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Fuel supplier selection for large scale UK bioenergy schemes

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Abstract: This article presents a potential method to assist developers of future bioenergy schemes when selecting from available suppliers of biomass materials. The method aims to allow tacit requirements made on biomass suppliers to be considered at the design stage of new developments. The method used is a combination of the Analytical Hierarchy Process and the Quality Function Deployment methods (AHP-QFD). The output of the method is a ranking and relative weighting of the available suppliers which could be used to improve optimization algorithms such as linear and goal programming. The paper is at a conceptual stage and no results have been obtained. The aim is to use the AHP-QFD method to bridge the gap between treatment of explicit and tacit requirements of bioenergy schemes; allowing decision makers to identify the most successful supply strategy available.

Keywords: *AHP, QFD, Bioenergy, supplier selection*

1. Introduction

The UK Bioenergy industry is expected to undergo significant growth over the coming decade as utilities and government aim to reach renewable energy targets by 2020. This expected growth is due to increasing installations of biomass heating, biofuel production for transport, biochemical for oil substitution, combined heat and power production and centralized electricity generation from biomass. For the sector to succeed the rapid development of demand for biomass resources must be matched by a sustainable supply. The various different bioenergy conversion processes that can be used to supply this range of lower carbon products brings a diverse set of material suppliers to the attention of project developers and procurement managers.

These fuels are likely to arise from a wide variety of sources and will have greatly differing properties and characteristics such as varying moisture or energy content. Additionally there are likely to be both positive and negative impacts associated with deciding to use a particular supplier. These impacts are less well defined when compared to the explicitly expressed measures of material properties and cost. The more tacit properties of a biomass fuel could include labor hours, CO_2 emissions, air water and noise pollution, job creation, waste diverted from landfill, price fluctuation and reliability of supply are all examples of impacts a bioenergy scheme may have upon wider society and the environment. The challenge for the procurement manager is to decide which sources of materials to select and how much of each material to purchase from each supplier, thus creating a supply strategy.

Most conversion plants will have some technical parameters to which the input feedstock blend should comply with; these parameters define the desired fuel specification required of the blend. The problem of which blend to use lends itself well to goal programming techniques as the relationships are linear and the optimal blend can be expected to be a mixture of materials from different sources. Several methods have previously been successfully applied to the optimization of the bioenergy supply chain under various contexts. For instance for a multi-fuel problem and maximizing some objective function; energy efficiency, net CO_2 emissions, or labor hours [1]. The output of such decision models is to give recommendations on the optimal location and capacity of new bioenergy plants, or to suggest an optimal supply or logistics strategy.

Previous research on the tacit impacts of a bioenergy system also exists. Often these tacit requirements are described in the context of sustainability metrics described as social and environmental impacts. Key sustainability constraints for UK bioenergy schemes have been identified as greenhouse gas savings, land availability, air quality, and problems associated with facility siting [2]. In a study on decision making for sustainable energy schemes some assessment criteria were identified and categorized as ecological, social and economic and included factors such as *employment rate*, *land competition* and *supply security* [3]. Indeed the study of sustainability regarding biomass grown for energy use has attracted a great amount of academic and public attention over the past decade.

The understanding of these two sides of the supplier selection problem is fairly robust considering the relative immaturity of the sector and the small number of commercially operating schemes. There is a gap in the treatment of the supplier selection problem however and more widely in the design of the biomass supply chain. The existing studies are unable to fully combine the optimization algorithms used for explicit aspects with knowledge of tacit requirements made of suppliers. This work presents a possible method to bridge this gap between the treatment of tacit and explicit requirements. The output of the work will be a structured process for developers to follow which will allow a score to be generated for each supplier given the extent to which that supplier meets the requirements of the development and any identified critical stakeholders.

The method behind the proposed framework is the combined AHP-QFD supplier selection method [4]. The hypothesis is that by selecting biomass suppliers using the AHP-QFD method a combination of suppliers can be selected to provide a supply which more effectively meets the needs of the conversion facility whilst remaining within the feasible region of cost and technical requirements.

This approach allows developers to move their procurement strategy beyond the model of transaction cost theories which are not suitable for the non-commodity market faced by the bioenergy industry sector at present. Building relationships between suppliers and conversion facilities will allow suppliers to better understand and meet the requirements of the conversion facility. Increasing the degree to which requirements are satisfied and maintaining a competitive cost for the fuel compared to other supply options. This is expected to be a better model for all parties than either the transaction cost model or the vertically integrated supply chain model.

2. Methodology

The AHP-QFD method has been applied in several previous cases for the selection problem under various multi-criteria conditions. The AHP-QFD method has been frequently applied in the manufacturing sector to select engineering projects [5] and more commonly to the area of product design [6, 7] that QFD was initially developed for. Elsewhere the method has also been applied to selecting budgets, teams and facility locations within logistics problems.

Current practice is for developers to select supply blends based on a mixture of experience and market knowledge as well as the price of each supply. The AHP-QFD method will be used to generate a recommended supply blend for a given scheme with a supply blend designed using current practice. The two recommended supply blends will then be compared with one another to determine the extent to which key tacit requirements are met by each approach.

2.1. The QFD Method

Quality Function Deployment (QFD) allows the requirements of a customer to be mapped against the characteristics of a product. The House of Quality technique is closely associated with QFD and allows for this translation or mapping to be done systematically. The method uses one or more interrelationship matrices to relate the properties of the product to the requirements of the customer. The customer requirements are given a weighting related to its importance to the customer. The person or team of people completing the matrix is required to judge to what extent each requirement is met by each product characteristic. The output of the process is an importance score for each of the product characteristics.

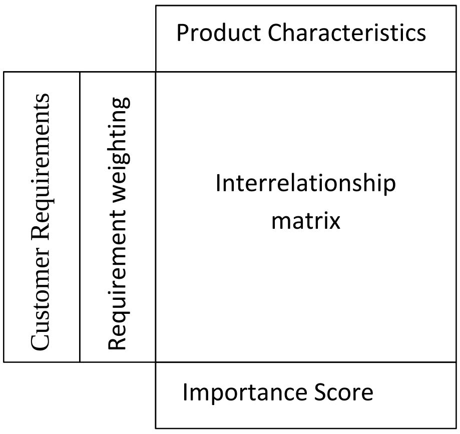

Fig. 1. A typical construction of a product HoQ.

The great advantage of the HoQ and QFD method is that each product characteristic is given a relative importance related to the degree to which that characteristic meets the customers' requirements. The weakness of the method is that the assigned importance is heavily reliant upon accurate completion of the interrelationship matrix. Any inconsistency or inaccuracy in this part of the HoQ process will lead to misleading final importance scores. Obtaining accurate weightings for the customer requirements is also important. This weakness is overcome when the Analytical Hierarchy Process (AHP) is applied.

2.2. The AHP-QFD Method

This section describes the steps used to determine the relationship weightings between the list of product characteristics and the customer requirements thus completing the interrelationship matrix. The following steps describe the AHP for use in a House of Quality.

Step 1: Construct a comparison matrix A with a customer requirement for each row and a product characteristic for each column.

$$A = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{12} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{bmatrix}, \qquad (1)$$

Where n is the number of elements in the top array (Product Characteristics), and a_{ij} is the comparison of element i to element j using a 9-point scale shown in table 1.

Step 2: AHP Synthesization
Divide each entry of the matrix A by the column total. This creates a normalized comparison matrix *A'*.

$$A' = \begin{bmatrix} \frac{a_{11}}{\sum_{i\in R} a_{i1}} & \cdots & \frac{a_{1n}}{\sum_{i\in R} a_{in}} \\ \vdots & \ddots & \vdots \\ \frac{a_{n1}}{\sum_{i\in R} a_{i1}} & \cdots & \frac{a_{nn}}{\sum_{i\in R} a_{in}} \end{bmatrix}, \qquad (2)$$

Where *R* is a set of customer requirements *R* = {1, 2, …, *n*}.

Step 3: Create a column vector *C* from the averages of each row of matrix *A'*.

$$C = \begin{bmatrix} \overset{1}{c}_{1k} \\ \vdots \\ \overset{1}{c}_{nk} \end{bmatrix} = \begin{bmatrix} \dfrac{\left(\frac{a_{11}}{\sum_{i\in R} a_{i1}} + \frac{a_{12}}{\sum_{i\in R} a_{i2}} + \cdots + \frac{a_{1n}}{\sum_{i\in R} a_{in}} \right)}{n} \\ \vdots \\ \dfrac{\left(\frac{a_{n1}}{\sum_{i\in R} a_{i1}} + \frac{a_{n2}}{\sum_{i\in R} a_{i2}} + \cdots + \frac{a_{nn}}{\sum_{i\in R} a_{in}} \right)}{n} \end{bmatrix}, \qquad (3)$$

Where c_{ik}^{1} denotes the relationship weightings between the product characteristics *i* and the corresponding customer requirement *k*.

Step 4: Verify Consistency of AHP
To ensure that the respondent has assigned values from table 1 in a consistent way a consistency test should be carried out. Create a further column matrix by multiplying each entry in column *i* of matrix *A* by the column vector c_{ik}^{1} from step 3 then divide by the sum of values in each row *i* by c_{ik}^{i}.

$$\overline{C} = \begin{bmatrix} \overset{-1}{c}_{1k} \\ \vdots \\ \overset{-1}{c}_{nk} \end{bmatrix} = \begin{bmatrix} \dfrac{\overset{1}{c}_{1k} a_{11} + \overset{1}{c}_{2k} a_{12} + \cdots + \overset{1}{c}_{nk} a_{1n}}{\overset{1}{c}_{1k}} \\ \vdots \\ \dfrac{\overset{1}{c}_{1k} a_{n1} + \overset{1}{c}_{2k} a_{n2} + \cdots + \overset{1}{c}_{nk} a_{nn}}{\overset{1}{c}_{nk}} \end{bmatrix}, \qquad (4)$$

Where $\bar{C}$ is a weighted sum vector.

Table 1. AHP scale for completing the HoQ comparison matrix.

Intensity	Importance	Explanation
1	Equal	Two activities are equally important
3	Moderate	One is slightly more important than the other
5	Strong	One is strongly more important than the other
7	Very Strong	One is dominant of the other
9	Extreme	Highest possible affirmation of evidence favoring one over another.
2,4,6,8	Intermediate	Used for compromise when desired value falls between above scales
Reciprocals of the above numbers		Used for inverse relationships

Step 5: Calculate the averages of values in vector $\bar{C}$ to give the maximum Eigenvalue (λ_{max}) of matrix *A*.

$$\lambda_{\max} = \frac{\sum_{i\in R} \overline{C}^{1}_{ik}}{n}, \qquad (5)$$

Step 6: Calculate the consistency index.

$$CI = \frac{\lambda_{\max} - n}{n-1}, \qquad (6)$$

Step 7: Compute the consistency ratio,

The consistency ratio is based on RI(*n*), a random index taken from table 2 based on the value of *n*.

$$CR = \frac{CI}{RI(n)}, \qquad (7)$$

The consistency ratio is a measurement of consistent responses when completing the relationship matrix. If the measurement is greater than 0.10 the process is considered inconsistent and should be repeated in the hope of realizing a more consistent response. This measurement of consistency gives greater confidence when using the AHP-QFD method over the QFD method alone.

Table 2: List of Random Index values

n	2	3	4	5	6	7	8	9
RI(n)	0	0.58	0.90	1.12	1.24	1.32	1.41	1.45

Assuming consistency is acceptable the matrix will be populated with relationship weightings that link the top matrix with the left hand side matrix (Product characteristics with Customer Requirements from Fig. 1). The importance rating of each product characteristic can then be calculated.

Step 8: Compute importance rating

$$w_i^1 = \sum_{k \in S} p_k c_{ik}^1 , \qquad (8)$$

Where S denotes the set of customer requirements $S=\{1, 2, \ldots, m\}$, and p_k denotes the importance rating given to that requirement.

The result of step 8 is an importance score for each product characteristic which has been obtained from the requirements of customers. The AHP-QFD method can also be applied to a selection problem. By using the QFD to link the requirements made on a supplier, to the characteristics displayed or possessed by any given supplier, qualitative aspects of supplier selection can be managed in a systematic and robust way.

2.3. The AHP-QFD approach for bioenergy suppliers

The QFD method can deal with both qualitative and quantitative aspects of a product or service [7], several other techniques are available for the explicit optimization of fuel blends, therefore the QFD-AHP process will be used to better analyze and understand the qualitative requirements made of suppliers. The method is intended to be applied from a developer perspective as it is the developer that will make the initial decisions on the supply strategy for the scheme. Therefore rather than customer requirements being used as the success criteria the requirements of the developer and the scheme should be identified and weighted.

Many of the requirements of a good biomass supplier are likely to be in line with the requirements on suppliers from other industries. Reliability, company size, responsiveness and quality control are likely to be important tacit requirements. Other requirements may be more unusual and regard the material itself such as accreditation by sustainable forestry bodies, the local or national sourcing of waste, compliance with best practice and the method of delivery may be important aspects not covered by the technical fuel specification.

Having identified the requirements the developer places upon potential suppliers the relative importance of each requirement should be identified. This is done using the first HoQ matrix. The developer is likely to consist of several teams or members of staff with different perspectives on the project. These different teams will place differing importance weightings on different requirements. In this case the developer teams are considered to be equally important, typical developer teams may consist of planning, technical/design teams and finance teams.

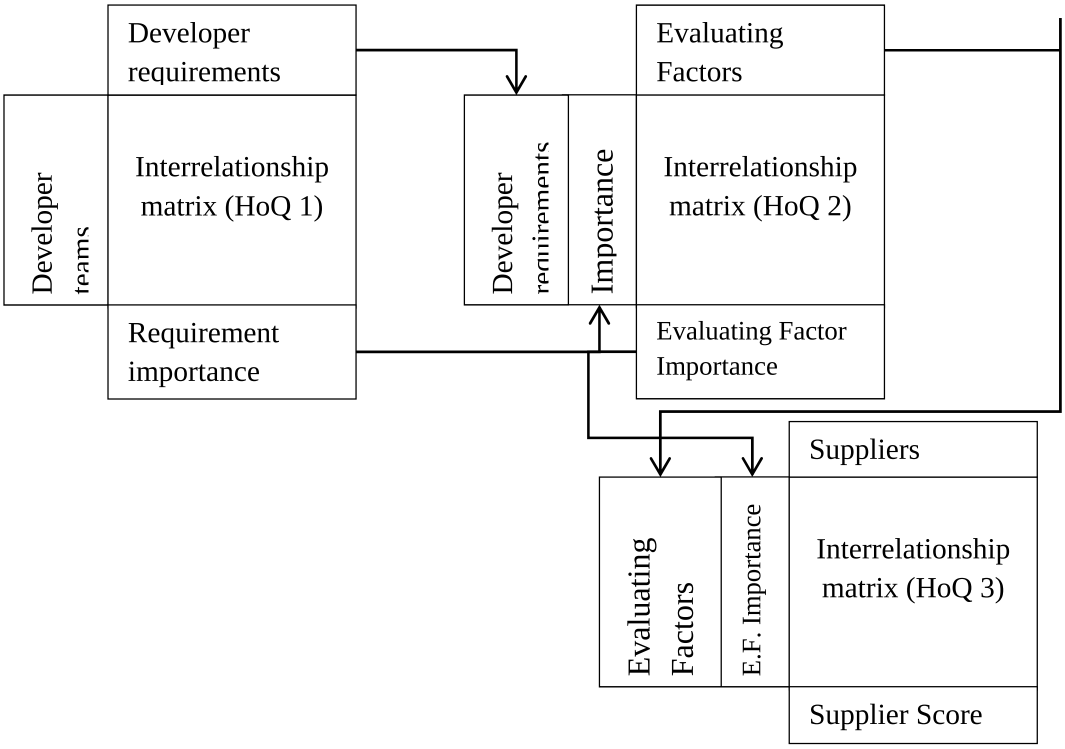

Fig. 2. HoQ 1 giving the importance of each requirement as determined by the developer. HoQ 2 linking the developer requirements with available evaluating factors for potential suppliers and HoQ 3linking those evaluating factors with the available suppliers to the bioenergy scheme.

The output of HoQ 1 is then used in HoQ 2 which links the developer requirements to externally observable characteristics possessed by the suppliers. These characteristics take the place of product characteristics and allow the decision maker to determine to what extent each requirement would be met by certain aspects of a supplier. For instance a requirement for sustainable fuel would be significantly met by a supplier approved by some sustainable forestry stewardship scheme. The use of organic wastes may be negatively related to a requirement to keep site odors to a minimum whilst a guarantee to deliver at within a narrow band of moisture content may score highly against a requirement for consistent fuel characteristics.

A final House of Quality table HoQ 3 can then be constructed which links the evaluating factors and their relative importance with the suppliers available. Here the decision maker must decide to what extent each supplier matches the evaluating factors identified. The output of HoQ 3 is a score for each supplier based on the ability of that supplier to meet the tacit requirements of the developer. Those suppliers that score highest should be favored.

3. Discussion

The weighted ranking score of each supplier assists decision makers in determining which suppliers to use when creating a strategy for biomass supply to large scale facilities. The massive quantity of materials required for large scale conversion facilities mean supply chain managers are forced to source from a range of materials and sources. The objective function for optimization algorithms can, using the presented method, incorporate the tacit requirements made on suppliers to create a model constrained by the explicit requirements of material specification imposed by equipment specifications. The objective function therefore could take a form similar that shown in equation (9).

$$\max\left(w_1 S_1 + w_2 S_2 + \ldots w_m S_m\right) \tag{9}$$

Where w_m denotes the score for each supplier S_m for m different suppliers. This approach would ensure the resulting suggested strategy is technically feasible, whilst also ensuring the best possible combination of suppliers is contracted.

The AHP-QFD method is suitable for application within developing companies as it is simple to apply and gives predictable and clear outputs for the decision maker. An inherent weakness of the approach is the subjective viewpoint of the decision maker compiling the list of requirements. In this application this weakness is minimized by considering only requirements of the teams within the developer company, not the wider stakeholder group. The AHP-QFD method also has an advantage over other weighting or ranking methods that could be incorporated into the objective function as it directly translates the requirements made on suppliers into their performance score using a robust method rather than a user estimate.

As the research develops more stakeholders could be interviewed for requirements and asked to complete the AHP-QFD process. This would allow developers to gain insight into the requirements that should be satisfied to make the scheme more successful from the perspective of other development stakeholders. As the framework is applied to different stakeholders a database of requirements can be constructed showing global and scheme specific requirements of different stakeholders.

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Bioenergy Decision Support Systems: Worth the Effort?

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Abstract: The purpose of this research is to explore the disparity between the existing model-orientated bioenergy decision support system (DSS) functions and what is desired by practitioners, in particular bioenergy project developers. This research has compiled the published bioenergy project development models, to highlight the characteristics emphasised by academics. When contrasted against a UK practitioner's perspective through the administration of a Likert style questionnaire, it is clear that the general DSS issues still persist. Finally, the research suggests how this 'theory-practice' divide could be addressed. The research contributes by giving a unique insight into the demands of a practitioner, but is currently limited by a small sample size.

Keywords: *Decision Support System, Bioenergy Project Development, Theory-Practice Divide*

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1. Introduction

Developing a bioenergy project requires large volumes of complex information to be gathered and processed by project developers. This information tends to be fairly structured and accessible; although, often not easily retrievable for use in a timely manner [1]. The difficulties faced in progressing through the necessary phases in bioenergy project development encourage a dependence on experts, which restricts knowledge transfer and non-expert project developers entering the industry – ultimately constraining sector growth. This could be one explanation why growth in the UK bioenergy market, in particular has been slower than expected, with some referring to growth as 'slight' [2].

Academic literature supports the use of model-oriented decision support systems as a proven method to aid both expert and non-expert decision-makers [3], with a substantial amount of bioenergy support systems being assembled to address a multitude of development problems in countries such as: Japan, Greece and Italy. Although, this literature rarely considers the most critical issue; the theory-practice divide in DSS research [4]. At present, there is no research to understand the lack of practical application of decision support tools in the bioenergy sector. With the dire need for bioenergy project support tools to aid decision-making and in turn sector growth in the UK, but with a persistent disconnect between theory and practice [4, 5], a lack of relevance [5] and little evidence to show that these tools are ever really adopted [6] – can a decision support system really ever have a pragmatic contribution.

1.1. *Objectives*

The research objectives are to ascertain whether bioenergy DSS are worth the effort, by:

- reviewing published bioenergy project development DSS models;
- critically comparing these models to the requirements of the industry practitioner;
- discussing how future research could be more applicable to the practitioner.

1.2. *Contribution*

The contribution of this research is two-fold: it is the first paper to analyse the characteristics of all existing model-orientated DSS papers in developing bioenergy projects; and it increases understanding of the theory-practice gap by assessing these characteristics against a practitioner's perspective.

2. Developments and Issues with Decision Support Systems

Since the term decision support system' was coined by Gorry and Scott-Morton [7] when suggesting a framework for improving management information systems (MIS), there have been many developments in this discipline. One of the most successful attempts to classify the characteristics of a DSS was by Alter [8] who created a taxonomy of seven categories, which could be further condensed down to two: data-orientated or model-orientated support systems. The bioenergy DSS models reviewed in this research are all model-orientated, spanning the *representation* and *optimisation* categories in Alter's [8] classification, most support systems in use today are in these two categories [4]. Model-orientated decision support systems are typified by their user(s) and whether they integrate knowledge. This can be seen in the table below:

Table 1. DSS types [9].

Type	Description
Personal DSS (PDSS)	Small-scale systems that are normally developed for one manager, or a small number of independent managers, for one decision task.
Group support systems (GSS)	Decision responsibility is shared by a number of managers and a number of managers need to be involved in the decision process.
Intelligent DSS (IDSS) / knowledge-based DSS	Intelligent DSS can be classed into two generations: the first involved the use of rule-based expert systems and the second generation uses neural networks, genetic algorithms and fuzzy logic [Turban et al., 2005 cited 9].
Knowledge management-based DSS	Involves the combination of several areas including IT, organizational behaviour, organizational structure, economics and organizational strategy.

Table 1, also illustrates the chronological order in which the field has developed. The earlier PDSS were intended for a single decision-maker or user. As the field developed, multiple decision-makers were accounted for in the DSS design. More recently, in the last two decades researchers have built in expertise to support systems to further support decision-making.

Decision support systems have been extensively applied to a myriad of industries and problems over the past four decades, with Eom [4] reviewing over 25,000 published articles; however, he concluded theory-practice divide issues still persist. A paper by Arnott and Pervan [5] reduced the field's problems to eight issues, of which the research has selected four relating to the theory-practice divide have been selected, listed in table 2:

Table 2. DSS discipline key issues [adapted from 5].

Key Issue	Comments
Professional relevance	Most DSS research is disconnected from practice.
Research methods and paradigms	DSS is more dominated by positivism than general IS [information systems]. Case study research is under represented. A long history of design science research could contribute methodologically to IS research.
Theoretical foundations	Around half of the papers have no explicit foundation in judgement and decision-making. Much DSS research is based on a relatively old theoretical foundation.
Inertia and conservatism	The relatively older types of PDSS and GSS still dominate research agendas.

The first and foremost issue is 'professional relevance', Arnott and Pervan [5] found "only 10.1% of research is regarded as having high or very high practical relevance. On the other hand, 49.2% of research was regarded as either having low practical relevance or none at all". Two of the papers, Hirschheim and Klein [10] and Banbasat and Zmud [11], which are cited in the focal article as giving possible explanations, point toward the disconnect between these two groups; both articles focus on the researcher and academia as the cause of the divide. With Hirschheim and Klein [10], in particular, analysing the performance of the discipline from an external, management viewpoint. They show how the practitioners' expectations were not fulfilled – no matter how unrealistic. The issue with this defence is that it is bias and fails to consider, the practitioners' role in this 'disconnect'.

There are a variety of possible explanations why decision support systems fail to get adopted by practitioners. The first being given by Rizzoli and Young [12] who found that decision-makers lack trust in a DSS even if it is proven to be effective, opting for their own often sub-optimal decisions. A case in point is a study of forestry operations decision-makers in Canada, who would rather rely on their own ability than computer software's [Rooney, 1996 cited 1]. This was also found by Wierzbicki and Wessels [13:37] who discovered "the higher the level and experience of a decision-maker, the less inclined she/he is to trust in various tools and methods of decision analysis and support". The second explanation may be as Brown and Vari [6] suggested "the practical impact of decision aids on business decisions is less easy to establish, due to the cloak of commercial secrecy…" with the successful DSS being used to achieve a competitive advantage rather than for publication.

The second issue shown in table 1 is the research method and paradigm typically applied in DSS research. Arnott and Pervan [5] found that the discipline is still overwhelmingly positivist, their conclusion to remedy this was a greater reliance on case study research, and adoption of the interpretive paradigm. This issue is inextricably linked to 'practical relevance', possibly because academia has been guilty of pursuing 'rigour over relevance'[11], and the classical hypothetico-deductive positivist paradigm is the most suitable method for achieving this rigour. Although, an interpretive case study would increase the practical relevance of a DSS publication, it is not necessarily the only method of addressing this issue. It is possible to increase relevance without requiring a paradigm shift; an experimental positivist or post-positivist DSS could increase practical relevance with the empirical testing of the model(s) through actual cases application.

The third and forth issues follow on from the preceding problems in the general discipline. Arnott and Pervan [5] classified a paper as having a theoretical foundation if there was theory cited in the research design and result interpretation, they stated that the results in general DSS research was quite alarming, after finding just under half of all papers reviewed (47.8%) lacking a theoretical foundation. Additionally, they discovered that the older – more popular – types of DSS (PDSS and GSS) performed better than other DSS types. Finally, their research found that inertia and conservatism in the discipline, even accounting for the publication lag, meant that the newer types of DSS were not being fully adopted by academia.

These four issues in the general decision support system field are still present, and have not been fully addressed over the past four decades. It is unclear who is at fault: practitioners, academia, or both. However, it is clear in the context of this research problem, that if these issues are addressed by the bioenergy industry, their use and contribution will greatly increase.

3. Decision Support Systems in the Bioenergy Industry

There have been many bioenergy decision support systems created for academic papers which address different issues in developing bioenergy projects. The research has excluded a small group of sustainability DSS papers, as they are beyond the scope of this research. A timeline of all the relevant bioenergy DSS literature has been compiled in figure 1; this is a substantial number of research papers considering this is a relatively new academic field. The extent to which DSS tools have been utilised in academic journals could be attributed to the complexity of effectively making decisions in the energy sector, making it is necessary to utilise some form of support model [14].

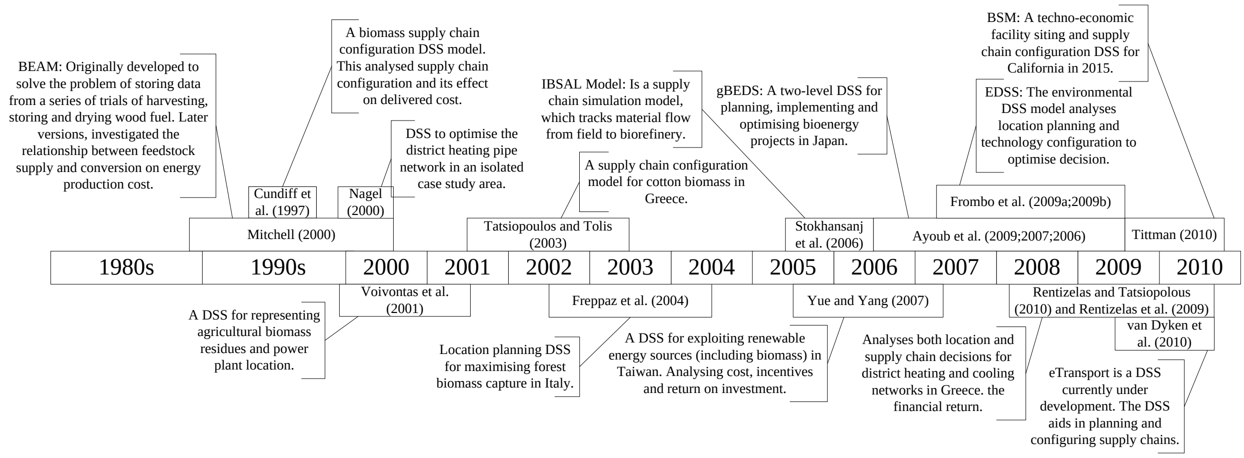

Fig. 1. Annotated timeline of model-oriented bioenergy DSS research.

The timeline highlights 13 DSS models created for developing bioenergy projects, primarily spanning two decades, with most models being created in the last 10 years. The timeline gives a brief overview of each DSS and shows the publication lag, or when explicitly stated in the article, when research began.

4. Methodology

The paper gives an exploratory insight into what a bioenergy project developer requires from a DSS. The primary data for this research was gathered by creating a questionnaire for practitioners, which analyses their opinion on the existing bioenergy research papers traits.

From the descriptive statistics gathered from the analysis of the DSS characteristics (table 3), a scale of importance was attributed to each characteristic. The frequency ranking scale was: low (0-2 articles); medium (3-5 articles); high (6-8 articles); very high (9 or more articles).

4.1. Bioenergy DSS Characteristics

Before it is possible to assess the focus of bioenergy decision support systems, it is necessary to analyse their characteristics. To achieve this key attribute categories have been created, some relate to the configuration of the DSS, such as: type of DSS, intended user(s), research paradigm etc; whereas, the remaining characteristics relate to the professional relevance and model application. The scales attributed to each of the characteristics varies, most are non-parametric nominal scales. In some cases a simple dichotic yes/no choice was utilised, as seen in table 3.

Table 3. DSS Characteristic Classifications.

Category	Classification
Type of DSS	This characteristic refers to the DSS design. The bioenergy DSS models are categorised as: personal (PDSS), group (GSS), intelligent or knowledge-based, or knowledge management-based.
User(s)	The categories for this measure are: national or regional planners/developers, local developers, investors and not stated. Importantly, if the intended user of the decision support tool is not explicitly stated in the research paper then they are categorised as not stated.
Research method	The research method and paradigm categories are based on the Arnott and Pervan [5] classification: non-empirical conceptual, illustrative or applied concepts; empirical objects or events and processes.
Practical relevance	This is the foremost issue with decision support systems. As the Arnott and Pervan [5] paper utilised a subjective scale, administered by a group of experts to judge whether the article had practical relevance (none, low, medium, high, very high). It was important to implement a similar system, with a less interpretive grounding. Table 4 applies a measure for each existing bioenergy articles.
Theoretical foundation	The method of judging whether a bioenergy DSS paper has a theoretical foundation will be the same as applied in Arnott and Pervan [5]. They distinguished between only citing other theory in the introductory chapters and citing theory in the method and discussion sections, as no theoretical foundation or having a theoretical foundation respectively.
Project lifecycle	The research also categories the DSS models by the targeted phase in the bioenergy project lifecycle, the phases are: planning, construction and operation [15]. As decisions are made throughout a project's lifecycle phases, it was important to ascertain where the current support systems focused.
Model output	The bioenergy model output(s) were also recorded as: financial, non-financial or multiple.

As the theory-practice divide and whether decision support systems are worth the effort, is the primary focus of this research, emphasis has been placed on creating a practical relevance scale, as seen in the table below:

Table 4. Scale for establishing practical relevance.

Relevance	Measure
Low	Hypothetical case
Medium	Single application or case study
High	Multiple practical uses
Very high	Multiple practical uses and application examples

This research argues that a DSS which is possesses multiple practical uses; meaning it can be applied to multiple cases to solve problems (generalisable), will have the highest practical relevance. Moreover, if this is also demonstrated in the academic article, as opposed to merely stating a support system's generalisability, then this achieves 'very high' practical relevance.

4.2. Practitioner Questionnaire

A simple closed choice questionnaire, with a five-point Likert style scale for importance (none, low, medium, high, very high) was designed to explore whether bioenergy project developers placed similar emphasis on the characteristics in the existing bioenergy support systems. Due to the constraints of the research paper, the questionnaire is not included, but is available on request. The results of the questionnaire can be seen in table 5. The respondent organisation is a SME developer of biomass combined heat and power projects in the UK.

4.3. Research Limitations

The research is currently limited to one organisation, but this is because the research is on-going. Although, this is presently a limited sample size, its contribution remains as the first study to explicitly state the practitioner's view.

5. Results

The results table (5) below, illustrates the comparisons between the academic and practitioner weighting:

Table 5. Results table.

Characteristic	Application	Academic Weighting (no.)	Practitioner Weighting
Type of DSS	PDSS	Very high (10)	High
	GSS	Low (0)	High
	Knowledge-based	Medium (3)	Very high
	Knowledge mgmt' based	Low (0)	Low
User(s)	National or regional	Low (1)	Very high
	Local	Low (0)	Very high
	Investor	Low (1)	Very high
	Implied/not stated	Low importance (10)	Very important
Method	Empirical	High (7)	High
	Non-empirical	High (6)	Low
Practical relevance	Low/med (single application)	Very high (10)	High
	High/v.high (multiple applications)	Medium (3)	Very High
Theoretical foundation	Yes	Low (2)	Very high
	No	Very high (11)	-
Bioenergy lifecycle phase	Planning	Very high (13)	Very high
	Construction	Low (0)	Very high
	Operation	Low (0)	Very high
Model output	Financial	High (7)	Very high
	Non-financial	Low (2)	High
	Both	Medium(4)	-

5.1. Analysis

The results highlighted that the foremost issue of practical relevance in the bioenergy sector was an improvement on the Arnott and Pervan [5] findings, with 3 models or 23.1% classified as having a high or very high practical contribution, as opposed to only 10.1% of their sample were categorised as such. Although, it is not possible to truly know if the criteria for assessing this were exactly the same, this verifies the research paper's interpretation of the practical relevance scale.

Moreover, the user(s) of the bioenergy DSS tended not to be mentioned or explicitly stated (76.9%) in the bioenergy publications, this can only support the argument for the lack of relevance, as the user is most likely the practitioner. This is something that the respondent organisation felt particular strong about, stating that it is very important to target each user group, and to explicitly tailor a DSS to their requirements. However, there is a general agreement between the academic and practitioner viewpoint on the most suitable output of the model, with the most emphasis placed on financial performance measures.

The bioenergy lifecycle phase results are also particularly interesting, as all of the 13 bioenergy models supported decision-making in the planning phase: in supply chain planning, location planning or both. None of the existing models supported the decision-maker in the later phases of a project's lifecycle; this highlights a need for further work considering that the respondent classified all phases as equally important.

The second issue raised was the lack of case study research and positivist paradigm dominance in the general DSS field. This was found to still be present in the bioenergy development models, with all papers reviewed having a positivist paradigm. Although, there was a high level of case study research found, with more than half of the bioenergy support systems possessing empirical data from case studies. This importance was also expressed in the respondent organisation's support for empirically grounded case studies.

The existing bioenergy research performed worse than the general discipline with regard to the theoretical foundation. This category classified 11 of the 13 models as not having a theoretical foundation in the model development and result analysis sections of the academic paper, this is considerably higher than the 47.8% found by Arnott and Pervan [5]. Furthermore, PDSS represented the majority of existing models, illustrating the inertia and conservatism within the discipline; although, it can be seen that group support systems were not adopted, the more recent knowledge-based DSS did quite well in this sector (23.1%).

6. Conclusion

From analysing the current issues in general DSS research (section 2), it is clear that the four issues relating to the theory-practice divide are interlinked; what wasn't clear was whether the bioenergy DSS research suffered from the same shortcomings. The bioenergy article analysis and the primary research in this paper have shown that for the most part they are still present. This could, therefore, explain why there is little evidence of practical adoption.

Arguably, if the purpose of building a DSS is to support decision-making, then practical application has to be regarded as the most important parameter. The most suitable way of addressing this issue is to design a system tailored to the decision-maker – this does not appear to be a priority of the existing research. Acknowledging and explicitly integrating the requirements of the user into the model building and testing stages will undoubtedly increase adoption. Furthermore, if generalisable model-orientated support systems have the highest level of practical relevance, then where possible they should take preference over a single use model. Finally, creating knowledge-based or intelligent DSS models which allow for group decision-making will not only reduce the conservatism issue but also allow for a potentially greater contribution. Addressing the issues raised in this paper is undoubtedly the first barrier to realising the full potential of decision support systems in the bioenergy industry.

6.1. Further Work

Firstly, as the research presented is at an early stage, the next step is to increase the respondent sample size to include national and regional developers and investors, to better ascertain what functionality bioenergy project developers require. Moreover, a larger sample size would allow for inferential statistical analysis, adding a greater level of depth to the research. Secondly, as there is no research into decision support models for the latter phases of a bioenergy lifecycle, this presents an interesting new avenue of enquiry.

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Options for Increased Use and Refining of Biomass – the Case of Energy-intensive Industry in Sweden

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Abstract: Events in recent decades have placed climate change at the top of the political agenda. In Sweden, energy-intensive industries are responsible for a large proportion of greenhouse gas emissions and their ability to switch to renewable energy sources could contribute to the transition to a decarbonised economy. This interdisciplinary study has its starting point in three energy-intensive industries' opportunities to take part in the development towards increased refining and use of biomass. The study includes the pulp and paper industry, the iron and steel industry and the oil refining industry, each exemplified by a case company. It can be concluded that there are several technological options in each industry. On the other hand, implementing one option for increased use of biomass in each case company could demand up to 34% of the estimated increase in Swedish biomass supply, in 2020. Additionally, in a longer time perspective none of the case companies believes that the amount of biomass in the Swedish industrial energy system have the possibility to increase significantly in the future.

Keywords: *Biomass, Energy-intensive industry, CO_2 emissions, Case study.*

1. Introduction

Increased awareness of the effects of climate change has placed mitigation of greenhouse gas emissions at the top of the political agenda, urging a transition to a decarbonised economy. Sweden has taken a prominent position in the international discussions about this transition and is simultaneously creating national policies to mitigate climate change, for example the green certificates for generation of electricity from renewable energy sources. In Sweden, the industrial sector represents one third of the total energy use and in 2008 this sector used 151 TWh [1]. The Swedish pulp and paper, iron and steel and oil refining industry accounted for more than 70% of the energy use (50%, 15%, 7% resp.) in the industrial sector and were responsible for 44% of the CO_2 emissions from Swedish companies (that are a part of the European Emission Trading Scheme) in 2008 [2]. Therefore their ability to switch to renewable energy sources could contribute to mitigate climate change effects. Since a large part of Sweden is covered by forest or agricultural land, biomass has the potential to be one of these renewable sources.

Several studies have analysed the options for biomass use in Sweden [3; 4]. More specifically, the potential for increased biomass use and refining in the pulp and paper industry is analysed by e.g. Andersson [5]. Berntsson et al [6] and Johansson et al. [7] analyses the biomass use in the oil refining industry and Norgate and Landgate [8] investigates the same issue for the iron and steel industry. This study includes these three industries in order to get a comparative view on the potential for biomass use and refining in Swedish energy-intensive industry. However, it is important when studying these industries jointly to take into account their different prerequisites for use and refining of biomass, regarding current feedstock as well as processes. The aim of the study is to investigate how these industries can contribute towards a future increased use and refining of biomass. A case study approach is used and three case companies are studied, one for each industry. The aim of the study is evaluated through three research questions; 1) What are the possible technological options for increased use and refining of biomass for the studied industries? 2) If implemented in the case companies, what amount of biomass would these technological options require compared to the potential of increased biomass supply in Sweden 2020? 3) What possibilities and obstacles do the case companies recognize for increased use and refining of biomass in their industry?

2. Methodology

This interdisciplinary study illuminates both technological options and business strategies, revealing conflicting and co-operational interests and creates the potential for a profound understanding of sustainable future development in this area. The study is based on a case study approach and both interviews and literature surveys are used to collect data. For research question 2 and 3 each industry is represented by a case company, which are presented at the end of this section. The case companies are chosen since they all have an ambitious attitude to climate change mitigation activities and have shown interests in collaborations with universities.

The first research question is answered by a literature survey, in which the following commercial technologies are included; pyrolysis, catalytic cracking, hydro cracking and production of wood-fuel pellets. Not commercially available technologies included are second generation ethanol fermentation, biomass gasification, lignin extraction and black liquor gasification.[1] Technologies in an early stage of development or with a limited potential to increase the use and refining of biomass in the industrial sectors were not included in this study. The included technologies are based on wood and agricultural biomass and do not compete with the core capabilities of the case companies. For the second research question the result of the first is combined with the different preconditions at the case companies and the potential future biomass demand. However, only technologies that are possible to implement at each case company are evaluated. The results for the third research question are based on qualitative and semi-structured interviews. Two representatives for each case company were interviewed, one at corporate group level and one at facility level.

In this study biomass is considered to be a limited resource. The biomass required to implement a technology is therefore compared to the future potential of increased biomass supply in Sweden. Several studies have estimated the increase in supply of wood and agricultural biomass, in Sweden. In this study a moderate increase of biomass supply has been used, estimated of 38 TWh/year in 2020 in reference [9].

The studied case companies are; Södra Cell for the pulp and paper industry, SSAB for the iron and steel industry and Preem AB for the oil refining industry. For the calculations in research question 2, the following specific facilities are used; Södra Cell Värö that produced 380 ktonnes of kraft pulp [10], SSAB Strip Products in Luleå that produced around 2.2 Mtonnes of steel slabs and 750 ktonnes of coke [11] and Preem's refineries in Lysekil and Gothenburg with annual oil refining capacities of 11.4 Mtonnes and 5 Mtonnes of crude oil respectively in 2008[12]. The choice of facilities limits the study to kraft pulp mills[2] for the pulp and paper industry and to integrated steel plants[3] for the iron and steel industry. Additionally, the refinery in Gothenburg is smaller and less complex than the refinery in Lysekil.

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[1] More information about these biorefining technologies can be found in Johansson et al [13].

[2] Chemical pulp and not paper is the final product.

[3] The processes are based on iron ore.

3. Results

This section presents opportunities for increased use and refining of biomass in the three energy-intensive industries studied. Furthermore, the amount of biomass required for the options are related to the estimated increase in biomass supply in Sweden in 2020. Additionally, the case companies' views on future increased use of biomass in their industry are presented. To distinguish the results based on interview outcomes from results based on calculations or literature studies all interview references are marked with an asterisk.

3.1. Pulp and paper industry

For the pulp and paper industry, with its wood biomass based processes and extensive experience of logistics of timber, the increased demand for biomass has lead to increased competition for the industry's raw material but also opened new opportunities for increased refining of intermediate and by-products. The existing infrastructure for transportation of raw materials, storage possibilities on site and knowledge of handling of biomass can facilitate increased import of biomass as well as export of products based on biomass.

Like the industry in general, the case company Södra Cell is affected by the changes in its environment. The price of biomass, chemicals and energy affect the production cost, on the other hand energy prices also affect Södra Cell's incomes positively [14]*. Södra Cell's strategy is to increase energy efficiency in order to minimise purchased energy so that only raw material is bought and additionally the company wishes to become independent from fossil fuel [14]*. This is achieved by increasing the efficiency of the production processes, through technological choices adapted to the different prerequisites at Södra Cell's three Swedish mills. The mill in Mönsterås has invested in a condensing turbine to increase electricity production, Södra Cell Mörrum is planning a LignoBoost[4] process and Värö's mill installed a bark drier during 2009. The company is interested in using new technologies for producing non-cellulose-based products, e.g. district heating, electricity, lignin or tall oil, but only as long as these are produced from residues and thus do not compete with pulp production [14]*. All these alternatives offer the possibility of increased export of energy products without increasing the total import of biomass to the facilities. Policies, particularly the green certificates for electricity, have contributed to justify activities that improve energy efficiency and investment in new technologies.

In the case of replacement of the recovery boiler or increase in production capacity in a kraft pulp mill, gasification of black liquor could be an interesting alternative. The technology is currently at the demonstration plant level and it is argued by Pettersson and Harvey that a large scale implementation is unlikely to occur before 2020 [15]. Their conclusions are based upon a study of energy and material balance consequences of implementation of black liquor gasification for production of DME in a model mill. They argue that pulp mills will be more energy efficient by 2020 (using best available technology of today). The study shows that one consequence would be an increased biomass demand that, in the case of Södra Cell Värö would correspond to about 700 GWh/year. Södra Cell claims that the main barrier for implementing this technology is the high investment cost of the gasifier [14]*. Ekbom et al. [16] estimated the investment cost for a large scale gasifier to be more than twice the cost for a recovery boiler with the same capacity. Furthermore, the technology would also compete for biomass feedstock with the LignoBoost process [14]*. Finally, a sign of another path of development with a slightly different character is Södra Cell's research on green chemicals,

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[4] A process for separating lignin from black liquor. The lignin is sold as high value fuel.

which is conducted at the headquarters in Växjö by an R&D team of 50 peoples based in Värö [14]*.

3.2. Iron and steel industry

The spectrum of options to increase use and refining of biomass in an integrated steel plant is narrow, but the existing options have great potentials to reduce the industry's CO_2 emissions. An integrated steel plant can replace some of the coke used as reducing agent in the blast furnace, with biomass derived products such as charcoal, syngas, methane and ethanol. However, it is not possible to substitute all the coke in the blast furnace as coke acts as a physical support material and hence ensures correct gas permeability, process temperature and process drainage. Moreover, gasified biomass can be used as fuel in the steel plant's heating furnaces and replace the fossil fuel used today. Another option for an integrated steel plant is a partnership in an industrial symbiosis together with a biorefinery. For example, excess heat from the steel plant can be used by an ethanol plant and the ethanol can be used as reducing agent in the blast furnace or as transportation fuel in the steel plant's vehicles. Furthermore, an integrated steel plant can cooperate with a gasification plant and a Direct Reduced Iron (DRI) plant. The DRI plant can use syngas from the gasifier together with coke oven gas as reducing agent and DRI can be charged into the blast furnace or into the converter.

The interviewed representatives at the case company SSAB Strip Products state that a large scale replacement, of for example coke with products derived from biomass in the blast furnace, would need an extensive amount of biomass which makes it unlikely to be realized [17]*. Calculations for SSAB Strip Products demonstrate that a replacement of the pulverised injection coal with pulverised charcoal would demand approximately 4.4 TWh/year[5] of dry wood. If instead bio-methane was considered for injection, it would be possible to replace one third of the injection coal without affecting the blast furnace process [17]*, which would demand approximately 1.5 TWh/year of methane. If the methane is produced through gasification of biomass it would demand about 2.5 TWh/year[6] of dry wood. However, SSAB Strip Products identifies a risk in substituting coke with products derived from biomass as a substitution could affect the quality of the products, before the process is optimised, which could reduce the company's competitiveness [17]*.

The development of CO_2 prices and the global raw material markets will probably have the greatest impact on SSAB Strip Products' choice of future development path [17]*. Currently, energy-rich process gases are exported from SSAB Strip Products and used as fuel in a combined heat and power (CHP) plant. With regard to biomass use, the representatives from SSAB Strip Products consider it a better option to investigate possibilities to use excess energy-rich gases from the steel production internally at SSAB Strip Products and use biomass in a CHP plant [17]*. As a result of this line of reasoning, the company is increasing the efficiency of its energy system and aims at reducing its CO_2 emissions by 2% by 2012, which corresponds to 130,000 tonnes of CO_2 [11].

3.3. Oil refining industry

In a transition to more sustainable production and use of fuels the oil refining industry could play an important role with its extensive experience in processing and converting petroleum oil products into valuable fuels. The oil refining industry has the opportunity to use existing equipment for refining of biomass. By using the existing catalytic cracking unit or the

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[5] Calculations were based upon a biomass-carbonisation kiln with a weight-basis yield of 37%.

[6] In the calculations, a gasification plant with a biomass to SNG conversion efficiency of 60% is used.

hydrotreating unit bio-oils can be upgraded to transport fuels that meet the existing fuel standards. At present, there is an increasing demand of hydrogen in the oil refining industry which is due to a process change into more valuable products, e.g. diesel, aviation fuel etc. This increasing demand can be supplied by production of hydrogen trough gasification of biomass. Moreover, hydrogen could also be produced by natural gas steam reforming and indirect use of biomass via production of synthetic natural gas (SNG). Another option for utilisation of biomass in the oil refining industry is gasification followed by Fischer Tropsch synthesis. This process could be placed on-site at the refinery or off-site, closer to the biomass feedstock. To maximise the production of Fisher Tropsch diesel and improve the efficiency, the by-products from the process, naphtha and wax, could be further utilised in existing refinery processes.

Results from the interview with the case company for the oil refining industry, Preem AB, show that they considers biomass as a raw material that could be used in their processes, since this offers a new business opportunity and the company seems eager to be an early mover in the market for green diesel [18]*. On the other hand this can also be regarded as a matter of survival for Preem AB, since many European oil refineries of the same size as Preem AB's refinery in Gothenburg have faced bankruptcy lately [18]*. Preem's strategy for the future consists of two parallel paths: developing the Gothenburg refinery towards the production of green diesel and increasing the complexity of the Lysekil refinery for refining of crude oil [18]*. This strategy includes a recently started biomass-based hydrotreating process in Gothenburg, which is regarded as a step between the first and second generation renewable fuel, i.e. fuel production based on gasification. Karlsson and Nyström [18]* explain that regarding the development of gasification, they consider cleaning after the process as a huge challenge which demands co-operation by industry, universities and the government, in order to reduce risks and exchange competencies.

Calculations for Preem AB´s refineries in Sweden show that replacement of the total hydrogen demand through gasification[7] of solid biomass would demand approximately 1.2 TWh/year at Gothenburg refinery and 6.60 TWh/year at Lysekil refinery. However, if hydrogen is produced through gasification of pyrolysis oil, i.e. including a pyrolysis pre-treatment step for the biomass, biomass requirements of 1.7 TWh/year in Gothenburg and 9.2 TWh/year in Lysekil are needed. With regard to hydrogen production trough steam reforming of SNG, supplying Preem's refineries in Gothenburg and Lysekil would require approximately 1.8 and 9.5 TWh/year biomass respectively. It is important to stress that these requirements are based on the current total hydrogen demand and on the assumption that it is possible to replace the whole demand. More detailed calculations about biomass gasification in Gothenburg are found in Johansson et al. [7].

The adjustment of the refinery in Lysekil for optimal use of crude oil, is motivated by the belief that there will continue to be a market for liquid fuel from crude oil, due to crude oil's efficiency as an energy carrier and its relative low cost [18]*. Since biomass is a limited resource Preem AB's plan is a 30% blend of green diesel into fossil diesel. Calculations shows that the production of 100 000 m^3 diesel, with a 30% renewable content, will at the refinery in Gothenburg refinery demand 1.15 TWh/year of raw tall oil, requiring 55% of the total Swedish raw tall oil production. Although tall oil is the first biomass-based raw material Preem AB is investigating other options are for example used oils and oil from algae [18]*.

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[7] Calculations are based on assumptions presented in [13] and for gasification for hydrogen production updated with result from [7].

3.4. Future prospective

Even though current policies try to stimulate use of biomass as a source of energy and several technological options are possible, none of the case companies believes that biomass will increase significantly in the Swedish industrial energy system over a longer time perspective. The reason for this is that biomass is regarded as a limited resource and neither SSAB Strip Products nor Preem believe that biomass could represent a large-scale substitute for the currently used fossil fuel. The case companies' views on biomass as a limited resource are in line with the result that is obtained when calculating the biomass demand from the previous described technologies in comparison with the future increase in biomass supply in Sweden until 2020.

The biomass demand for the technological options that can be seen in Fig. 1 show a large share of the biomass considered to be available for new actors in 2020. However, it is important to note that the potential described above is the highest possible demand; some of the technologies may be implemented in a smaller scale, needing less biomass. Furthermore, it is not possible to implement all technologies described in section 3.1-3.3 in one facility within the case company at the same time as some of them compete for the same resources or supply the same feedstock.

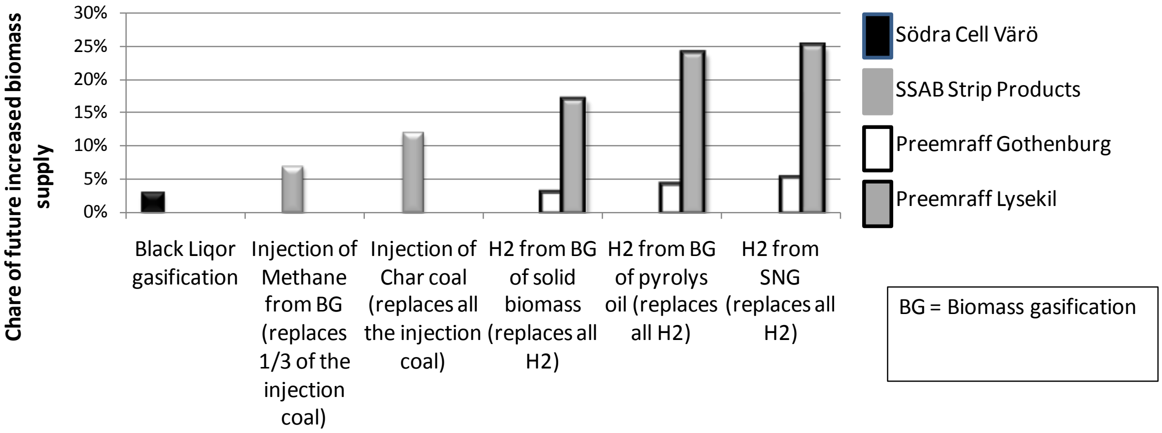

Fig. 1. The share of future increase in biomass supply that is needed if a technology to increase biomass use/refining would be implemented at each case company. Note that this is the highest biomass demand. Options not requiring increased import of biomass or do not significantly affecting the CO_2 balance at the case company are not included.

Adding the biomass demand for hydrogen production from biomass gasification at Preemraff Lysekil and Gothenburg, injection of pulverised charcoal at SSAB Strip Products and black liquor gasification at Södra Cell Värö would require 34 % of the total increase of biomass supply in 2020 (38 TWh/year [9]). For the pulp and paper industry the only option that requires increased import of biomass is included, in the oil-refining industry the hydrogen production alternative with the most efficient use of biomass is included and for the iron and steel industry the option substituting the largest amount of fossil fuel is included.

Despite the somewhat pessimistic view of biomass potential as a future feedstock the representatives we met at both Södra and Preem appreciate that the companies they represent have chosen to become actively involved in environmental issues. In a longer perspective, Södra hopes that they still can use biomass for their current core business, pulp production, and additionally for production of e.g. composite material, cloths, chemicals or medicine [14]*. SSAB Strip Products does not believe that any biomass technology will be implemented at their facility. Instead they believe that available excess heat will be integrated with surrounding energy systems, in which biomass could be one of several feedstocks [17]*. In contrast, Preem´s strategy for the refinery in Gothenburg to remain competitive is to modify existing infrastructure for production of both renewable and fossil diesel. Preem fears that competition for biomass as a feedstock between different industrial sectors will be more important in a longer perspective than competition within the oil refining industry [18]*.

4. Discussion and Conclusions

The study shows several possibilities for increased use and refining of biomass in the three industries studied: Kraft pulp mills can export by-products either unrefined or refined into higher value added products. Additionally, oil refineries can import biomass feedstocks for the production of green diesel or hydrogen and integrated steel plants can use biomass-derived products as reducing agent in the blast furnace. Finally, all three industries have options to export excess heat to biorefineries with demand for heat.

This study shows that technologies for increased use and refining of biomass implemented at three energy-intensive industries would require up to 34% of the Swedish potential for increased supply of biomass in 2020. Although estimations of the increase in biomass supply is very uncertain, the fact that biomass is a limited resource have been recognized by the case companies. Hence, it is important to evaluate the options in relation to alternative scopes of use for the biomass before any new investments are made. One important issue to address is how the biomass is most efficiently used in order to reduce CO_2 emissions. Furthermore, the market for biomass is global and biomass price and expected profits for the purchaser will probably have an impact on where the biomass will be used in the future. There are large differences in required amounts of biomass for the different industry sectors, which could affect the probability of realization of the options. Companies located near harbours may have a financial advantage on the global biomass market since transportation costs can be reduced.
Finally, it is vital from an environmental point of view that the biomass resources are exploited in a sustainable way with re-planting and responsible land-use.

Regarding the case companies, both Södra Cell and Preem are investigating possibilities to introduce new technologies for increased use and refining of biomass and have identified this as a new business opportunity. On the other hand, SSAB Strip Products considers biomass a too limited resource, especially compared to coal and coke, which the company uses today, and is not interested in investing in facilities not related to its core capabilities. The interview results for Södra and SSAB Strip Products are in line with the results from the calculations. For Preem, the calculations indicate that a large amount of biomass would be required for the different options (see Fig 1), which would constitute a barrier for implementation. In the interviews the company has an optimistic view on implementing options for increased use and refining of biomass. However, these options are based on using existing infrastructure but adopting it to biomass based feedstock and are thus not the same technologies as in our calculations.

This study concludes that opportunities for Swedish energy-intensive industry to increase use and refining of biomass exist, but with many potential barriers for implementation. However, the study points towards a trend in Swedish energy-intensive industries; the industries are more aware of their CO_2 emissions and seek options to be more climate neutral.

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Is Bioenergy the Big Bad Wolf in the Forestry Sector? A discussion about the sustainable supply chain management role in bioenergy systems

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Abstract: The paper's aim is to use a bioenergy supply chain management approach in order to reinforce sustainable development in a likely scenario of competition between bioenergy and the production of other goods extracted from wood. This competition is perceived as a threat because it may lead to an increase in raw material and energy prices and reduce the competitiveness of the European pulp & paper industry compared to other regions of the world. The key question is then: is bioenergy the big bad wolf in the forestry sector or an opportunity for improving the sustainability of biomass-based supply chains? The work assumes bioenergy as an opportunity because a systemic approach to bioenergy systems' optimization can lead to performance improvement beyond the boundaries of a single company and increase the sustainability aspects of the entire network. The results are based on content analysis conducted by a literature review and information gathering from relevant publications in the field.

Keywords: *Bioenergy Systems, Sustainable Supply Chain Management, Systems Analysis.*

1. Why sustainable supply chain management is important?

The energy price shocks of the 1970s served as a major incentive to revisit energy practices. As a result, several nations launched efficiency programs and tried to develop solutions to replace hydrocarbon fuels. However, for some time low oil prices has been a barrier and preventing renewable energy from taking up on large commercial scale [1]. More recently, renewables gained new momentum as a result of favorable policies, such as in the EU where the target is to reach 20% of renewables by 2020. Nevertheless, the development of renewables is by no means given. The increasing availability of gas and the delayed removal of fossil fuel subsidies could again hamper the competitiveness of renewables for many years to come [2].

At present, we are facing a new crisis based on the depletion of natural resources, expected scarcity of fossil fuels, increasing energy prices worldwide, increasing global competition for fuels, and global efforts to reduce greenhouse gas emissions. In this context, energy from renewable sources remains a key component to mitigate environmental risks and increase energy security. According to the International Energy Agency, renewable energy sources – such as wind power, solar energy, hydropower and biomass – responded for only 12.9% of the global primary energy supply and 18.7% of the global electricity production in 2008. IEA calculates that, without new policies in place, global primary energy demand could increase by 45% by 2030 compared to 2006 levels. Transportation could account for 57% of the global primary oil consumption, compared with 52% now and 38% in 1980. The agency emphasizes the need for policy actions in order to change the so-called *"business-as-usual"* scenario and foster an increased share of renewables in the future global energy mix [3].

Certainly, the need to shift energy systems towards renewable sources is well recognized. This tends to put a lot of emphasis on technology development. However, intensifying the use of renewable energy systems is not only a technological challenge. To optimally explore constrained renewable resources (e.g., forest-based biomass), technological management challenges have to be faced. This paper assumes that a strategic use of bioenergy supply chains, in particular the use of the concept of sustainable supply chain management in the forest-based bioenergy systems can improve the sustainability aspects throughout the chain.

1.1. Sustainable Supply Chain Management

Lambert *et. al.* (1998, p.1) describes supply chain management (SCM) as *"the integration of key business process from end-user through original suppliers, that provides products, services and information that add value for customers and other stakeholders"* [4]. In 2001, Mentzer *et. al.* (2001, p.18) has outlined a complementary definition that defines SCM as *"the systemic , strategic coordination of the traditional business functions and the tactics across these business functions within a particular company and across businesses within the supply chain, for the purposes of improving the long-term performance of individual companies and the supply chain as a whole"* [5]. Nowadays, the Council of Supply Chain Management Professionals (CSCMP) describes supply chain management as *"the planning and management of all activities involved in sourcing and procurement, conversion, and all logistics management activities. Importantly, it also includes coordination and collaboration with channel partners, which can be suppliers, intermediaries, third party service providers, and customers. In essence, supply chain management integrates supply and demand management within and across companies"* [6]. Svensson (2007, p.263) and Cater & Rogers (2007, p.368) argue that in order to SCM become sustainable it should integrate and equalize economic profit, environmental and social goals to long-term performance of individual companies as well as their supply chains [7] [8].

In this context, the sustainable supply chain management concept in general is understood as the management of services, products and raw materials along the chain – from suppliers to manufacturer and/ service provider to final consumer and back again in the cycle – with improvements to the environmental and social goals. The interaction between suppliers and consumers is understood by this work as the flows of energy, materials, and greenhouse gases emissions from suppliers to consumers.

This study assumes that if forest-based biomass is to compete with fossil fuels, there is a need to create more reliable and constant supplies of bioenergy on a long-term basis and a more efficient distribution to points of consumption in more sustainable ways.

1.2. Methodological approach

The paper's originality is the use a bioenergy supply chain management approach instead of the commonly used *"Command & Control"* mechanisms (i.e., legal standards, taxation and/or subsidies) in order to reinforce sustainable development in a likely scenario of competition between bioenergy transformation (e.g., heat and electricity) and the production of other goods extracted from forest-based biomass.

In order to complete this work, the methodological approach was based on a content analysis conducted by a literature review and information was gathered from relevant publication found on hard copy publications and electronic journals provided by well-known publishers (e.g., Willey and Elsevier).

1.3. Work Structure

This paper is divided into 4 main sections. First section has introduced the sustainable supply chain management concept used in the paper and background information about the management challenge and the methodology used in the study. Second section presents the findings related to biomass as an important renewable source and the significance of adding value along its production chains. The third section discusses the need to understand the re-distribution of available resources in an increasing competitive environment. Finally, the forth section indicates an option to shift from the perspective of bioenergy as a threat to the perception of opportunity in the forest-based supply chain.

2. Forest-based biomass: now and beyond

The EU RES Directive aims to promote the use of energy from renewable sources. Each Member State has to achieve a specific target so that, as a whole, the EU shall have 20% of the total energy based on renewables by the year 2020. The Directive sets a common vision for the EU. It also contains a roadmap to cut down 20% of the EU greenhouse gases emissions [9]. The Directive sets an important framework alongside with the European Strategic Energy Technology Plan (SET-Plan) for reducing the EU's oil dependence, which is also illustrated by the target set for the transport sector: 10 % biofuels by 2020. Although the EU is expected to fall short on the 2010 target of 5.75% biofuels, it is expected to reach beyond the 2020 target.

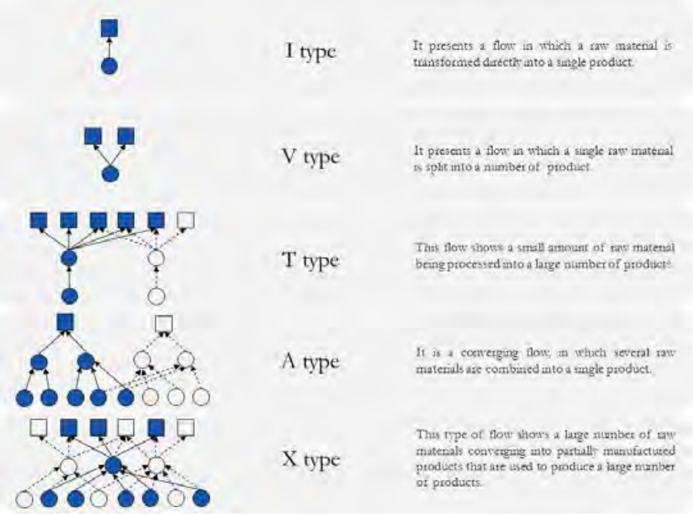
In this context, renewable energy is assuming an increased prominence among Member States, mostly motivated by security of supply as well as greenhouse gases emissions reduction objectives. Among the Member Countries, Sweden is often regarded as one of the frontrunners concerning the development, promotion and implementation of renewable energy policy and technology. The Swedish mandatory target for the share of energy from renewable source in gross final consumption of energy in 2020 is 49%. On the other hand, the proportion that is forecasted by the Swedish Energy Agency (SEA) sums up to 50.2% in the same period. This means that Sweden shall reach beyond the binding national target by 1.2% and this trend can be traced in the considerable expansion of renewable energy of the last years [10].

In 2008, the Swedish share of renewables was 44.1%. This corresponds to an excess of approximately 2.5% already above the indicated trajectory for 2011-2012 period [11]. A very important part of this success lies on the national expansion of the bioenergy sector during the last few decades [12].

The RES Directive is not the only driving force affecting bioenergy utilization. Ling and Silveira (2005) consider that current policies being applied in the EU enhance the condition but there are also other important forces such as internationalization of the bioenergy segment, integration of bioenergy systems with other transformation processes, and the fact that bioenergy is becoming a mainstream alternative. In line with this perception, a biomass study carried out by McKinsey and Pöyry for the Confederation of European Paper Industries (CEPI) indicates that meeting bioenergy targets set by the RES Directive could lead to a wood deficit of 200 up to 260 million m^3 in Europe by 2020. This has worried, for example, the pulp & paper sector which is afraid of potential competition in the markets for raw materials [13].

Bioenergy contribution has grown from the second largest source of energy in 2003 to the leading position in the final energy use in Sweden. In the last couple of years, the bioenergy share has increased from 28.6% in 2007 to 31.7% in 2009 and it is still growing. As a result, biomass is not just an alternative but has turned into a major reliable energy source [11].

An important aspect of the bioenergy segment in Sweden is the fact that most of the biomass used for heat and electricity generation in the country comes from forests. Despite of its importance in the transition to a long-term sustainable energy system, the strategic use of bioenergy supply chain management and its overall impacts in the forestry sector are still very much restricted to cost effectiveness and excellence in customer service in pursuit of profit and competitive advantage [14] [15] [16] [7]. As a result, the majority of the current models for analyzing it do not consider the overall value of a supply chain [17]. They frequently focus on improving the individual performance of the various actors along the chain (e.g., company level approach). This is because there are a variety of flow structures and each one of them has a direct impact in the supply chain organization, which makes difficult to foster overall performance. Figure 1 presents a variety of flows based on the work of Haartveit *et al.* (2004) and their specific characteristics that directly define supply chain structure configuration and its complexety [18].



I type	It presents a flow in which a raw material is transformed directly into a single product.
V type	It presents a flow in which a single raw material is split into a number of product
T type	This flow shows a small amount of raw material being processed into a large number of products
A type	It is a converging flow, in which several raw materials are combined into a single product.
X type	This type of flow shows a large number of raw materials converging into partially manufactured products that are used to produce a large number of products.

Fig. 1. Types of flows structures within a supply chain adapted from Haartveit et.al.(2004)

Independent from its configuration, the supply chain concept intuitively implies a network of actors divided into a variety of organizational structures operating at different stages/structures/levels and combining efforts in order to deliver products to customers. This means that management and control of flows involve collaboration among actors and, as any complex system structure, the supply chain might need several strategies and information flows operating at different structure levels. At an overarching level, this includes general information such as inventories, statistics, policy targets, etc. This information could be in the public domain while specific information (e.g., detailed information about a region) may require further investigation. At the company level, there are strategies related to the business model, market competition, planned production, price mechanisms, etc. These strategies are not in the public domain but reflect the response of various actors to opportunities in the market [17] [18]. As a result, an effective strategy for supply chain management depends on the specific characteristics and complexity of the chain under study.

It is clear that a renewable energy source can play a major role in addressing environmental degradation at large. This is because a renewable source such as biomass, if used in a sustainable way, is not depletable and produces less greenhouse gases emissions than fossil fuels. However, an important finding was that supply management improvements could add value along various production chains to reinforce, optimize, and operate the whole network and achieve a sustainable development.

3. From threat to opportunity: a discussion

Among the renewable energy resources, wood is one of the most important renewable sources for achieving the 2020's target in the EU. Today in Europe, wood already represents over 50% of the total renewables [19]. In addition, wood is expected to continue playing a key role in the development of renewables in the continent. However, increasing extraction of forest biomass for energy purposes could have impacts on other segments of the forestry sector as a whole. The current perception among some market actors is that meeting bioenergy targets set by EU will only be possible by increasing the biomass extraction from forest [20].

In the short term, strategies endorsing *status quo* practices could lead to enlarged extraction of forest resources. Although this could result in immediate direct positive benefits in the local economy (e.g., work generation and income), it could also lead to loss of biodiversity as well as environmental impacts on soil and water that can compromise the total resource productivity in the long run.

In the middle run, competition between bioenergy use and the production of other goods extracted from wood may induce to an increase in raw material and energy prices and reduce the competitiveness of the European pulp & paper industry compared to other regions of the world (e.g., South America, especially Chile and Brazil).

In the long term, intensified competition among different segments of the forest-based industry could lead to the closing down of industrial plants following on production relocations. This implies lay-offs, initially to rescue companies' productivity levels, but eventually to deal with competitiveness at an international scale.

By being a traditional and well-established sector from the start, the forestry sector – especially the pulp & paper companies – perceives bioenergy targets more as a threat than an opportunity. In this perspective, the RES Directive and, especially, forest-based bioenergy becomes *the big bad wolf in the forest.* If perceived negatively, there is risk that administrative barriers more than financial and technical obstacles may hold back or – at the least – delay further bioenergy development, above all in the pulp & paper segment.

Considering that a *"sustainable energy solution needs to be motivated beyond their technical performance and economic efficiency, and become attractive in the context of regional development, environmental and social benefits"* [21]. It is necessary to understand the re-distribution of available resources and the process along the bioenergy value chain network in order to tackle the potential obstacles (i.e., administrative barriers in the pulp & paper sector).

New actors and new configurations of value chains can be perceived as a threat by conservative segments because they can – in a very short time – increase the demand of raw materials, increase competition in an already aggressive environment, change land use, and create an uneven biomass supply. However, this is also an opportunity for creating new alliances, facilitating transitions, and opening new markets. In order to shift from the perspective of threat to the perception of opportunity, it is necessary to understand the process along the bioenergy value chain network and re-distribution of available resources. This is because a performance frontier of any given supply chain should be understood as a system performance due to its complexity and interconnected nature (see Figure 2). In doing so, the real competitive position or the performance frontier of a supply chain becomes based on the supply chain's weakest link [17].

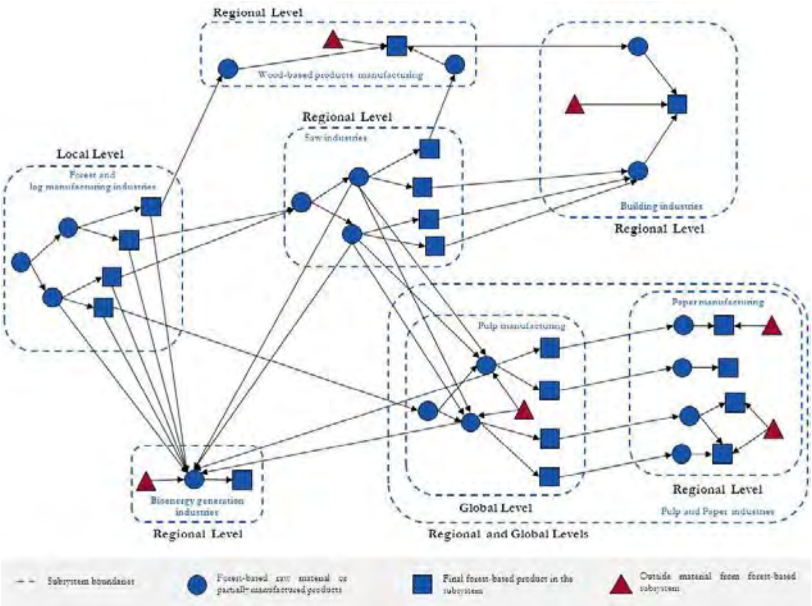


Fig. 2. Generalized structure of the forestry industry supply chain

As the Figure 2 has presented, the forestry industry supply chains are complex and characterized by multitude of flows resulting in many products and services, as well as by-products along the chain. In addition, Haartveit *et al.* (2004) describes that the roles of individual actors in the supply chain are highly dependent on the supply chain own structure and specific characteristics. This is because material and information flows, as well as the product flow can vary in levels (i.e., from local to regional and/or global levels) and structure.

The initial question is bioenergy is the big bad wolf in the forestry sector or an opportunity for expansion, given the uncertainty of future costs of oil. In any case – threat or opportunity – , it is clear that a systemic approach in such complex network makes the strategic configuration of the bioenergy supply chain a critical task for management decisions and a major administrative challenge [16] [7] (22].

4. Conclusion remarks: a way of getting through

The rapid expansion in global trade of biomass (i.e., wood pulp) is expected to continue over the next years. On the other hand, a likely new international biomass commodity (i.e., wood chips and pellets) could also rise as direct result of more countries favoring renewable energy and relatively inexpensive local supplies of biomass reaching their limits. In this respect, the new competition may well rearrange the forestry industry supply chain structure presented in Figure 2 by redefining the boundaries' levels.

In short, the devil is in the details. This is because forthcoming competitions will strength the need for actions. At the same time, external triggers (i.e., environmental and social standards) placed by governmental agencies, stakeholders and consumers are going to continue playing a major role. By doing so, a sustainable bioenergy system has to become focused more in a systemic approach process and less in single individuals' efficiency, which is currently in place. In other words, a systemic approach means that bioenergy systems' optimization must aim at the overall supply chain by asking for performance improvement beyond the boundaries of the single company in order to improve the sustainability aspects of the entire network. An increased system understanding will allow not only a better estimation of the potential effects of the RES Directive on existing supply chains but also an evaluation of the improvements that are necessary while planning future bioenergy supply chains. Moreover, it would assist us in identifying challenges in the bioenergy sector and leverage points in its system that could be used to foster climate change mitigation and energy security.

This study is the starting point of the author's doctoral research and for that reason has its limitations which open opportunities for future research. Like all content analysis the empirical validity of the bioenergy as an opportunity to the forestry industry needs to be tested in case studies. Future studies should examine not only operations, logistics, structures and other activities but also the flows of material, energy and greenhouse gases emissions to comprehend if there are other important aspects to be considered by a sustainable supply chain management for bioenergy systems.

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Bioenergy production in the Toruń biogas plant (Poland)

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Abstract: This paper describes the work of the biogas plant in Toruń (Poland). Biogas has been obtained from municipal waste since 1998 at the Municipal Waste Landfill Site in Toruń. Biodegradable waste constitutes about 45-50% of the waste dumped into the site. These municipal wastes have been disposed of at this site since 1964. Biogas is obtained during approximately 8000 hours per year from 62 wells. The highest methane contents in biogas (>60%) were achieved between 2000-2003 and in 2008. As a result of biogas combustion, thermal and electrical energy is produced. The total quantity of energy produced during a year is 11 000 MWh, but higher amounts were achieved in 2004 and 2008 (nearly 12 500 MWh). The heat and electrical energy obtained is supplied to the city inhabitants by the Power Station Toruń S.A. and the Thermal Energy Station Toruń Co. Ltd.

Keywords: *bioenergy, biogas, Toruń, municipal wastes*

1. Introduction

Biogas is one of the most important renewable energy sources [1,2]. Known also as a waste site gas, biogas is heavier than air. Regardless of the substrate, it has two major components – methane and carbon dioxide. Biogas is obtained from waste biomass [3,4]. This covers a wide and difficult to manage range, starting from forest and farming wastes (including fermented liquid manure) through sewage sludge to municipal wastes [5,6].

The Municipal Waste Landfill Site in Toruń (Fig. 1) is designated, mostly, for municipal wastes. The site is located in the northern part of the city, in the industrial district, 10 km away from the city centre. The location complies with the local spatial management plan -in the area designated for the municipal waste disposal complex. The site is located on a plain with little altitude differences, with ground declination toward the south and the current Vistula Valley, located 3.5 km away.

Fig.1. Location of biogas installation.

The wastes have been disposed of at the site since 1964. Originally solid and liquid wastes were dumped without any formal or legal agreement in an unregulated manner. Since its

modernisation in 1993, the waste landfill site has been functioning as a legally sanctioned waste site for the city of Toruń.
The total area of the site is 12.1 ha, including:

- two landfill sections of total area of 8.5 ha, exploitation time 1964/86 and 1992/95 – there are no safeguards against leaches to underground waters; these are the areas the waste site gas-biogas is obtained from,
- post-discharge terrace of total area of 1.7 ha; until 1991 in this area there used to function two partially proofed landfill sections for industrial post-discharge sludge,
- landfill section of area of 1.9 ha, used since 1995, so called "basin" – proofed with geo-membrane HDPE 1.5 mm with a built-up sewage drainage system.

On December 31st 2009 the waste site was closed. It is estimated that biogas from the dumped waste will be exploited for the next 15-20 years. In the near future a further biogas installation is to open at a new, nearby waste site.

1.1. The type and amount of waste dumped at the site

The landfill waste site in Toruń is a target place for municipal waste disposal as well as the disposal of industrial waste, qualified to be disposed there, as a result of the decisions of the competent administration authorities. At the site there are no wastes considered to be dangerous substances according to environmental protection regulations. Table 1 shows the composition of wastes. The major components of municipal waste are organic wastes, which are subject to the natural process of biodegradation. In Toruń biogas is obtained from non-segregated waste, which is a result of the lack of pro-ecological management in the 1970s in Poland. The biodegradable wastes constitute about 45-50% of the stream of municipal wastes. The amount of dumped waste is estimated at 2 500 000 Mg.

Table 1. The composition of municipal waste of the city of Toruń (%).

Fraction	Year		
	1991	2000	2009
Plant food waste	25.2	14.8	14.4
Animal food waste	4.3	1.0	0.0
Other organic waste	3.4	8.8	14.2
Paper and cardboard	13.4	18.7	12.3
Plastics	5.1	19.9	11.2
Textile waste	4.4	3.5	2.5
Glass	6.9	12.0	7.6
Metals	3.4	2.8	5.4
Other mineral waste	6.9	4.7	3.4
Fraction < 10 mm	27.0	13.8	29.0

2. The system for obtaining biogas in the Toruń biogas plant

In 1991-1992, within the framework of the programme to improve the natural environment, research was conducted in Poland to examine 15 municipal waste landfill sites in order to check the amount and quality of biogas. At the waste site in Toruń, 6 gas wells were built that ran 16 m deep into the bowl of the site. After 800 hours of work, the mean parameters of obtained biogas were satisfactory (61.1% CH_4, 28.8 CO_2, 0.1% O_2). The initial analysis, as well as the further research, confirmed that the biogas produced at the municipal waste landfill site in Toruń is adequate for commercial use.

In 1993 a request was made for financial support from the Thermie programme in order to build a pioneering installation for obtaining and utilising waste site gas in Toruń. With the support of the European Union Commission, a contract was signed to realise this project and to finance it at 30% of net costs. In order to build and operate a modern waste site gas utilisation unit, a new company was established – Biogas Investor Co. Ltd. The investment was partially financed by the National and Voivodship Environmental Protection Fund as well as by 30% subvention from the European Union, allocated as a part of the Thermie programme.

The gas from waste landfill piles started being used on 10 September 1997. On 10 September 1999 additional works were finished and a use permit was obtained. In 2001 the maximum technical and production parameters were achieved. The gas production covered 11 ha of the waste site near Kociewska Street in Toruń. In this area 40 gas wells were drilled (Fig. 2), which are boreholes 16 m deep and suction pipes were laid. The system is equipped with a technical biogas suction apparatus (MPR), gas mains, thermal-electric mains (CHP) of power 550 kW_e and 770 kW_t. The thermal-electric power station is connected to the heating and power network. The whole system is totally automatic and computer directed. In April 2002 a further 3 ha of the waste landfill site were covered by degassing equipment as 12 new biogas wells were built and utilised as a part of the system.

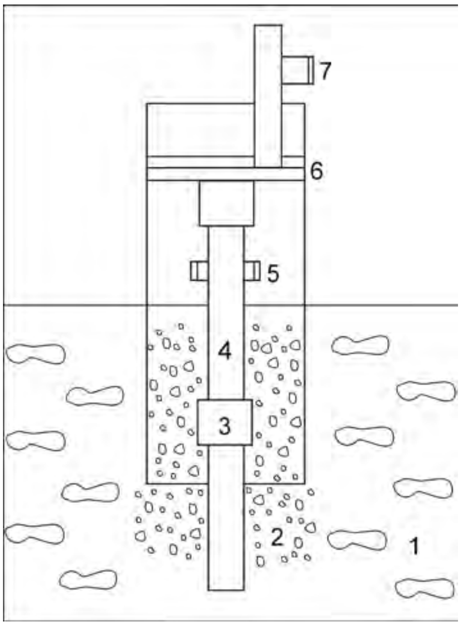

Fig. 2. Construction of wells: 1 – waste, 2 – gravel, 3 – plug-in muff, 4 – degassing pipe, 5 – gas intake, 6 – gas proof cover, 7 – pipe line.

In January 2004 the second power-producing unit of power 324 kW_e was opened, which marked the end of the first stage of development of the system for obtaining and utilisation of waste site gas. During this stage, 12 wells, 2 788 m of gas pipes, a transformer station, wire line NN were built and a power-generating system was bought. Since 1 March 2004 the biogas system has been working at the power of 698 kW_e and 770 kW_t – utilising 440 Nm^3/h of waste site gas obtained from municipal waste piles of 16 m height and 14 ha base.
In 2007 and 2009 respectively 17 and 5 new wells were built. In 2009 12 wells of low efficiency were closed. Currently, biogas is obtained from 62 wells.

3. Biogas production in the Toruń biogas plant

The biogas obtained from the degassing wells is transported via gas pipes to an MPR module, where suction and pumping equipment, a gas composition analyser and flow meters showing the flow in particular gas wells**.** Transported from an MPR module by a common pipe, gas from individual wells is then sent to the decanter, where water contained in the biogas is outdropped. After drying, depending on the requirements, biogas is directed to the module generating electrical power and heat or to the power generating system operating since 2004. The composition of gas taken from each well is constantly monitored using the stationary analyser SATGAS 800 (S.A. TechnikAS, Denmark). The content of CH_4, CO_2 and O_2 is analysed, the remaining part is assumed to be N_2. The collection of biogas is fully controlled: in situations where the methane concentration decreases below 40% or oxygen concentration increases above 0.3%, the well is closed.

Fig. 3 represents the amount of biogas obtained between 1998 and 2009. The least amount of biogas was obtained at the first start-up (1998), and in 2002 when maintenance work was carried out. Since 2003 when 12 new wells were opened, the amount of obtained biogas has risen by 50%. The highest methane content in biogas (>60%) was achieved in 2000-2003. Since 2004 a decrease in methane content has been observed, which is contributed to the ageing of resources from which biogas is obtained. This phenomenon is partially caused by the common use of virtually non-degradable foil bags for rubbish collection in Poland. Having arrived at the site, these bags create a specific geo-membrane, making it difficult for nutrients and water to penetrate into deeper parts of the waste site. Water content is essential to the development of microorganisms. When the content of dry matter is higher than 40%, the life processes of microorganisms are disturbed, which leads to a lower methane content of the biogas and smaller quantities of biogas produced. One of the solutions aimed at avoiding the geo-membrane issues created by the waste foil is to use a mill to crush waste prior to dumping it onto the waste site. When the methane content drops below 40%, it is planned to use natural gas to aid the biogas stream fed into the engine. This will make the combusted gas more calorific and extend the working lifetime of the biogas site. It will also mean that the power of installed equipment is fully used. Opening new wells as well as closing the inefficient ones leads to increased methane content in biogas.

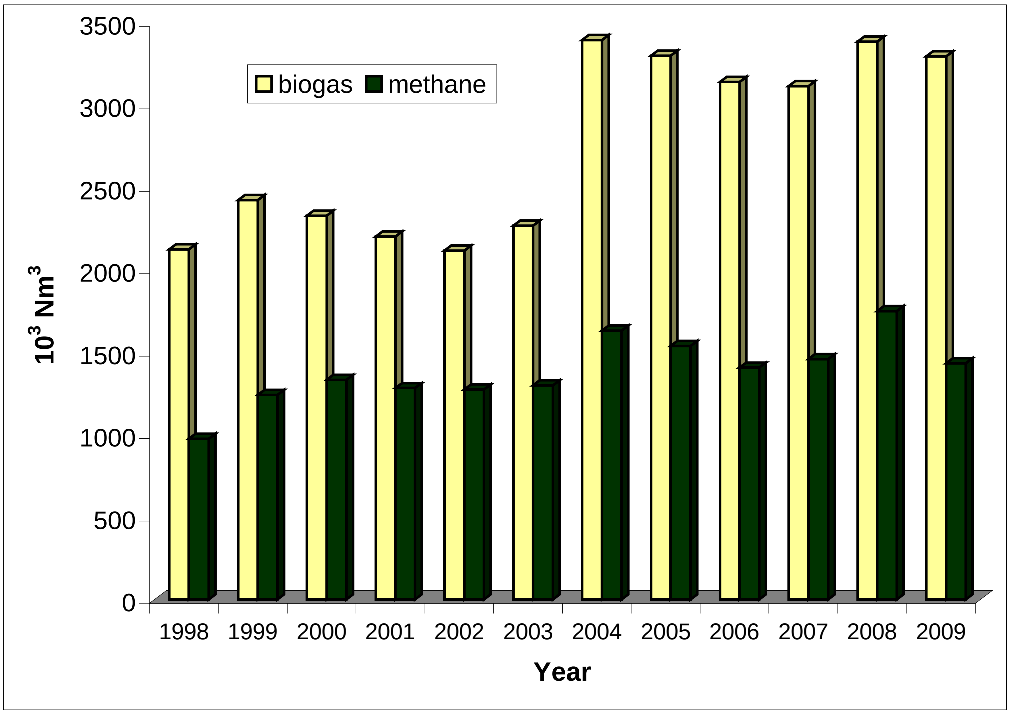

Fig. 3. The amount of biogas and methane obtained in 1998-2009.

Biogas is obtained during 8 000 hours annually. The highest mean electric power generated was achieved during the last six years, which was influenced by the new wells and the second power-generating system being opened. Apart from the first year of start-up (1998), the mean thermal power has remained at the same level. The amount of heat produced was 25% higher than the amount of electrical power over the years 1998-2007. Since 2008 the amounts of heat produced and electric power have been at a similar level (6000 MWh).
The total amount of energy produced over a year stays at the level of 11 000 MWh (Fig. 4), but the highest amounts were achieved in 2004 and 2008 (nearly 12 500 MWh). The obtained heat and electric energy is supplied to the city inhabitants by the Power Station Toruń S.A. and the Thermal Energy Station Toruń Co. Ltd.

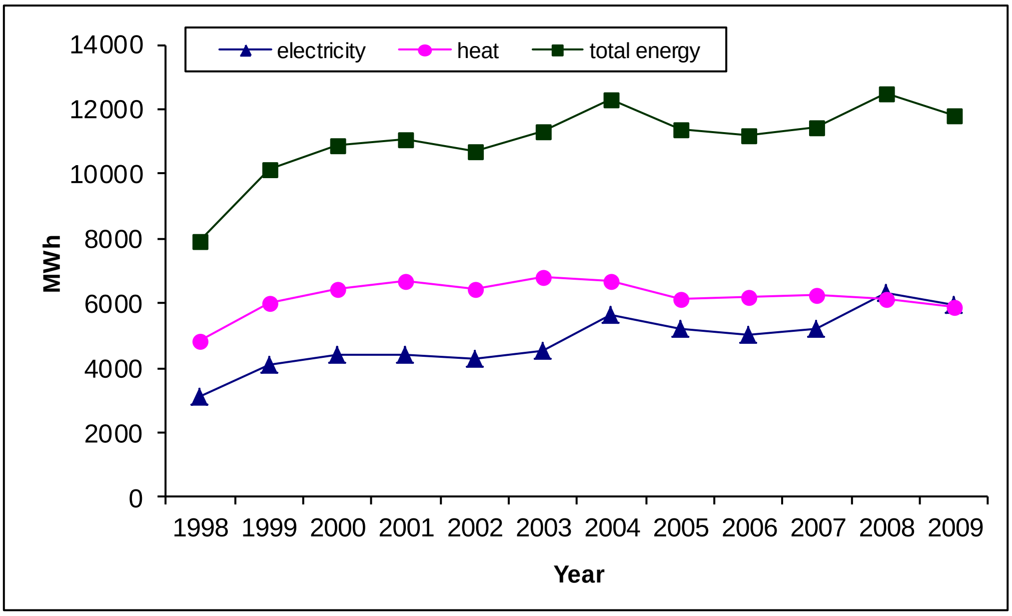

Fig. 4. Electricity and heat prduction in 1998-2009.

4. Perspectives of biogas production in biogas plant in Toruń

During most of the operation time of Toruń landfill installation there was no record of waste deposited there. Apart from the municipal waste, the industrial (hazardous) waste was also deposited, including bricks, tires and chemical waste. Thus, it is only possible to estimate the amount of biogas and methane content in landfil gas using the results obtained so far. Currently, the next twenty wells are to be built at the landfill site in 2011, which is going to increase the amount and quality of biogas in comparison to the previous years (Fig. 3). Within the following years (after 2011) the quality of biogas as well as methane content in LFG will continue to deplete and biogas parameters will be gradually decreasing. In the near future a new biogas installation will operate at a new municipal landfill site in Toruń.

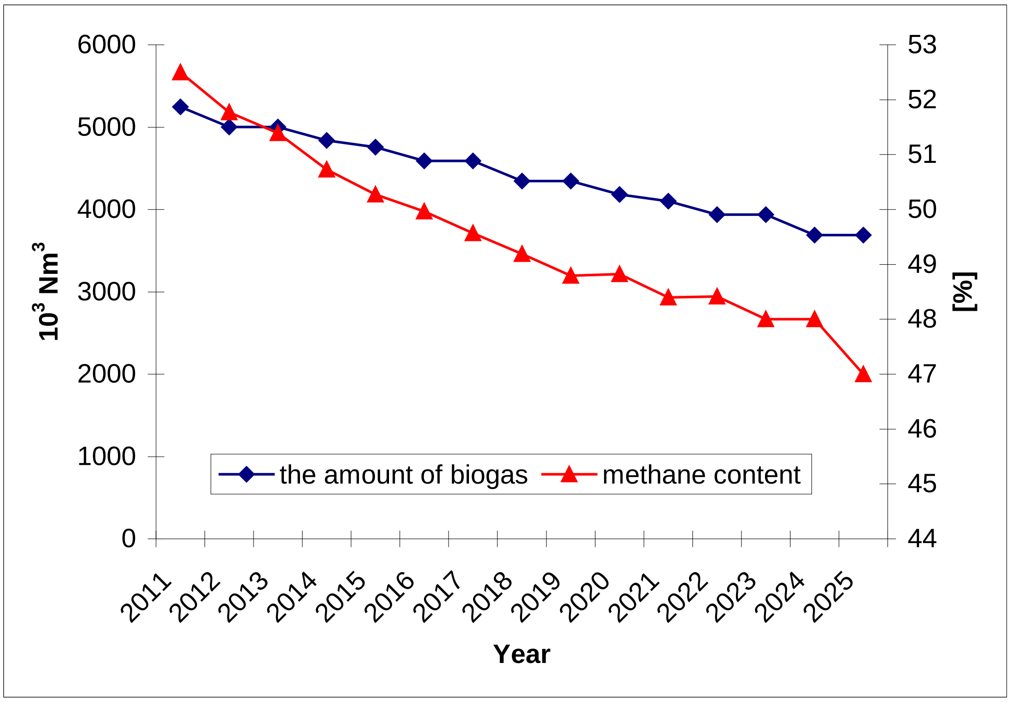

Fig. 5. Estimated amount of biogas and methane content.

5. Ecological effect of biogas production

The biogas installation in Toruń ensures the utilisation of biogas created at the municipal waste landfill site. The major component of biogas – methane – is a highly flammable and explosive gas. A fire at the waste site could be very difficult to control and could last over months, emitting during this time considerable amounts of CO_2, CO, dioxins, furans and soot. Methane is one of the gases with a strong impact on the green house effect. Research has shown [9] that methane emission from waste landfill sites causes the green house effect 25 times higher than that caused by carbon dioxide [10].

Between 1998-2009, 33095283 m^3 of biogas was utilised, including 16626081 m^3 of methane, which corresponds to 75 213 Mg of lignite ("brown coal") or 30815 Mg of hard coal. Combustion of such an amount of coal would lead to the emission of CO_2, CO, SO_2, NO_x and of dusts. Obtained biogas is burnt at the location where it is produced (Toruń), whereas hard coal needs to be transported from the mines (Upper Silesia – 300-400 km), which also involves the emission of harmful gases and increases the cost of its production [11,12].
In the near future it is planned for all the public transport vehicles and the Municipal Waste Management Services vehicles to be fuelled by natural gas with the addition of treated biogas.

The Gas Fuels Station in Toruń was opened in 2008 for this purpose and the first buses are now testing the gas fuel [2,13].

6. Conclusions

Toruń waste site gas recovery and utilisation installation, combines the production of electrical and thermal energy, it is the first one in this part of Europe to be equipped with such modern technology. It eliminates the negative impact of waste site gas emission, which would enhance the greenhouse effect and contribute to ozone layer destruction. Additionally it also produces green thermal and electrical power, which improves the environment of historic Toruń, the Old Town of which is on the UNESCO heritage list [13].
Summing up the possibilities offered by alternative energy sources, it must be stressed that their use seems essential to the country that wants to lead a policy of balanced development. Before we ask how many new coal power plants to build and whether nuclear energy should be developed, we should try to answer the alternative questions – what resources there are in rationalization and how much energy can be provided by renewable, environmentally friendly energy sources.

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Influence of different cell disruption techniques on mono digestion of algal biomass

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Abstract: Due to high growth rates microalgae provide an enormous potential as a source for biomass besides conventional energy crops. The algal biomass can be used for bioenergy production. Anaerobic digestion to biogas is one of the most energy-efficient and environmentally beneficial technologies for alternative energy carrier production. The resistance of the algal cell wall is generally a limiting factor for cell digestibility. In the present work different cell disruption techniques (microwave heating; heating for 8 hours at 100°C; freezing over night at -15°C; French press; ultrasonic) on algal biomass of *Nannochloropis salina* were carried out. The disrupted material was digested to biogas in batch experiments according to VDI 4630. The results indicate that hydrolysis of algal cells is the rate-limiting step in anaerobic digestion of algal biomass. Cell disruption by heating, microwave and French press show a considerable increase in specific biogas production and degradation rate. Compared to the untreated sample the specific biogas production was increased for the heating approach by 58 %, for the microwave by 40 % and for the French press by 33 %.

Keywords: *Anaerobic digestion, Microalgae, Cell disruption, Specific biogas production, Pretreatment*

1. Introduction

Microalgae are microscopic algae and cyanobacteria, which use sunlight and atmospheric carbon dioxide for growth by photosynthesis. The common doubling time is 3.5 to 24 hours in the exponential growth phase [1]. Compared to terrestrial plants with biomass production rates of 20 to 25 tons per ha and year, production rates of more than 100 tons per ha and year have been obtained for microalgae in photobioreactors or in high-rate raceway ponds [2]. Besides the reduction of carbon dioxide emission by using algae as source for biofuels, the production of algal biomass is not competing with conventional agriculture for resources [3], [4].

Anaerobic digestion of biomass to produce biogas is, concerning the multiple utilization, a promising technology for bioenergy production [5]. The fermentation process of organic matter is divided into four steps conducted by different consortia of microorganisms and leads to a gas, which mostly consists of methane and carbon dioxide. The rate of organic degradation depends on the particle size and the access of the microorganisms to the particular components of the substrate at hydrolysis step. For substrates with high amounts of complex biopolymers like lipids, cellulose and proteins the hydrolysis is the rate-limiting step. For easily biodegradable material like dissolved carbohydrates (e.g. glucose) methanogenesis and acetogenesis are rate-limiting due to lower growth rates of the involved bacteria. Algal biomass contains high amounts of lipids and proteins and the resistance of the cell wall is one of the limiting factors for cell digestibility [6]. Many green microalgae possess a thin trilaminar outer wall (TLS) with a very high resistance to chemical and enzymatic degradation based on the incorporation of insoluble, non-hydrolysable aliphatic biomacromolecules called algeanans [7, 8]. For *Nannochloropsis salina* (*N.salina*), a unicellular marine eustigmatophyceae, 1-2% of dry matter was detected as algeanans [8].

Aim of the current work was to show one of the two bottlenecks of *N.salina* biomass as mono-substrate in anaerobic digestion processes: the resistance of algal cell walls to enzymatic hydrolysis beside the unbalanced chemical composition due to low C/N-ratio. Batch experiments of physically disrupted cell material were carried out in comparison to untreated algal cells.

2. Methodology

2.1. Substrate

As substrate for the batch tests algal biomass from *N.salina* was used. Algal biomass was taken from Phytolutions Ltd., Bremen. Algal sludge was harvested by centrifugation to dry matter content of 35 wt%. For disruption the algal biomass was suspended in tap water. The content of total solids (TS) and volatile solids (VS) before and after digestion was determined according to DIN 12879 and DIN 12880 [9, 10].

2.2. Cell disruption

Cell disruption of algal biomass was performed by different physical methods. Experimental conditions were optimized according to different sources (e.g. protein purification, lipid extraction), since less data for pretreatment of algae in biogas fermentation is available [11-14]. The influence of temperature was examined by freezing over night at -15°C, heating for 8 hours at 100°C in a compartment dryer (Function line, Heraeus) and by microwave heating (five times until boiling at 600 W and 2450 MHz; Inverter Grill, Panasonic). For ultrasonic treatment the cell suspension was disrupted three times for 45 seconds at 200 W with 30 kHz output (Sonifier 250, Branson). Influence of high pressure homogenization was examined by French press (French pressure cell press, TermoSpectronic). Two runs at 10 MPa were conducted for each sample.

To validate the disruption success the absorption of centrifuged samples (3 min at 13400 rpm; dilution 1/10) were photometrically measured. The three aromatic amino acids phenylalanine, tyrosine and thyptophan show maximal absorption at 280 nm. These values correlate with the amount of released protein.

2.3. Anaerobic digestion experiments

Anaerobic digestion of *N. salina* was carried out as batch tests according to VDI 4630 [15]. Digestate from a biogas plant (input material maize silage and cattle dung) was taken as inoculum in a ratio of 2/1 compared to the substrate. 7 g VS were appointed from the digestate, 3.5 g VS from the algal biomass. The difference to 400 ml (sample volume) was filled up with tap water. In addition the inoculum was mono-digested. All approaches were investigated in triplicate batch tests at 38°C about a period of 40 days. The produced biogas volume was recorded by measurement of the displacement of a seal liquid (55.2 g/l sulphuric acid; 200 g/l sodium sulphate decahydrate) in 400 ml eudiometers. Dry gas volumes were corrected to standard temperature and pressure conditions (STP: 0°C, 1013 hPa).For calculation of the biogas volume produced by the algal biomass, the inoculum gas volume was deducted.

2.4. Regression equation

An equation (Eq. (1)) was fitted to every sample to illustrate the daily gas production over retention time.

$$V_{STP,dr}(t) = a + \frac{b}{2} \cdot (\tanh(c \cdot (t-d)) + 1) + \frac{e}{2} \cdot (\tanh(f \cdot (t-g)) + 1) \qquad (1)$$

where $V_{STP,dr}$ is the dry biogas volume under standard temperature and pressure conditions, t is the time and a to g are fitting parameters used to describe the progression. Eq. (1) was used to combine the triplicate approaches and to deduct the gas production of the inoculum.

3. Results

All exerted disruption techniques were successful and showed higher absorption compared to the untreated sample (Figure 1). Photometrical measurement due to released cytosolic protein by cell wall deletion was highest in French press treated samples (2.18). Decreasing amounts were detected in high temperature (1.74) and microwave (1.3) samples. Cell disruption in ultrasonic (0.79) and frozen (0.31) samples was less successful.

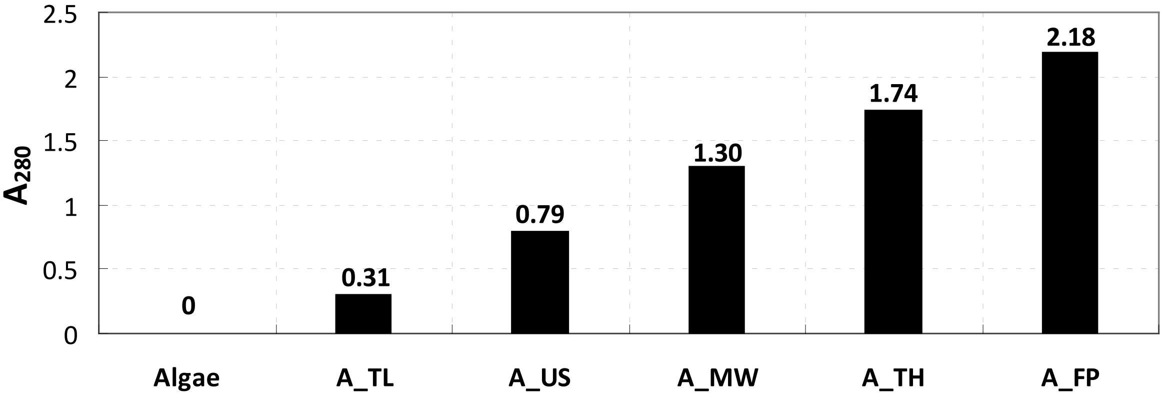

Fig. 1. Absorption at 280 nm (A_{280}) of disrupted cell suspensions compared to the untreated sample (Algae). (A_TL) = low temperature, (A_US) = ultrasonic, (A_MW) = microwave, (A_TH) = high temperature and (A_FP) = French press.

VS were determined before and after anaerobic digestion. The VS degradation was calculated for the substrate (Figure 2). For all disrupted samples the VS degradation was higher than for the untreated sample (25.2%). High temperature (53.8%), French press (54.5%) and microwave (58.7%) were in the same range between 50 and 60%. Lower degradation rates were determined for ultrasonic (41.4%) and the frozen sample (35.4%).

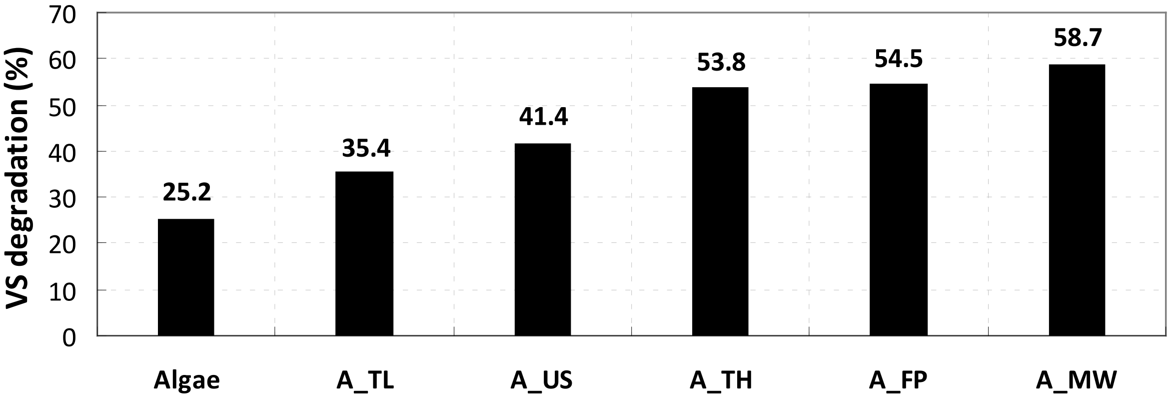

Fig. 2. Volatile solid (VS) degradation of disrupted samples compared to the untreated sample (Algae). (A_TL) = low temperature, (A_US) = ultrasonic, (A_MW) = microwave, (A_TH) = high temperature and (A_FP) = French press.

To compare the digestion progression of the different samples the determined biogas volume was calculated by regression analysis (Eq. (1)). The biogas produced by the inoculum was deducted (Figure 3). High temperature (A_TH) and microwave (A_MW) disruption showed the highest biogas volume and exhibited a saturation curve, where biogas volume of A_TH (2150 mL) was above A_MW (1900 mL). Biogas volume of the French press sample (A_FP; 1800 mL) was highest during the first 13 days and dropped then below A_TH and A_MW. The untreated sample (Algae; 1265 mL) exhibited a plateau after ten days and reached saturation after 30 days. The progression of produced biogas volume for ultrasonic (A_US) and the frozen sample (A_TL) are similar to the untreated sample. Evolved biogas was for A_US (1080 mL) at the beginning higher and at the end below the Algae, whereas the produced biogas volume for A_TL (920 mL) was below the untreated sample for the whole experiment.

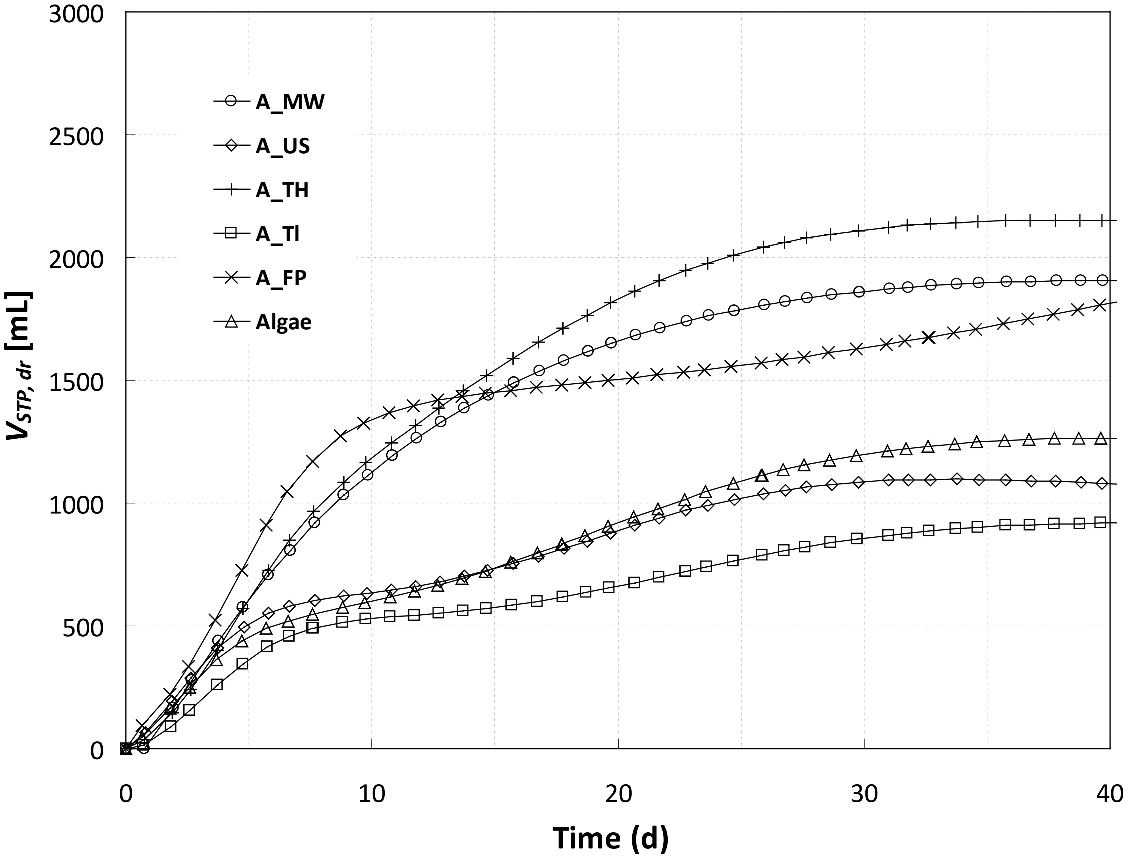

Fig. 3. Biogas production. Biogas volume is indicated in mL as dry gas under standard temperature and pressure conditions (STP, dr). High temperature (A_TH), microwave (A_MW) and French press (A_FP) show different progression and higher biogas volume compared to the untreated sample (Algae). The biogas production progression for ultrasonic (A_US) and the frozen sample (A_TL) is similar, the biogas volume lower as in the untreated sample. VS content was from 3.7 to 3.9 g.

Specific biogas production referred to the added amount of VS was determined for comparability (Figure 4). Compared to the untreated sample (Algae; 347 mL$_{STP,dr}$/g VS) frozen (A_TL; 233 mL$_{STP,dr}$/g VS) and ultrasonic (A_US; 247 mL$_{STP,dr}$/g VS) samples showed lower specific biogas production. In French press (A_FP; 460 mL$_{STP,dr}$/g VS), microwave (A_MW; 487 mL$_{STP,dr}$/g VS) and high temperature (A_TH; 549 mL$_{STP,dr}$/g VS) treated samples the biogas yield was higher than in untreated samples. Due to similar VS content order of specific biogas production is comparable to produced biogas volume stated above.

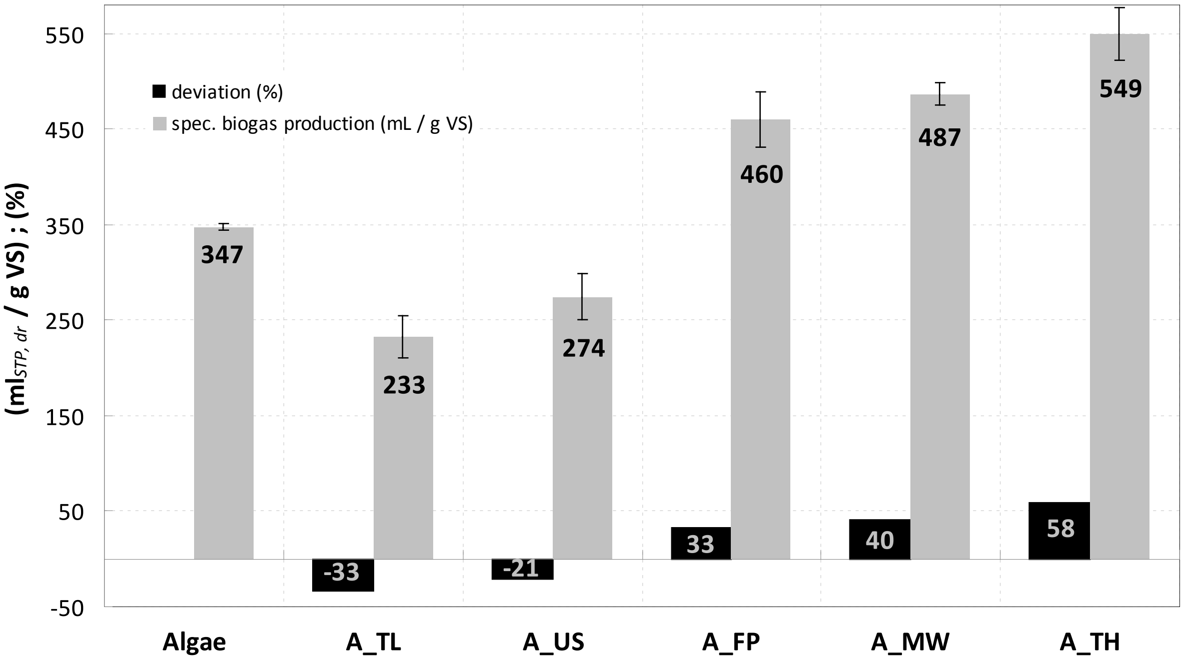

Fig. 4. Specific biogas production of disrupted samples in comparison to the untreated sample (Algae). The freezing (A_TL) and ultrasonic treatment (A_US) showed lower specific biogas production. Increasing biogas yields were determined for French press (A_FP), microwave (A_MW) and high temperature (A_TH) samples. In addition deviation of specific biogas production from the untreated sample was stated.

4. Discussion and conclusions

The results indicate that effectively cell wall degradation is a limiting factor in anaerobic mono-digestion processes of *N.salina* biomass. The validation of cell disruption efficiency shows enhancement for all disruption techniques. Higher VS degradation and lower specific biogas production for the frozen (A_TL) and the ultrasonic (A_US) treated samples are a sign for loss of volatile organic material during cell disruption. Gas bubbles due to cavitation in ultrasonic samples were not yet examined. Microwave (A_MW) and French press (A_FP) samples showed higher VS degradation than high temperature samples (A_TH) with less specific biogas production. Organic material must have been lost in these processes, too.

The appropriated cell disruption techniques showed different efficiency and effects on anaerobic digestion. Thermal pretreatment exhibited the best results as indicated by Chen and Oswald in previous studies, where methane formation efficiency was improved by up to 33% [11]. Ultrasonic treatment improved substrate solubility, whereas a negative effect on specific biogas production was observed as indicated by Samson and LeDuy for *Spirulina maxima* algal biomass [12]. The effect was explained by changes in the chemical composition of the culture media due to cell disruption. VS degradation was differently to the data obtained in this work below the untreated sample. Sonification and high pressure homogenization (French press) are standard methods for disruption of algal and bacterial cells in protein purification. Microwave irradiation gains significance in lipid extraction from algae for biofuel production [13, 16]. For French press and microwave no comparative data of algal fermentation after cell disruption is available.

In this work one major limiting factor for *N.salina* mono-digestion was revealed: the resistance of the algal cell wall against enzymatic hydrolysis. Mussgnug et al. showed that without pretreatment the accessibility to cell disintegration is a Major factor for efficiency of fermentative biogas production [17]. Easy degradable microalgae were found to have no cell wall (*Dunaliella salina*) or a protein-based cell wall without cellulose or hemicellulose (*Chlamydomonas reinhardtii*). Specific biogas production of untreated *D.salina* (505 $mL_{STP,dr}$/g VS) and *C.reinhardtii* biomass (587 $mL_{STP,dr}$/g VS) was in the range of high temperature samples (549 $mL_{STP,dr}$/g VS) with highest specific biogas production after pretreatment in this work. The cell degradation was 100% for *D.salina* and 70% for *C.reinhardtii*. After pretreatment of *N.salina* a maximum of about 60% (A_MW) degraded VS were determined. Consequently, *N.salina* cell wall is resistant against enzymatic hydrolysis and degradability was improved by physical pretreatment. Whether the cell wall is partly resistant against the different disruption techniques or other limitations like low C/N-ratio or ammonia-inhibition affect the low degradability after pretreatment, is ambiguous. A control with 100% cell disintegration was not conducted in this work.

The potential of microalgae for biogas production is depending on the selected strain [17]. Besides the cell disintegration due to cell wall structure, factors like growth kinetics, biochemical composition or biomass yield are important selective parameters for evaluation. Combined biorefinery concepts can be a possible solution to reduce the influence of cell wall hydrolysis. Anaerobic digestion of pretreated microalgae after lipid extraction for biodiesel production can be the key process to make microalgae sustainable as a source for biofuels by nutrition and energy recovery [6].

In further studies the rated ranges with positive effects have to be investigated for the different disruption approaches. Energy balances with regard to commercial applications have to be examined.

Acknowledgements

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Scale up of laboratory scale to industrial scale biogas plants

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Abstract: Industrial biogas plants often do not operate in their optimum. To investigate limits of anaerobic digestion processes experiments are necessary. Economically it would be feasible to perform these tests at laboratory scale, if the tests could be transferred to industrial scale. This work presents a preliminary study, in which two different scales of laboratory digesters are compared and reproducibility of tests is investigated.
Therefore, three identical glass digesters with a liquid volume of up to 22 liter and a steel-digester with a liquid volume of 390 liter were used. All digesters were started up with digestate from an industrial biogas plant, were fed with cow manure and corn cob mix, and were operated at the same process parameters like temperature, organic loading rate and retention time. Gas volumes were measured continuously. Twice a day the composition of the biogas was analyzed. Dry matter and volatile solids were quantified once a week.
The presented data show a good reproducibility between biogas plants of the same scale. The transferability to a bigger scale is in an acceptable range, but depending on the organic loading rate the deviation between the different scales varies.

Keywords: *biogas plant, laboratory scale, comparison, reproducibility, transferability*

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1. Introduction

Sources for renewable energy become more and more important. Among the renewable energies biogas has the advantage that it is a not fluctuating source. When being used in the existing pipeline infrastructure, it can even be stored to compensate for fluctuations in consumption. Storage for short periods is possible directly in most plants. Biogas can be gained in an anaerobic digestion process from different organic substances, e.g. from energy crops, agricultural waste or municipal organic waste.

Industrial biogas plants often do not operate in their optimum. To reach a higher efficiency for biogas plants it is necessary to know the limits for the anaerobic digestion process. These limits have to be identified in experiments. Economically it is not feasible to perform these tests on an industrial scale biogas plant since they involve the risk of long lasting production curtailments. Therefore, experiments at laboratory scale are the most common way to study the anaerobic digestion process. To use the results of laboratory scale experiments, it is essential to know whether the results are transferable to industrial scale and whether the experiments are reproducible.

To answer these questions it is necessary to use exactly the same inoculums for all digesters used in one test series and the same substances for feeding, because the anaerobic digestion process is a strongly dynamical process and depends very much on the used material. Furthermore, all digesters investigated should be operated with the same process parameters such as temperature, organic loading rate (OLR), hydraulic retention time and liquid volume for studies on reproducibility. For transferability studies only the liquid volume is allowed to vary. Transferability and reproducibility were investigated by Brunn et al. [1] with a non identical OLR for the different scales. Gallert et al. [2] operated their digesters with different OLR and hydraulic retention times. This work presents results of a pre study in which two different scales of laboratory digesters are compared keeping all process parameters as equal as possible. Furthermore, a reproducibility test was carried out with identical digesters. In coming tests a laboratory scale digester will be compared with an industrial scale biogas plant.

2. Methodology

To prove the reproducibility of experiments on the anaerobic digestion process, three identical continuous (22 liter laboratory) digesters were used. The transferability of experimental results to different scales was investigated comparing the 22 liter digesters to a 390 liter continuous digester.

2.1. Experimental setup

One of the three identical digesters with a liquid volume of 22 liter is shown in Fig. 1. The double glass shell of the digester is used for heating and gives the possibility to observe mixing and liquid level. Mixing is realized by a central stirring system with three mixing elements. These are propeller mixers with three blades for every mixing element. At the bottom a ball valve allows to discharge the digester or to take samples. For feeding a ball valve connected with the lid is used. From the top of the digester a gas-pipe leads to a 5 liter gas sampling bag. The gas sampling bag is necessary, to avoid low pressure by draining during feeding or taking samples. From the gas sampling bag a heated pipe leads to a drum type gasmeter (TG 05; Ritter). The gasmeter has a PT-100 thermometer and a manometer to be able to calculate the standard volume flow.

Fig. 1. Left: One of the three continuous 22 l digesters; Right: continuous 390 l digester.

Two identical gas chromatographs (GC) (Focus GC, Thermo Electron Corporation, Axel Semrau) are used to analyze the gas composition. One is equipped with a thermal conductivity detector (Thermo Fisher Scientific, Axel Semrau) with a micropacked column (ShinCarbon ST 100/120, Restek) for analyzing methane (CH_4), carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2). The other GC is connected to a mass spectrometer (DSQ II, Thermo Electron Corporation, Axel Semrau) with a capillary column (GS-GasPro, J&W Scientific Products) for hydrogen sulfide (H_2S). Furthermore a variable over pressure function is connected to the top. To determine the temperature in the digester a PT-100 thermometer is used.

The biogas plant with a liquid volume of 390 liter is shown in Fig. 1. It is made of stainless steel. The geometry of the digester is a scale-down of an industrial plant with 3000 m^3 liquid volume. The gas flow is much higher in the 390 liter digester. Therefore, no problems with low pressure occur during feeding or taking samples and a gas sampling bag is not needed. A constant liquid level is held due to a siphon which connects the digester with a storage tank. The digester is mixed by a central stirring system with three mixing elements. These are pitched blade impellers with two blades. This means, that they differ in their geometry compared to the ones of the 22 liter digesters. Temperature is measured on three levels. The digester is equipped with the same metrology as the smaller digesters. The measured quantities and their uncertainties are summarized in Table 1.

Table 1. Measured quantities and their uncertainties.

T (mK)	p (mbar)	$\dot{V}$ (%)	CH_4 (mol-%)	CO_2 (mol-%)	O_2 (mol-%)	N_2 (mol-%)	H_2S (ppm)
± 31,0	± 1,5	± 0,2	± 4,0	± 3,4	± 0,2	± 0,3	± 615,3

2.2. Experimental performance

All four digesters were filled with digestate from an industrial biogas plant (fed with maize silage (MS), corn cob mix (CCM) and cow manure (CM)) at the beginning. During the test period of 40 days the digesters were run at the same temperature level of ca. 38°C. The test period of 40 days was considered to be sufficient, after the digesters showed a good reproducibility and transferability even with changing organic loading rates (OLR). Once a day they were fed with the same mixture of CCM and CM, which was mashed with digestate. CM was chosen because of its good buffer capacity. CCM and CM are, compared e.g. to MS, very homogeneous and well suited for reproducibility and transferability tests. The chosen feeding rates ensured the same OLR for all digesters. The OLR is calculated according to

$$OLR = \frac{\dot{m}_{VS}}{V_{liq}} \tag{1}$$

where $\dot{m}_{VS}$ is the input mass flow of volatile solids (VS) and V_{liq} the liquid volume of the respective digester. The OLR was increased from 0.20 to 2.54 $kg_{VS}m^{-3}d^{-1}$ during the test period. The steps are shown in Fig. 2.

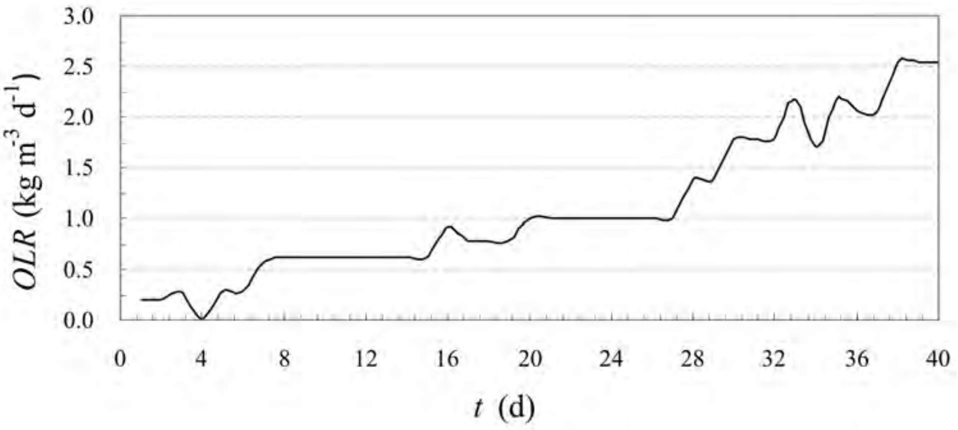

Fig. 2. OLR over test period for all digesters.

Before and after feeding gas samples were taken for gas quality analysis. During the whole test period the gas flow was measured continuously and the digesters have been stirred without any interruptions. Six times during the test period of 40 days dry matter (DM) and volatile solids (VS) where determined according to DIN 12879 [3] and DIN 12880 [4], respectively.

3. Results

During the test period the four plants showed a good agreement with respect to the analyzed parameters. Fig. 3 and Fig. 4 give an overview of the performance for two different days. The diagrams show the standard volume flow reduced by the liquid volume of the digester over one day. The reduction is necessary, because otherwise it would not be possible to compare the 22 liter digesters to the 390 liter digester. The drop in Fig. 3 and at 05:00 and 08:00 o'clock in Fig. 4 result from sampling for gas analysis. The fluctuations between 10:00 and 15:00 o'clock are caused by feeding and taking samples for gas analysis.

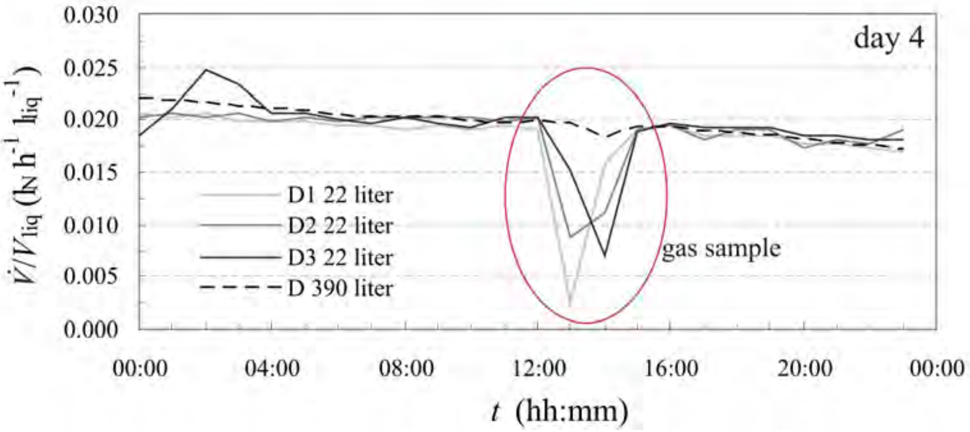

Fig. 3. Volume flow referring to the filling volume for fourth day (D: Digester).

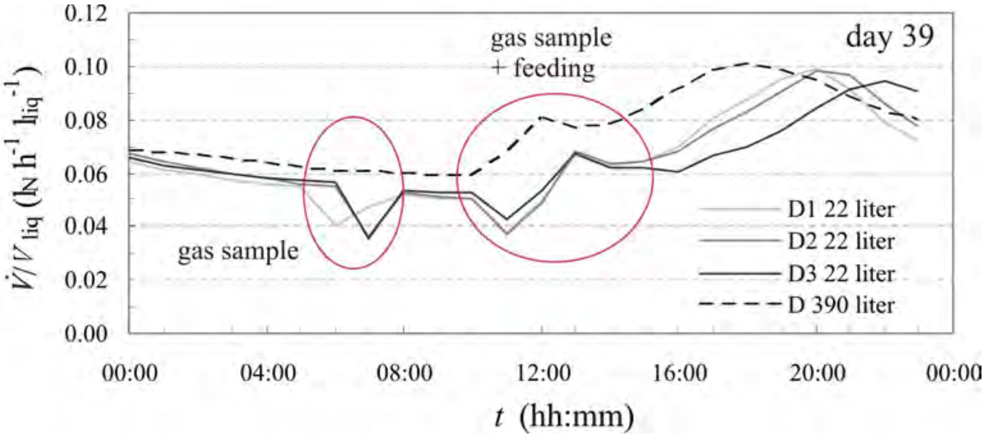

Fig. 4. Volume flow referring to the liquid volume for 39th day (D: Digester).

Fig. 3 shows a nearly identical shape of the curve with very similar results for all four digesters. In Fig. 4 the curve of the 390 l digester deviates from the ones of the 22 l digesters. The trends at the two different scales are comparable at any time, for derivates. In this example the curve of the third 22 liter digester is displaced on the time-line, but shows the same trends.

Fig. 5 shows the daily average of the absolute standard deviation for the 22 liter digesters, as well as the daily average of the absolute deviation between the 390 liter digester and the average of the three 22 liter digesters. To calculate the deviation the values during feeding or taking gas samples, as described in Fig. 3 and Fig. 4, and outliers were excluded. On the second axis the average of the daily gas volume flow to the liquid volume of the digesters is shown. Here the outliers are excluded as well.

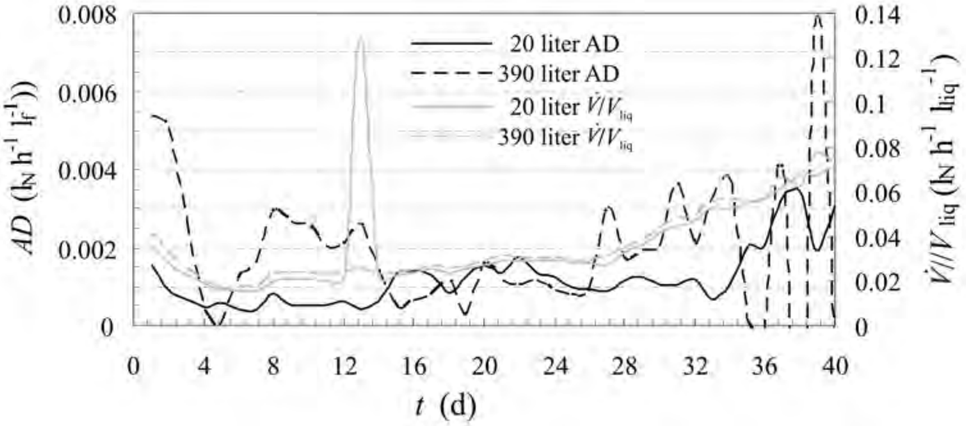

Fig. 5. Daily average of the absolute standard deviation (AD) for the three 22 liter digesters and daily average of the absolute deviation (AD) between 390 liter digester. Also the average of the three 22 liter digesters and the daily average of the gas volume flow reduced by the liquid volume for 22 liter and 390 liter digesters.

Fig. 5 shows a good reproducibility of the three 22 l digesters among each other. The relative standard deviation is between 1.42 and 5.96 % (excluded one outliner with 21.58 % on day 13) for the 22 liter digesters among each other. Comparing the average of the 22 l digesters to the 390 l digester the relative deviation is between 0.68 and 18.07 %. This and the shape of the curves for the gas volume flow in Fig. 5 for both digester scales are an evidence for a possible transferability of experimental results in different scales.

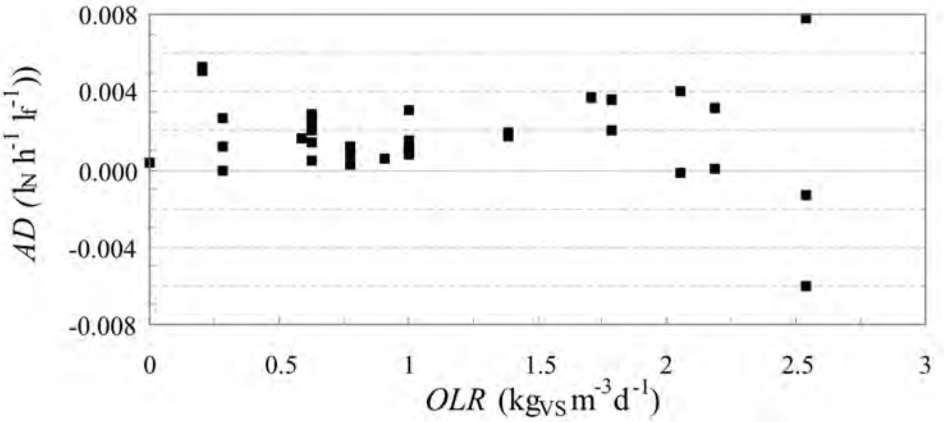

Fig. 6. Absolute deviation (AD) of the 390 liter digester to the average of the 22 liter digesters over OLR.

Fig. 6 shows the absolute deviation of 390 liter to 22 liter digesters (referring to gas volume flow to liquid volume) over OLR. For each OLR, expect 2.53 $kg_{VS}m^{-3}d^{-1}$, the deviation is between 0.0002 and 0.0053 $l_N h^{-1} l_f^{-1}$. For an OLR of 2.53 $kg_{VS}m^{-3}d^{-1}$ the absolute deviation is between -0.0061 and 0.0078 $l_N h^{-1} l_f^{-1}$.

To compare the biogas quality, Fig. 7 shows the plot of the measured methane concentration. Expect for the curve of the first 22 liter plant at days 14-18 and a single peak of the 390 l digester at the end of the test period, all curves show a good agreement. The difference between the two scales till day 6 results from the gas sampling bags used for the 22 liter digesters, which contain air at start up.

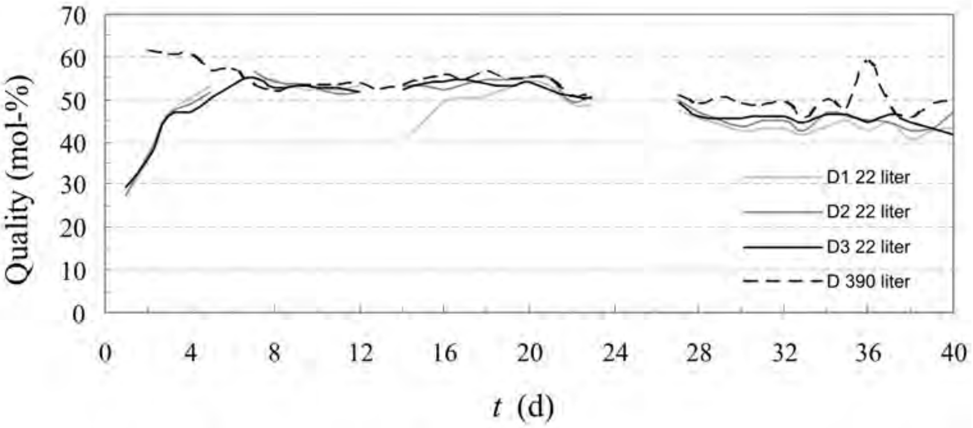

Fig. 7. Methane-rate over test period.

Table 2 shows results for DM and VS determined during the test. Day 0 represents the starting point, at which all digesters have been filled with the same inoculum. After the first week the DM in the 390 l digester decreases more than in the smaller digesters. This indicates a higher conversion of the substrates to biogas. This is also shown in Fig. 5, where the production rate of the 390 liter digester is always above the one of the 22 liter digesters.

Table 2. Dry matter (DM) and organic dry matter (VS) of all digesters through the test period.

t	(d)		0	7	16	23	29	36
DM	(% FM*)	BP1 22 l	8,37	8,10	7,85	7,61	7,47	7,63
		BP2 22 l	8,37	8,30	7,67	7,42	7,67	7,81
		BP3 22 l	8,37	8,33	7,55	7,37	7,48	7,61
		BP 390 l	8,37	7,72	7,38	7,11	7,11	7,57
VS	(% FM*)	BP1 22 l	6,47	6,00	5,65	5,50	5,64	5,76
		BP2 22 l	6,47	5,83	5,56	5,53	5,47	5,88
		BP3 22 l	6,47	6,00	5,65	5,39	5,45	5,73
		BP 390 l	6,47	5,92	5,63	5,43	5,43	5,76

* fresh mass

4. Conclusion and Outlook

The presented results show a high degree of reproducibility at equal experimental conditions. During the test period the daily relative standard deviation of the three 22 liter digesters is between 1.42 and 5.96 %. Reasons for this deviation are the heterogeneity of the fed substrates and small differences in liquid volume and digester temperature.

The relative deviation of the 390 l digester to the three 22 liter digesters is between -6.92 and 18.07 % with an average of 6.33 %. This is not caused by the OLR, which was varied during the test. The reasons for the deviation have to be searched in the same causes as the ones for the reproducibility. Additional reasons are the differences in geometry, in materials used for the digesters and in mixing.

Good correspondence between a laboratory scale digester and a full scale digester was observed by Gallert et al. [2]. This is a good indicator, that experiments in laboratory scale can be transferred to industrial scale. Aivasidis and Wandrey [5] concluded, that it is possible to scale up anaerobic digesters and that experiments in laboratory and pilot scale can provide data to design an industrial scale digester.

Also Brunn et al [1] figured out a good reproducibility for digesters of the same scale, but not for transferability. The industrial scale digester produces 36% more gas, compared to the used laboratory scale digester. As explained by Brunn et al. this causes in different feeding schedules and substrates (substrates for the laboratory digester were taken once a week). This shows the importance of similar process parameters for tests relating to reproducibility and transferability.

The next step in studying the transferability of experimental results should be a comparison between a digester at laboratory scale with one at industrial scale. All process parameters have to be chosen as identical as possible, as the presented results underline the importance of synchronicity of all process parameters. Currently the industrial biogas plant is being equipped with the necessary measure devices.

Acknowledgements

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The effect of distinct operational conditions on organic material removal and biogas production in the anaerobic treatment of cattle manure

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Abstract: Although very difficult to treat due to their complicated composition, the increasing amounts of cattle manure generation makes their purification a compulsory task for environmental engineers to prevent their adverse environmental impacts. Historically, these wastes have been used as a fuel or a soil fertilizer. The generation of cattle manure even in increasing amounts in Turkey, however, makes this kind of use unfeasible. Therefore, new methods to dispose of these wastes are required. This study focuses on the anaerobic digestion process for the treatment of cattle manure. In the study, two lab-scale anaerobic reactors were employed to investigate the effects of different operating temperatures (35 ºC and 55 ºC), of different total suspended solids concentrations (%5 and 10%), of different hydraulic retention times (20 days and 40 days), and of the addition of corn silage on the treatment performance. The performance of the reactor was evaluated with respect to total solids (TS), volatile solids (VS) and biogas production. The results of the study suggested that the thermophilic reactor showed a good treatment performance (59% VS removal and 0.29 L methane per VS added) when the cattle manure of 10% solids content together with corn silage were fed. Besides, it was concluded that the addition of corn silage to the reactors improved the treatment efficiencies and that the addition of irrigational organic materials increases biogas production rate. The results of the study point out that anaerobic digestion process is a viable option for cattle manure stabilization and valuable gas production.

Keywords: *Anaerobic Digestion, Cattle Manure, Biogas, Methane*

Nomenclature

TS	*total solids*	*mg.kg^{-1}*	*TOC*	*total organic carbon*	*mg.kg^{-1}*
VS	*volatile solids*	*mg.kg^{-1}*	*COD*	*chemical oxygen demand*	*mg.L^{-1}*
HRT	*hydraulic retention times*	*day*	*cfu*	*colony forming unit*	

1. Introduction

The number of cattles have shown an increasing trend in Turkey. In 2007, the capacity of cattles in Turkey reached over 11 millions [1]. This increase, unfortunately, led to an increase in the environmental problems caused by inappropriate disposal of cattle manures into the environment, due to which the proper treatment of these wastes gained attraction in last years. Current disposal methods (burning and using as fertilizer) have proven to be inadequate and research is ongoing for new treatment methods.

Cattle manure can be as harmful as other industrial wastes in environmental aspects. Therefore, development of new treatment methods for the safe disposal of these wastes would prevent endangering the public health. Besides, the end product of the anaerobic digestion process could easily be used as an organic fertilizer and this use would contribute to sustainable development strategies.

In addition to the severe environmental impacts caused by the uncontrolled disposal of cattle manure, possible future energy crisis makes the environmental engineers to provide solutions both economically and environmentally sound. Production of energy through biomass along with a by-product that can be used as a natural fertilizer are the major advantages of this process.

Although being a very complicated process, anaerobic digestion simply involves three stages as (1) the conversion of high-density organic materials into low-density materials by hydrolysis, (2) the conversion of low-density organics into acetate by acid bacteria, and (3) methane production by methane bacteria by consuming acetate, carbon dioxide and hydrogen [2]. Coskun et al. (2009) listed the factors affecting the anaerobic digestion of cattle manure as (1) solids content and hydraulic retention time, (2) pH and alkalinity, (3) trace elements and nutrients, (4) temperature, (5) toxic content of the waste, (6) C/N ratio, and (7) dilution ratio of the waste [3].

This study aims at the evaluation of anaerobic digestion alternatives for cattle manure treatment with differing hydraulic retention times, feed contents and feed solids contents. The investigation involved the determination of the most feasible anaerobic digestion method for the treatment of cattle manure in Turkey.

2. Methodology

2.1. Characterization of cattle manure

Cattle manure contains insoluble organic materials as well as soluble organics such as polysaccharides, fats, and volatile fatty acids. Their high chemical oxygen demand (COD), ammonia and phosphorous content make them very complicated and extremely difficult to treat [4]. The cattle manure used in this study was obtained from Gebze District of Kocaeli of Turkey and the characteristics of the waste are given in Table 1.

Table 1. General characteristics of the raw cattle manure (Gebze-Kocaeli)

Parameter	Unit	Value
pH	-	7.41
Moisture	%	80.98
Volatile solids (VS)	%	73.58
Ash	%	5.12
C	%	39.12
N	%	1.35
C:N	-	28.94
P	%	0.96
H	%	5.01
S	%	0.40

2.2. Measurement methods

TS, VS, total organic carbon (TOC), biogas production and methane content of the biogas were continuously monitored during the study. For TS and VS, the method “DS/EN 12879 Characterization of sludges” was followed. TOC analyses were conducted using Hach-Lange IL 550 TOC/TN device. TOC analyses were conducted in the effluents from the reactors starting from the sixth week of the study. The biogas production was measured daily via a Ritter Drum-type gasmeter and LMSx Multigas Analyser was used to assess the biogas composition. *Salmonella spp.* was measured according to “ISO 6579/April, 1996 Salmonella measurement methods” while “NF-ISO 166492 (June 2001) Horizontal method for the enumeration of glucuronidase-positive Escherichia coli β – Part 2: Technique of colony count at 44 °C by means of 5-bromo-4-chloro-3-indolyl-β-D-glucuronate acid (IC: V08-031-2)” was used for E.coli measurement.

2.3. Experimental setup

Two lab-scale, completely mixed, stainless-steel, cylindrical anaerobic reactors with 10 L of active volumes were operated at 35 ºC and 55 ºC, simultaneously, for the treatment of cattle manure. The solids contents of 5% and 10% along with the hydraulic retention times of 20 days and 40 days were used during the study. Solids content of the manure was set to 5% or 10% with tap water before feeding. Further, mixtures of cattle manure and corn silage were fed to determine the effects of the use of a supplementary organic material. The reactor performances were evaluated with respect to TS, VS, *Salmonella spp.*, and E.coli removal efficiencies as well as biogas production rate. The experimental setup is shown in Figure 1.

Fig. 1. Lab-scale anaerobic treatment system [3].

3. Results

3.1. Cattle manure feed at 5% solids content

First of all, the reactors were fed with only cattle manure of 5% solids content and were operated at 20 days of hydraulic retention time (HRT) at 35 ºC (mesophilic range) and 55 ºC (thermophilic range), respectively. After 10 weeks of successful operation, the retention times were increased to 40 days. Figure 2 shows the change of TS, VS and TOC when only cattle manure of 5% solids content was fed to the reactors.

The TS concentration in the effluent of mesophilic reactor at HRT=20 days changed between 39,000 and 43,000 mg/kg while values of same range were obtained in the effluent of thermophilic reactor. The TS removal efficiency of the mesophilic reactor was calculated between 14% and 21% while that of thermophilic one ranged between 10% to 21%. After increasing the HRT to 40 days, the TS content of the effluents were increased first and then decreased to 31,000 mg/kg for mesophilic reactor and 32,000 mg/kg for thermophilic one in 16th week. At the end of the study, the TS removal efficiencies reached to about 38% and 36% for mesophilic and thermophilic reactors, respectively. The reason for the TS removal efficiency to drop first when the HRT was increased from 20 days to 40 days is the reaction of microorganisms to the changing environmental conditions [3].

During the study, VS concentration of the waste was determined to be 38,800 mg/kg. For HRT=20 days, effluent VS concentrations ranged from 27,000 to 30,000 mg/kg and from 28,000 to 31,000 mg/kg for mesophilic and thermophilic reactors, respectively. The VS removal efficiencies ranged from 23% to 30% and from 20% to 29%, respectively. After increasing the HRT to 40 days, the effluent VS concentrations increased first and decreased to around 23,000 mg/kg for both reactors. At the end of the study, the VS removal efficiencies were about 41% for both reactors.

TOC concentration of the waste was measured as approximately between 15,600 and 19,900 mg/kg. For HRT=20 days, average effluent TOC concentrations were around 11,700 mg/kg and 12,300 mg/kg for mesophilic and thermophilic reactors, respectively. After increasing the HRT to 40 days, average effluent TOC concentrations were increased to about 12,000 and 13,300 mg/kg, respectively. The effluent TOC concentrations averaged over the whole study were 11,900 and 13,000 mg/kg for mesophilic and thermophilic reactors, respectively, and average TOC removal efficiencies of the reactors were calculated as 32.8% and 25.4%, respectively.

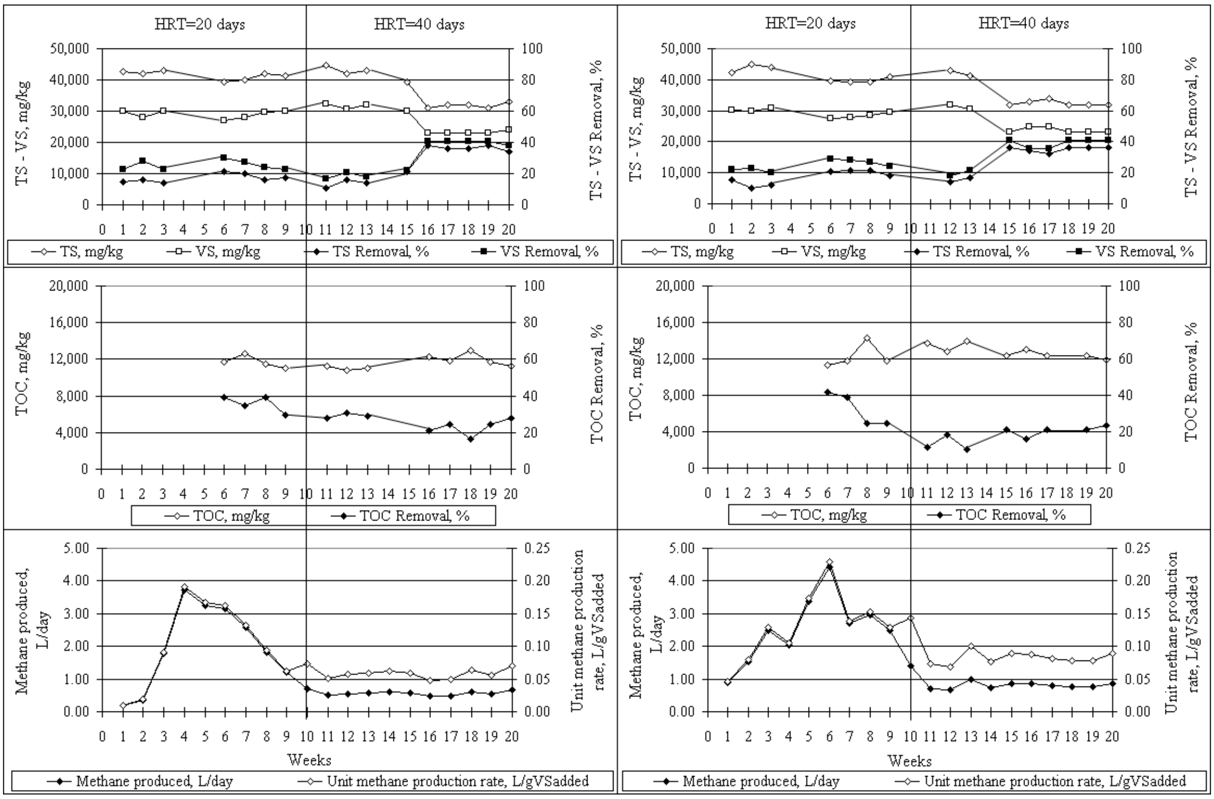

Fig. 2. TS, VS and TOC concentrations in the effluents from mesophilic (A) and thermophilic (B) reactors when only cattle manure of 5% solids content was fed.

Starting with the second week of the study, biogas production rate showed an increasing trend for both reactors. However, the rate was decreased after increasing the HRT. The biogas production rate was measured as between 0.10 and 0.34 L_{biogas}/ gVS_{added}, and between 0.15 and 0.41 L_{biogas}/ gVS_{added} for mesophilic and thermophilic reactors according to the HRTs of 20 days and 40 days, respectively. During the whole study, methane content of the biogas was between 45% and 55% for both reactors. Therefore, the methane production rates for mesophilic and thermophilic reactors ranged from 0.06 to 0.19 $L_{methane}$/ gVS_{added} and from 0.08 to 0.23 $L_{methane}$/ gVS_{added}, respectively.

Salmonella spp. was not detected in both effluents during the whole study. For thermophilic reactor, E. coli was determined to be 10 cfu/kg while this value reached up to 1,000 cfu/kg for mesophilic one. The results showed that the mesophilic range of operating temperature (35 °C) was less effective in E.coli removal while they are completely removed in thermophilic temperature (55 °C).

3.2. Cattle manure feed at 10% solids content

In this stage of the study, the solids content of the raw waste was increased to 10% and the reactors were operated at HRT of 40 days. Average concentrations of TS, VS, and TOC in the raw waste were determined to be 100,000 mg/kg, 82,400 mg/kg, and 36,400 mg/kg, respectively. The results of TS, VS, and TOC analyses in the effluents are shown in Figure 3. For mesophilic reactor, TS, VS, and TOC removal efficiencies were around 20.3%, 23.8%, and 21.3%, respectively. The removal efficiencies for the thermophilic reactor were calculated as 24.9%, 28.3%, and 22.1%, respectively.

In this stage, the mesophilic and thermophilic reactors produced 0.12 to 0.23 L_{biogas}/gVS_{added} and 0.16 to 0.32 L_{biogas}/gVS_{added} of biogas, respectively. The methane production rates were measured as between 1.17 to 2.16 L/day and 1.47 to 2.89 L/day, respectively. In terms of VS fed to the reactors, mesophilic reactor produced 0.06 to 0.10 L methane per gVS_{added} while the rate for thermophilic one was measured as between 0.08 and 0.14 $L_{methane}/ gVS_{added}$.

In the aspect of *Salmonella spp*. removal, both reactors produced perfect effluents. However, this was not the same for E.coli. E.coli was not detected in the effluent from the thermophilic reactor while the mesophilic one was less effective in E.coli removal.

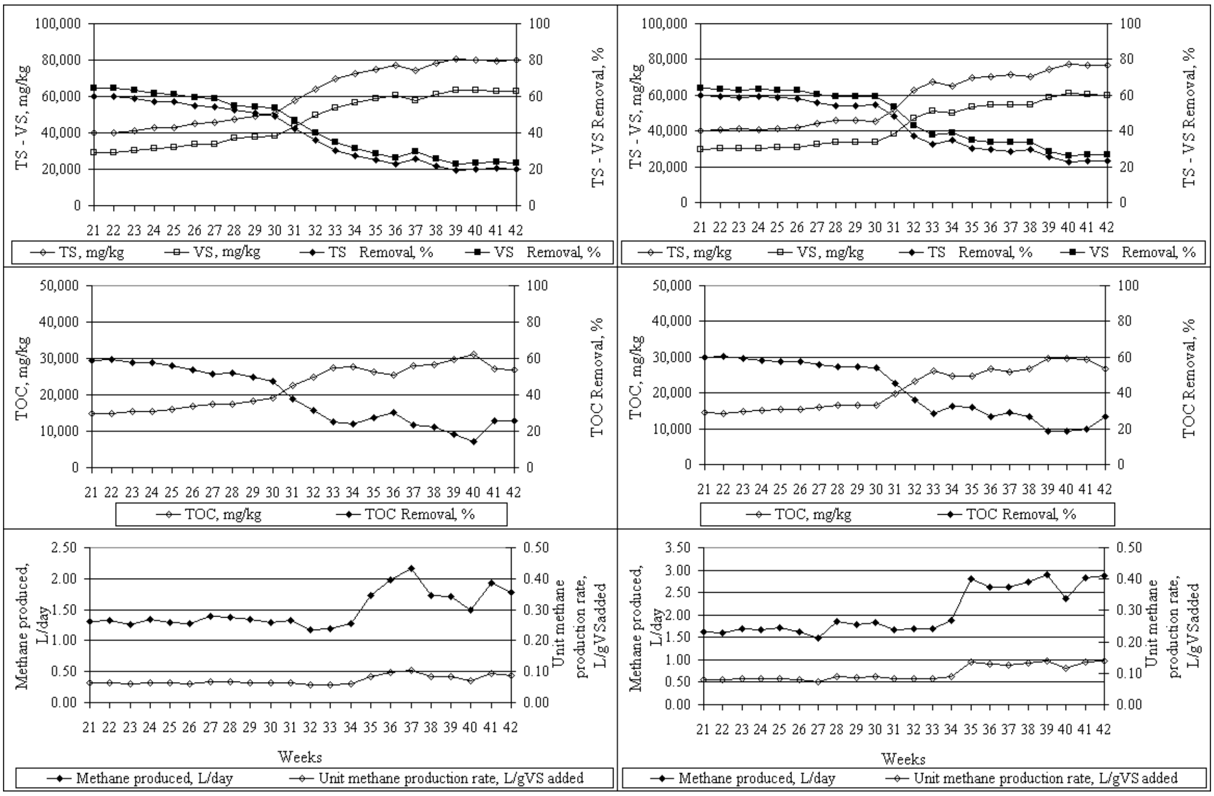

Fig. 3. TS, VS and TOC concentrations in the effluents from mesophilic (A) and thermophilic (B) reactors when only cattle manure of 10% solids content was fed.

3.3. Mixture of cattle manure and corn silage feed at 10% solids content

In this stage of the study, anaerobic digestion of cattle manure along with corn silage as supplementary organic waste was investigated. In this stage of the study corn silage was added to cattle manure of 10% solids content and the reactors were operated at an HRT of 40 days. TS, VS, and TOC concentrations of the corn silage were measured as 230,000 mg/kg, 205,000 mg/kg, and 83,000 mg/kg, respectively. Those of the mixture of cattle manure and corn silage were determined to be 161,600 mg/kg, 140,600 mg/kg, and 58,400 mg/kg, respectively. TS, VS, and TOC concentrations measured in the effluents from the reactors are shown in Figure 4.

TS removal efficiencies of the reactors were calculated as around 47.5% for mesophilic one and around 51.4% for thermophilic one while VS removal efficiencies were observed as about 53% and about 59%, respectively. 49% and 52.4% of TOC removal efficiencies were obtained for mesophilic and thermophilic reactors, respectively.

After feeding the mixture of cattle manure and corn silage together, the biogas production rate was measured as between 0.16 and 0.37 L_{biogas}/gVS_{added} for mesophilic reactor and between 0.31 and 0.54 L_{biogas}/gVS_{added} for thermophilic reactor. For mesophilic and thermophilic reactors, methane production rates were observed to range from 0.08 to 0.19 $L_{methane}/gVS_{added}$ and from 0.15 to 0.29 $L_{methane}/gVS_{added}$, respectively.

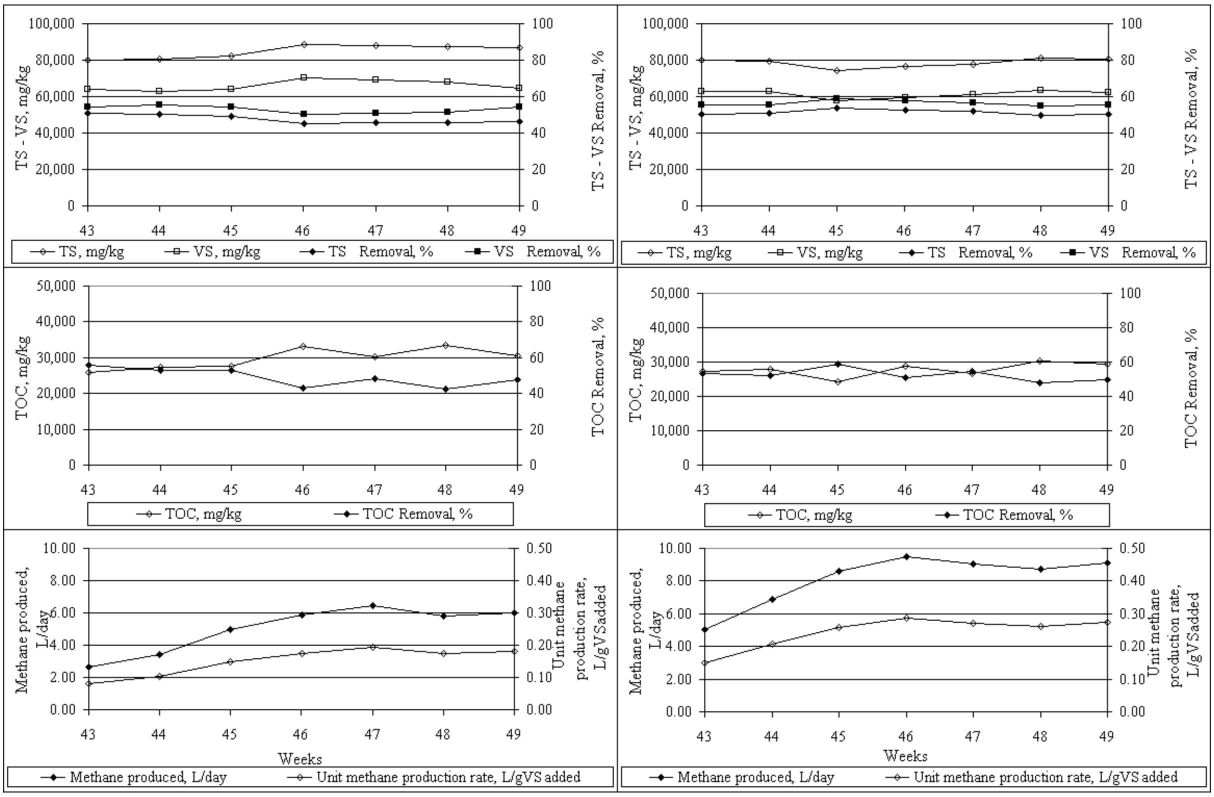

Fig. 4. TS, VS and TOC concentrations in the effluents from mesophilic (A) and thermophilic (B) reactors when a mixture of cattle manure and corn silage of 10% solids content was fed.

Although the removal efficiency in mesophilic reactor increased considerably by the use of corn silage as a supplementary organic waste, the reactor was still less effective in E.coli removal than thermophilic reactor which completely removed E.coli and *Salmonella spp*.

4. Discussion

The results from the both reactors, which are used to treat cattle manure of 5% and 10% solids content anaerobically, suggests that TS, VS, and TOC removal efficiencies as well as biogas and methane production rate per gram VS added were quite similar. The highest removal efficiencies and the highest biogas/methane production rates were obtained in the stage in which cattle manure and corn silage were mixed to obtain 10% of solids content. The results from this stage were compared to the literature data (Table 2). The results shown in Table 2 suggest that study results (VS removal efficiency and methane production rate) are satisfactory compared to literature data. Finally, it is necessary to state that the thermophilic reactor was successful in both *Salmonella spp.* and E.coli removal in stages of the study while mesophilic one was not satisfactory in E.coli removal although it successfully removed *Salmonella spp*. Related Turkish legislation suggests that *Salmonella spp*. and E.coli must not be detected in the effluent [5].

Table 2. Comparison of the study results with literature data.

Reference	Reactor type	VS removal (%)	Methane production ($L_{methane}/gVS_{added}$)
Current study*	Complete mix	59	0.15 – 0.29
[6]	Fill-decant anaerobic	48 – 53.6	0.24 – 0.25
[7]	Anaerobic hybride	59 – 68	0.19
[8]	Two-phase anaerobic digester	30.3 – 62.4	0.07 – 0.24
[9]	Temperature-phased anaerobic digester (TPAD)	37 – 41.5	0.15 – 0.22
[10]	Complete mix	28	0.20
[11]	Temperature-phased anaerobic digester (TPAD)	42.6	0.23
[12]	Anaerobic SBR	22	0.07 – 0.15
[13]	Complete mix	38.4	0.25
[14]	Fill-decant type	42 – 52	0.17 – 0.22
[15]	Complete mix	24.7	0.09

*Cattle manure of 10% solid content mixed with corn silage

5. Conclusions

The performance of anaerobic digestion process for the treatment of cattle manure was investigated in this study. The results of the study, in which the effects of different operational temperatures (35 ºC and 55 ºC), different solids content of the feed (5% and 10%), different hydraulic retention times (20 and 40 days) and the addition of corn silage to the feed on the TS and VS removal performances of the reactors and on the biogas production, suggests

- that cattle manure is possible to treat by both feeding alone and feeding mixed with an organic supplementary material (corn silage for the case),
- that the addition of corn silage to the cattle manure increases the treatment efficiency in both reactors,
- that higher VS removal efficiencies and higher methane production were observed if corn silage are provided to the feed,
- that the thermophilic range of operational temperature shows higher performance in the aspects of both methane production and pathogen removal,
- and that cattle manure can be stabilized by anaerobic digestion in an economical and environmentally beneficial way.

Considering all results from the study, it was concluded that thermophilic reactor was satisfactorily effective in pathogen microorganisms removal and VS stabilization. Besides during the stabilization process the use of a supplementary organic material (corn silage) was proven to sustain high energy production potential.

Acknowledgement

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Slaughterhouse waste co-digestion
- Experiences from 15 years of full-scale operation

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Abstract: At Tekniska Verken in Linköping AB (TVAB) there is a long time experience of handling and producing biogas from large volumes of slaughterhouse waste. Experiences from research and development and plant operations have lead to the implementation of several process improving technological/biological solutions. We can in this paper describe how the improvements have had several positive effects on the process, including energy savings, better odor control, higher gas quality, increased organic loading rates and higher biogas production with maintained process stability. In addition, it is described how much of the process stability in anaerobic digestion of slaughter house waste relates to the plant operation, which allow the microbiological consortia to adapt to the substrate. Since digestion of proteinaceous substrates like slaughterhouse waste lead to high ammonia loads, special requirements in ammonia tolerance are placed on the microbiota of the anaerobic digestion. Biochemical assays revealed that the main route for methane production proceed through syntrophic acetate oxidation, which require longer retention times than methane production by acetoclastic methanogens. Thus, the long retention time of the plant, accomplished by a low dilution of the substrate, is a vital component of the process stability when treating high protein substrates like slaughterhouse waste.

Keywords: *Anaerobic digestion, co-digestion, full-scale, slaughterhouse waste, syntrophic acetate oxidation*

1. Introduction

Slaughterhouse waste is the very energy-rich waste stream of meat industry [1]. As such, it is an attractive material to treat through anaerobic digestion for the production of biogas. However, there are many potential technical and microbiological problems associated with anaerobic digestion of slaughterhouse waste. These include the practical handling according to European Union Animal By-Products (ABP) Regulation [2], protein content [3] and high degradation and volatile fatty acid (VFA) formation rates [4,5]. Reported here are the experiences, production results and R & D activities at the full scale co-digestion biogas plant treating slaughterhouse waste in Linköping, Sweden, for the period 1997-2010.

1.1. Anaerobic digestion of protein-rich substrate

Anaerobic digestion of organic material is a complex microbiological process requiring the combined activity of several groups of microorganisms with different metabolic capacities which need to work in a synchronized manner in order to obtain a stable biogas process [6]. One type of key organisms are the methanogens, producing methane mainly from acetate or hydrogen and carbon dioxide. Protein-rich substrate, such as slaughterhouse waste, is a well-known source of sulfide formation during anaerobic degradation. The increased concentration of sulfides in the digester lead to higher concentrations of corrosive H_2S in the biogas and can further lead to sulfide inhibition of the methanogens [7,8]. When the proteins in slaughterhouse waste are degraded, not only sulfides are formed but also ammonia [3]. The released ammonia increases the pH in the digester and with a large ratio of slaughterhouse waste in the substrate mixture, the pH tends to reach over 8.0, which can be growth limiting for some VFA consuming methanogens [9]. The above optimal pH, together with a high fermentation rate of proteins and fats in the slaughterhouse waste can lead to an accumulation of fatty acids. Thus, if the organic load to the digester is not decreased at that point, the process overload can lead to increasing concentrations of process inhibiting fatty acids, the consequential pH drop and finally to a total inhibition of methanogenesis and process collapse will follow. The released ammonia (NH_3) from protein degradation is in equilibrium with the less harmful ionized ammonium species (NH_4^+). However, the non-ionized form is itself also a source of inhibition of microorganisms, since the neutral NH_3 can easily pass through cell membranes of bacteria and archaea and upon entering the cell disrupt *e.g.* intra-cellular pH and concentrations of other ions [8]. Thus, methods to lower ammonia levels in anaerobic digesters treating high-protein substrates are desirable and subject to active research [10,11]. Furthermore, at increased pH and temperature, the equilibrium is shifted towards the toxic ammonia, resulting in a positive correlation between toxicity effects and increasing pH and temperature [12]. Among the methanogens, the acetate-utilizing methanogens have been suggested to be responsible for 70-80 % of the methane produced [6]. However, recent results suggest that an alternative methane producing pathway is activated at elevated levels of ammonia [13]. In this pathway, acetate is converted to hydrogen and carbon dioxide by syntrophic acetate oxidizers (SAO), followed by the subsequent reduction of carbon dioxide to methane by hydrogen utilizing methanogens, *i.e.* by this pathway methane is produced by hydrogenotrophic methanogens only. Development of SAO has been shown to occur due to a selective inhibition of acetate-utilizing methanogens by ammonia, released *e.g.* during the degradation of proteins [13].

1.2. Co-digestion plant design and operation

The plant for co-digestion of slaughterhouse waste started operation in 1996. The plant is operated by the company Svensk Biogas AB (SvB), a subsidiary to TVAB, and has since start-up continuously supplied upgraded vehicle-fuel quality biomethane. TVAB has an in-house Biogas R & D department, which continuously work to support production and improve plant performance. Biogas process research is further conducted in collaboration with Linköping University and the Swedish University of Agricultural Sciences [14,15].

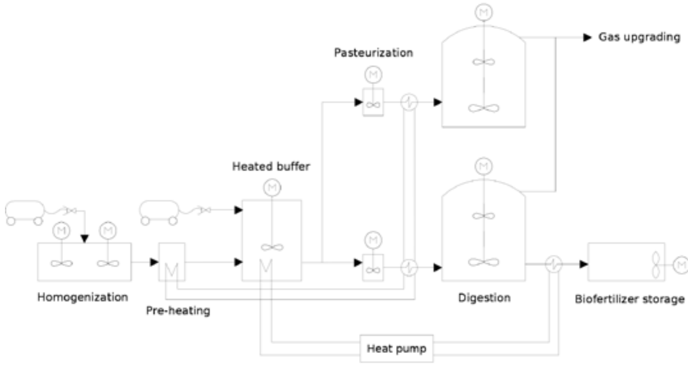

Figure 1. Schematic diagram of the process at Linköping Biogas plant.

The co-digestion plant consists of three basic parts: 1) substrate reception and storage, 2) pasteurization equipment, and 3) anaerobic digesters (Fig. 1). Yearly capacity of the plant is 55 000 metric tons, and the proportion of slaughterhouse waste in the total substrate mixture has varied between 35 and 75 % (w/w, yearly average). During 2010, the capacity of the plant was expanded to 100 000 tons/year.

Slaughter house waste is treated with formic acid at the slaughter house and all waste is delivered to the plant by closed trucks in a grinded (≤ 12 mm) pumpable form and is either transferred into a combined homogenization and buffer tank or directly into a second, heated buffer tank. After homogenization the substrate mixture is continually pumped to the second heated buffer tank. The target temperature of the second buffer tank is above 75 °C to avoid foaming, to pre-heat the material before pasteurization and to provide a stable thermal disintegration of the substrate. Substrate which is delivered warm is pumped directly to the heated buffer tank to save energy on substrate heating. Before loading of the digesters, the substrate is pasteurized in a batch process for one hour at 70 °C, to fully comply with the EU ABP regulation for category three materials [2]. The anaerobic digestion takes place at mesophilic conditions (38 °C) and the process heat is supplied through the city's waterborne district heating system. The two digesters are continuously stirred tank reactors (CSTR) run in parallel, with a total volume of 7400 m^3 and a hydraulic retention time (HRT) of 45-55 days. The gas composition is, on average, 68 % CH_4, 31 % CO_2 and <100 ppm H_2S. No significant modification to the plant has been necessary, as a consequence of ABP regulation implementation, since the plant was already equipped with the required pasteurization function. However, the precise categorization of different substrates of animal origin has changed over the years, as legislation and its interpretation have changed.

2. Materials and methods

2.1. Operation and analysis data

Operational data on biogas production, biogas composition and the amount and type of incoming substrates were collected from the plant's SCADA-system. pH was analyzed with a WTW 526 pH meter (WTW Inolab, USA), according to Swedish Standard SS 028122:2. Partial (bicarbonate) alkalinity was analyzed by titration to pH 5.4, with simultaneous removal of CO_2, in accordance with Swedish standard SS-EN ISO 9963 Part 2.

Total solids (TS) and volatile solids (VS) were analyzed according to Swedish Standard SS 028113. VFAs were analyzed with a modified spectroscopic HACH method (HACH no. 8196). Dissolved free ammonium nitrogen was analyzed according to FOSS Tecator's Kjeltec method, on a Kjeltec 2200 (Foss Tecator, Denmark). The method gives the concentration of total dissolved free ammonium including a minor fraction of dissolved ammonia nitrogen. (NH_4^+-N (aq) + NH_3-N (aq)).

2.2. Labeling experiments

Inoculation of digester samples with isotopically labeled acetate was performed in order to distinguish between methane formation by acetate utilizing methanogens or via syntrophic acetate oxidation and hydrogenotrophic methanogens. Aliquots of digester content (20 ml) were transferred during flushing with N_2/CO_2 (80/20 percent) to sterile serum vials (118 ml). The bottles were closed with butyl rubber stoppers and aluminum caps and the labeling studies were started by the addition of (2-^{14}C)-acetate (Amersham, England) to a final concentration of 10 kBq/ml. The culture was incubated at 37 °C and the degradation of (2-^{14}C)-acetate and the concomitant formation of $^{14}CH_4$ and $^{14}CO_2$ were determined by scintillation counting. The labeling pattern was analyzed when approximately 90 % of the labeled acetate had been converted. Finally, the ratio of $^{14}CO_2/^{14}CH_4$ was determined and values above 1 were considered as evidence for SAO.

3. Results

3.1. Operational strategy development

During the two first years of operation about 50 % (w/w) of the substrate consisted of cattle manure. This is a common way to avoid problems with process overloading, nitrogen/ammonia inhibition and micronutrient deficiency [16,17]. However, diluting the substrate mixture with manure has the negative effect of decreasing the amount of methane produced per reactor volume, since the methane yield of manure is far lower than that of slaughterhouse waste [18]. To increase the profitability of the plant, and to meet the increased demand for biomethane as a vehicle fuel, a gradual replacement of manure with more slaughterhouse and other organic wastes with higher methane potential have been implemented (fig. 2B).

3.1.1. Organic load of digesters and biogas production

At start-up, the plant was designed for a substrate mixture with a TS maximum of 8 %. However, as a result of the constant endeavor to increase the organic load and thereby methane production, the TS of the incoming substrate mixture, sampled in the heated buffer tank, has during 2009/2010 reached a TS of 17 % as a yearly average (Fig. 2A), with individual samples during 2009/2010 sometimes reaching 20 %. A replacement of steam injection with district heating for pasteurization in 2007, also led to a thicker substrate mixture, since added water no longer enter the system through the steam.

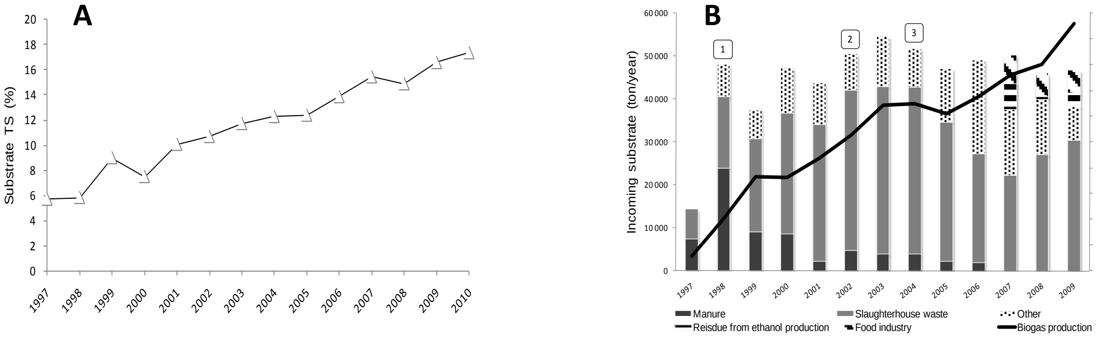

Figure 2. A) Total solids (TS) of incoming substrate (yearly average) during 1997-2010 (data for 2010 up until 2010-05-06), sampled in the heated buffer tank. B) Annual amount of substrate, substrate composition and biogas production during 1997 - 2009. Number captions denote implementation of process additives: [1] $FeCl_2$; [2] hydrochloric acid; [3] KMB1.

As can be seen in Fig. 2B, the plant has experienced an almost unbroken increase of yearly biogas production. In 2009 the average volumetric biogas production reached an average of $3.6\ \text{Nm}^3/(\text{m}^3\_\text{R}\cdot\text{d})$ and a yearly total production of 9.6 million Nm^3.

3.2. Main achievements in process stabilization and optimization

The cut down in manure usage put a focus on process development, which was facilitated by three main appendages to the operational strategy of the plant; 1) addition of ferrous chloride, 2) addition of hydrochloric acid and 3) addition of the process additive KMB1 (Fig. 2B).

3.2.1. Addition of ferrous chloride

Sulfide-associated problems, such as corrosive H_2S in the biogas and sulfide-inhibition of the methanogenesis are both reduced by precipitation of sulfides with Fe(II). At the plant, the addition of ferrous chloride to the homogenization and pasteurization tanks commenced in May 1998 and as a result, the sulfide concentration in the digesters and the concentration of H_2S in the biogas were reduced, as well as the sulfur load on the water scrubbers [19]. The use of ferrous chloride has continued since 1998 and because the addition of the precipitant is made already in the homogenization and pasteurization tanks, the H_2S-induced odors from the buffer and pasteurization tanks are also reduced.

3.2.2. Addition of hydrochloric acid

Laboratory tests, with addition of hydrochloric acid to co-digestion reactors operated under mesophilic conditions were performed in 1999-2000 [20]. Positive effects on volumetric gas production and VFA levels were noted in the digesters where pH was lowered with hydrochloric acid and full-scale acid addition was started at the plant in March 2002. On comparison of the operation performance of the plant in 2000-2001 with 2002-2003, the following direct and indirect effects were observed [19]: digester loading rate could be increased with 70 % on VS basis, gas production increased, acetate concentration decreased by 43 % and partial alkalinity concentration increased from 11 000 mg/L to 17 000 mg/L. On average, between the two periods, the amount of material increased by 20 % (fig 2B) whereas the dry substance of the material increased with 26 % during the same period (fig. 2A). Since also the percentage of slaughter house waste increased from 59 to 72 % in the material, the VS percentage of TS increased. Thus, the gas production increase was a result of the increased loading rate since the specific methane yield per kg VS was unchanged.

3.2.3. Addition of process additive KMB1

To further enhance process stability, and to increase the efficiency of the plant, a process additive known as KMB1 was developed at TVAB [21]. The main effects of the additive were: (1) more stable production, enabling (2) higher organic loading rate without process disturbances and heavy foaming [19], leading to (3) higher methane production. Also, the additive enabled the decrease and final removal of manure in the substrate mixture, and has been added to the plant since November 2003.

3.3. Plant performance after process improvements

After implementation of the three process improving additives mentioned above, a closer study of the process reveal the positive effects (data from 2004-2005). In the heated buffer tank the VFA levels fluctuate to a great extent and can occasionally get very high (up to 16 000 mg/L) while the pH is low (Fig. 3A). However, even though the buffer tank substrate display a low pH and high, fluctuating VFA concentrations (average 8400 mg/L, pH 5.5), the concentration of VFA in the digester is low and stable (average 1600 mg/L, max 2800 mg/L) and the digester fluid has a stable pH of 8.0 (7.9-8.1).

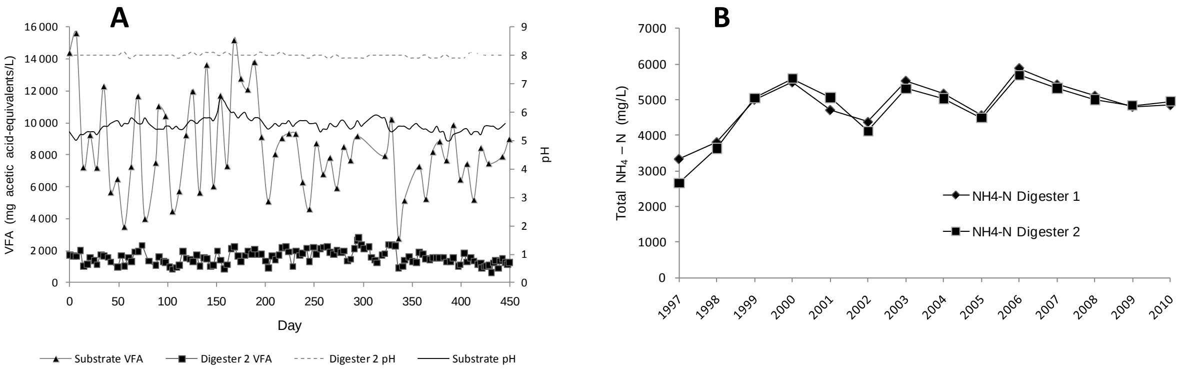

Figure 3 A). Volatile fatty acid (VFA) concentrations (mg acetic acid-equivalents/L) and pH levels in the heated buffer tank (denoted: substrate) and in the biogas digester (data from 2004-2005). B) Total ammonium (NH_4^+-N (aq) + NH_3-N (aq)) concentrations (mg/L) in the digesters during 1997-2010.

Since the plant's early years of operation, the total NH_4-N concentration has been high. The average for both digesters during 1999-2010 has been 5060 mg/L, with a maximum yearly average of 5880 mg/L (digester 1, 2006) and a minimum yearly average of 4120 (digester 2, 2002) (Fig. 3B). Labeling experiments were performed in 2008 to establish what type of methane formation pathway is prevalent – methane formation by acetate utilizing methanogens or via syntrophic acetate oxidation and hydrogenotrophic methanogens?

The labeling analysis showed production of high levels of labeled carbon dioxide in relation to labeled methane. The $^{14}CO_2/^{14}CH_4$ quota was determined to be 16; clearly showing that methane production in the digester occurred mainly through syntrophic acetate oxidation and hydrogenotrophic methanogenesis. Since the digester is operated at high ammonium levels (5300 mg NH_4^+-N/L at the time of sampling) this is a result that was expected and in accordance with the previous studies that have shown development of SAO in response to increasing ammonia levels[13]. The development of this prevailing metabolic pathway is likely the explanation to the stable operation of the process even at high ammonia levels. Given that methanogenesis via syntrophic acetate oxidation involves a hydrogenotrophic methanogen, that tolerates higher levels of ammonia than acetoclastic methanogens, methane production from acetate can still proceed even though the acetoclastic methanogens are inhibited. Furthermore, isolation and characterization of several ammonia tolerant hydrogen utilizing methanogens, as well as ammonia tolerant syntrophic acetate oxidizing bacteria, support this suggested mechanism for ammonia adaptation in biogas processes [22-24]. However, the generation time of a SAO culture was calculated to be approx. 28 days [13] which can be compared with the times of around 2 - 12 day for acetate utilizing methanogens [25]. Thus, the long retention time would seem to be a prerequisite to allow SAO to establish in the digester.

3.4. Practical experiences

The general plant operation experiences of anaerobic digestion of slaughterhouse waste concern two main themes: 1) logistics and transportation and 2) process and technology. At the slaughterhouse, the waste is grinded to ≤12 mm and treated with formic acid. The grinding at the slaughterhouse allows for transportation of the substrate in slurry form, and thereby a closed-system handling at the biogas plant, which prevents odor problems. Treatment with formic acid prevents foaming which would otherwise cause significant problems during transport and storage at the biogas plant. The thermal disintegration of the substrate in the heated buffer tank, and the fact that the substrate temperature is over 70 °C in large parts of the system, reduces potential problems with clogging and eases pumping of the substrate due to reduced viscosity. Furthermore, to achieve a stable process the type of material co-digested with the slaughterhouse waste is important, and the complimentary substrates should work well in the plant, both from a practical and a process point of view, which will lead to an even substrate mixture over time and thus an even organic loading rate and a stable biogas process.

4. Conclusions

From the long time experiences the following conclusions are established:

- It is possible to operate CSTR co-digestion of slaughterhouse waste, at substrate TS levels significantly over the original design level.
- The plant is operating well at high levels of ammonium, and the long HRT (45-55 day) enables establishment of a mesophilic syntrophic acetate oxidizing culture.
- With optimization of process parameters, substrate composition and through the addition of process additives, it has for 15 years been possible to achieve a continued increase of the biogas production, with basically the original plant capacity.

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Development of Process Technology to Produce Low Cost Biofuel I - Minimization of Operating Parameters during Preparation of Biodiesel

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Abstract: Fatty acid methyl ester (FAME), a renewable liquid biofuel popularly known as biodiesel, is emerging as a suitable replacement to common diesel fuel (CDF) in unmodified Compression Ignition (CI) engine. Present article reports the development of a process to reduce the operating cost during the conversion of vegetable oil to biodiesel through the application 1kW sonication techniques at various stages of the composite process. Around 98 % yield was achieved by employing minimum quantity of excess alcohol and alkali catalyst in transesterification reaction. After the completion of reaction, instantaneous separation of FAME from glycerol is a noticeable advantage. Its reaction parameters such as time and temperature have been reduced drastically. The ultrasound energy had also produced excellent benefit during purification of crude FAME through the efficient removal of mono and diglyceride from FAME. The analysis of the products was done as per ASTM methods and its fuel characteristics were evaluated using a research engine.

Keywords: *FAME, Biodiesel, Transesterification, Ultrasonication, Compression Ignition engine*

1. Introduction

Stupendous efforts have been made during the last few decades on bio-fuel chemistry. Amongst these, biodiesel in particular, has captured the world attention as an impressive substitute to common diesel fuel (CDF). It is the monoalkyl esters of long chain fatty acids (FAME) derived from vegetable oil and animal fats. The feedstock composed of mainly triglycerides with high viscosity, very low vapor pressure and impurities like free fatty acid (FFA), phospholipids, moisture, vegetable sediments and gum hence cannot act as ideal fuel for CI engine [1]. On being converted to FAME (having both carbon and viscosity equivalent to CDF) through a chemically reversible reaction called transesterification [1, 2], it becomes suitable to replace CDF, hence called biodiesel. Transesterification reaction is the vital step of the composite process where the vegetable oil (triglyceride) is treated with a short chain alcohol viz. methanol, in presence of a catalyst (acidic/basic) at a suitable temperature and reaction time to produce corresponding FAME as per gross reaction (1). It is renewable, biodegradable with relatively less emission profile, admissible viscosity, flash point and a high cetane number [3].

$$\text{Triglycerides} + 3\ CH_3OH \rightarrow \text{Glycerol} + \text{FAME} \qquad (1)$$

Even though the synthesis of FAME from vegetable oil is relatively facile its economization is challenging. The major drawback of the composite process lies largely on the costly feedstock, inefficient extraction of oil from seed, complicated purification of crude oil and product, high reaction parameters of transesterification, ineffective separation of products and loss of homogeneous catalyst. The difficulty involved with purification step of FAME comprises utilization of vast quantity of fresh water, loss of small quantity of the product with water followed by waste water treatment.

The present paper attempts to develop a process to produce biodiesel from refined soybean oil and sunflower oil by overcoming major hurdles involved in both transesterification and purification steps. Reduction of reaction parameters and other improvements in the various working steps have been tried with the help of ultrasonic waves [4, 5]. The purified biodiesel was subjected for exploration of its fuel characteristics in an unmodified CI engine.

2. Materials and methods

2.1. Materials

Refined soybean oil of nature fresh brand and sunflower oil of fortune brand were procured from local dealers. Anhydrous methanol (MeOH) (99.5%) and sodium hydroxide (NaOH) pellets were procured from M/s Finar, Ahmedabad. Fatty acid profile of the feedstock was evaluated by Gas Chromatography while moisture by using Karl Fischer (Systronics make) and phospholipids by classical method. Refined vegetable oil are found to contain negligible quantity of free fatty acid, moisture phospholipids, and used as feedstock for biodiesel preparation without further purification. The Ultrasonic Processor of Sonapros PR-1000 model of 1kW was used to generate sonication in a special designed three necked glass reaction vessel housed in a sound dampener. Gas Chromatograph of model CERES 800 plus of M/s Thermo Electron LLS Pvt. Ltd was used for the analysis of glycerol, monoglycerides, diglycerides, triglycerides, methyl esters of various fatty acids. Kirloskar make compression ignition engine with variable compression ratio was procured to study its performance with different biodiesel and evaluate their respective fuel properties.

2.2. Method

2.2.1. Transesterification reaction for the conversion of vegetable oil to FAME

All the ingredients of transesterification such as vegetable oil, anhydrous methanol was kept over freshly dried anhydrous sodium sulphate for over 10hours before use. Clearly homogeneous stock solution of desired strength of sodium hydroxide-methanol was prepared and also stored over freshly dried anhydrous sodium sulphate to remove any possibility of moisture formation. Exactly weighed quantity of vegetable oil was taken in the sonication vessel and preheated to a temperature 5^{o}C below the operating temperature. Methanol-sodium hydroxide catalyst solution was added into the sonication vessel very slowly without lowering the pre set temperature of the vessel. Appropriate horns/probes of the ultrasonic processor were inserted into the sonicator vessel so that its tip dips about 5mm into the alcohol phase. Reflux condenser, thermocouple, and dropper to draw sample time to time were placed with the reactor and appropriate sonication energy was applied. The experiments were conducted over wide range of methanol and oil molar ratio between 3:1 to 15:1, varying quantity of sodium hydroxide catalyst ranging from 0.1% to 1.5% with respect to oil and reaction times varying from 5 minutes to 45 minutes as well as wide temperature range of 30 to 70°C. After the completion of the reaction, heavier glycerol was gravity separated instantaneously from the reacted mixture leaving FAME as upper layer in a separating funnel.

2.2.2. Purification of Products

Crude FAME containing free glycerol, small amount of alkali and partial unconverted portion of triglycerides usually are usually done complicated water washing or vacuum distillation methods [6]. Disadvantages associated with such classical process is the partial loss of biodiesel and poisonous methanol, total loss of costly homogeneous catalyst, use of large quantity of fresh water followed by adopting costly waste water treatment process. While purification through distillation under reduced pressure was found to make partial oxidation of biodiesel due to the presence of double bond with fatty acids of FAME. Moreover, both methods failed to reduce mono- and diglycerides impurities from it [7]. In order to overcome the difficulties a novel method was adopted to purify FAME after its separation from reaction mixture. The neutralization of the alkali content of the product was done with dilute sulphuric acid [8] followed by counter current water washing to remove entire unreacted alcohol and residual free glycerol. By this way the requirement of fresh water was reduced to only 2 liters per litre of FAME in compare to large quantity of water utilized earlier [9]. The methanol was recovered from the waste water by distillation. About 90% methanol content of washed water was recovered by distillation. The waste of small quantity of FAME through washed water was minimized by reusing the distillate as washing fluid. The purified product was dried under by purging dried air. The mono- and diglycerides were reduced from the product by treating with silica gel of particular surface property and of particular mesh size under ultrasonication for 15-20 minutes. This purification method without thermal treatment prevents partial decomposition of the relatively unstable FAME containing un-conjugated double bonds.

2.2.3. Analysis of biodiesel

The ester content of soybean oil methyl ester and sunflower oil methyl ester was determined using Gas Chromatography with Flame Ignition Detector (FID), % yield was calculated following ASTM: D 6584-00 and moisture, viscosity, flash-fire point, density, etc as per the ASTM6547 method and GC graph is shown in Fig. 1.

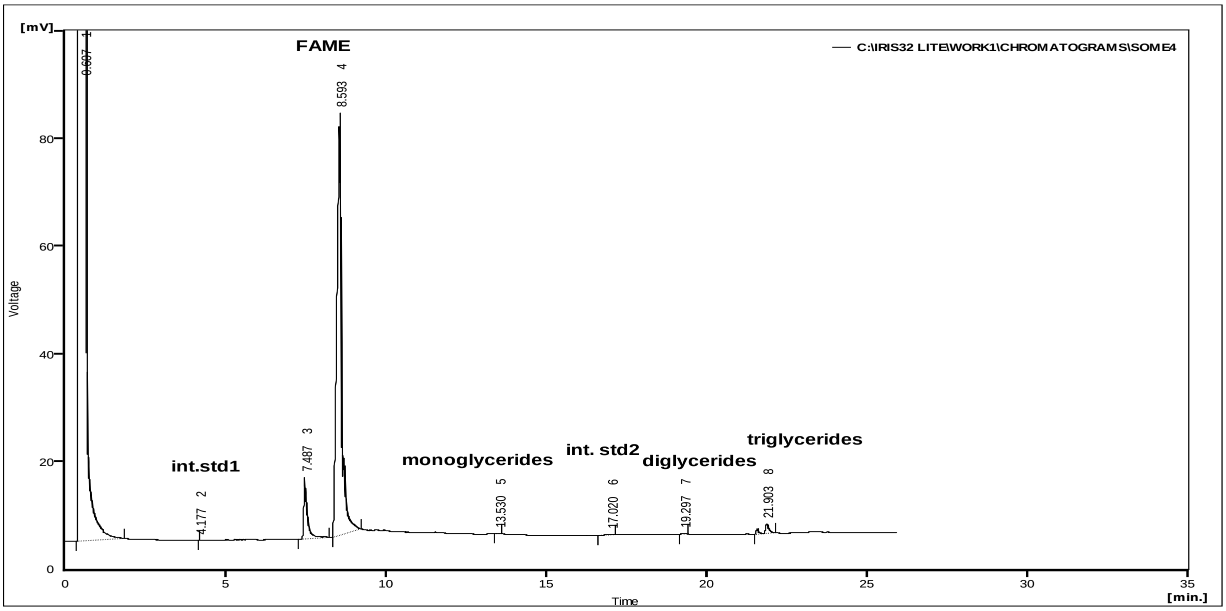

Fig. 1. Soy-FAME Gas Chromatogram

3. Results and Discussion

3.1. Effect of alcohol oil molar ratio:

The theoretical molar ratio of alcohol to oil in the transesterification reaction is 3:1. The higher molar ratio of methanol to oil is involved with catalytic braking of carbonyl bond with glycerides under strong thermal turbulence created by sonication. Availability of more solvent brings poorly soluble oil slowly into the homogeneous reaction phase. The nascent fatty acids after its liberation from glyceride are highly acidic for esterifiation with vast quantity of methanol available as medium. The presence of alkali catalyst in the reaction mixture probably helps the esterification. It is observed that with 5:1 to 9:1 molar ratio of alcohol-oil, ester formation (shown in Fig. 2) is more than 98%. When it is increased to 15:1 the yield of esters dropped to 80%. Such higher molar ratio of alcohol to oil probably reduces the adequate homogeneous catalytic concentration by dilution as well as interferes with the separation of glycerin as it is dispersed in large volume of solution thereby lowers the yield of esters. FAME yield is drastically reduced when molar ratio goes down from 5:1 which may be due to the fact that insufficient solvent fails to bring poorly soluble oil for reaction zone. Sonication technique proved to be more beneficial leading to an enhancement in the yield.

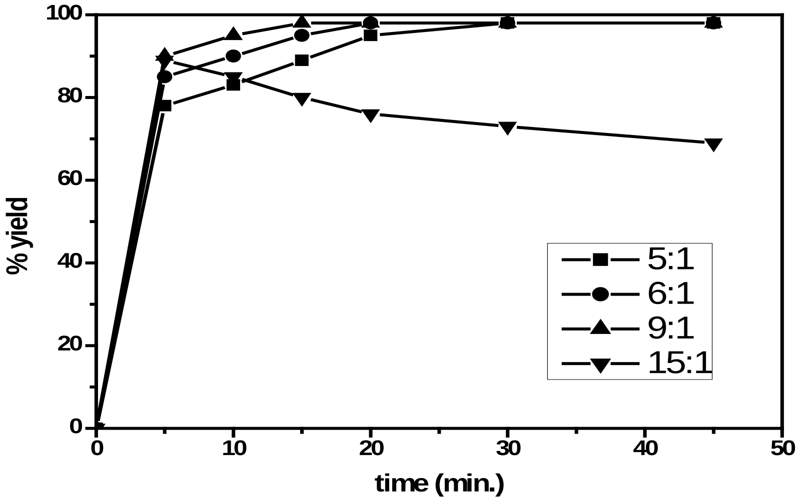

Fig. 2. Percentage yield of soy-FAME at varied methanol-oil molar ratios and different interval

3.2. Effect of catalyst concentration:

Methanolysis of soybean and sunflower oil is done by taking low cost NaOH as catalyst over the concentration range of 0.3 to 1.2 % wt with respect to oil. With alcohol-oil molar ratio 6:1 and temperature 60°C the product is analyzed at different time intervals starting from 5 min to 45 minutes. The results are displayed in Fig. 3. It is observed that the reaction has shown a yield of around 85% even with a low catalyst concentration of 0.3% in 45 minutes. Unlike the mechanical stirring method where the yield of products with low catalyst concentration is quite low, the sonication technique proved to be more beneficial leading to an enhanced increase in yield of methyl esters. However the maximum 98% yield is obtained at catalyst concentration of 1% wt. of oil in less than 15 minutes time. Longer reaction time found to increase the viscosity of FAME may be due to back reaction of FAME with glycerol.

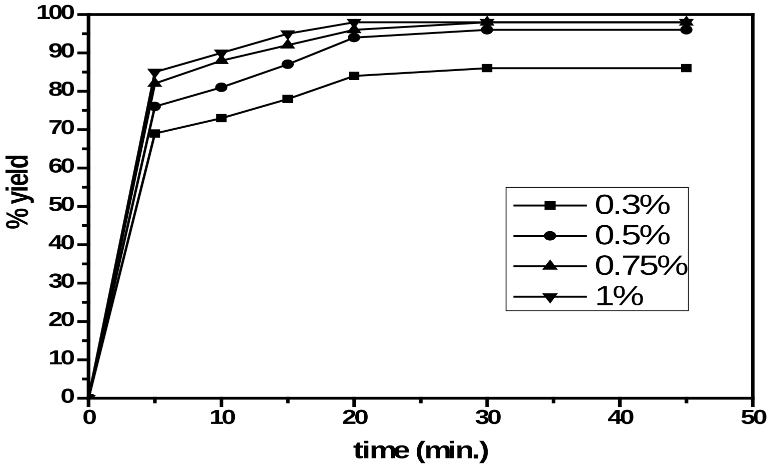

Fig. 3. Percentage yield of soy-FAME at varied catalyst concentrations and different time intervals

3.3. Effect of temperature:

It is observed that transesterification under sonication is temperature dependent. At temperature 60-65°C more than 90% conversion is achieved in just 5 min (shown in Fig. 4). The gas chromatogram for this conversion is shown in Fig. 1. The ultrasound technique involves the formation of a fine dispersion between oil and alcohol due to micro-turbulence generated by cavitations bubbles creating enormous interfacial area. Thermal input between two immiscible liquids under sonication forms more dispersion and thus accelerates chemical reactions especially between two immiscible ingredients.

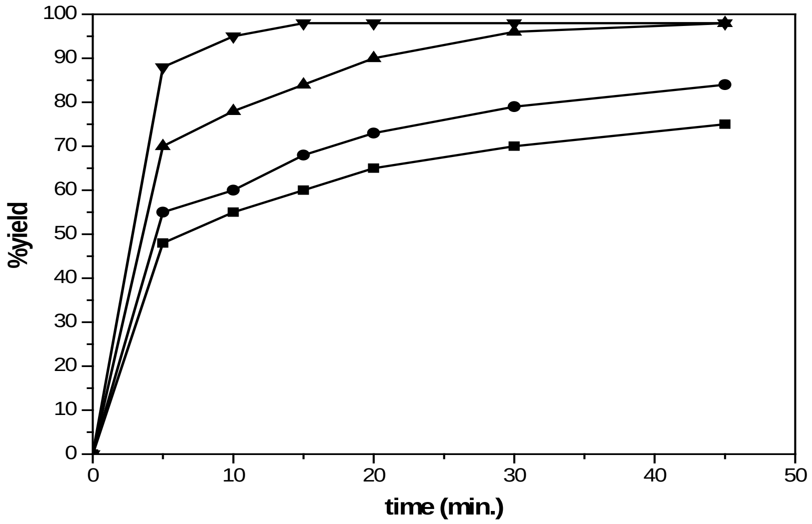

Fig. 4. % yield of soybean oil methyl ester at varied temperature and different time intervals

3.4. Performance of biodiesel in IC engine

The biodiesel with maximum conversion (98%) after purification and analysis is taken up for the evaluation of its fuel properties in a CI research engine. Due to low vapour pressure of FAME the flash point is found to be more than 130^0C. Hence it cannot be used as a direct fuel in the unmodified CI engine. Hence, FAME is blended with CDF in the proportion of 5% and 10%, called as B-05 and B-10 and used as fuel [6] in the unmodified CI engine.

The density and kinematic viscosity of FAME is equivalent to CDF. The gross calorific value (GCV) is 1-2% lower than diesel. The brake specific fuel consumption (BSFC) i.e. the ratio of fuel mass flow of an engine to its output power were drawn for soybean FAME-CDF blended B-05 and B-10 at low engine load under variable compression ratio (CR). BSFC is found to be higher at lower loads and as the load increased its value decreased. It is also noticed that the BSFC for B-05 is greater than that of B-10. The difference between BSFC values for both the blends is reduced with rise in load (Fig. 5 & 6). Due to higher flash point and lower calorific value, the BSFC should rise with biodiesel content in the biodiesel-diesel blended fuel, but at lower loads this does not happen. It may be due to the presence of oxygen (attached to carbonyl carbon) content in biodiesel as well as its better spray characteristics (due to its lower viscosity) and comparable energy density for which the brake power is improved [10]. Overall, BSFC of biodiesel is at par with CDF, may be due to the presence of un-conjugated double bonds with fatty acids of FAME.

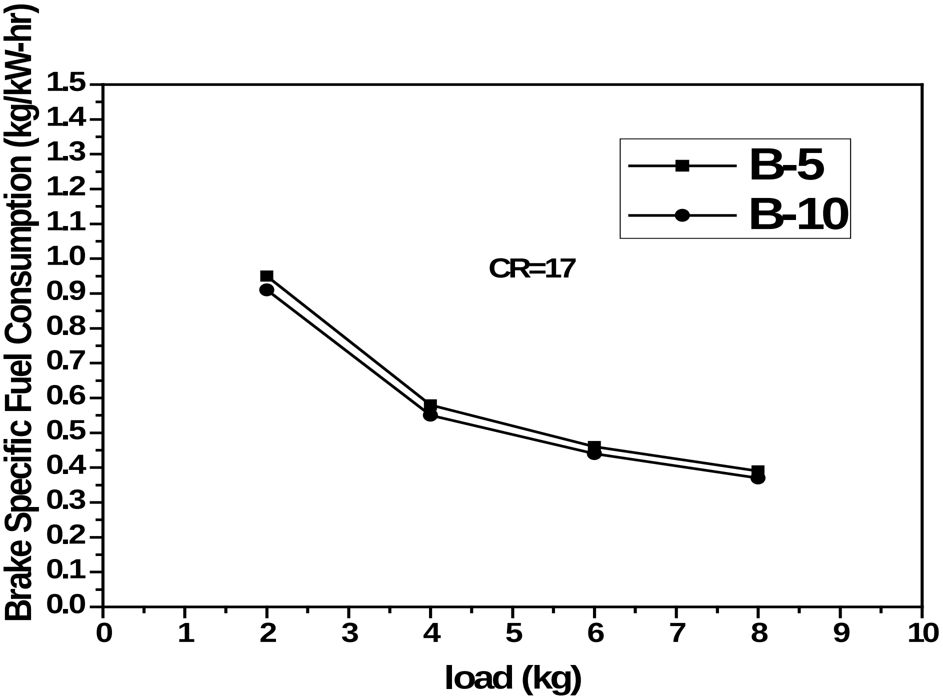

Fig. 5. Variation of Brake Specific Fuel Consumption with different loads at CR of 17 for B-05 & B-10

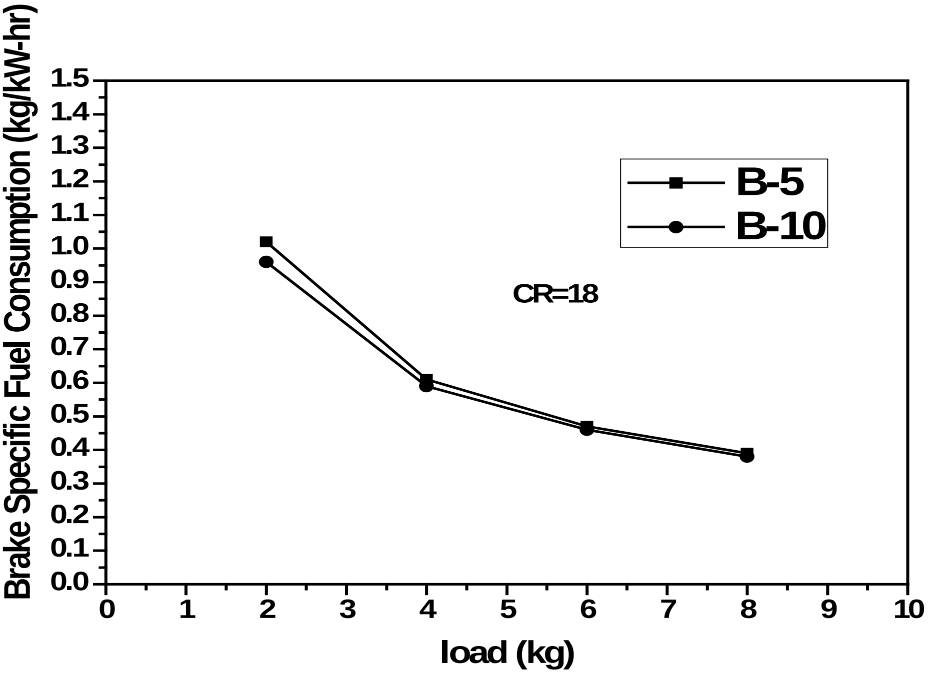

Fig. 6. Variation of BSFC with different loads at compression ratio 18 for B-05 & B-10

4. Conclusion

The paper puts up a composite process to produce biodiesel from vegetable oil with reduced operating parameters such as the reduction of reaction time, reaction temperature, reduction in quantity of unrecoverable homogeneous catalyst, utilization of lesser amount of excess methanol for achieving excellent yield by the application of low energetic (1kW) ultrasonication. However, the transesterification reaction under sonication is found to be temperature dependent. The separation of FAME from glycerol under the present working condition is instantaneous. The complicated purification step has been simplified. Use of silica gel along with sonication found to reduce the impurities of crude FAME such as free glycerol, mono and diglycerides. Hence, the application of sonication is found to be beneficial with composite process of synthesizing biodiesel from refined vegetable oil. Brake Specific Fuel Consumption of biodiesel prepared through the application of ultrasonication found to be at par with that of Common Diesel Fuel although the gross calorific value of biodiesel is 1.5% lower than CDF, which may be due to the presence of un-conjugated double bonds with many fatty acids of FAME that could replace it in CI engine.

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Orthogonal array design for biodiesel production optimization - using ultrasonic-assisted transesterification of *Camelina sativa* L. Crantz oil

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Abstract: Camelina seed oil has recently attracted great interest as a low-cost feedstock for biodiesel production because of its high oil content and environmental benefits. In the present study, an orthogonal array design was used to optimize the biodiesel production from camelina seed oil using ultrasonic-assisted transesterification. Four relevant factors are investigated: methanol to oil ratio, catalyst concentration, reaction time and temperature to obtain maximum fatty acid methyl ester (FAME) yield of biodiesel. An OA_{25} matrix was employed to study the effect of the four factors, by which the effect of each factor was estimated using statistical analysis. Based on the results of the statistical analysis after the orthogonal experiments, maximal biodiesel FAME yield (98.6 %) was obtained under the conditions of 8:1 methanol to oil molar ratio, 1.25 wt.% catalyst concentration (KOH), 50 min reaction time, and 55 ℃ reaction temperature. Other properties of the optimized biodiesel, including density, kinematic viscosity, and acid value, were conformed to the relevant ASTM and EN biodiesel standards and thus the optimized biodiesel from camelina oil basically qualified to be used as diesel fuel.

Keywords: Biodiesel, Orthogonal experiment, Optimization, Ultrasonic-assisted, Camelina oil.

1. Introduction

In recent years, biodiesel, as a low-emission renewable fuel, has attracted great public interest and there is a huge demand for biodiesel in the renewable fuel market. At present, most ~~of~~ biodiesel is produced from vegetable oils, such as soybean and rapeseed [1]. However, many vegetable oils for biodiesel production are edible and compete with the edible oil market. It will increase the cost of vegetable oils and cause deforestation since a lot of forests have to be felled for plantation purposes [2]. Moreover, the cost of raw materials accounts for 60-80 % of total biodiesel production [3]. Increasing cost of vegetable oils also causes the cost of biodiesel production higher. Therefore, many researchers focus on different feedstocks of biodiesel and explore non-edible vegetable oils for biodiesel production, such as jatropha curcas oil and algae oil [4].

Camelina (*Camelina sativa* L. Crantz), is a spring annual oilseed plant originated in Germany in about 600 B.C.. It grows well in temperate climates and matures earlier than other oilseed crops [5]. In comparison with common oilseed crops, camelina has lower agriculture inputs, such as lower water, pesticide and fertilizer requirements, and higher cold-weather tolerance. Therefore, camelina may avoid deforestation in certain extent since it can be cultivated in agriculturally undesirable lands which are not suitable for normal crops, hence improving the quality of lands [6]. Furthermore, camelina seeds have an oil content as high as 28 to 40 %, which makes camelina a high oil-bearing crop [7]. Therefore, the use of camelina oil as feedstock for biodiesel production can greatly reduce the production cost of biodiesel and offer some environmental benefits.

Frohlich and Rice [8] already evaluated the possibility of using camelina oil as a source for biodiesel production and Patil et al. [9] also tried to produce biodiesel from camelina oil using supercritical and subcritical methanol with cosolvents. Although there are some studies related to biodiesel produced from camelina oil, the optimal production conditions have never been investigated. Most optimal conditions were attained using a stepwise approach, which examined one process condition at a time [10]. This method was time-consuming and might not get the right optimal conditions because some process conditions affect the yield of biodiesel simultaneously. This paper used an orthogonal array experimental design to optimize the biodiesel production conditions from camelina seed oil in order to avoid these problems. The use of the chemometric method: Orthogonal Array Experimental Design for process optimization has already found many applications elsewhere. It involves the selection of some representative combinations of factors and levels for the experiments to reflect the situation of the whole selected examined area. It is a cost-effective optimization strategy that can obtain the optimal level of each factor in a limited number of experimental trials [11]. This paper discussed the main process conditions in the transesterification reaction using orthogonal array experiments to optimize biodiesel production. To confirm whether or not the final product can be used as a qualified fuel, this study ~~will~~ also examined its compliance with international biodiesel standards.

Normally, a stirred reactor is used as the reaction vessel for continuous alkali-catalyzed biodiesel production. However, ultrasonic irradiation has proved to be a useful tool for strengthening the mass transfer of immiscible liquids. It can cause cavitation of bubbles near the phase boundary between immiscible liquid phases and then the asymmetric collapse of the cavitations bubbles disrupts the phase boundary and causes emulsification. Micro jets, which are formed by impinge one liquid to another, lead to intensive mixing of the system near the phase boundary and thus reactants can be produced more quickly [12, 13]. Therefore, assisted with ultrasound, the reaction time may be reduced dramatically and the high reaction temperature may be lower than in traditional mechanical stirring production process. That would reduce the production cost of biodiesel and save more energy.

2. Methodology

Reagents and catalysts

Cold-pressed camelina seed oil, obtained from Campressco Products Inc. (Saskatchewan, Canada), was used for the experiments. The main chemical compositon of the oil was, expressed in wt.%, 5 % palmitic acid, 16.7 % oleic acid, 16.9 % linoleic acid, 16.1 % cis-11-eicosenoic acid and 38.1 % linolenic acid. Analytical grade methanol (99.9 %) was used in the experiments and potassium hydroxide (>85 %) in pellet form was used as the catalyst for the alkaline transesterification reaction.

2.1. Experimental process

Around 100 g (±0.1) of camelina oil was weighted and placed in a 250 ml glass bottle. The amount of methanol used was calculated based on its molar ratio with oil. The catalyst was first dissolved completely in methanol with a prefixed amount using a standard mixer, and then the mixture was added into the oil. The whole reaction was carried out in an ultrasonic bath obtained from Jeio Tech Co., Ltd. (model: US-05; frequency: 40 KHz; volume: 5L) and operated at 40 KHz. To enhance mass transfer and the reaction rate, the bottle was shaken for about 20 seconds by hand for every 10 minutes. Until reaching the preset reaction time, the glass bottle was then removed from the bath and the products of the reaction were settled down overnight at the room temperature. Two major products was observed in the bottle: crude biodiesel phase at the top and glycerol phase at the bottom. These two phases were separated by centrifugation (rotating speed: 8000 rpm; time: 5 min). After that the crude biodiesel was washed several times by deionized water assisted with ultrasound to remove the impurities and unreacted catalyst. The use of ultrasound reduced the washing times.

2.2. Orthogonal experiment design

In the study, the experiments were based on an orthogonal array experimental design (OA_{25} matrix) where the following four variables were analyzed: methanol to oil molar ratio (factor A), catalyst concentration (factor B), reaction time (factor C) and reaction temperature (factor D). These variables were identified to have significant effects on the yield of biodiesel produced from other feedstocks [10]. An OA_{25} matrix was employed to assign the considered factors and levels as shown in Table 1. Twenty-five trials were carried out according to the OA_{25} matrix to complete the optimization process. Each row of orthogonal array represents a run, which is a specific set of factor levels to be tested. The run order of the trials was randomized to avoid any personal or subjective bias. Here the matrix denotes four factors each with five levels and the extra column remained could be used as experimental error to indicate the reliability of the whole experiments. Statistical analysis was carried out to reflect the optimal reaction conditions and their magnitudes.

Table 1 Levels and factors affecting the FAME yield of biodiesel.

Level	Factors			
	Alcohol quantity (Molar ratio) A	Catalyst concentration (wt.%) B	Reaction time /min C	Reaction temperature /°C D
1	2:1	0.75	10	25
2	4:1	1	30	35
3	6:1	1.25	50	45
4	8:1	1.5	70	55
5	10:1	1.75	90	65

2.3. Fuel properties of biodiesel

The whole experiments of biodiesel were aimed at increasing the fatty acid methyl ester (FAME) yield. This yield determines the quality of the biodiesel product and indicates the efficiency of oil conversion. The EN standard (EN14214) requires FAME content of biodiesel to be over 96 % [14]. In the present study, the FAME yield was analyzed by a Hewlett-Packard 6890 Series gas chromatograph (Palo Alto, USA) according to the AOCS official methods Ce 1-62 [15], equipped with a flame ionization detector (FID) operating at 300 ℃ and a capillary injection system operating at 250 ℃. The carrier gas was high-purity helium, with a constant flow of 1.0 ml/min, and samples of 1 μL were injected in split mode with a split ratio of 80:1. The column was a BD-EN14103 HP-INNOWax column (J&W Scientific, USA) with 30 m in length, 0.32 mm internal diameter and 0.25 μm film thickness. To minimize the experimental error, a known amount of a specific component methyl nonadecanoate (C19:0), used as the internal standard, was added into the sample prior to the GC injection. Other properties of the final biodiesel product, including density, kinematic viscosity and acid value, were determined in order to evaluate its suitability as diesel fuel substitute. The density was determined at the room temperature by using a density bottle while its kinematic viscosity was determined with an ubbelohde glass capillary kinematic viscometer according to the ASTM D445 method. The acid value (AV) was calculated according to the ASTM D644 method. All data reported were arithmetic means of triplicate assays.

2.4. Statistical analysis of orthogonal experiments

The statistical analysis included a range analysis and an analysis of variance (ANOVA). Range analysis was used to indicate the effect of each factor and determine the optimal level of different factors. The mean value of the sum of the evaluation indexes of all levels in each factor ($\overline{K_{ji}}$) was used to determine the optimal level and the optimal combination of factors. The range (R_j) was defined as the range between the maximum and minimum value of the mean values and used to evaluate the importance of the factors. The optimal level for each factor could be obtained when $\overline{K_{ji}}$ is the largest and larger R_j means greater significance of the factor [16]. Although the optimal value of different factors can be easily determined by the range analysis, this method cannot distinguish whether the difference between the data fluctuation of each factor level was caused by experimental conditions or by experimental errors. Due to the limitation of the range analysis, analysis of variance was necessary to obtain the magnitudes of the factor affecting the result [17]. In the ANOVA, the data were analyzed by a F-test. The F value of each factor (F_j) implies the ratio of the variance for the each factor (V_j) to that of the experimental error (V_e) [16, 18]. During the F-test, F_α was a constant and defined as a critical value of the F-value for different inspection levels and can be found from the distribution table of the F-values [18]. When F_j is larger than F_α, the factor effect for the results is prominent; otherwise the factor effect for the results is not prominent. Moreover, the percentage contribution of each factor (P_j) was the percentage of the purified sum of square deviation for each factor (SS_j') in the total sum of square deviation (SS_T). It reflects the factor's influence and the percentage contribution due to experimental error providing an estimate of the adequacy of the whole experiments. Larger percentage contribution means more significant factor influence. When the percentage contribution due to error is low, say 15 % or less, it can be assumed that no important factor has been omitted and the whole experimental results are reliable [18, 19].

3. Results and discussion

3.1. *Fatty acid methyl ester yield and statistical analysis*

According to the OA_{25} matrix, twenty-five experiments were carried out and the results were shown in Table 2. As mentioned before, the extra column was used as the experimental error to indicate the reliability of the whole experiments. These data were taken as the original data and used in the statistical analysis.

The mean values ($\overline{K_{ji}}$) and the relative data of range analysis were shown in Table 3. The highest FAME yield of each level was clearly distinguished when methanol to camelina seed oil molar ratio was 8:1 (93.4 %), catalyst concentration was 1.25 wt.% (89.5 %), reaction time was 50 minutes (87.8 %) and reaction temperature was 55 ℃ (86.9 %) since $\overline{K_{ji}}$ at these combinations ($A_4B_3C_3D_4$) was the highest. Since larger R_j means bigger impact on the product yield, compared with the range values of different factors (R_j), the order of significant factors was: methanol to oil ratio (36.9) > catalyst concentration (14.8) > reaction time (10.3) > reaction temperature (7.3). The mean values of each factor ($\overline{K_{ji}}$) were shown in Fig.1. It should be noted that these lines were only used to show the trend of each factor, not for predicting other values that were not experimented [20]. Based on the changes of $\overline{K_{ji}}$, it can be observed that the FAME yield was dramatically increased from 56.5 % to 93.4 % with the ratio of methanol to oil increased from 2:1 to 8:1, and then slightly decreased. It indicated that increasing methanol amount immediately speeded up the transesterification reaction and shifted the reaction equilibrium toward the product side to form more FAME. However, further increasing the methanol amount beyond the optimal ratio reduced the yield since methanol also acts as an emulsifier that enhances emulsion. This caused a drop in FAME yield and complicated the washing process. The FAME yield increased with increasing catalyst concentration and reached maximum (89.5 %) at 1.25 wt.%. Beyond the optimal point, the yield slightly decreased to 86 %. It indicated that sufficient amount of catalyst was required for complete conversion but excessive catalyst might activate the oil to react with the alkali catalyst, and thus formed more soaps and reduced the FAME yield. For reaction time, the FAME yield increased steadily first, and reached a maximum (87.8 %) at 50 min, and then the yield reduced slightly. Theoretically, FAME conversion would increase with reaction time. However, beyond the optimal time, the FAME yield slightly reduced because of the backward reaction and the saponification reaction [10]. Finally, reaction temperature seems to have little effect on the FAME yield with a change from 79.7 % to 86.9 %. Since the reaction was carried out in an ultrasonic bath, the cavitation led to a localized increase in temperature at the phase boundary and thus the influence of reaction temperature was small.

Table 2 FAME yield of biodiesel in OA_{25} matrix.

Trial no.	Factors					Results
	A	B	C	D	Experimental error level	FAME yield (wt.%)
1	2:1	0.75	10	25	1	28.5
2	2:1	1.00	30	35	2	53.6
3	2:1	1.25	50	45	3	68.4
4	2:1	1.50	70	55	4	67.6
5	2:1	1.75	90	65	5	64.2
6	4:1	0.75	30	45	4	84.1
7	4:1	1.00	50	55	5	93.4
8	4:1	1.25	70	65	1	95.2
9	4:1	1.50	90	25	2	90.5
10	4:1	1.75	10	35	3	85.9
11	6:1	0.75	50	65	2	88.5
12	6:1	1.00	70	25	3	91.6
13	6:1	1.25	90	35	4	95.8
14	6:1	1.50	10	45	5	92.5
15	6:1	1.75	30	55	1	96.2
16	8:1	0.75	70	35	5	88.5
17	8:1	1.00	90	45	1	94.6
18	8:1	1.25	10	55	2	93.6
19	8:1	1.50	30	65	3	96.9
20	8:1	1.75	50	25	4	93.3
21	10:1	0.75	90	55	3	83.8
22	10:1	1.00	10	65	4	87.1
23	10:1	1.25	30	25	5	94.4
24	10:1	1.50	50	35	1	95.6
25	10:1	1.75	70	45	2	90.3

Table 3 Range analysis data of biodiesel FAME yield.

	Alcohol quantity (Molar ratio) A	Catalyst concentration (wt.%) B	Reaction time /min C	Reaction temperature /℃ D
$\overline{K_{i1}}$	56.5	74.7	77.5	79.7
$\overline{K_{i2}}$	89.8	84.1	85.0	83.9
$\overline{K_{i3}}$	92.9	89.5	87.8	86.0
$\overline{K_{i4}}$	93.4	88.6	86.6	86.9
$\overline{K_{i5}}$	90.2	86.0	85.8	86.4
R_j	36.9	14.8	10.3	7.3

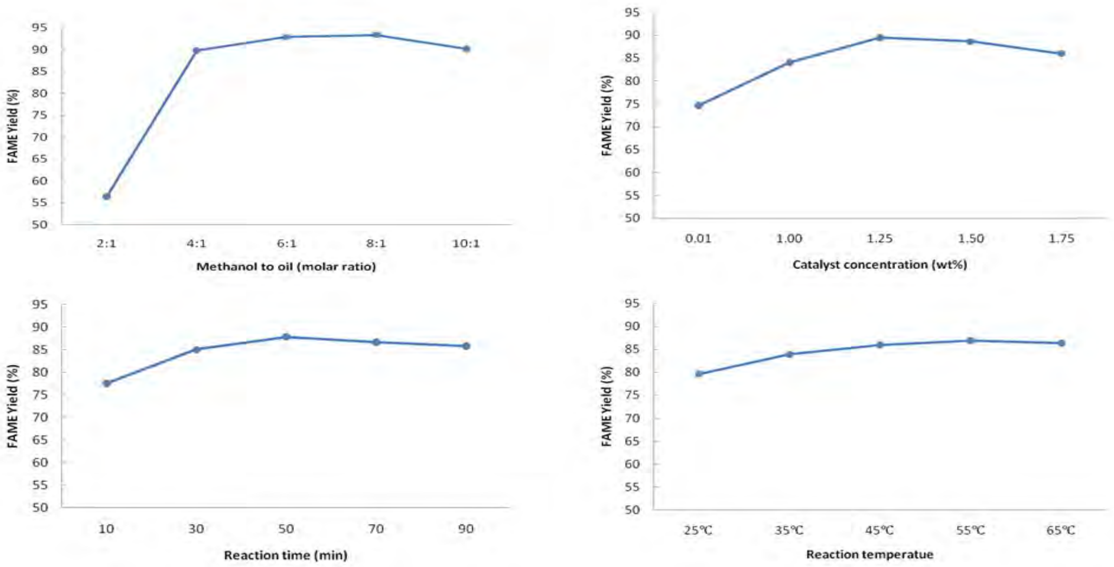

Fig.1. Relationship between the mean values of various influence factor and FAME yield.

The data of ANOVA for the FAME yield was shown in Table 4. For the inspection level, $\alpha=0.05$, the critical value can be found from the distribution table of F-value: $F_a(4,4) = 6.39$. It was obvious that F_A (72.2) > F_a, F_B (10.2) > F_a. It indicated that methanol to oil ratio and catalyst concentration were the prominent factors affecting the FAME yield of biodiesel, when the regression curve and analysis were within a 95 % confidence level. Furthermore, from the percentage contribution, it was deduced that the most important factor contributing to the product yield was factor A (methanol to oil ratio, 78.5 %), followed by factor B (catalyst concentration, 10.1 %), whereas factors C (reaction time, 4.2 %) and factor D (reaction temperature, 1.7 %) were not the significant factors for the change of FAME yield. Since the percentage contribution due to error was low (5.5 %), it was assumed that no important factor had been omitted and the whole experimental results were reliable.

Table 4 ANOVA results of the FAME yield in OA_{25} matrix.

Source	SS_j	df	V_j	F_j	$F_a(4,4)=6.39$	SS_j'	P_j (%)
A	4986.1	4	1246.5	72.2	>	4917	78.5
B	702.9	4	175.7	10.2	>	633.8	10.1
C	331.8	4	83.0	4.8	<	262.7	4.2
D	176.9	4	44.2	2.6	<	107.8	1.7
e	69.1	4	17.3	—		345.5	5.5
T	6266.8	20				6266.8	100

3.2. Optimization of the experimental conditions

According to the statistical analysis, the four experimental conditions affected the FAME yield of biodiesel differently. The amount of methanol and catalyst influenced dramatically the FAME yield and reaction temperature had a few effect on the FAME yield. The results indicated that increasing the level of these factors speeded up the reaction and the FAME conversion. However, beyond the optimal level, the FAME yield slightly reduced because of the backward reaction, such as emulsion and saponification. On the other hand, reaction temperature had little effect on the FAME yield since assisted with ultrasound already led to a localized increase in temperature at the liquid phase boundary.

Finally, the experiment was repeated under the optimal process conditions to confirm the validity of the optimization. A FAME yield of 98.6 % was obtained, which was higher than any former orthogonal experimental result. Compared with the data of the Trial 18 experiment, it was obvious that there was slight difference in the FAME yield (93.6 %) because of the influence of reaction time (10 min in Trial 18 and 50 min under optimal conditions). This result was consistent with that of the statistical analysis. And compared with the results of the traditional mechanical stirring production process, the FAME yield under optimal conditions with ultrasonic-assisted was much higher. Both the reaction time and the amount of catalyst used were reduced [8]. Other properties of biodiesel produced under the optimal conditions were also measured. The density of biodiesel was 0.882 g/cm^3, while the kinematic viscosity was 3.66 cst at 40°C, and the acid value was 0.217 mg KOH/g. Compared with the ASTM D6751 and EN 14214 standards, all the tested fuel properties of biodiesel produced under the optimal production conditions met the requirements. Therefore, optimized biodiesel basically qualified to be used as the diesel fuel.

4. Conclusions

In this research, the alkali-catalyzed ultrasonic-assisted transesterification reaction of camelina seed oil was studied and optimized through the orthogonal experiments with an OA_{25} matrix and a statistical analysis. According to the range analysis, the FAME yield of biodiesel increased sharply with increasing the amount of methanol used and catalyst concentration but was slightly reduced after the optimal point. The FAME yields also increased with increasing reaction time and temperature but the change was small. According to the ANOVA, the amount of methanol and catalyst used were significant factors for the FAME yield. After the whole statistical analysis, the optimal FAME yield of biodiesel (98.6 %) was obtained to be methanol to oil molar ratio of 8:1, catalyst concentration of 1.25 wt.%, reaction time of 50 min and reaction temperature of 55 ℃. Since the tested fuel properties of biodiesel conformed to the ASTM D6751 and EN 14214 standards, camelina seed oil biodiesel produced under the optimal conditions basically can be used as a qualified fuel.

Acknowledgement

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Lipase catalyzed transesterification of tung and palm oil for biodiesel

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Abstract: The tung oil and palm oil were subjected to enzymatic transesterification. Immobilized lipase (Novozyme 435) was used at 10 % w/v vs. oil. The reactions were conducted at 40°C to 60°C with methanol and ethanol at a molar ratio of 1:3 for 24 hours. Temperature was found critical for the conversion efficiencies. Under 55°C after 24 hour, the optimal conversions of tung oil and palm oil fatty acid methyl esters (FAMEs) were 48 % and 63 %. The optimal conversions for tung oil and palm oil fatty acid ethyl esters (FAEEs) at 50°C were 20 % and 55 % respectively at 50°C. It was found the effciencies of FAEEs conversion were lower than the ones of FAMEs conversion. It was found that the tung oil consisted of 80 % unsaturated fatty acids, and palm oil consisted by just over 50% saturated fatty acids, by contrast. The results showed that the fatty acid composition of oil could directly impact on the efficiencies of enzymatic transesterification. A numerical model was derived to describe the reaction in this two-phase system. It was found that fitted mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction were consistent to experimental results.

Keywords: *Biodiesel, Lipase, Palm oil, Transesterification, Tung oil.*

1. Introduction

Tung Tree (*Vernicia fordii*) is widely distributed in Taiwan, as well as in southern China, Burma, and northern Vietnam. Its seed oil, as known as tung oil, had been conventionally used in lamps for lighting, as well as an ingredient for wood paint and varnish. Currently, non-edible oils have been more favourable to serve as biodiesel feedstocks to avoid competitions with food sources under increasing population pressures. The utilization of seed oil from tree sources can have synergistic benefits with afforestation, like carbon sequestration and climate mitigation. Lipase transesterification of triglycerides is an eco-friendly alternative to chemical process due to a lower process temperature and an improved selectivity [1, 2]. In addition, many operational advantages of using immobilized lipase were reported [3, 4]. Few catalytic transesterification of tung oil were reported [5], and even fewer lipase transesterification of tung oil for biodiesel production was reported [6].

In order to characterize the enzymatic transesterification for tung oil, various temperatures were employed with methanol and ethanol. The results were compared to the ones of the palm oil. In contrast to mono-phase three-step reactions [7-9], fewer models were considering two-phase mass transfers for immobilized lipases [10, 11]. A numerical model, considering dual phase mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction, was derived to describe the reaction in this two-phase system. No other published studies compared the differences for transesterification by immobilized lipases between two plant oils with different degree of unsaturation in a two-phase system.

2. Methodology

2.1. Experimental

2.1.1. Materials and analytical methods

The locally obtained tung and palm oils were de-waxed by dichloromethane [12]. Their fatty acid contents were verified using a G C/MS following protocols described by Chinese National Standard (CNS) 15051 (2007) and ISO 5508 (1990). The composition is listed in Table 1. Lipase immobilized onto catalytic exchange resins (Novozyme 435, B aesvegard, Denmark) was used without further treatments.

Table 1. Fatty acids composition of tung oil and palm oil.

Plants	C16:0	C18:0	C18:1	C18:2	$C18:3^{\Delta 9,11,13}$
Tung oil	2.67	2.4	7.88	6.6	80.46
Palm oil	52.71	3.8	36.73	6.7	--

2.1.2. Reaction Conditions

Tung and palm oils were subjected to enzymatic transesterification, with parameters from the studies cited in a recent review [13]. Immobilized lipase was used at 10 % w/v vs. oil [14]. The reactions were conducted at the oil to alcohol molar ratio for 1:3. The reaction temperature was set at 40°C, 45°C, 50°C, 55°C, 60°C with methanol for 24 hours. A stirring rate of 700 rpm was applied. Conversions by enzymatic transesterification were also quantified using a GC/MS based on the above protocols.

2.2. Numerical model

2.2.1. Mass transfer

Lipase was a water-soluble enzyme, and the catalyst particles are surrounded by a hydrophilic film consisting of methanol/ethanol and glycerol. The immiscible mixture of methanol/ethanol and tung/palm oil formed a film consisting mass transfer resistance:

$$-\frac{dC_A}{dt} = k_1(C_A - C_{As}) \tag{1}$$

where k_1 was the mass transfer coefficients of tung/palm oils; C_A and C_{AS} were the tung/palm oil concentrations in the oil phase and on the interfacial area, respectively, and t was time. In a mass-transfer limiting case, C_{AS} could be ignored:

$$-\frac{dC_A}{dt} = k_1 C_A \tag{2}$$

$$-\frac{dC_{A0}(1 - X_A)}{dt} = k_1 C_{A0}(1 - X_A) \tag{3}$$

$$\frac{dX_A}{dt} = k_1(1 - X_A) \tag{4}$$

X_A was the conversion of tung/palm oils.

2.2.2. *Pseudo steady-state second order reaction*

After mass transfer resistance was overcome, a pseudo steady-state second order reaction was assumed:

$$-\frac{dC_A}{dt} = k_2 {C_A}^2 \qquad (5)$$

$$-\frac{dC_{A0}(1-X_A)}{dt} = k_2 C_{A0}^2 (1-X_A)^2 \qquad (6)$$

$$\frac{dX_A}{dt} = k_2 C_{A0}(1-X_A)^2 \qquad (7)$$

k_2 was the rate constant of the pseudo-steady-state second order reaction; C_A and C_{A0} were the tung/palm oil concentrations at $t = t$ and $t=0$.

2.2.3. *Numerical procedures*

The parameters k_1 and k_2 were obtained from non-linear regression of the experimental oil conversion versus time data using Eq. (1-7) using SigmaPlot for Windows Version 10.0.

3. Results and Discussions

3.1. *Effect of Alcohols*

Figure 1 shows the effect of alcohols on the conversions of tung and palm oils at 50°C. The model fitted well with the experimental data. Conversions of tung oils at 24 hours were very sensitive to alcohol used in the transesterification: 40 % with methanol and 18 % with ethanol. Although conversions of palm oils at 24 hours were not very sensitive to alcohol used, the system using methanol demonstrated greater initial conversions for the first 12 hours than the one using ethanol.

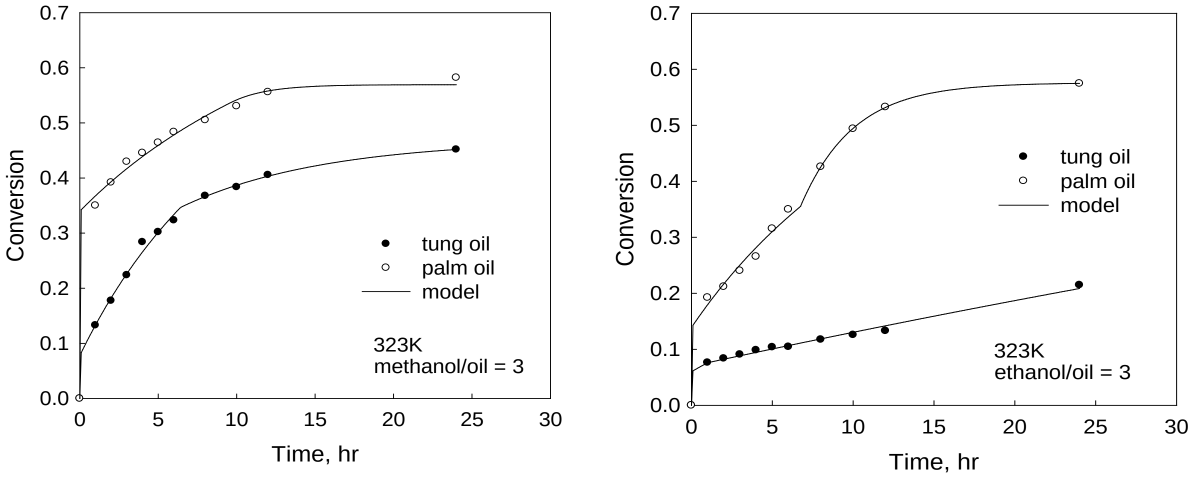

Fig. 1. Effect of alcohols on the conversions of tung/palm oils at 50°C. Left panel: methanols; right panel: ethanol.

3.2. *Effect of Temperature*

3.2.1. Reaction with methanol

Figure 2 shows the effect of temperature on the conversions of tung/palm oils using methanol from 45 to 55°C. The model fitted well with the experimental data. Conversions of both oils at 24 hours were slightly increased with this temperature increment. Again, greater initial conversions for the first 12 hours were shown for both oils.

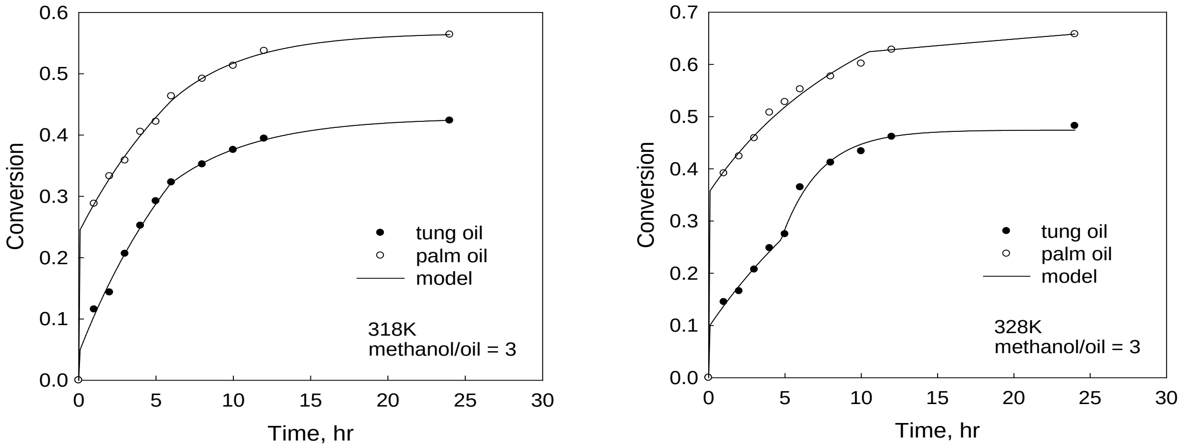

Fig. 2. Effect of temperature on the conversions of tung/palm oils using methanol. Left panel: 45°C; right panel: 55°C.

3.2.2. Reaction with ethanol

Figure 3 shows the effect of temperature on the conversions of tung/palm oils using ethanol from 40 to 50°C. The model fitted well with the experimental data. Conversions of both oils at 24 hours were increased with this temperature increment. Grater initial conversions for the first 12 hours were shown for both oils.

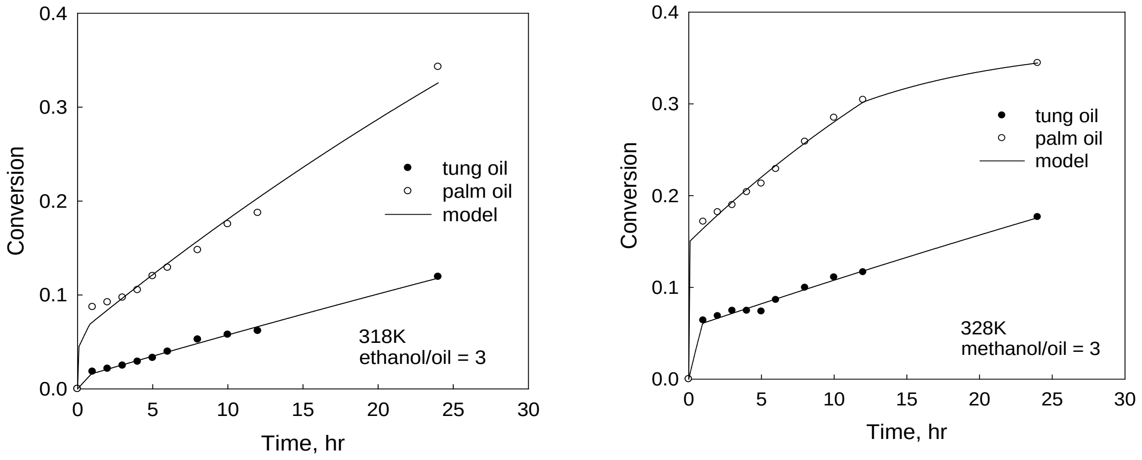

Fig. 3. Effect of temperature on the conversions of tung/palm oils using ethanol. Left panel: 45°C; right panel: 55°C.

3.3. *Comparison of the kinetic parameters*

Shown by Figure 1 to 3, the model fitted well with the experimental data for all cases. Trends of the obtained kinetic parameters were consistent to the conversions of experimental data. Then the physical meanings of the obtained kinetic parameters could be further discussed. Effect of reaction temperatures on the obtained kinetic parameters are listed in Table 2.

Table 2. Effect of reaction temperatures on the obtained kinetic parameters

T (°C)	Tung oil				Palm oil			
	Methanol		Ethanol		Methanol		Ethanol	
	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)
40	214	0.050	0.0052	0.0076	--	--	--	--
45	378	0.072	8.6E-06	0.018	939	0.087	315	0.037
50	508	0.070	0.0391	0.019	1153	0.067	692	0.058
55	570	0.073	5.6E-06	0.068	1182	0.100	719	0.071
60	770	0.088	7.8E-06	0.041	915	0.093	250	0.061

The mass transfer coefficients (k_1) of tung oil with methanol were from 214 to 770 h^{-1}, generally less than 915 to 1182 h^{-1} of palm oil system. The highest mass transfer coefficients (k_1) of tung oil and palm oils were exhibited at 60 and 55°C, respectively. The mass transfer coefficients (k_1) of ethanol system were generally less than the ones of methanol system for both oils. The magnitude of order was similar for mass transfer coefficients (k_1) of palm oils but the differences between using methanol and ethanol were much greater for tung oils. The above finding for the difference caused by different alcohols was consistent to previous work using waste animal fats [15].

The reaction rate constants (k_2) of tung oil system using methanol were much greater than the ones using ethanol. However, the values in Table 2 for tung oils were of same magnitude of order. In the other hand, the reaction rate constants (k_2) of palm oil showed the same trend as tung oils. And the differences for palm oils were even smaller between methanol and ethanol. The above results implied that the safer ethanol could be employed for enzymatic transesterification.

The above finding suggested that the mass transfer of triglycerides into the surface of the immobilized lipase could play a deciding role for reduced conversions shown by Tung oils. The majority of highly unsaturated chain of Tung oils fatty acids may contribute higher affinities among tung oil triglycerides.

4. Conclusions and Recommendations

The present study showed that the fatty acid composition of oil could directly impact on the efficiencies of enzymatic transesterification. A numerical model with mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction were successfully employed to describe the conversion. It was found that the mass transfer played a more important role than the one by reaction during enzymatic transesterification. The above finding suggested that the increased mixing could improve the processes for biodiesel conversion from tung oils.

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Study on Reaction Conditions in Whole Cell Biocatalyst Methanolysis of Pretreated Used Cooking Oil

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Abstract: Biodiesel fuel (fatty acid methyl esters; FAMEs) can be produced by methanolysis of waste edible oil with a whole cell biocatalyst which is an attractive alternative to fossil fuel because it is produced from renewable resources. Utilizing whole cell biocatalyst instead of free or immobilized enzyme is a potential approach to reduce the cost of catalyst in lipase-catalyzed biodiesel production. *Rhizopus oryzae* (*R. oryzae*) PTCC 5174 cells were cultured with polyurethane foam biomass support particles (BSPs) and the cells immobilized within BSPs were used for the methanolysis of pretreated used cooking oil (UCO) for biodiesel production in this research. UCO is the residue from the kitchen, restaurant and food industries which promotes environmental pollution and human health risks. The inhibitory effect of undissolved methanol on lipase activity was eliminated by stepwise addition of methanol to the reaction mixture. The optimum conditions for the reaction were as follows: 50 BSPs, molar ratio of methanol to UCO 3:1, 15.54% (wt) water (in the form of buffer phosphate with pH= 6.8) based on UCO weight and temperature 35°C in three-step addition of methanol. The maximum methyl ester yield of 98.4% was obtained after 72 h of reaction in a shaken Erlenmeyer at mentioned conditions.

Keywords: *Biodiesel, Whole-cell biocatalyst, Methanolysis, Pretreated UCO*

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1. Introduction

With the reduction of energy sources from fossil fuels, increase of the crude petroleum price and public awareness on impacts of its emissions on environment and their potential health hazards have created an interest for alternative fuel sources. Biodiesel is renewable, biodegradable, non-inflammable and non-toxic and it also has a favorable combustion emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum based diesel. The biodiesel fuel (fatty acid methyl esters), is defined as the mono-alkyl esters of fatty acids produced by transesterification of triglycerides [1-6] obtained from vegetable oils like soybean oil, jatropha oil, rapeseed oil, palm oil, sunflower oil, corn oil, peanut oil, canola oil and cottonseed oil [7]. Apart from vegetable oils, biodiesel can also be produced from other sources like animal fat (beef tallow, lard), waste cooking oil, greases (trap grease, float grease) and algae [8]. Because of the high price of high-quality virgin oils, the cost of biodiesel from these resources is higher than petroleum-based diesel [9]. The increasing of production of UCO from household, restaurants and industrial sources and to pour down it into drain has resulted in problems. The production of biodiesel from waste cooking oil to partially substitute petroleum diesel is one of the measures for solving the twin problems of environment pollution and energy shortage [10].

A number of processes have been developed for biodiesel-Production involving chemical or enzyme catalysis or Critical alcohol treatment [11-14]. Presently, industrial production of biodiesel from waste cooking oil is performed by chemical alkaline or acidic processes. Chemical catalysts including alkaline have been employed most widely since they give a high conversion of triglycerides to methyl esters in a short reaction time. However, chemical transesterification has some unavoidable drawbacks such as high energy and methanol consumption, difficulty in glycerol recovery, the need to eliminate the catalyst and salt and a large amount of alkaline wastewater from the catalyst [15-18]. In the case where supercritical alcohol was used, higher rates of reaction were observed when it was compared to conventional transesterification. However, the requirements of high temperature, high pressure and high molar ratio of alcohol to oil make the process costly for industrial scale [8].

In recent times, there has been a growing interest in the use of enzymes such as lipases as biocatalyst for biodiesel production. Some advantages of lipase biocatalyst over the chemical-catalyzed reactions include the generation of no by-products, easy product removal mild reaction conditions (reaction temperature of 35-45°C) and catalyst recycling [19]. It has been reported that enzymatic reactions are insensitive to FFA and water content in waste cooking oil [19-21]. Hence, enzymatic reactions can be used in transesterification of used cooking oil [22]. But the cost of enzyme remains as a challenge for its industrial implementation. In order to enhance the cost effectiveness of the process, the enzyme (both intracellular and extracellular) is reused by immobilizing in a suitable biomass support particles of polyurethane that has resulted in considerable improvements in process efficiency [18].

In this work, waste edible oils obtained from MERC restaurant was used to produce biodiesel employing immobilized *R. oryzae* cells within biomass support particles of polyurethane foam. Furthermore, The effect of several parameters such as the molar ratio of methanol to UCO, water content, the enzyme content with the BSPs content and reaction temperature in three-step addition of methanol was determined on enzymatic methanolysis of pretreated UCO in a shaken Erlenmeyer for 72 h.

2. Methodology

2.1. Procedure of immobilization

All lipase catalyzed experiments were carried out using the filamentous fungus *R. oryzae* PTCC5174. Basal medium for growth of *R. Oryzae* which contained of polypepton 70 g; $NaNO_3$ 1.0 g; KH_2PO_4 1.0 g; $MgSO_4 \cdot 7H_2O$ 0.5 g and olive oil 30 g in 1 l of distilled water). Erlenmeyer (500 ml) containing 100 ml of the basal medium with biomass support particles (BSPs) were inoculated by aseptically transferring spores from a fresh agar slant using from 4% potato dextrose agar and 2% potato dextrose agar, and incubated at 30°C for 90h on a reciprocal shaker (150 oscillations/min, amplitude 70 mm). The *R. oryzae* cells became well immobilized within the BSPs as a natural consequence of their growth during shake-flask cultivation. Immobilization was effected by placing 150 particles inside an Erlenmeyer together with the medium, subjected to prior sterilization. The pH of the medium was initially adjusted to 5.6 and then allowed to follow its natural course. Reticulated polyurethane foam with a particle voidage of more than 97% and a pore size of 50 pores per linear inch (ppi) was cut into 6mm×6mm×3mm cuboids. After cultivation, the BSP-immobilized cells were separated from the culture broth by filtration, washed with tap water, and dried at room temperature for around 24h. To stabilize the lipase activity, the dried cells were treated with a 0.1% (v/v) glutaraldehyde solution at 25°C for 1h, washed with tap water, dried at room temperature for more than 24h, and then used as whole-cell biocatalyst for methanolysis reaction [23-24].

2.2. Methanolysis reaction

Methanolysis reaction was carried out in a 50 ml Erlenmeyer flask while incubated on a reciprocal shaker (150 oscillations/ min, amplitude 70 mm) at the temperature range of 25°C to 45°C for 72 h. First, raw UCO was filtered by applying a reduced pressure system using a filter paper (Whatman42) to eliminate the indiscerptible impurities and was heated for 15 min at temperature of 90-110°C to eliminate extra water that has an influence on the transestrification reactions yield with methanol as an alcohol. The reaction mixture UCO 9.65 g, 0.1M phosphate buffer (pH 6.8) 0.5-3.5 ml and molar ratio of methanol to UCO 2-9:1 (one molar methanol (0.35 g) equivalent to 9.65 g UCO) was dispensed with 30-90 BSPs into an Erlenmeyer. The total of methanol was equally added to the reaction mixture at 0, 24 and 48 h reaction time. After the reaction, the whole cell biocatalyst was separated from the reaction mixture by filtration. Samples (200 µl) were withdrawn from the reaction mixture at specified time, centrifuged at 12,000 rpm for 5 min, to obtain the upper layer and were analyzed by capillary gas chromatography.

2.3. Gas chromatography (GC) analysis

The methyl esters content in the reaction mixture were quantified by using a gas chromatography/mass spectrometer (GC–MS) which was equipped with a HP-5 column with 30 meter long, internal diameter 0.25 millimeter. The column temperature was held at 160°C for 2 min, heated to 300°C with rate 8ºC/min and then maintained for 5min. The temperatures of the injector and detector were set at 280 and 230ºC; respectively. The total time of the process is 29.5 minute. For GC-MS analysis, 5µl of the aforementioned mixture and 300 µl of 1.4 mmol/l heptadecanoic acid methyl ester (hexane as the solvent) which is served as the internal standard were precisely measured and mixed thoroughly. A 1.0 µl of the treated sample was injected into a gas chromatograph column.

3. Results

Figure 1(a, b) and (c, d) shows the SEM micrographs of polyurethane foam particles surface with 2 magnifications before and after cell immobilization. The images are shown that the immobilization process was successfully preformed. Also, the weight of polyurethane foam particle after immobilization has increased almost twice. The efficiency of the process was checked by employing GC-Mass analysis of biodiesel product.

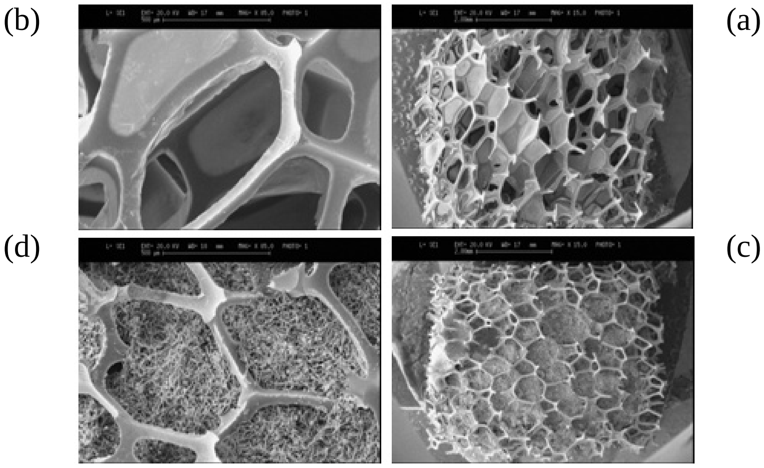

Fig. 1. SEM micrograph of foam particles: a. low magnification and b. high magnification, before immobilization; c. low magnification and d. high magnification, after immobilization.

3.1. Effect of temperature on the reaction

The reaction temperature is an important parameter in enzymatic catalysis. Higher temperatures can give a faster transformation, but too high temperature will lead to enzyme denaturing [25]. The effect of temperature on the lipase activity was examined by using a temperature range of 25°C to 45°C as shown in Fig. 2 with a constant content of 50 BSPs, molar ratio of methanol to UCO 3:1, 15.54% (wt) water based on UCO weight, the reaction time of 72 h and in three-step addition of methanol. The lipase activity increased sharply when temperature enhanced from 25°C to 35°C, The highest yield was observed at 35°C. However, a further increase above 35°C in temperature leads to decrease in the reaction yield. This decrease in methyl ester yield can be explained by enzyme thermal denaturation.

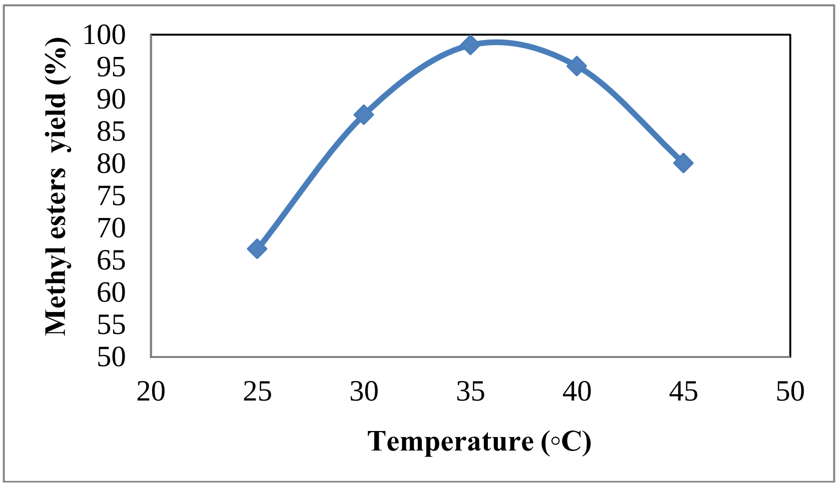

Fig.2. Effect of temperature on lipase-catalyzed methanolysis reaction. Reaction conditions: 50 BSPs, molar ratio of methanol to UCO 3:1, temperature of 25°C to 45°C,15.54% (wt) water based on UCO weight, the time of 72 h and in three-step addition of methanol.

3.2. Effect of water content on the reaction

It is well known that lipase, as a form of protein, requires the presence of water to maintain its live structure, and the activity of the enzyme in non-aqueous media is affected by the water content [10]. The reaction was examined in cases of water content (in the form of phosphate buffer with pH= 6.8) ranging from 5.18% to 36.27% (wt) water based on UCO weight, 50 BSPs, temperature 35°C, molar ratio of methanol to UCO 3:1, the reaction time of 72 h and in three-step addition of methanol. The result is shown in Fig. 3. As indicated in Fig. 3, the FAME content rose gradually as water content increased from 5.18% to 15.54% (wt) water based on UCO weight, and then declined as water content rose from 15.54% to 36.27%. This result indicates that the excessive water content affects the mass transfer of the oil phase of the reaction product, and inhibits esterification. It was observed that the FAME content reached its maximum at a water content of 15.54 wt% which was about 32.4% higher than water content of 5.18 wt%.

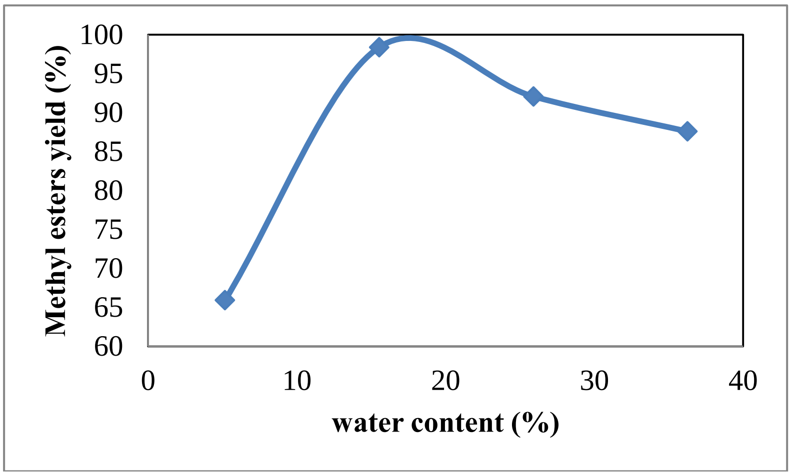

Fig. 3. Effect of water content on lipase-catalyzed methanolysis reaction. Reaction conditions: 50 BSPs, temperature 35°C, molar ratio of methanol to UCO 3:1, 5.18% to 36.27% (wt) water based on UCO weight, the time of 72 h and in three-step addition of methanol.

3.3. Effect of immobilized microorganism on the reaction

The enzyme activity produced of immobilized microorganism within BSPs increases with the immobilized microorganism content [10]. The effect of enzyme content on the transesterification reaction was examined with the BSPs content range from 30 to 90, temperature 35°C, molar ratio of methanol to UCO 3:1, 15.54% (wt) water based on UCO weight, the reaction time of 72 h and in three-step addition of methanol. As shown in Fig. 4, the FAME content increased along with the increase in enzyme content, because the more lipase available, the more substrate molecules were absorbed into the active center of the lipase, but the increase rate of FAME content declined as BSPs rose from 50 to 90. This phenomenon can be explained that the UCO content was excessive when enzyme content was under 50, and that as the enzyme content rose to become sufficient from 50 to 90, the FAME content increased only 0.88%. From an economic point of view, 50 BSPs is the most feasible content level for lipase in reaction of biodiesel synthesis from UCO.

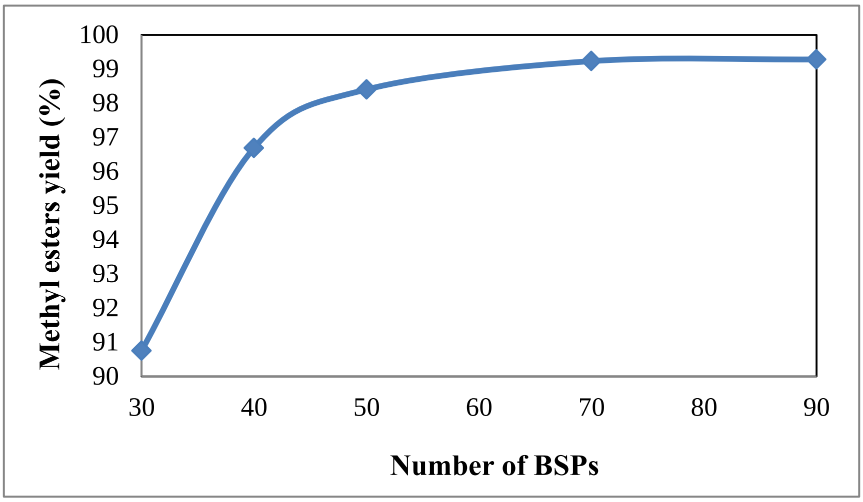

Fig. 4. Effect of BSPs content on lipase-catalyzed methanolysis reaction. Reaction conditions: BSPs content range from 30 to 90, temperature 35°C, molar ratio of methanol to UCO 3:1, 15.54% (wt) water, the reaction time of 72 h and in three-step addition of methanol.

3.4. Effect of Molar Ratio of Substrates on the Reaction

Methanolysis reaction was performed by using different substrate molar ratios of methanol to oil varying in the range of 2–9. The results (Fig.5) demonstrate that the methyl esters yield initially increases with increasing the methanol to oil molar ratio from 2 to 3 and reaches to its maximum at 3. However, a further increase in the methanol to oil molar ratio leads to decrease in the reaction yield. The highest methyl ester yield of 98.4% was achieved at a methanol to oil molar ratio of 3:1, and decreased to 50.68% when the molar ratio of 9:1 was utilized. This is in agreement with the earlier observation that excessive methanol concentration lead to lipase enzyme inactivation. The addition of methanol more than stoichiometric amounts exerts an inhibitory effect on enzyme performance. This could be due to the fact that the immiscible methanol was accumulated around the lipase structure including its active sites, reaching a concentration level sufficient to cause a denaturation of the protein. This phenomenon might lead to enzyme inactivation [24].

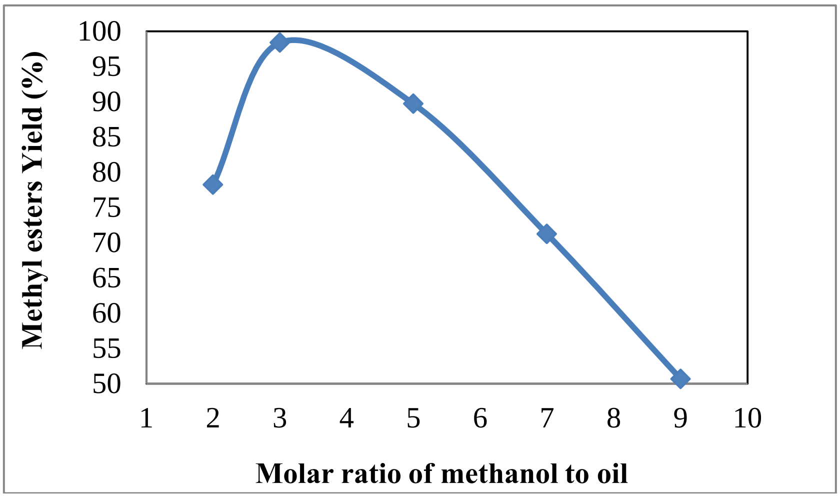

Fig. 5. Effect of methanol to oil molar ratio on lipase-catalyzed methanolysis reaction. Reaction conditions: 30 BSPs, temperature 35°C, molar ratio of methanol to UCO 2-9:1, 15.54% (wt) water, the reaction time of 72 h and in three-step addition of methanol.

3.5. Product analysis

The result of GC-Mass analysis indicated that the main components In the UCO-derived biodiesel were methyl octadecenoate, methyl hexadecenoate, methyl octadecadienoate, methyl octadecanoate, methyl tetradecanoate, methyl heptadecanoate, methyl dodecanoate and methyl pentadecanoate. These components account for 98.4% of the FAME.

3.6. Conclusions

The study shows that pretreated used cooking oil (UCO) can be efficiently converted to biodiesel fuel in a shaking Erlenmeyer methanolysis reaction using immobilized *Rhizopus Oryzae* (PTCC 5174) on polyurethane foam biomass support particles (BSPs). Therefore, this is an effective approach to reduce the cost of biodiesel feedstock and pollution problems.The optimum reaction conditions for the reaction were as follows: 50 BSPs, molar ratio of methanol to UCO 3:1, 15.54% (wt) water (in the form of buffer phosphate with pH= 6.8) based on UCO weight and temperature 35°C in three-step addition of methanol. The maximum methyl ester yield of 98.4% was obtained after 72 h of reaction in a shaken Erlenmeyer at mentioned conditions.

Based on GC-Mass analysis, the main components in UCO-derived biodiesel are methyl octadecenoate, methyl hexadecenoate, methyl octadecadienoate, methyl octadecanoate, methyl tetradecanoate, methyl heptadecanoate, methyl dodecanoate and methyl pentadecanoate, which are the most compositions of FAME.

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EN 14103 adjustments for biodiesel analysis from different raw materials, including animal tallow containing C17

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Abstract: EN 14103 is suitable to quantify the ester content in biodiesel free of heptadecanoate ester (C17:0), because it is employed as internal standard (IS). But EN 14103 cannot be applied to the analysis of tallow biodiesel because C17:0 is found in animal fats. This work proposes an improved method, based on EN 14103 capable to determine ester content in tallow biodiesel. Twenty samples from tallow, soybean, babassu and palm biodiesels and its blends were used to carry out the analysis. Chromatograms of ethylic biodiesel were analyzed using separately methylic and ethylic C17:0 (IS). The results showed that some peaks from tallow biodiesel co-eluted with both IS peaks, confirming the impossibility to quantify ethylic esters using those standards. Despite this, in all analyzed samples it was observed a constant relationship between two neighbor peaks occurring naturally in the tallow samples. The rate between them was measured and applied as a correction factor to measure the real influence, caused on methylic C17:0 IS by natural C17:0. As a result, the original equation from EN 14103, modified by the introduction of a correction factor (F), resulted in another equation more adequate to analyze the ester content in tallow biodiesel and its blends. Pure tallow biodiesel presented ester content around 4.3% greater, when quantified using the equation containing the correction factor, instead of the original equation.

Keywords: *EN 14103, Tallow Ethylic Biodiesel, Heptadecanoate.*

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1. Introduction

Biodiesel is a biofuel produced worldwide from several oils and fats, obtained from both vegetable and animal sources. This fuel is capable to work in diesel engines and hence be mixed to mineral diesel or replace it completely [1, 2]. Many countries around the world produce, import and/or export fuels, thus it is necessary to promote the internationalization of standards that specify the methods of analysis and maximum/minimum limits for quality parameters in order to allow a technically effective commerce worldwide. Technical data are used to set those limits. To harmonize the biodiesel specifications, the limits set in a global standard need to be carefully considered, since specification limits have arisen based in different utilization contexts [3]. Currently the evaluation of the biodiesel quality is a global concern. In this way experts from standards elaboration organizations from Brazil, United States and European Union, have participate of meetings with the objective of discuss standards for the evaluation of biodiesel quality.

The ester content is the most important biodiesel quality parameter, since the ester is the biodiesel itself. EN 14103 is a standard that evaluates chromatographically the ester content of biodiesel [4] and was developed for analysis of methylic biodiesel obtained from vegetable oils predominantly found in Europe. So this standard contemplates only methyl biodiesel obtained from oils which composition has the majority of carbon chains from C14:0 to C24:1 and which does not contain C17:0 in its composition. The wide feedstock diversity used to produce biodiesel around the world [5] makes the use of EN 14103 inadequate not only when we consider the composition of the oils, but also the choice of applied alcohol. That standard can be useful to measure the ester content of soybean, sunflower, rapeseed and other methylic biodiesels, but do not makes mention to ethylic biodiesel and is not capable to measure the ester content of tallow biodiesel itself or when present in blends.

Biodiesel from tallow has C17:0 in its composition. This represents a major concern in Brazil in relation to assessment of its quality, once biodiesel from tallow is already inserted in the national and international market [6].

One Brazilian solution to overcome the limitations of EN 14103 was the development of NBR 15764 [7]. This standard allows biodiesel quantification produced from different types of oils fats and alcohols, using external standardization. However this method has a weakness even more critical when compared with all the EN 14103 limitations. The NBR 15764 states the use of chloroform as solvent. This solvent is incompatible with the (GC-FID) detector since it promotes corrosion of the detector during use with the consequent loss of sensitivity. Compounds containing chlorine atoms in its structure, when burned in the detector flame, produce hydrochloric acid, promoting the corrosion of the detector, and can infer the reliability of analysis results [8].

A large number of biodiesels from different raw materials are produced around the world and being marketed pure or as blends. Tallow biodiesel is possibly present in those blends. The possibility of using ethanol as reactant is another important factor that must to be taken in account because its choice for biodiesel preparation makes the analysis of ester content particularly impaired.

Thus, this paper proposes an evaluation and adjustment of the EN 14103 analytical conditions in order to quantify adequately total ester content not only from methylic but also ethylic biodiesel, even in matrices containing the C17:0 in its composition, taking in to account that the global trends are the commercialization of biodiesel "blends". The biodiesels used in this approach were prepared from soybean, palm, babassu oils and bovine tallow, the mostly used raw materials in Brazil.

2. Methodology

2.1. Raw materials, solvents and standards

Four different types of raw materials were used: soybean, palm, babassu oil and bovine tallow. Industrialized oils purchased in local shops were used and the tallow experienced craft process of grinding and frying before being used. Anhydrous ethanol was synthesis grade (Synth, lot 118784) Internal standards (IS) were methyl myristate (C14:0), methyl nervonate (C24:1), methylic and ethylic heptadecanoate (C17:0) (Nu-Chek, >99%). Heptane (Vetec-0803307) HPLC grade was used for sample dilutions.

2.2. Biodiesel

Eight ethylic biodiesels were prepared, by transesterification, two from each oil and fat selected. The preparations were performed in two conditions: varying the key variables responsible for the total or partial conversion into esters. Four biodiesel were made under conditions that present high conversion rate with the heating time of 120 min, molar ratio alcohol/oil 9:1 and 1% of catalyst. The other four biodiesel, were made under conditions to present low conversion rates with heating time of 30 min, molar ratio alcohol/oil 6:1 and 0,3%

of catalyst. All biodiesels were prepared at 75 °C, next to the boiling point of ethanol. The choice of conditions was performed according to a review of the literature [9-12]. The transesterification reactions were performed using ethanol and catalyzed by sodium hydroxide.

2.2. *Blends*

The eight biodiesel were mixed forming blends with different levels of esters, totalizing 20 samples. 10 mL of each sample was prepared containing equal volumes of each biodiesel with the aid of a micropipette.

2.3. *Analysis of samples*

The quantifications of ester content in biodiesel samples were performed, in triplicates, according to EN 14103 [Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of Ester and linolenic acid methyl esters contents] in a Shimadzu GC 2010 gas chromatograph with flame ionization detector (GC-FID). The chromatograph was configured with injector in split mode coupled to auto-sampler AOC 5000 for liquid samples. EN 14103 establishes the chromatographic conditions used in the quantification of fatty acid esters: sample injection volume = 1 mL, split = 1:20, injector and detector temperatures = 250 °C, isothermal oven temperature = 210 °C, pressure of helium carrier gas = 83 kPa due to "split" or adjusted to visualize clearly the peak of the methyl standard C24:1. Because of difficulties in visualize clearly the peak of the methyl standard C24:1, under isothermal conditions, in this study the isothermal condition of the oven was replaced by programmed temperature conditions. 120 °C for 2 minutes, heating rate 10 ºC/min to a temperature of 180 °C, where it remained for three minutes, new heating rate of 5 ºC/min until 240 ºC where it remained for 10 minutes. The capillary column used was a Restek-Carbowax 30 m long, 0.25 mm internal diameter and 0.25 mm stationary phase thickness.

2.4. *Quantification of ester contents*

20 mg/mL stock solutions of methyl myristate (C14:0) and methyl nervonate (C24:1) standards were prepared, while methylic and ethylic heptadecanoate standards were prepared in 10 mg/mL stock solutions. Methyl esters standards C14:0 and C24:1 were used to identify the range of integration. In addition, we used the methylic and ethylic (C17:0) esters as IS. The ester contents were obtained by integrating the peak areas ranging from C14:0 to C24:0 and subtracting heptadecanoate area, as showed in Eq. (1).

$$\% \text{ Ester} = \frac{\Sigma_A - A_{C17\,IS}}{A_{C17\,IS}} + \frac{(C_{EI} * V_{EI})}{m} * 100 \qquad (1)$$

where:

ΣA = sum of areas of all peaks ranging from C14:0 and C24:0
$A_{C17\,IS}$ = C17:0 IS area
C_{EI} = concentration (mg/mL) of C17:0 solution
V_{EI} = volume of C17:0 solution added to sample
m = mass of the sample (mg).

3. Results and Discussion

3.1. EN 14103 for ethylic biodiesel

To quantify ethyl esters in biodiesel according to EN 14103, a study was conducted using methyl and ethyl standards under the conditions described in 2.4. The retention times (RT) of methyl and ethyl standards were: methyl C14:0 (8.6 min), ethyl C14:0 (9.2 min), methyl C24:1 (26.5 min) and ethyl C24:1 (27.2 min). From these results is possible to note that there is only a small variation on the beginning and the end of integration intervals. It was not observed any new peak in both intervals; hence the ester quantification accuracy will be not affected by using methyl standards to analyze ethyl esters. The 20 samples of biodiesel used in this study were quantified using the method 1 (EN 14103) and method 2 (conditions of EN 14103 unchanged, except for the integration of the ester peaks performed using the ethyl standards RT). The results were compared using the Student T test. The value of t-calculated to a limit of 95% of confidence was 0.81 while the theoretical value is 1.98, meaning that there is no significant difference between the two methods of quantification. Furthermore, in both cases the ester content results variation were below the method repeatability, that is 1.6 % m/m.

3.2. EN 14103 applied to biodiesel containing C17

Biodiesels containing heptadecanoate (C17:0) in their composition, (e.g. beef tallow), needs two chromatographic runs to be analyzed; one with IS and another without the addition of the C17:0 IS. The reason for this is that C17:0 IS is necessary to assist the quantification, but if C17:0 is already present in the sample (e.g. tallow biodiesel) the C17:0 of the standard co-elutes and consequently presents an area bigger than that corresponds to itself. Looking at the chromatogram of a sample without C17:0 IS (Figure 1), it is possible to found the co-eluted peaks (A when using methylic IS and B if it is used ethylic IS). Therefore it is necessary to run another chromatogram without IS. After that, the peak area at the same retention time of C17:0 IS must be subtracted from it and included in the total peaks sum.

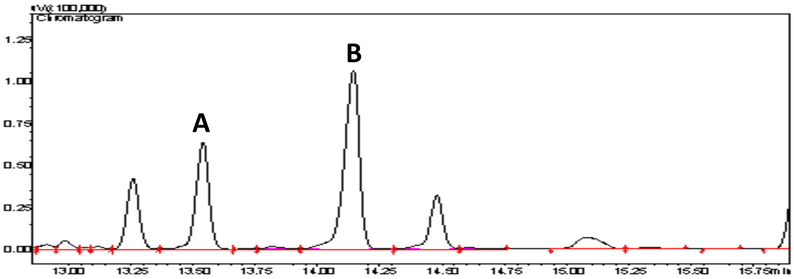


Fig. 1. Chromatogram window of a biodiesel blend showing the peaks A and B (A co-elutes with methylic C17:0 and B co-elutes with ethylic C17:0

During the development of the procedure, to overcome the need of two chromatographic runs, firstly, two chromatograms of ethyl and methyl C17:0 standards were obtained. The RTs were 13.5 min for methylic and 14.2 min for ethylic standards. The biodiesels of soybean, palm and babassu were diluted in heptane (without addition of C17:0 IS) in order to verify the occurrence of peaks in the RT 13.5 and 14.2 min. These chromatographic runs were successful, since they did not show any peaks in the regions of those RT. This fact showed the possibility of using both IS for ester quantification in the studied biodiesels samples.

Beef tallow biodiesel was then diluted with heptane and its chromatogram was compared with C17:0 standards methyl and ethyl chromatograms. Both, the methyl and ethyl standards co-elute with peaks of esters present in tallow biodiesel (Fig. 2).

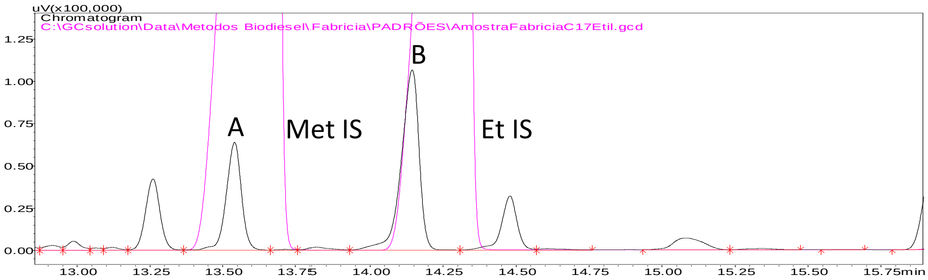


Fig. 2. Chromatogram window showing methyl (Met IS – black colour) and ethyl (Et IS - pink colour) IS peaks that co-elutes with A and B peaks from tallow biodiesel, respectively.

Thus, it is not possible to quantify correctly the ester content in tallow biodiesel or its blends using methylic or ethylic C17:0 IS. But, an accurate analysis of the chromatograms, allow to perceive a constant ratio between the two peaks areas A and B, that co-elute with C17:0 IS. To confirm how useful and confident would be this relationship between A and B peak area, a C17 external calibration curve was performed intending to support the quantification of C17 from samples. A seven point curve was produced using concentrations from 0.5 to 5 percent of ethylic C17 in heptane. Chromatographic conditions were similar to those used for ester content analysis official method EN 14103. Equation 2 is the curve calibration equation used to calculate A and B peak areas of the samples ($R^2 = 0.9999$). After that, seven biodiesel samples were analyzed from which five were mix of soybean and commercial beef tallow biodiesel and two of them were samples were pure biodiesel of soybean and beef tallow.

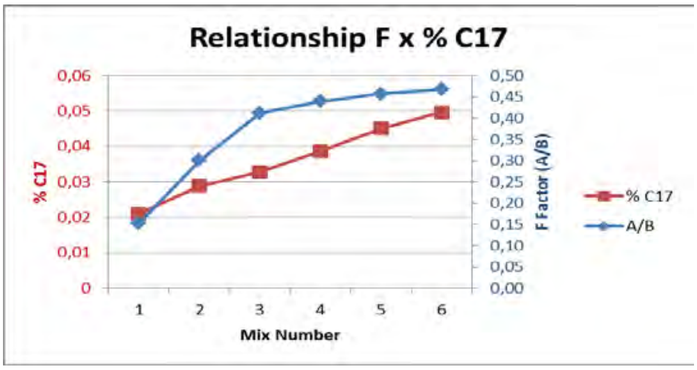
$$\%_{C17} = A_{peak} * 1{,}24638^{-7} + 1{,}59447^{-2} \quad (2)$$

Table 1 presents the percentage of tallow biodiesel in blends, C17 content into each sample and the ratio A/B results for every blend. The A and B peaks were quantified using the external calibration curve.

Table 1. Blends of tallow biodiesel with soybean, the % C17 found and ratio A/B peak.

	Mix 0 (0%)	**Mix 1 (5%)**	**Mix 2 (25%)**	**Mix 3 (45%)**	**Mix 4 (65%)**	**Mix 5 (85%)**	**Mix 6 (100%)**
Tallow Biodiesel	0	5	25	45	65	85	100
Soybean Biodiesel	100	95	75	65	45	15	0
%C17	-	0.021	0.028	0.328	0.0386	0.0451	0.049
A/B ratio	-	0.15	0.30	0.41	0.44	0.46	0.46

In the Graph 1 we can observe the behavior of A/B ratio related to C17 percentage. They are much correlated, especially when tallow biodiesel percentage is above fifty percent. In other hand, for pure tallow biodiesel or rich blends A/B variation curve is practically stable what shows that is possible to use an average A/B ratio value in order to correct the ester content analysis results without needs to proceed another GC analysis.



Graph 1. Behavior of A/B ratio related to C17 percentage in samples

Taking into account the relationship between the A and B peak areas and C17 percentage of pure beef tallow biodiesel (Graph 1), it was possible to establish a correctional factor that should be introduced into original formula of EN 14103 for quantify the ester content. The value adopted was the average of A/B ratio considering samples Mix 3, Mix 4, Mix 5 and Mix 6. That way we recommend to use 0,45 as a correctional factor “F”.

For this, the area of methylic C17:0 IS used in Eq. 1 was replaced by other term containing F (A/B). In this new term, the methylic C17:0 IS area was subtracted of: ethylic C17:0 IS area (RT 14.2 min.) multiplied by F. Moreover, this last product represents the peak co-eluted with methylic IS, so it was added to total peak sum. Thus, for quantification of samples containing beef tallow biodiesel, the Eq.(1), was replaced by Eq. (3).

In Eq. (2) the $A_{C17\,IS}$ was replaced by $A_{C17\,IS} - (A_{C17et} * F)$.

$$\% \ \text{Ester} = \frac{[(\Sigma_A + (A_{C17et} * F)) - (A_{C17\,IS} - (A_{C17et} * F))]}{A_{C17\,IS} - (A_{C17et} * F)} + \frac{(C_{EI} * V_{EI})}{m} * 100 \qquad (3)$$

where:

A_{C17Et}= Area of C17:0 ethylic present in the sample.
F = Correction factor

The mean value of F found was applied in the further experiments. Table 2 shows the study of F behavior to several samples of tallow biodiesel pure and its blends with soybean, babassu and palm oil biodiesel. Those samples were designed to present different ester levels intending to confirm F efficiency when applied to any matrix.

Although the t test did not show significant differences (t-calculated 0.78 and theoretical 1.03) for the sample of beef tallow biodiesel when using Eq. (1) and (3), the difference between results reach value bigger than the repeatability (1.6% m/m) of the method. A difference of 2.5% for beef tallow biodiesel was detected in its ester content. This difference is bigger than C17 ester content found by some authors [13] (1,7% of C17), however the complex biosynthesis of fatty acid can provide different level of this bioproducts available on fatty issue. Other works [6] presumes levels that can reach almost 5% of C17.

Table 2. Study of F behavior in different tallow biodiesel samples and blends.

Samples containing tallow	**% ester no using F correction**	**% ester with F correction**
Tb^{a}	7,4	7,5
$Tb^{c/a}$	46,3	46,5
$Tb^{d/a}$	52,8	53,0
$Tb^{e/a}$	49,6	49,7
Tb^{b}	91,6	93,1
$Tb^{c/b}$	96,8	98,9
$Tb^{d/b}$	97,1	99,2
$Tb^{e/b}$	94,2	96,3

a) Tallow biodiesel type low ester content; b) Tallow biodiesel type high ester content; c) soybean biodiesel type; d) babassu biodiesel; e) palm oil biodiesel.

In this sense, it was necessary to identify what substance is assigned to A peak. Since B is heptadecanoate. Some studies [6,13] concludes that A peak can be isomers of C17:0, like heptadecenoate and/or branched C17:0 fatty acid esters. Therefore, is comprehensible the fact of A and B present a regular proportion.

Within this context, we note that the difficulty in using the EN 14103 to quantify the levels of esters in biodiesel produced from different matrices was overcome. These achievements support us to propose the results of this work as a new standard, since the NBR 15764 is not suitable for quantifying the ester content in biodiesel.

4. Conclusions

Through an evaluation and adaptation of EN 14103, the limitations on feedstock and alcohol used in the production of biodiesel were effectively circumvented. Analyses performed using methyl and ethyl IS showed that there were no significant differences when comparing the results of ester content using both types of standards (methods 1 and 2). So ethyl and methyl biodiesel can be quantified using both methyl and ethyl IS using EN 14103 conditions.

For the ester quantification of ethyl beef tallow biodiesel, is necessary to introduce a correction factor (F) in the original equation of EN 14103 (Eq. 3), keeping the methylic standard C17:0 established by original method. In the cases when methylic beef tallow biodiesels are analyzed, it is necessary to do another few adjusts, however it should be used a similar procedure. Thus, it was possible to quantify adequately all peaks related to the esters in beef tallow ethylic biodiesel. In the other samples (soy, sunflower, rapeseed, babassu and palm biodiesels), there is no problem in using Eq. 3 because the final result will be equal. We recommend a study about composition of other fats in order to confirm existence and proportionality between A and B peaks.

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Indian-nut (*Aleurites moluccana*) and tucum (*Astrocaryum vulgare*), non agricultural sources for biodiesel production using ethanol: composition, characterization and optimization of the reactional production conditions

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Abstract: Indian-nut (*Aleurites moluccana*) and tucum (*Astrocaryum vulgare)* are oleaginous non eatable that present excellent oil content (about 60% and 30%, respectively) compared to soy bean grains (20%). Biodiesel production from these oils, using bioethanol as reactant, is an alternative for renewable energy source. In this paper, experimental design was used to determine the influence of these different kinds of oils on the transesterification reaction in order to evaluate the viability of biodiesel production process using ethanol as reactant. The most influential variables on the transesterification reaction yield were: alcohol to oil molar ratio, mass of catalyst, temperature and reaction time. In this paper, the variables was operated using experimental design with central composite. Compositional difference between both tucum and *Aleurites* oil has been verified by ^{1}H-NMR and GC analysis. Physicochemical properties presented by *Aleurites* biodiesel are in accordance with ANP Regulation n. 07. On the other hand, the same conditions were not adequate to achieve a high transesterification yield from handmade *Astrocaryum* oil. In this case, better conditions were only obtained from refined oil. The reactional conditions optimized based on a kind of oil sometimes can't be suitable for any biodiesel production reaction.

Keywords: *Biodiesel, Bioethanol, Aleurites, Optimization, Experimental design.*

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1. Introduction

Vegetable oils are one of the most commonly used biofuels raw materials. The main reason is their great versatility in the industrial transformation and environmental gains of their processing, in relation to petroleum, due to the absence of sulfur and heavy metals in their composition [1]**.** In this way, vegetable oils enable the production of biodiesel, a biofuel with very similar features as petrodiesel. The biodiesel is obtained from the chemical transformation of the oils (glycerides) by a transesterification process. In this case, the glycerides react with an alcohol of short carbon chain in the presence of a strong acid ou alkaline catalyst, to produce a mixture of fatty acid alkyl esters and glycerol [2].

The alcohol generally employed in transesterification reactions to biodiesel production is methanol, however, it presents some disadvantages, such as: mostly of it is obtained from non-renewable sources, presents high toxicity and Brazil do not produces sufficient amount for internal consumption. In other hand, ethanol, even deprecated due some reactional inconveniences, becomes very attractive under economic, strategic and environmental points of view; presents low toxicity and can be produced from sugar-cane, a highly renewable source. Brazil is currently the world's leader in bioethanol production obtained from sugarcane. Because of government subsidies, large sugarcane crops, and high sales taxes on gasoline, Brazil has built a profitable national bioethanol industry. Sugarcane is grown in the country as the climate presents perfect conditions for its cultivation and production. It is very easily converted to ethanol, and provides Brazil with huge supplies of bioethanol [3,4].

Lima *et al.* (2007; 2008) used bioethanol to prepare biodiesel from glycerides abundant in vegetable sources present in Brazil Midwest, North and Northeast regions, by homogenous catalysis reaching quantitative yield on catalytic process. These results became the motivation for a research aiming to overcome the reactional limitations for bioethanol and to improve its insertion into biodiesel energetic matrix.

Brazil has a lot of oleaginous vegetables with huge potential to produce biodiesel. The *Aleurites moluccana* seeds (so called indian nut or "noz-da-índia" in Brazil or "nogueira-de-iguapé") has been employed as an oil source for several years. *Aleurites* is original from tropical Asia and pacific islands; In Brazil, it is broadly spread in Atlantic Forest. The species is a tree with 10 meter height, that produces green fruits having one or two seeds. The percentage of oil extracted from *Aleurites* seeds is higher than soy bean grains, for example. It is about 63% composed of oleic glycerides that have excellent properties for biodiesel production. The oil obtained from *Aleurites* seeds is mostly used to make soaps, candles and varnish [6] and was already used to produce methylic biodiesel [7] but, to the best of our knowledge, there are no reports on its use to produce ethylic biodiesel.

There is a great biodiversity of palm trees in Brazil and among them there is a palm tree, *Astrocaryum vulgare,* Mart. (popularly known as "tucum" or "tucumã" in Brazil) not used as a source of oil for biodiesel production. The "tucum" is a palm tree that grows up to 10 m high, in a highly dry soil and those that floods occasionally. The almond supplies eatable white grease used to produce soaps, cosmetics and medicines. The fruits are very appreciated and the fruition occurs between November and May [8]. The "tucum's" mature fruits are yellow and consist of the pulp and the almond that correspond respectively to about 53.2% and 24.5% of the fruit weight [9]. The pulp produces orange oil (18.18% w/w) in which polyunsaturated fatty acids predominate and the almond produces a white grease (29.59%) rich in lauric and myristic fatty acids. In Brazil it is possible to found the "tucum" tree in the Amazon and Northeast regions. The majority of its fatty acids consist of short chain, mainly lauric (52.51%) and myristic (25.04%). This property facilitates the kinetic of the transesterification reaction for biodiesel production leading to a product with more oxidative and thermal stabilities than biodiesel obtained from other oils, such as soybean [9].

As discussed earlier, nowadays, the optimization of biodiesel production mainly applying ethylic route, is of great relevance. The use of experimental design is a powerful tool to process optimization. The experimental design is a technique able to rationalize the application of experiments, to investigate, simultaneously, all potential variables that affect the results of a process. The advantages of working with experimental design are the achievement of more information using a smaller number of experiments, to perform studies about individual effect of each variable, how these variables interact independently and more than this, to analyze the results with a model that allows previsions of what will happen for any experiment into studied range. The response surface methodology, also, is a statistic tool for optimization based on factorial designs, to denote the response of the system, under study, with alterations in the variables [10].

According to Sarin *et al.* (2010), the properties of a biodiesel are influenced by the structure and amount of the component fatty acid esters, which depends on the oil source. So, the main objective of this work is to discuss the application of experimental design based on a specific oil to a different oil, for the production of biodiesel. Moreover, we intend to propose "tucum" and indian nut oils as raw materials for biodiesel production using the ethylic route. In such way we intend to improve the reactional conditions, using experimental design, to obtain biodiesel from indian nut seeds oil, by ethylic route (NaOH as catalyst). Then, the best conditions should be applied to prepare biodiesel from almond oil of "tucum". Ester content, and other physico-chemical properties established by Resolution n. 07/2008, from Brazilian Regulatory Crude Oil, Natural Gas and Biofuels Agency [12], will be the principal reference parameters to verify the efficiency of reactional conditions obtained from experimental design.

2. Methodology

2.1. Experimental design for ethylic biodiesel preparation from Aleurites oil.

In order to obtain the response surface, it was applied an experimental design with central composite design. All variables: heating time, temperature, ethanol/oil molar ratio and mass of catalyst, were evaluated under five levels. These variables are shown in Table 1, together with their respective levels. A total of twenty six experiments were predicted. The results were analyzed using the software Statistica 7.0 [13].

Table 1. Variables and studied levels for the preparation of biodiesel from Aleurites seeds oil and ethanol (NaOH catalyst).

Variables	Level				
	-1,41	-1	0	+1	+1,41
Heat time /min.	50	70	90	110	130
Molar ratio /ethanol/oil	6:1	7:1	8:1	9:1	10:1
Temperature /°C	40	50	60	70	80
Catalyst /% w/w	0.6	0,7	0,8	0,9	1,0

2.2. Materials, methods and instruments

Ethanol (Synth, lot 118784) and sodium hydroxide (Qhemis, lot Q0011) of analytical grade were used without additional purification. Indian nut seeds were gathered at the city of Araraquara-SP, Brazil. The oil was obtained by milling the seeds and extracting the resulting material with hexane in a Soxhlet system during 10 hours. The yield was calculated dividing the final mass of oil extracted by the mass of the milled seeds. The "tucum" oil was obtained from the municipal district of Altos, PI, Brazil, and extracted by handmade way, in other words, it was extracted by milling and heating in water.

2.3. Preparation of the tucum and Indian-nut biodiesel

The transesterification of oils with ethanol, catalyzed by sodium hydroxide, were made using a three necked flask over a heating plate with magnetic stirrer. A condenser and a thermometer were connected to the flask. The third neck was closed with a rubber septum, through which the catalyst solution in ethanol was introduced using a syringe with a long needle under the heated ethanol/oil mixture surface. The reaction time began to be counted from this moment. The reaction mixture was kept in the flask under magnetic stirring. After the reaction time be completed, the final products were separated by centrifugation and the biodiesel (upper phase) was washed with distilled water. The biodiesel was, then, dried by heating at 60 ºC about 40 minutes under argon flow.

2.4. Physicochemical characterization of the tucum and Indian-nut biodiesel

The "tucum and Indian nut biodiesels were characterized by: visual aspect; ^{1}H NMR spectra; viscosity at 40 ºC (ASTM D445), specific gravity at 20 ºC (ASTM D4052), cupper corrosivity (3h at 50 ºC - ASTM D130); cold filter plugging point (ASTM D6371), acidity index (ASTM D664); ester content (EN/ISO 14103); free and total glycerol and glycerides index (EN 14105); iodine index (EN 14111), water content measured by the Karl Fisher method (ASTM D6304), content of sodium, potassium, calcium, magnesium and phosphorus (ICP-OES - NBR 15553) and oxidative stability analysis (Rancimat - EN 14112).

^{1}H NMR spectra were obtained in a equipment Varian Inova of 500MHz. $CDCl_3$ was applied as solvent (30 µL of sample and 600 µL of solvent). ^{1}H NMR spectrum was obtained at 300K temperature using 64000 acquisitions with pulse standard (s2pul), and tetramethylsilane TMS as reference. The spectral profile was used to observe the conversion of oil to biodiesel and to verify the oils composition.

3. Results / Discussion

Aleurites moluccana presented fruits with a high content of oil (60 %), such as found in other researches [7]. Tucum, how presented in the introduction [9], can produce around 30% of oil. This yield is better than soybean that shows an oil content around 25%, for example.

3.1. Experimental design for Aleurites biodiesel synthesizes

After all of the twenty six experiments and measure the ester content were done, were built six surface designs where the Y axis represents the percentage of ester content. The best results was obtained employing heat time about 90 minutes, molar rate alcohol/oil 8:1, temperature of 60 ºC and 0.8% of catalyst. Was reached more than 99% of conversion. However, we can see other conditions that could be applied considering the little difference at the final results. In other words, when employed 70 minutes; 9:1 molar rate; 60 °C and 0.8 % of catalyst we achieved nearby 100% of yield. These conditions were used to synthesize both Indian-nut and Tucum biodiesel.

3.1.1. Preparation of the tucum and Indian-nut biodiesel

It is necessary remember that the oils are from different sources and they were obtained by different process too. The optimization process has been done employing Indian-nut oil only.
Exactly 100 g of oil was put into a flask and heated until 60 °C. After then, was added the ethylic alcohol containing the total mass of catalyst. There were not troubles during the reactional time. The purification process was done using distillate water at room temperature. It was around 30 °C. No special process was necessary to segregate the glycerin phase.

3.2. Physico-chemical characterization of the tucum and Indian-nut biodiesel

Physico-chemical properties showed that both biodiesel were very similar at rheological viewpoint, because their viscosity and density are practically equals. Table 2 shows analysis results. The water content proves the efficiency of drying process using argon gas. It was below the maximum limit of 500 ppm. Some ions level like sodium, potassium, calcium, magnesium and phosphorus are below quantification limit of ICP equipment. That way, the biodiesel are in accordance to ANP Resolution. The tucum biodiesel's low iodine index (14.6 g/100g) denotes his saturated character and hence his cloud point (5.0 °C) will be bigger than *Aleurites* biodiesel (-5.0 °C). The iodine index of *Aleurites* biodiesel (150.36 g/100g) reflects a high level of unsaturated chains on his composition. These unsaturated chains can resist lower temperatures than the saturated compounds without freezing.

Table 2. Aleurites and Tucum biodiesel physicochemical parameters.

PARAMETERS	UNIT	LIMIT	METHOD	RESULTS	
				Tucum	Aleurites
Aspect	-	LII*	Visual	LII	LII
Density at 20º C	kg/m3	850-900	ASTM D4052	0,8770	0,8789
Kinematic viscosity at 40ºC	mm2/s	3,0-6,0	ASTM D445	4,54	4,12
Water mass, max.	mg/kg	500	ASTM D6304	261,6	160,1
Sodium + Potassium, max.	mg/kg	5	NBR 15553	<LQ**	<LQ
Calcium + Magnesium, max.	mg/kg	5	NBR 15553	<LQ	<LQ
Phosphorus, max.	mg/kg	10	NBR 15553	<LQ	<LQ
Cupper corrosivity, 3h a 50 ºC, max.	-	1	ASTM D130	1 a	1 a
Cloud filter point pour, max.	ºC	19	ASTM D6371	5,0	-5,0
Iodine índex	g/100g	Anotate	EN 14111	14,67	150,36
Free glycerin	% mass	0,02	EN 14105	0,00	0,00

* Impurities free and limpid.; ** LQ: Quantification limit.

Total glycerin and glycerides content are not displayed because they are a parameter directly linked to ester content. Thus, in the tucum biodiesel we can not expect them are according to maximum limit due tucum ester content is only 79.8%. In other hand, total glycerin of *Aleurites* biodiesel (0.075%) was completely in agreement with that limit which can not be more than 0.25% of total glycerin. Free glycerin is an important parameter, especially in order to provide information about purification process. In this case, two biodiesel presented non quantitative mass of glycerin due to efficient washes.

3.3. ^{1}H NMR biodiesel analysis

When comparing indian nut and “tucum” biodiesels ^{1}H NMR spectra (e.g. Fig. 1 and 2) is possible to see differences, such as unsaturation level and compositional profile. Absence of representative peaks around 2.1 ppm in “tucum” spectrum, assigned to the methylene protons attached to the unsaturated carbon, shows its high degree of saturation.

Beyond this, near to 5.3 ppm the peak assigned to the H from CH unsaturated is in agreement with the previous observation about pi bonds. In the Glycerides chains presents in tucum biodiesel there is almost none pi bond beyond those of carbonyl groups. Observing chromatograms overlap (e.g. Fig.3), we can note the real composition`s difference between both oils and biodiesel from tucum and *Aleurites*.

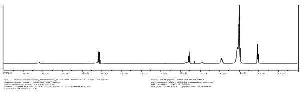

Figure 1. ^{1}H NMR Aleurites biodiesel spectrum.

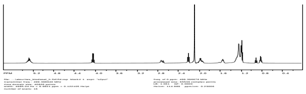

Figure 2. ^{1}H NMR "tucum" biodiesel spectrum.

3.4. Ester content

One of the most important reactional results is the ester content. This parameter represents how efficient was the reactional process. The principal target of this paper is to show how useful can be the optimization from an experimental design in order to apply it to others oils with different properties. If the ester contents yield are similar, so these same conditions could be applied. The *Aleurites* biodiesel synthesize presented yield about 99%. This result is almost the same as the one previously obtained during the optimization process. When those reactional conditions were applied to synthesize ethylic tucum biodiesel, the result achieved was only 79.8% for ester content. The minimum level described on Brazilian national legislation is 96.5%.

The chromatograms superimposed, e.g. Fig. 3, shows the composition differences between biodiesels from "tucum" and indian nut in terms of carbon chain length. In order to prove this, some ethylic ester standards were run on GC and their retention time (RT) were registered: C8:0, RT= 2.5 min; C12:0, RT=7.0 min; C14:0, RT= 8.0 min; C17:0, RT=14.2 and C24:1, RT=25.4 min. With this data, we can prove the saturated character of tucum oil. In the chromatogram could be seen that the majority of compounds from tucum biodiesel are between 2.5 and 15.0 minutes. In this interval there are C8:0, C10:0, C12:0, C14:0 and C16. Even a little after that, there are some peaks attributed to C18:0, or a small peak assigned to C18:1, but nothing after 17.5 minutes. Regarding *Aleurites*, most peaks are above 12.0 min and below 18 min. That interval covers saturated and unsaturated chains like C16:0, C18:0, C18:1, C18:2 and C18:3. Among those peaks, majority lies above 15.0 minutes, region of occurrence of peaks corresponding to esters with more than 17 carbons.

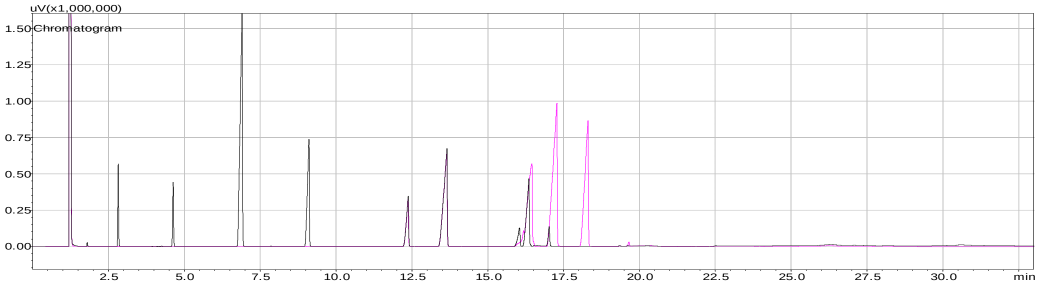

Figure 3. Superimposed "tucum" and indian nut biodiesels chromatograms (pink: Indian-nut biodiesel; black: tucum biodiesel.

3.5. "Tucum" biodiesel preparation yield under the best conditions found to indian nut biodiesel preparation.

The yield achieved to "tucum" biodiesel prepared, applying the best conditions developed by experimental design on indian nut oil, was very low. The preparation procedures were the same to both oils. Only during work up procedures there were some differences between them. Because of the acidity presented by "tucum" oil (soap generation) and its shorter carbon chains, the washing process generated more emulsions than during indian nut biodiesel work up; "tucum" biodiesel was washed much more times to remove soap excess and to break any emulsions. This can be one of the causes for the low yield of esters obtained from "tucum" oil. Other causes for the unsuitable behavior of "tucum" oil under the best experimental conditions developed for indian nut oil conversion to biodiesel may be its impurities, not removed during manual oil extraction process, and the manual oil extraction itself.

4. Conclusions

The oil content of "tucum" and indian nut seeds is greater than soybean grain. Ethanol showed technically suitable as a reagent to biodiesel production from indian nut and "tucum" oils. Indian nut oil has considerably more unsaturated esters than "tucum" oil, what explains its lower resistance to oxidation. Experimental central compound design and surface response methodology were efficient for optimization of the reactional conditions (time, temperature, molar ratio ethanol/oil and mass of catalyst) to obtain biodiesel from ethanol and indian nut oil. The optimized conditions led to an almost stoichiometric yield of biodiesel confirming the forecast of the technological viability of indian nut oil to obtain high yields of ethylic biodiesel. The same optimized conditions did not apply for "tucum" oil. Further experiments with "tucum" oil obtained by the same extraction procedure used to indian nut oil are necessary. Experimental design is an important tool to optimize chemical preparations. However, its relationship with raw materials characteristics must be carefully observed.

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A bubbling fluidized bed combustion system for forest residues

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Abstract: The main objective of the project was to develop or adapt a combustion technology that would permit a stable operation of a boiler fed with a combustible with a high level (50%) of humidity. The size of the unit was determined by the heating demand of a lacto-serum plant. Computer simulations and small scale laboratory experiments were used to design a fluidized bed, then fluid flow and heat transfer calculations were carried out to verifiy the heat balance (or energy balance) of an existing fixed boiler to be converted into à fluidized bed one. A grid involving 130 nozzles with 6 equally distributed holes (10 mm) was designed. The intake has a 23.37 mm I.D. It has been in operation for more than a year now and operation results are presented. It was found that the key aspect of the combustion process in such boilers is the homogeneity of the fluidized bed and the temperature control. We are now working on a way to broaden the range of type of wood and humidity levels.

Keywords: *Renewable energy source, Boiler, Bubbling fluidized bed*

Nomenclature

ΔP	*effective pressure drop across the bed*	*Pa*
A	*area of the bed*	m^2
Ar	*Archimedes number*	-
D	*particle diameter*	*m*
g	*gravity*	$m{\cdot}s^{-2}$
h	*convective transfer coefficient*	$W\,m^{-2}\,K^{-1}$
H	*height of the bed*	*m*
K	*fluidized bed constant, usually 5*	-
Nu	Nusselt number	-
Pr	Prandtl number	-
Re	*Reynolds number*	-
S	*surface to volume ratio*	-
T	*temperature*	*K*
U	*fluidization velocity*	$m{\cdot}s^{-1}$

Greek symbols

ρ	*density*	$kg{\cdot}m^{-3}$
λ	*thermal conductivity*	$W\,m^{-1}\,K^{-1}$
μ	*dynamic viscosity*	$kg{\cdot}m{\cdot}s^{-1}$
ε	*bed porosity*	-

Indices

mf	*minimum fluidization*
g	*gaz*
p	*solid particles*
r	*radiation*

1. Introduction

1.1. Context

The ever increasing level of greenhouse gas emissions combined with the overall rise in fuel prices (although fluctuations occur) are the main reasons behind efforts devoted to improve the use of various sources of energy. Economists, scientists, and engineers throughout the world are in search for: (1) strategies to reduce the demand; (2) methods to ensure the security of the supplies; (3) technologies to increase the energy efficiency of power systems; and (4) new and renewable sources of energy to replace the limited and harmful fossil fuels.

Nowadays, biomass (organic wastes) receives an ever increasing interest for energy production because this renewable source of energy:

- reduces the demand of fossil fuels,
- diversifies the sources of traditional energy,
- ensures the supplies at a local level,
- is carbon neutral?

Fluidized beds found several industrial applications such as coal and biomass combustion. Boilers involving such a technology are generally more efficient that their counterparts with fixed or mobile grids and this is why bubbling fluidized beds combustors (BFBC) are often selected to transform waste into energy. An efficient combustion for low calorific power fuels is possible with appropriate controls: according to Oka [1], it could reach up to 99%. Moreover, bubbling fluidized bed combustion of solid residues also becomes attractive for thermal steam generators because it can allow for variations in the regime by up to 4% per minute [2].

1.2. Fluidized beds combustion

Fluidization refers to the conditions for which a granular material behaves such as a fluid. To obtain fluidization, a gas (generally air) crosses a bed of particles with an appropriate upward flow rate to create forces that separate particles: the result is a turbulent mixing of gas and solids. The key idea is to obtain the highest mixing rate possible. In practice, the mass flow rate must be high enough to ensure an appropriate mixing and low enough to keep the particles in the mixing. The rationale behind this technology is that the tumbling action provides more effective chemical reactions and heat transfer in the solid fuel particles that are added to the bed.

In this paper, the process involves BFBC. During preheating, the bed is heated up with an auxiliary source (here natural gas). Then, the process is fed with biomass. This initialization process is critical to ensure proper operation. During combustion, part of the ashes and fine particles must be collected with a cyclone. The other part of the ashes is recovered through the sand circulation. The bed temperature – which influences the stability of combustion, the efficiency of the steam generator, and the rate of pollutants are the preponderant factors for this type of system.

1.3. Process characteristics

BFBC boilers operate at lower temperature than other types of boilers (800-850°C). This may lead to less NOx emissions. However, burning at low temperatures also causes increased polycyclic aromatic hydrocarbon emissions. The temperature upper limit is intrinsically due to the melting point of the most commonly used solid particle: sand. The development of eutectic within the sand is a crucial phenomenon to avoid. The creation of agglomerates will seriously impact the efficiency and may stop fluidization and, eventually, the whole process. The melting point of silica diminishes when it is mixed with ashes and eutectics are formed when hot spots occur in the bed. BFBC reduces the amount of sulfur produced in the form of SOx.

1.4. Overview of the installation

The whole factory into which the boiler is installed produces lactoserum which requires 6MWth and electricity (1MWe). The boiler produces 10T/h at 32 bars and 315^{o}C. The whole plant is shown in Fig. 1. On the left-hand side the storage and feeding systems (a) are shown while the boiler (b) is located in the center of the right-hand side of Fig. 1. The feeding system is a key element of the design as the process is continuous and cannot be stopped. The homogenization of the bark in terms of size and humidity is another key aspect. In Fig.1, the fuel is grabbed and thrown into the feeding system where some sorting occurs to avoid having large chunks of wood to get into the 40 cm worm gear. This gear feeds the combustion chamber. The fluidization grid is another key aspect of the process. The shape and size of the nozzles, the numbers and diameters of the orifices as well as the air outlet velocity have to be selected to maximize the homogenization. The height of the bed and the pressure drop are other key parameters [3,4] discussed in subsequent sections.

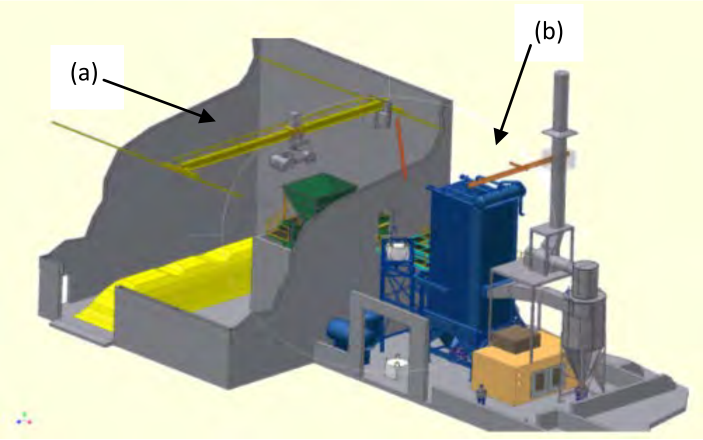


Fig. 1: Layout of the complete plant with: (a) Feeder and storage; (b) boiler, turbine and stack.

1.4.1. The storage system

In this area of the plant, the raw material is treated to maximize homogeneity in size, calorific power, and humidity. A mechanical treatment is applied to tear the biggest chunks of wood this to avoid mechanical failure of the feeding system. During winter, humidity and ice were initially found to cause mechanical blocking along the conveyors. Nowadays, by use of specific materials and appropriate controls of the feeding system, this problem vanished. Several tons of material can be stored in the area.

1.4.2. The feeding system

The feeding system has been designed for a rate of 4 tons per hour. Initially, the rough surface of the drop feed, made of refractory, involved too much friction. Suddenly, clusters of bark accumulated in the drop feed were inappropriately falling in the bed. A defluidization was occurring followed by several local hot spots in the bed. There was a high potential for eutectic formation. The refractory has been replaced to solve the problem.

1.4.3. The boiler

The Falmec boiler (B.F.I) was originally designed for a fixed grid (water tubes type). The main design limitation was then the size of the combustion chamber itself which limited the width of the fluidized bed. The overall area of the bed, A, was hence predetermined (2,3m x 2 m) and thus the imposed the minimal fluidization velocity (which also depends upon the particles size): U_{mf} =1,5 m/s. The primary fan delivers 75 kW with a pressure of 1,27 m CE (or 0,12 bars) during normal operation. This pressure allows for the circulation of the air through the sand bed. The secondary fan as a power of 30 kW with a pressure of 0,38 m CE (or 0,04 bars).

1.5. Start-up and control specifications

1.5.1. Start up

As mentioned earlier, during the start-up, the bed is preheated with an auxiliary burner then the biomass is fed-in. The crucial steps of this initialization process are: (1) verification of the minimal sand thickness of height; (2) start of the primary fan (to initiated fluidization); (3) start of the auxiliary burner; (4) heating of the sand until auto-ignition temperature (about

700°C); (5) low speed feeding; (6) progressive increase of the biomass flow rate to reach the appropriate average temperature of 850°C.

In the proposed boiler, the main difficulty with the auxiliary burner is that it is located above the bed and this causes poor heat transfer to the bed (between the flame and the sand). Afterwards, we realized that, due to its position, the auxiliary burner was undersized slightly. Moreover, the fluidization (process) air should have been heated to shorten the start-up procedure. One way to enhance the start-up process was to add oil (on a temporary basis) in attempts to improve it. Since then, we rely on drier bark at the beginning.

1.5.2. Controls

The control of a steam generator is largely documented [5,6] while that of fluidized beds is also quite documented [7, 8]. Start-up procedures are also documented [2]. The main parameters to control are the flow rates of the two fans, the stability of the combustion, and the bed temperature, with emphasis on the latter. An increase of the mass flow rate of fluidization air increases the temperature (increase in the combustion rate, internal heat release) and inversely [9, 1]. This indicates that the combustion takes place partly within the bed and partly above the bed (appearance of flames above the bed) in the combustion chamber. Several methods allowing for the control of the fluidization regime with primary air and bed temperature measurements could be carried-out but these methods have not been considered in our installation. It is the variation of the bark or wood chunks humidity, needed at about 50%, which was found to require a rigorous control and measurement here.

The system was started during winter 2009 and a data acquisition system permitted the continuous recording of the most important variables: (1) three thermocouples immersed in the bed; (2) the fan speed (primary, secondary, exhaust); (3) percentage of oxygen in the combustion products; (4) steam pressure. In this study, the fluidization regime was said to be in steady state when the three thermocouples showed similar temperatures (Fig.3 and 4).

2. The fluidized bed design and method

2.1. The pressure drop and critical velocity

The fluidization velocity is a basic parameter but its evaluation is rather complicated. Several correlations based on the pressure drop across the bed are available and this pressure drop varies linearly or nearly linearly with the fluidization velocity. In the case of a turbulent flow, Ergun [10] proposed the following expression:

$$\frac{-\Delta P}{H} = 150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu U_g}{D^2} + 1.75\frac{(1-\varepsilon)}{\varepsilon^3}\frac{\rho_g {U_g}^2}{D} \tag{1}$$

In the fluidization regime, the pressure drop in the bed corresponds to the weight of the particles minus the Archimedes force divided by the surface area of the bed. Since the solid volume is H x A x (1-ε), this yields:

$$-\Delta P = \frac{HA(1-\varepsilon)(\rho_p - \rho_g)g}{A} \tag{2}$$

It is possible to obtain the minimal fluidization velocity when the pressure drop, eq. 2. is inserted into eq.1, yielding:

$$(1-\varepsilon)(\rho_p-\rho_g)g = 150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu U_g}{D^2}+1.75\frac{(1-\varepsilon)}{\varepsilon^3}\frac{\rho_g U_g{}^2}{D} \tag{3}$$

Introducing the relevant Archimedes and Reynolds numbers gives:

$$\mathrm{Ar} = 150\frac{(1-\varepsilon)}{\varepsilon^3}\mathrm{Re}_{mf}+1.75\frac{1}{\varepsilon^3}\mathrm{Re}_{mf}{}^2 \tag{4}$$

Several researchers tried to correlate their results with this expression to evaluate the minimal fluidization velocity:

$$U_{mf} = \frac{\mu\left[\left(C_1^{\,2}+C_2*\mathrm{Ar}\right)^{0.5}-C_1\right]}{D*\rho_g} \tag{5}$$

where C_1= 27.2 and C_2= 0.0408 according the results of Grace [11].

2.2. *Heat transfer and energy balance*

First, the heat transfer characteristic into the fluidized bed
The predominant parameters which influence the heat transfer coefficient are the fluidization velocity, the particle size and the temperature. The Nusselt number for a fixed object immersed in a particle bed was correlated by several researchers. For particle size lower than one millimeter, the refined correlation proposed by Baskakov [12] was used:

$$\mathrm{Nu} = 0.85\mathrm{Ar}^{0.19}+0.006\mathrm{Ar}^{0.5}\,\mathrm{Pr}\,0.33+\frac{h_r D}{\lambda_g} \tag{6}$$

This equation stands for an Archimedes number ranging between 10^2 and 10^9 and involves the radiative component of heat transfer calculated with respect to the bed and wall temperatures.
The overall energy balance was established to ensure that the existing boiler combined with the fluidized bed could reach the expected parameters (flow, temperature, pressure). A code was developed based on the temperature of the bed for overall balance calculations. The heat transfer by convection, radiation, and conduction was taken into account. This code permits to show that the combustible moisture level of 50% should be respected to ensure a proper operation in term of bed temperature.

2.3. *The nozzles design*

The Ergun software [13] has been used to design the bed. The software allows to obtain the suitable air velocities as a function of the fluidization regime, the temperature, the particle size, the height of the bed, and the heat transfer. It enables one to account for pressure drops and homogenization of fluidization. Although not straightforward to use, Ergun permits to correlate the number of holes in the nozzle, the diameter, the minimal fluidization velocity, and the exit nozzle velocity. Whereas several installations may use a perforated plate at the bottom, our combustion calls for a continuous ashes recovery. Hence, fluidization nozzles where used.

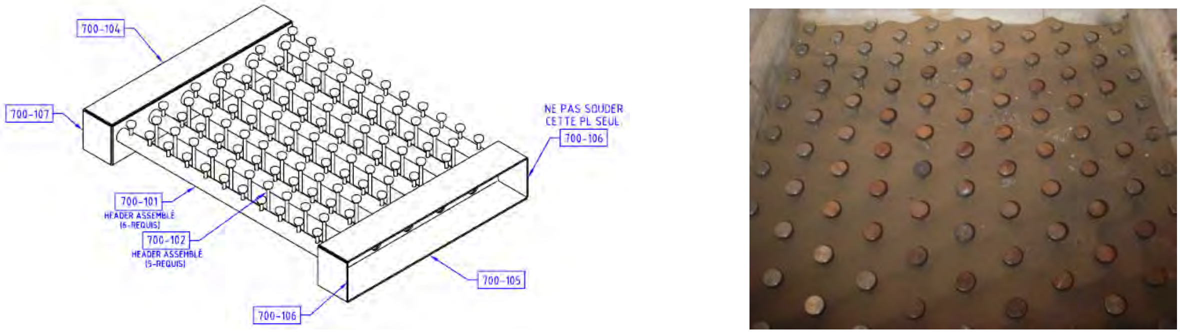
Fifteen different nozzles where designed, built, and investigated (two of them are shown in Fig.2a). All were satisfying the design constraints and criteria. The one respecting the minimum pressure drop required to ensure a stable and homogeneous fluidization was ultimately selected. The tests were then carried out in the lab without combustion in a cylindrical sand bed (Fig. 2b).


(a) (b)

Fig. 2: (a) Two of the eight nozzles that were simulated. (b) The laboratory test bench.

Four different sizes of sand particles, ranging from 1 to 2mm, 0.841 to 1mm, 0.500 to 1mm, and 250 to 500μm were tested. Mixing was also carried out with bark samples of about 1 cm by 2 cm. We found that the bark size did not matter and that the mixing was occurring only in the upper level of the bed, close to the surface. It is however important to note that the cold tests were quite different than the flowing full-scale results.

Finally, a bed involving 130 nozzles (Fig. 3) with 6 equally distributed holes (10 mm) was selected. The intake has a 23.37 mm I.D. The pressure loss is 5kPa when the flow rate is maximum. This flow rate varies from 0.0185 m^3/mn at 20ºC. 300 mm of sand was found to be the lowest limit for an homogeneous distribution of air while 600 mm was identified as the upper limit to avoid the over sizing of the fan.



(a) (b)

Fig. 3: The fluidized bed: (a) Full scale model; (b) Actual bed with uncovered heads.

3. Results

Several preliminary tests (not reported here) were needed to fine-tune the operations at the beginning. We worked until uniform temperatures were obtained, thus obtaining a suitable fluidization regime. We also found out that the content of oxygen remained constant with the temperature increase which in turn was proportional to an increase in the mass flow rate of combustible. We noticed that the biomass (fir bark) involved sand that progressively increased the level of the bed (after 10-12 hours of operations) which had to be lowered (by a simple control of the sand circulation). Our first series of tests showed a temperature variation between 730°C and 838°C. The content in oxygen varied from 1% to 13%. A high content (near 21%) indicates that the combustion is almost completed while à low content shows that there is a high combustion.

Fig. 4 presents two test cases at two different temperatures and same pressure levels. Temperature and boiler pressure are indicated on the left axis (0-1000 range) while the oxygen content and the fan speed is reported in % on the right axis (0-100% range). The abscissa is time in hours.

Fig.4a shows, over a period of about one hour, that the control system maintains the steam pressure (represented by ×) constant at about 350 PSI (the set-point). Indeed, the pressure varied between 320 and 356 PSI (± 9%). In Fig. 4, decreases in the pressure occur with increases in the primary fan velocity (represented by ✳). This corresponds to a simultaneous increase in combustion as the content in oxygen (left axis, represented by Δ) decreases. This content is always below 16%, which is excellent. The temperature here varied from 650ºC to 785ºC.

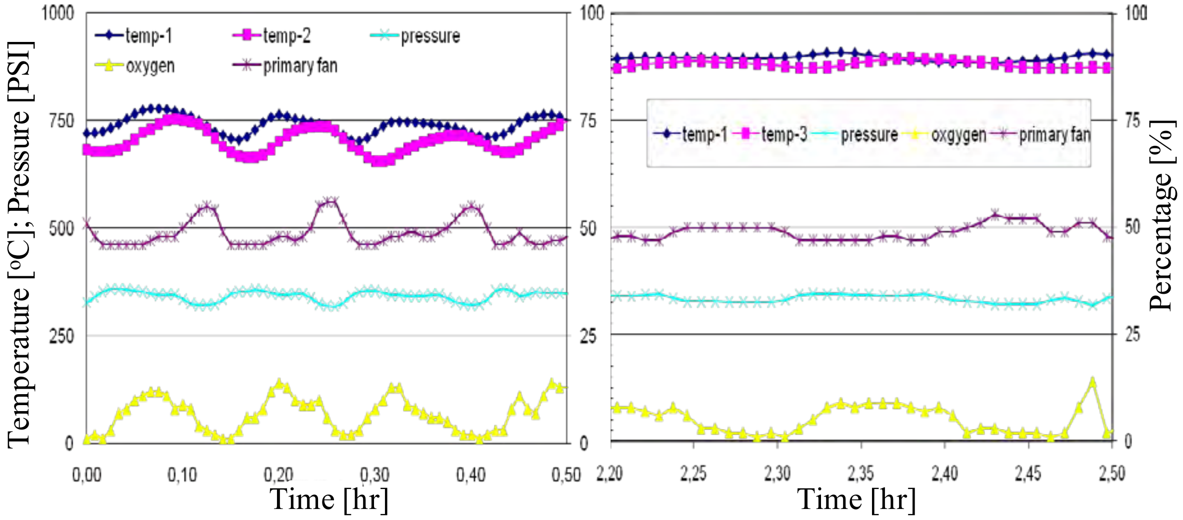


Fig. 4: Temperature, pressure, oxygen content and primary fan power as functions of time: (a) lower regime; (b) higher regime.

Fig. 4b illustrates, over a period of about one quarter of an hour, that the control system maintains the steam pressure constant at about 340 PSI (± 7%): A more stable regime is shown. In Fig. 4b, the trends are similar to those reported in its twin but the regime is higher with temperature ranging between 865ºC and 915ºC. This indicates a higher combustion regime also shown by a lower content in oxygen for the period. The temperature is also more homogeneous in this test case as the control loop improved with time and experience with the boiler.

An interesting feature of the installation is that the pressure settings remained constant during the test showing no need for manual adjustments after the tuning of controls.

4. Conclusion

A bubbling fluidized bed for the combustion of moist wood residues has been designed for an existing steam generator originally involving a fixed grid. The objective was to allow this generator to accept combustibles with a high level of humidity with no compromise over performance. This paper first presented the complete installation and insisted on a few design parameters and issues that pertain to the bed nozzles and lay-out. The format of the paper cannot permit to provide all relevant details.

When applied to the combustion of forest residues, the key aspects to address were found to be the proper size and humidity of the feed stock. And here, not only on an average basis: a homogeneous mixture ensures a stable process which avoids the generation of local hot spots that could provoke eutectics (agglomerates) and force the shut-down.

The positive points:

- The flexibility in terms of steam demand;
- The combustion efficiency (up to 99%);
- The low maintenance (changes of the sand) requirements.

The need for improvements:

- The design calls for a deep knowledge of fluidization which is not the case with other (simpler) technologies such as fixed grid boilers;
- The acceptance of a wider range of humidity variation of the feed stock;
- The training of the personnel.

The BFBC is nevertheless an excellent solution to burn humid residuals and recover the energy because of its flexibility, its efficiency, and its cleanness.

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Assessment of the energetic efficiency of a continuously operating plant for hydrothermal carbonisation of biomass

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Abstract: To date wet lignocellulosic biomass cannot be used efficiently for energy production. By hydrothermal carbonisation (HTC) wet biomass may be efficiently transformed to a solid, lignite-like fuel with good dewatering and grinding properties and a high calorific value. Energetic yields of the HTC reaction can be derived from lab scale experiments. However, for the assessment of energetic efficiencies of a HTC plant the amount of external energy consumption needs to be calculated. A model of a semi-continuously HTC plant is presented with a heat recovery system which is based on recycling of hot compressed water. Results of simulations with the program Engineering Equations Solver show that energy consumption can be significantly reduced by internal heat recovery. Efficiencies of a HTC plant model are presented based on experiments with beech wood chips as a model biomass. A sensitivity analysis of the water content of the biomass and the heat of reaction is presented.

Keywords: *Hydrothermal carbonisation, biomass, heat recovery, efficiency*

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1. Introduction

Hydrothermal carbonisation (HTC) is a pretreatment process of biomass in hot compressed water at around 200°C. Thereby the carbon content and higher heating value (HHV) is increased[1,2]. Apart from application as a soil ameliorant it therefore has been discussed as fuel[3]. The product (related to as “hydrochar” or “char”) leaves the reactor as a slurry and must be mechanically dewatered and dried for combustion. By removing water and further compression an energetically dense fuel can be formed facilitating transportation and storage. Good grinding properties make it applicable for gasification and further refining. Energetic yields of the solid of 75-90 % for the HTC process with regards to the HHV can be expected, because the whole fraction of lignocellulose is converted. The HHV of the solid increases when higher temperatures are applied. Yet, the energetic yield decreases for higher temperatures because of a decrease of the solid yield[2,3,4]. Potential feedstock includes digestate, municipal waste, grass, leaves, bagasse and wood[5]. Mass and energetic yields in this contribution are derived from lab scale and pilot scale experiments.

However, in order to assess the energetic efficiency of a HTC plant also external energy consumption must be taken into account - especially for heating the biomass to reaction temperature, for mechanical dewatering of the hydrochar slurry and for drying. The amount of energy needed to heat biomass with a water content of 80% to reaction temperature is app. 24% of the energy of the hydrochar. For drying of char with a water content of 30% app. 4% of its energy is needed. This shows that external energy consumption may decrease the efficiency of a HTC plant significantly and that heat recovery within an elaborated heat regime is crucial. In prior works it was shown that the use of flash steam from expansion of the hot slurry can significantly increase the efficiency of the process[6,7]. But release of pressure and the mixing of steam with colder water necessarily results in a loss of exergy, compared to direct recycling of hot compressed water which is proposed here.

1.1. Semi-continuous biomass feeding

Generally batch or continuous systems are applicable for a HTC plant. Yet, for continuous or semi-continuous systems, reaction heat can be used more efficiently. Also adjacent equipment can be utilized more efficiently and pressure changes in the reactor can be avoided. However, feed systems for solid matter against pressure are challenging – especially for heterogeneous biomass. Piston pumps usually can only pump biomass with a water content of 90%. For dry matter lock hopper systems are widely used, although they come along with a loss of gas for every cycle. Yet for the case of HTC this does not necessarily need to be a disadvantage because reaction gas needs to be discharged from a continuous reactor. Lock hopper valves are prone to abrasion and plugging. Here ball segment valves with a nominal diameter of up to 600 mm made of ceramic may be appropriate[8]. In order to reduce the loss of gas, further feeding systems have been developed including rotary feeders, plug-forming feeders, non-plug-forming feeders[9]. In this contribution we will present a model of a semi-continuously operating system with a lock-hopper feeding system.

1.2. Heat recovery

For a HTC plant an efficient processing of heat will be crucial. In a continuous HTC plant there are three mechanisms which require most of the energy and which are addressed by the plant model: (1) Much water along with the biomass needs to be heated to reaction temperature. This can be reduced if relatively dry biomass is fed via a lock hopper system. Additional water to fully cover biomass in the reactor and enhancing the reaction may be hot compressed process water which is recycled. However this requires mechanical dewatering of the hydrochar slurry after the reaction at elevated temperature and pressure. (2) Additional energy is used for drying wet hydrochar, which requires that the product is mechanically dewatered as well as possible. By dewatering at reaction temperature, a significantly lower water content can be expected. This is because of lower surface tension, density and viscosity of hot water, as was practically examined and realized for mechanical-thermal dewatering of lignite[10,11]. (3) By discharging reaction gas from the reactor a significant amount of steam is discharged as well. By increasing the absolute pressure in the reactor and hence the partial pressure of reaction gases, the loss of vapour can be decreased.

The model aims at using only internal heat sources for preheating of biomass and for drying. Only for the highest temperature level before the entrance of biomass in the reactor external energy is used for the supply of steam.

2. Modelling

For the simulation the program Engineering Equation Solver (EES) is used. Mass and enthalpy balances were entered for all mass flows. Enthalpy of components (except for steam) is set to zero for 0°C. The process is modelled in a steady state although lock hopper and piston press work semi-continuously in reality. Indirect heat transfer to solids or slurries is difficult and fouling on heat exchangers may increase considerably above 100°C[7]. Therefore in the model it is assumed that indirect heat transfer is only feasible up to a temperature of 100°C. The model assumes a capacity of the plant of 2000 kg/h of dry biomass. Below the model is described in detail and is depicted in Fig. 1.

2.1. Preheating of biomass

Biomass with a water content of 0.6 is heated by indirect heat transfer by low temperature waste water and vapour to 100°C at atmospheric pressure. The heat capacity of dry biomass and hydrochar is 1.6 $kJ/kg \cdot K^{-1}$ and 1.45 $kJ/ kg \cdot K^{-1}$ respectively. After preheating at atmospheric pressure biomass is fed to the lock hopper and is mixed with internal steam from the first flash tank. Then it is mixed with hot compressed water and is finally mixed with external steam from a steam generator until it reaches the necessary temperature and water to biomass ratio of 7:1. External steam is produced by a steam generator operated with natural gas with an efficiency of 0.9.

2.2. HTC reaction

The heat of reaction was measured by differential scanning calorimetry (PerkinElmer DSC-7). 4 mg of ground poplar wood were heated with 20 mg of de-ionized water to 220°C in stainless steel high pressure capsules. In the reference capsules only de-ionized water was used. The experiments were conducted according to ISO 11357-1:1997 and ISO 11357-5:1999. In [12] the applicability and uncertainty of this method for long lasting heat flows is discussed in detail. The mean heat released by the reaction within the first 4 hours was 500 J/g of dry biomass. The uncertainty of the experiments was 30% but could be higher if process water was recycled and therefore in the sensitivity analysis it is altered from 200 to 800 J/g.

In the model the biomass enters the reactor where it reaches the reaction temperature of 210°C by heat of reaction. Heat equilibration is assumed to be dominated by evaporation of water at superheated areas at the bottom of the reactor and condensation at relatively cold biomass on the top. Heat losses of the reactor were assessed to be 5-20 kW depending on insulation which accounts for 0.2% of the system power of the HTC plant. This shows that heat losses in an industrial scale may play a minor role which is not the case for lab experiments which require constant heating in order to maintain a certain temperature. In the model an overall heat loss of 20 kW is assumed and is completely attributed to the reactor.

The model uses experimental mass and energy balances of the HTC reaction. Solid yield, gas yield and heating values are derived from lab experiments with beech wood chips in a 200 mL reactor which could also be reproduced in a 250 L pilot scale reactor. The experiments were performed at the same conditions which are assumed in the model (reaction temperature 210°C, reaction time 4h, water to biomass ratio 7:1). The main results of the experiments which are used in the model are depicted in Table 1.

Table 1. Mass and energy balances of lab and pilot scale experiments with uncertainties shown in parenthesis.

	wood$_{dry}$	char$_{dry}$	solid yield	gas	gas yield	HHV	LHV	energetic yield$_{HHV}$
	mass(g)	mass(g)	(-)	mass(g)	(-)	(MJ/kg)	(MJ/kg)	(-)
Lab scale	19.98 (0.03)	12.88 (0.09)	0.644 (0.003)	0.69 (0.01)	0.035 (0.001)	23.27	22.01	0.781^1
Pilot scale	14710 (120)	9980 (860)	0.680 (0.064)	-		22.88	21.53	0.808^1

^{1} HHV$_{wood}$ =19.20 MJ/kg, LHV$_{wood}$=18.06 MJ/kg

Mass and energy yields could be well reproduced for lab experiments. Mass yields from pilot scale experiments altered mainly because the reactor could not be flushed as well. Solid and energetic yields are slightly lower and HHV is slightly higher than reported earlier for experiments at similar temperatures[3,4]. This can be explained by application of higher water to biomass ratio and longer reaction time in the experiments presented above, which will be discussed in detail elsewhere.

The ratio of reaction water and solved organic substances to biomass is 0.32 according to the experiments, yet in the model thermodynamic properties of pure water are assumed. It is assumed that reaction gas only consists of carbon dioxide. The partial pressure of the reaction gas in the reactor is assumed to be 0.9 MPa in order to be completely removed by gas loss of the lock hopper.

2.3. Mechanical dewatering and drying:

Electricity consumption of the piston press is calculated in two steps. First the char is dewatered to a water content of 0.6 with a pressure of 3 MPa. Then the char is dewatered to a final water content of 0.3 by a pressure of 10 MPa. The work is calculated by multiplying the volume of the displaced water with the respective pressure and assuming an efficiency of 0.9. The primary energy consumption of the piston press PEC_{press} is calculated by multiplying the electricity consumption with a primary energy factor. A factor of 2.5 is applied assuming an energy conversion efficiency of the char of 40% in a thermal power plant and thus resulting in a primary energy consumption of the piston press of 0.163 GJ/h.

The water content of the hydrochar after mechanical dewatering is assumed to be 30% corresponding to 31% achieved by pilot scale mechanical-thermal dewatering of lignite at 200°C[10,11]. After dewatering the pressure of the piston is released. In the model it is assumed that this results in evaporation of residual water and cooling to 105°C. Further assuming adiabatic conditions this results in drying to 22% water content which compares to 24% achieved at 200°C[10,11]. Relaxation steam is used for preheating biomass. Afterwards biomass is dried in a rotary drier using steam at 130°C from the second flash tank and abstracted reaction gas and steam from the reactor. Values for desorption heat of lignite[10] are used for the simulation of drying and no external energy is used for drying.

The efficiency of the plant in Table 2&3 is calculated according to Eq. (1):

$$efficiency_{HHV/LHV} = \frac{energy_{hydrochar,HHV/LHV}}{energy_{biomass,HHV/LHV} + energy_{natural\ gas} + PEC_{press}} \qquad (1)$$

3. Results

3.1. Simulation results

In Fig. 1 the model as presented before is depicted including mass flows and state variables. The biomass is heated by steam from the first flash tank to 156°C and then is mixed with the hot compressed water from the piston press.

This way the slurry reaches 196°C and only a limited amount of external heat is needed to finally heat biomass and water to 205°C. The amount of external energy needed for this step is 1.03 GJ/h which is 2.7% of the energy of the biomass and 3.4% of the energy of the hydrochar. Heat of reaction then is sufficient to heat biomass to reaction temperature of 210° and to make up for heat losses and gas losses via the lock hopper. The temperature of the waste water is 105°C and cannot be further used at this temperature level. The char can be dried to a water content of 7% by using only internal heat.

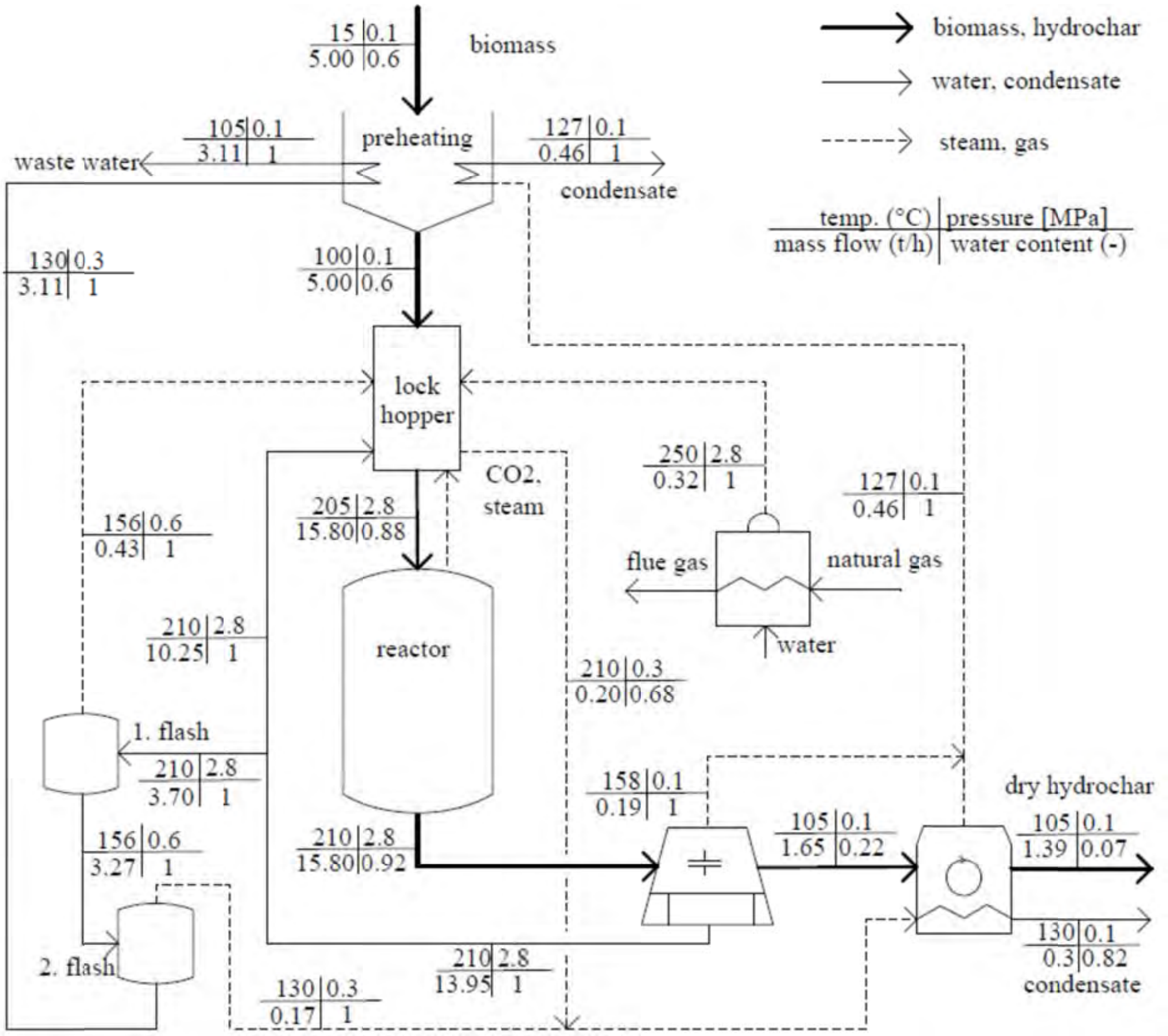

Fig. 1. *Model of HTC plant with mass flows and state variables.*

3.2. *Sensitivity analysis*

The water content of the biomass significantly determines the amount of energy needed to heat the biomass to reaction temperature. Therefore it was varied as an input parameter in the simulation from 0.5-0.75 and results are depicted in Table 2. For a higher water content the amount of natural gas needed increases and makes up between 2.2 % and 7.3 % of the energy of the hydrochar. On the other hand the water content of the dried char decreases significantly. This is because less water can be recycled allowing for a higher amount of steam from the second flash tank to be used for drying. The efficiency is calculated both on basis of the HHV and LHV. The efficiency of the HTC plant decreases with a rising water content on the basis of the HHV because more external energy is required. The efficiency of the plant increases on a LHV basis because the lower heating value of the biomass decreases significantly with a higher water content.

Table 2. Results from the variation of the water content of biomass.

water content		energy (GJ/h)					efficiency	
biomass (-)	char (-)	natural gas	biomass (HHV)	biomass (LHV)	char (HHV)	char (LHV)	(HHV) (-)	(LHV) (-)
0.5	0.104	0.650	38.40	31.24	30.06	28.07	0.767	0.876
0.55	0.088	0.819	38.40	30.16	30.06	28.13	0.763	0.903
0.6	0.069	1.032	38.40	28.80	30.06	28.20	0.759	0.940
0.65	0.044	1.307	38.40	27.06	30.06	28.29	0.754	0.992
0.7	0.011	1.675	38.40	24.73	30.06	28.40	0.747	1.069
0.75	0.000	2.191	38.40	21.47	30.06	28.43	0.738	1.193

For a very wet feedstock it may be favourable to mechanically dewater biomass before feeding it to the HTC plant. This would drastically decrease the amount of waste water by recycling a larger part of the water. Therefore it would also decrease the amount of energy needed to heat biomass to reaction temperature. Assuming a decrease of water content of 0.15 in a screw extruder and an electricity demand of 50 kWh/t_{DM}[13] and a primary energy factor of electricity of 2.5 the energetic breakeven point would be at a water content of 0.71 of the biomass.

The heat of reaction was varied in the model between 200 and 800 J/g while the water content of the biomass is set constant to 0.6. The results are depicted in Table 3. With increasing heat of reaction the amount of natural gas needed decreases significantly and would be zero for 840 J/g for the heat of reaction. As less external heat is consumed for heating the biomass, slightly more internal water is recycled. Therefore, less internal steam is available for drying the char, resulting in a small increase of the water content.

Table 3. Results from variation of reaction heat.

reaction heat	water content char	energy (GJ/h)	efficiency (-)	
(J/g)	(-)	natural gas	(HHV)	(LHV)
200	0.054	1.946	0.742	0.914
300	0.059	1.641	0.748	0.923
400	0.064	1.336	0.754	0.931
500	0.069	1.032	0.759	0.940
600	0.074	0.728	0.765	0.949
700	0.078	0.425	0.771	0.958
800	0.083	0.122	0.777	0.968

In the past it was disputed if a self sustaining heat regime was achievable for a HTC plant. As shown above heat demand both depends on the water content of the biomass and the heat of reaction. This means that at a certain water content the heat of reaction would have to be above a certain value. Eq. (2) describes the cases in which the condition of a self sustaining heat regime would be fulfilled for the configuration presented above:

$$h_{reac} \geq 245 * e^{2.1*WC} \qquad (2)$$

where h_{reac} is the heat of reaction (J/g) and WC is the water content (-).

4. Discussion & Conclusion:

It is shown that external energy consumption of a HTC plant can be significantly reduced by addressing the most energy consuming processes of biomass preheating, char drying and reaction gas abstraction. By recycling of hot compressed water efficient heat recovery can be achieved. By using internal heat only, biomass can be heated to 196°C and hydrochar can be dried to 7% water content. External primary energy is needed to further heat biomass to reaction temperature. Electricity is consumed for mechanical dewatering of the char. The total amount of external primary energy for the base case is 4% of the energy of the char which is about half as much as calculated earlier[6]. Depending on the amount of water content and heat of reaction it varies between 1-8%.

Efficiencies for the HHV of the presented HTC plant range from 74-78% based on lab experiments with beech wood chips. Further studies on energetic yields of the HTC reaction are necessary for different feedstock and reaction conditions. However, it can be assumed that external primary energy consumption mainly depends on the plant set up and on the water content of the biomass and the heat of reaction.

In previous publications the intensity of the heat of reaction was overestimated considerably by theoretical considerations. Here values from calorimetric measurements are used and it is shown that it is an important parameter for the assessment of the efficiency of a HTC plant. Therefore additional research is necessary for a better understanding of this parameter.

Recycling of process water is favourable because the amount of waste water can be reduced and heat can be recovered. It is shown that mechanical dewatering of biomass before the HTC reaction can reduce primary energy consumption for wet biomass. In addition a higher amount of recycled water may also slightly increase the energetic yield of the hydrochar because parts of the organic substances in the water may polymerize further. For quantification of this effect further studies are necessary which require extensive dewatering of samples after reaction. Also by further decreasing the ratio of water to biomass the solid yield can be increased. Both effects may increase the solid yield by a few percent.

Acknowledgements

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Minimization of exergy losses in combustion processes with an illustration of a membrane combustion

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Abstract: The efficiency of internal combustion engines and gas turbine processes are free from Carnot limitations as they are not performing cycle processes – the initial state of the thermodynamic system is the fuel with air, whereas the final state is the flue gas, whose chemical composition is different than fuel and air. Therefore, as we show here, the theoretical thermodynamic efficiencies of ideal combustion engines and gas turbine processes can be very high, the same as it is for fuel cells. The entropy generation analysis, what we have done for the internal combustion engines and gas turbines, shows that they suffer for relatively low efficiencies because of the exergy losses in the combustion processes, i.e. for the reason that the combustion reaction takes place quite far from the equilibrium state. We have studied several different combustion processes in the Exergy-project of MIDE-program to find a method for decreasing the entropy generation in the combustion. If the entropy generation can be reduced, by any means, then as a “reward”, we get the outlet pressure of the flue gas higher than the inlet air pressure without using any compressor which in turn would then increase the efficiency essentially. We present here a theoretical description of a membrane combustion method which, with the aid of gasification, suits for bioenergy. Shortly, it can be described as a molecular scale oxygen gas compressor driven by the combustion reaction, where the affecting force is amplified by the electric field across the membrane.

Keywords: *Entropy, exergy, combustion, membrane, efficiency, combustion engine, gas turbine process*

1. Introduction

In adiabatic combustion process the outlet temperature of the flue gas depends on the air factor λ and the fuel. It does not depend on the pressure as far as we consider the flue gas as an ideal gas, because then the specific enthalpy of the species (i) depends only on its temperature: $h_i = h_i(T)$. In very high pressures near to the critical pressure, where the ideal gas assumption is no longer valid, the pressure affects also on the specific enthalpy.

Hence, the pressure of the outflow gas does not follow from the energy balance, but it depends on the manner how the combustion process is realized. So we need the second law of thermodynamics to analyze this. The specific entropy of the gas species (i) depends on the temperature T, and also on its partial pressure p_i, i.e. according to the ideal gas model $s_i(T,p_i) = s_i(T,p_0) - R\ln(p_i/p_0)$, which shows that the higher the pressure p_i the smaller is the entropy s_i. Here the reference pressure $p_0 = 1\,bar$ and the gas constant $R = 8.314\ J/molK$. The entropy generation in the adiabatic combustion is

$$\sigma_{irr} = \sum_{out} n_i s_i - \sum_{in} n_j s_j \geq 0, \tag{1}$$

from which we see that the higher is the outlet pressure, the smaller is the entropy generation σ_{irr}. Instead of the entropy generation we may as well speak of the exergy loss defined as

$$T_{(-)}\sigma_{irr} = exergy\ loss, \tag{2}$$

which describes the loss of mechanical work in chemical combustion reaction, or the loss to increase the pressure of the flue gas by the chemical reaction. Temperature $T_{(-)}$ is defined with the aid of the real final state (B) and the ideal isentropic final state (B_s) as follows [1]:

$$T_{(-)} \equiv \frac{H(B_s) - H(B)}{S(B_s) - S(B)} \tag{3}$$

Usually the flue gases from the combustion chambers in the gas turbine processes flow out approximately at the same pressure as the inlet flow of the air, and we speak then about combustion at constant pressure. In our earlier paper [2] we have shown that in the conventional combustion with constant pressure the entropy generation is very high and the exergy loss $(T_{(-)}\sigma_{irr})$, depending on the air factor and the fuel, is about half of the heat value of the fuel.

In the classical form of the Guoy-Stodola, the exergy loss is defined as $T_o\sigma_{irr}$, where T_o is the lowest temperature of the surroundings with which the system is in thermal contact. As we have shown in our earlier paper [2] the choice of the temperature T_o for Eq.(2) does not give the accurate value for the lost of the work and for the efficiency of combustion engines (for Eq.(4) below), only an upper limit, and therefore, as shown in [2] we use the correct temperature $T_{(-)}$ instead of T_o.

2. Isentropic combustion

The ideal adiabatic combustion process is such that there is no entropy generation, $\sigma_{irr} = 0$. In the language of thermodynamics it is called an isentropic combustion, and it means a combustion process which proceeds via equilibrium states. In the following we discuss how important for the efficiency it is to keep the entropy generation σ_{irr} as small as possible in order to have a good efficiency.

2.1. Combustion engine

For the combustion engine the following general equation for the efficiency can be derived [1]

$$\eta = 1 - \frac{T_{(-)}\sigma_{irr}}{-[H(B_s) - H(A)]} \tag{4}$$

where σ_{irr} is the generation of entropy in the whole combustion engine process and $-[H(B_s) - H(A)]$ is the heat value of the isentropic combustion process from A to B_s, which is defined so that $S(A) = S(B_s)$. In the denominator of Eq.(4) there is the enthalpy difference $-[H(B_s) - H(A)]$ because our system is a closed system which makes transformation process in the engine during 720^o degrees of rotation of the crank shaft. The entropy generation σ_{irr} (J/K) means correspondingly the entropy generation during 720^o degrees of rotation.

We studied [1] the exergy losses of the diesel engine process, shown in Fig.1, and we found that 79% of all exergy losses took place between the combustion process steps 4-5-6-7. The whole efficiency of the diesel engine was 47.5%. Therefore, if we could eliminate the exergy losses of combustion, then the exergy losses left were 21% x 52.5% = 11% and the efficiency of the diesel engine would be $\eta = 89\%$. It can be so high as the theoretical efficiency can be even one as we see from Eq.(4). The reason for that is that the efficiency is not limited by Carnot formulae because the process is not a cycle process. The efficiency is under the same type of limitations as fuel cells, but for the combustion engine the reference process is an ideal reversible adiabatic process whereas for the fuel cells it is an ideal reversible isothermal process. Therefore, the maximum work out here is $-\Delta H(S = const)$, whereas for the fuel cell it is $-\Delta G(T = const, p = const)$.

How would then the ideal process without any exergy losses in the combustion steps look like compared to Figure 1a? First of all, the engine would be then a two stroke engine, but without having any dead volume. Suppose first that the piston is at left (with volume=0) and the hot flue gas starts to fill the cylinder by pushing the piston to the right in Fig.1b by constant pressure (say at 230 bar as in Fig.1a) from the point 4* to the point 5*. At that point the inlet valve is closed and the isentropic expansion process starts, during which the pressure and the temperature become lower. The length of the piston stroke is such that the point 9* is reached. After that the outlet valve is opened and the flue gas is flowing out to the turbocharger at constant pressure (3 bar in Figs.1a and 1b). All the flue gas is pushed off at constant pressure to the zero dead volume and then the process is repeated by filling the cylinder again by hot flue gas with a high pressure. The turbine unit of the turbocharger is rotating the shaft of the compressor which is feeding air into the special external membrane combustion chamber. That external membrane combustion chamber is assumed to produce the flue gas out at high pressure without any remarkable additional work (only the compression work for fuel feeding) and theoretically with zero entropy generation.

The efficiency of this type of a combustion engine shown Fig.1b is much higher than the engine in Fig.1a because the compression work (3-4 in Fig.1a) is not needed and because the expansion (point 8) continues down to 3 bar whereas it stops now (Fig.1a) at 12 bar, which means that more expansion work can be taken out to the crank shaft by the process.

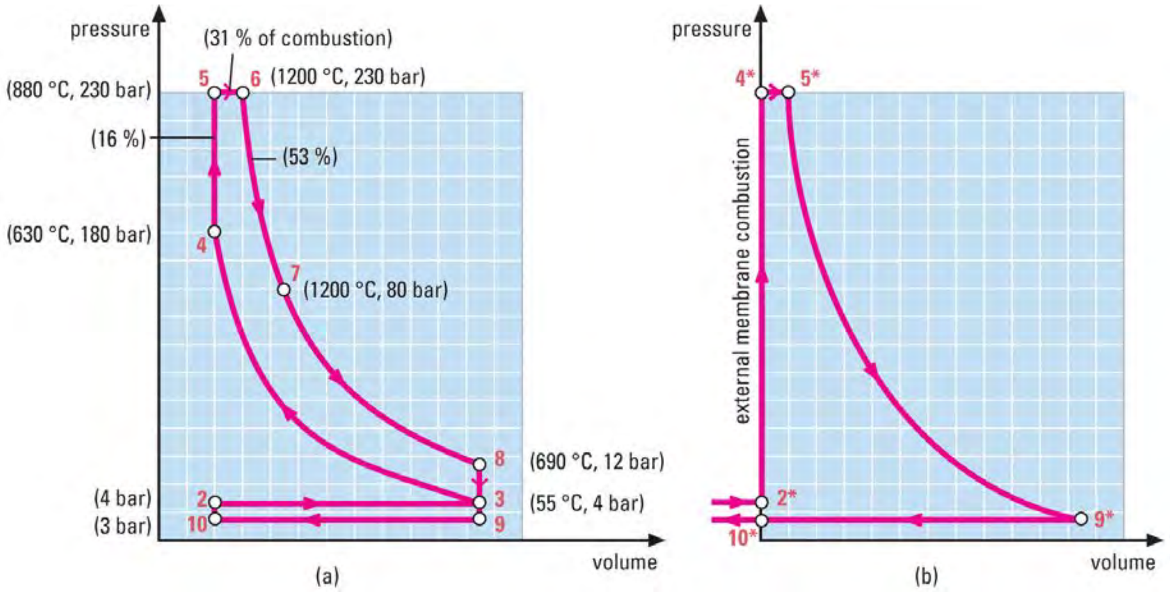

Fig. 1a. Turbocharged diesel engine process. Combustion takes place between 4-5-6-7.
1b. Turbocharged external membrane combustion engine. Combustion only between 2-4*.*

2.2. Gas turbine process

Also for the gas turbine processes the exergy losses in the combustion chamber are of crucial importance. In a methane gas driven power plant in Finland the gas turbine gives out 94 MW of shaft power with the flue gas inlet at 1100 ^{o}C and pressure 11 bar (abs). The compressor driven by the gas turbine takes 54MW which means that the shaft power delivered to the generator is 94 MW – 54 MW = 40 MW. By reducing sufficiently the entropy generation in the combustion unit the outlet pressure of 11 bar could be achieved without using the compressor at all, and thus the whole turbine power could be transferred to the generator which of course, would increase the efficiency essentially. The principal power process based on the use of the theoretical isentropic combustion chamber is shown in Fig.2.

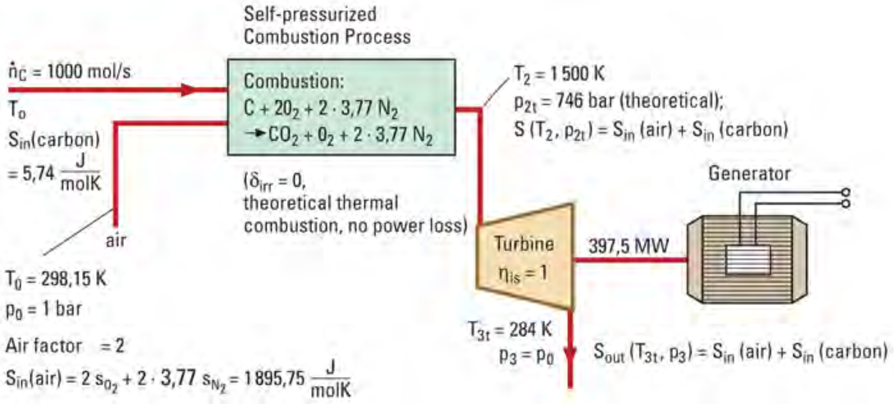

Fig. 2. Illustration of an ideal theoretical gas turbine process where the combustion takes place isentropically [1].

Figure 2 shows the theoretical limits for the gas turbine process if the entropy generation is zero in the combustion chamber and also in the turbine. If $\sigma_{irr} = 0$ in the combustion chamber, then as shown in Fig.2, the outlet pressure will be as high as $p_{out} = 746\ bar$. This is, of course just a theoretical number, but it shows that there is a great potential to improve the conventional combustion process. For instance, to achieve pressure ratio $p_{out} / p_{in} = 11$ in the combustion chamber with carbon as fuel and with λ=1, we need to decrease entropy generation from $\sigma_{irr} = 366\ J/molK$ only to $\sigma_{irr} = 270\ J/molK$. In the following we will shortly discuss how we could do this by a membrane combustion.

3. Principle of semipermeable membrane combustion

Ceramic membranes made of yttria-stabilized zirconia (in Fig.3: ZrO_2/Y_2O_3) has the property that in sufficient high temperatures (800-1000 °C) they start to conduct oxygen ions (O^{2-}). The ionic conductivity depends on the amount of yttria in the structure. Approximately half of the amount of yttria atoms in the crystalline structure can offer vacancies to be occupied by "hopping" oxygen ions. These materials are well known from Solid Oxide Fuel Cells and from lamda-sensors used in cars for measuring the oxygen concentration in flue gases.

As shown in Fig.3, the oxygen gas is consumed on the surface of the combustion side and therefore, the partial pressure of oxygen gas becomes there lower than on the surface of the airside. Because of the ionic form of oxygen, the difference of partial pressures generates a potential difference, which can be estimated by Nernst equation (see Fig.3). The electric field performed by the potential difference is the driving force for the oxygen transport through the membrane. Depending on the concentration of oxygen ions, the electric volumetric force field (ion charge density x electric field, N/m^3) can be amplified to several magnitudes higher than the partial pressure gradient of oxygen gas.

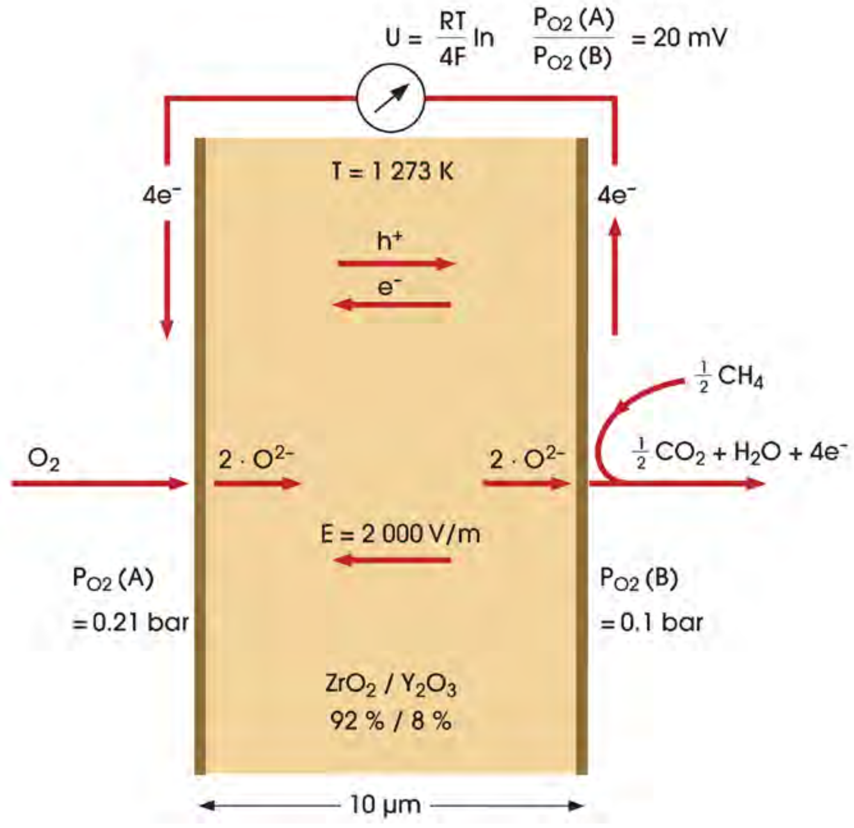

Fig. 3. Semipermeable oxygen gas membrane. Electric potential difference across the membrane is illustrated by assuming that the partial pressures of oxygen are 0.21 bar (on the air side) and 0.1 bar (on the flue gas side). The total pressure of the flue gas p(B) is kept higher than the total pressure of air p(A) by adjusting the outlet flow of flue gas accordingly.

Recently, it has been studied the ionic and electronic charge transport for single crystals of yttria-stabilized zirconia with additional nitrogen doping, e.g. [3] and [4]. At temperatures above 850 ^{o}C, even in the presence of a very small oxygen concentration in the surrounding gas phase, the nitrogen ion dopant becomes highly mobile, and thus diffuses to the surface where it is oxidized to gaseous N_2(g). The technical motivation for that study [3] has been to achieve sufficient nitrogen ion conductivity for the development of a nitrogen sensor or nitrogen pumps. In the membrane combustion the driving force for the nitrogen transportation comes also from the electric field generated by the oxidation of the fuel. The flow of nitrogen gas lowers the temperature of the membrane, which merely by oxygen combustion would be too high. A construction using nitrogen and oxygen gas semipermeable membranes is shown in Fig.4.

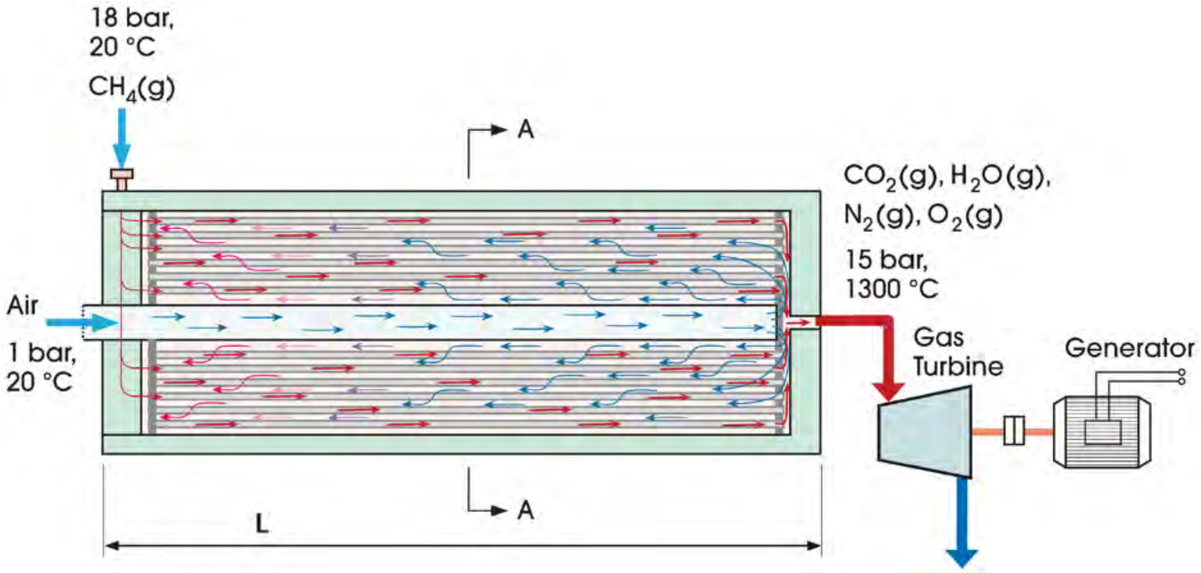

Fig. 4. Hollow ceramic fibers used in the membrane combustion. Fuel (here the methane gas) is fed in the fibers and air outside of the fibers.

4. Discussion

We have discussed here that the entropy generation in the combustion processes is the crucial point that reduces the efficiencies of combustion engines and gas turbine processes. We have presented here an illustration of a membrane combustion method which, with the aid gasification is quite suitable for bioenergy, and which can reduce the entropy generation by pressurizing the combustion chamber without using any external work. Shortly, it can be described as a molecular scale gas compressor driven by the combustion reaction, where the affecting force is amplified by the electric field across the membrane.

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Sugar Cane Trash Pyrolysis for Bio-oil Production in a Fluidized Bed Reactor

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Abstract: The objective of this work was to study bio-oil production from sugar cane trash by a pyrolysis process in fluidized bed reactor. The experiments were carried out at different temperatures ranging from 460 – 540 ^{o}C and at different medium gas flow rates between 120 -160 cc.s^{-1}. Two different gases, Nitrogen (N_2) and air, were used as the fluidizing medium in order to study the effect of a different medium on the yield and properties of the bio-oil. The experimental result showed that the maximum bio-oil yields of 46.2 wt% and 31.95 wt% were obtained at 500 ^{o}C and 160 cc.s^{-1} for air and Nitrogen medium, respectively. The bio-oil yield obtained when using air as a medium was higher than that when using Nitrogen medium. This was a result of the higher quantity of water content in the air. The properties of bio-oil were determined and the result showed that its heating value, dynamic viscosity, density, water content, and pH were 15.48 MJ.kg^{-1}, 2.31 cSt 1,019 kg.m^{-3}, 52 wt% and 3, respectively. By dehydration of the obtained bio-oil, the heating value, viscosity and density were increased to 19.81 MJ.kg^{-1}, 57.66 cSt and 1,260 kg.m^{-3}, respectively. These results show that the bio-oil can be used as a fuel oil for combustion in a boiler or a furnace without any modification. Furthermore, the energy consumption of the pyrolysis process was analyzed.

Keywords: *Sugar cane trash, Bio-oil, Pyrolysis, Fluidized bed reactor.*

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1. Introduction

Biomass is widely considered as a major potential for renewable energy in the future. Residual biomass and renewable materials can be converted by a pyrolysis process to a combustible liquid usually termed as bio-oil. Bio-oil is renewable and biodegradable and has some advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. The bio-oil can be used in engines, turbines and furnaces for power generation. The bio-oil obtained from agricultural residuals is a form of renewable energy. In principle, utilizing this energy, in contrast to fossil fuels, does not add carbon dioxide, a greenhouse gas, to the atmospheric environment. Therefore, bio-oil can be recognized as a potential source of renewable energy based on the benefits of both energy recovery and environmental protection. Due to the lower contents of sulfur and nitrogen in agricultural residuals, its energy utilization also creates less environmental pollution than fossil fuel combustion.

Sugar cane trash from agricultural residues is abundant in Thailand which has an annual production of more than 10 million-tons [1]. Traditional methods such as composting and incineration are not suitable to process these organic solid wastes, as they contain small concentrations of N_2 for composting and smoke would be released to pollute the environment during incineration. Therefore, a practical method would be to pyrolyze cane trash to provide bio-oil. Currently, the potential of pyrolysis conditions for bio-oil production have been investigated. Asadullah et al. [2] has studied the pyrolysis of jute stick for bio-oil production in a continuous feeding fluidized bed reactor. The experimental results showed that the maximum yield of bio-oil was 66.7 wt% at 500 ºC. Ji-lu et al. [3] pyrolyzed cotton stalk in a fluidized bed using nitrogen as the carrier gas to fluidize the cotton stalk with sand. From the experiment, the yield of bio-oil first increased and then decreased as a function of the combustion temperature and the maximum yield of bio-oil was 55 wt% obtained at 510 ºC.

Furthermore, bio-oil production from many kinds of biomass, such as China Fir, Manchurian ash, Padauk wood, rice straw and rice husk has been performed in a fluidized bed reactor by fast pyrolysis [4-5]. The experimental results showed that the yield of bio-oil varied with combustion temperature, heating rate and volumetric flow-rate of nitrogen gas. Besides, using a fluidized bed reactor for bio-oil production, a fixed bed reactor and an induction-heating reactor have also been investigated [6-8]. From the experiment, it was found that the temperatures, nitrogen flow rates, heating rates and particle sizes play the roles of important parameters for the yield of bio-oil production.

However, at present, there has not been comprehensive research about the bio-oil production from sugar cane trash. The fast pyrolysis of cane trash in a fluidized bed reactor under different conditions was performed in order to know the suitable conditions of the parameters to produce the maximum bio-oil production and to determine the properties of bio-oil obtained. The effects of combustion temperature, flow rate of carrier gas and type of fluidizing medium were investigated. Furthermore, the energy consumption for bio-oil production was also analyzed.

2. Experimental material, device, method and procedure

2.1. Experimental material

The experimental materials include cane trash, sand, air and nitrogen (N_2). The physical properties of the cane trash and sand, such as density, porosity and diameter, are listed in Table 1. The proximate analysis and ultimate analysis of the cane trash are listed in Table 2 and Table 3, respectively. The sugar cane trash had dimensions of 1 x 3 mm and 5.94 wt% of moisture content in feedstock. Sand was used as the thermal carrier to transfer heat quickly from the hot N_2 (or air) to the cane trash. N_2 (or air) was used as the carrier gas to fluidize the cane trash with sand in the fluidized bed reactor.

Table 1. Physical properties of experimental material.

Physical properties	Cane trash	Sand
Density (kg.m^{-3})	347.61	3,793.27
Porosity (%)	50.72	41.31
Diameter (mm)	1-3	0.332

Table 2. Proximate analysis of sugar cane trash.

Properties	Value
Fixed carbon (wt%)	21.26
Volatile matter (wt%)	70.86
Moisture content (wt%)	4.55
Ash (wt%)	3.33
Heating Value (MJ.kg^{-1})	18.3

Table 3. Ultimate analysis of sugar cane trash.

Properties	Value (wt%)
C	51.21
H	5.16
N	1.93
O	40.33
S*	1.37

* Sulfur calculated by difference.

2.2. Experimental set-up

As shown in Fig. 1, the experimental device consisted mainly of a hopper, two cyclones and a condenser as well as seven thermocouples. The hopper was used to contain feedstock such as cane trash. The two screw feeders had the same configuration and size; the first one was used to control the feeding rate and the second one operated at a relatively high speed to prevent jamming the feeding system. The fluidized bed reactor operated at atmospheric pressure using N_2 (or air) as the fluidizing medium gas. The reactor had a height of 1.54 meter and a diameter of 10 cm in which the cane trash was rapidly heated for pyrolysis. The 6,000 W electric heater was able to pre-heat the N_2 (or air) to a temperature range of 500 ºC - 620 ºC before entering the fluidized bed reactor. The two cyclones were used to separate solid particles, such as charcoal and ash, from the hot gas. The condenser was equipped with copper pipes and a cooling tank. The condenser was able to quickly cool the cleaned hot gas into a liquid. Thermocouples were used to monitor and control the pyrolysis system. The locations of all measurement sensors, including the seven thermocouples are shown in Fig. 1. The specification of the thermocouples is K Type, made from an alloy of chromel - alumel, measurement range from -200 ºC to 1,372 ºC with measurement accuracy of the thermocouples of ±2 ºC. The Fuzzy+PID logic was used in the temperature control system.

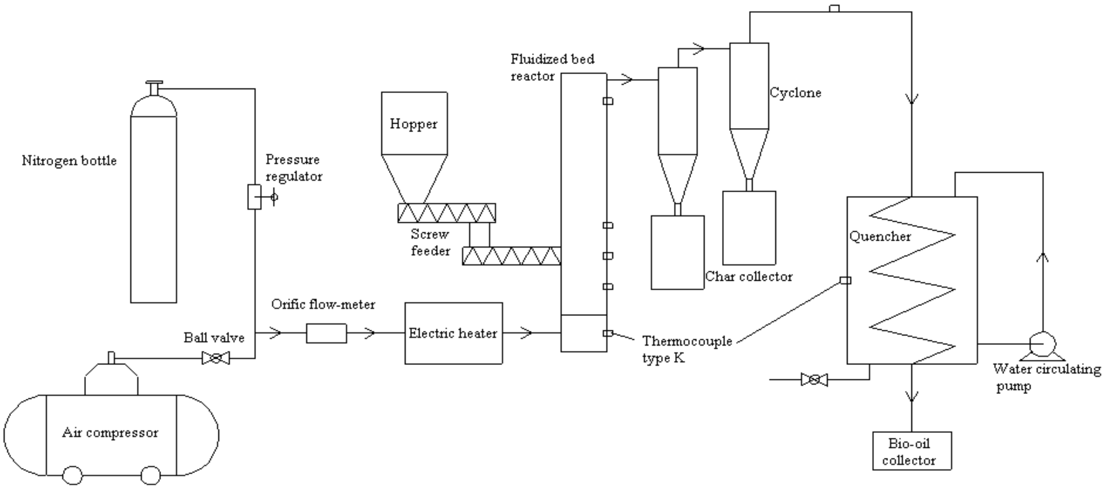

Fig. 1. The experimental set-up.

2.3. Experimental method

The experiment device was originally set up at Khon Kaen University in 2010 and presently scaled up to a cane trash feeding rates of 10 kg.h^{-1}. The cane trash powder had dimensions between 1 – 3 mm and was fed continuously into the reactor. The pyrolysis experiments using cane trash were performed at flow-rates of 120 cc.s^{-1},160 cc.s^{-1} and 200 cc.s^{-1} while the temperature was ranged from 460 ºC – 540 ºC under N_2 atmosphere., The pyrolysis experiments using cane trash were also performed in a different medium gas at a flow-rate of 160 cc.s^{-1} while the temperature was ranged from 460 ºC – 530 ºC under air static atmosphere. The yield of the bio-oil was heavily impacted by the rate of cooling in condenser. The cooling must be quick; otherwise, some condensable gas will be converted into non-condensable gas (NCG) [5]. Thus, in our experiment, the heat exchanger was operated in cool water and ice with a condensation temperature of - 4 ºC.

Besides bio-oil, two byproducts, namely charcoal and NCG, can also be obtained when cane trash is pyrolyzed. The yield of the bio-oil can be determined from the condensed liquid and the feedstock used. The yield of the charcoal can be calculated by dividing the ash contents in the feedstock with that in the charcoal. The yield of NCG can be determined from the fact that the sum of the three product yields should equal 100%.

2.4. Experimental procedure

1. Turn on the electric heater and turn on the 1st motor of the feeder to prevent jamming the feeding system.
2. Transport N_2 into the pyrolysis system with a flow rate of 120 cc.s^{-1}.
3. When the temperature of the fluidized bed reactor reaches the expected temperature, turn on the 2nd motor of the feeder to transport1 kg of cane trash into the fluidized bed reactor. The expected temperature was varied from 460 – 540 ºC.
4. After 45 minutes, stop transporting cane trash into the fluidized bed reactor.
5. Turn off the electric heater and the water circulating pump.
6. Then, stop transporting N_2 into the pyrolysis system.
7. Collect the bio-oil and charcoal for the experiment.
8. Perform the experimental steps (1)-(7) again by varying the flow rate of N_2 from 120 cc.s^{-1} to 160 cc.s^{-1} and 200 cc.s^{-1}, respectively.
9. Perform the experimental steps (1)-(8) again by changing the fluidizing medium from N_2 to air.

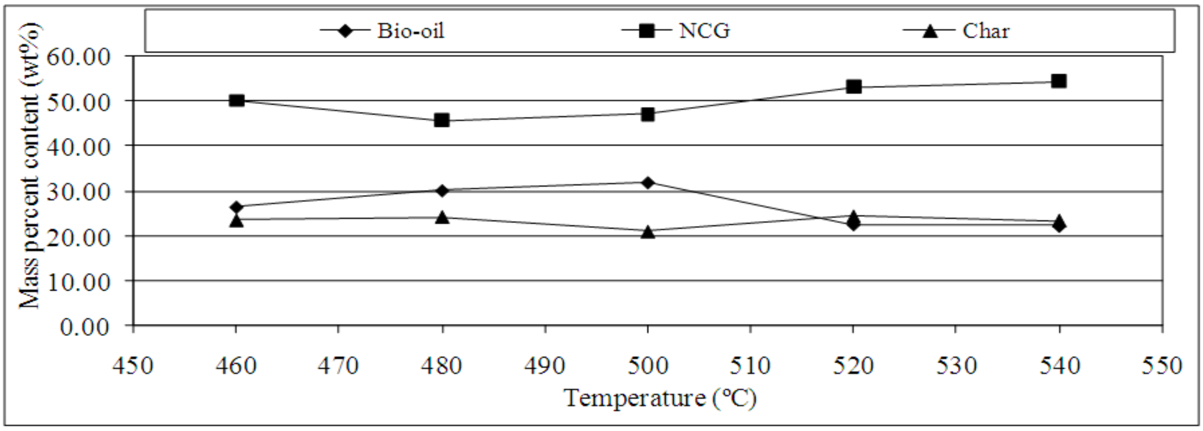

Fig. 2. Relationship between pyrolysis temperature and product yields for N_2 medium at flow-rate of 160 cc.s^{-1} and temperature between 460 ºC – 540 ºC.

3. Results and discussions

3.1. Effect of temperature on the product distribution

Our preliminary experiments show that a N_2 temperature below 460 ºC is not sufficient for pyrolysis, as some cane trash was found in the charcoal and ash. In contrast, N_2 temperatures above 540 ºC are too high, as the yield of bio-oil is quickly reduced. Therefore, for these particular materials, the optimum temperature for pyrolysis seems to be within the range of 460 ºC – 540 ºC. The relationship between the yields of the three products and the pyrolysis temperature at 160 cc.s^{-1} of N_2 volumetric flow rate is shown in Fig. 2.

From Fig. 2, it can be found that: (1) bio-oil yields first increase and then decrease with an increasing in N_2 temperature and the highest yield for cane trash is 31.95 wt% at 500 ºC, (2) NCG yields always increase with an increase in N_2 temperature and (3) charcoal yields always decrease with an increase in N_2 temperature. The influence of pyrolysis temperature is the same as the results of Z. Ji-lu et al. [3], S. Wang et al. [4] and Z. Ji-lu. [5], but the maximum yield of the bio-oil in their experiments is not equal to our experimental results.

The influence of pyrolysis temperature and the yield of the three products in air medium are shown in Fig. 3. It can be found that: the highest bio-oil yield of 46.2 wt% was obtained at an air temperature of 500 °C and a volumetric air flow rate of 160 cc.s^{-1}. The function of the air temperature to the product yields is similar to the function of N_2 temperature. The result showed that the yield of bio-oil from air medium was higher than the yield of bio-oil from N_2 medium. This is caused by the higher water content in the air.

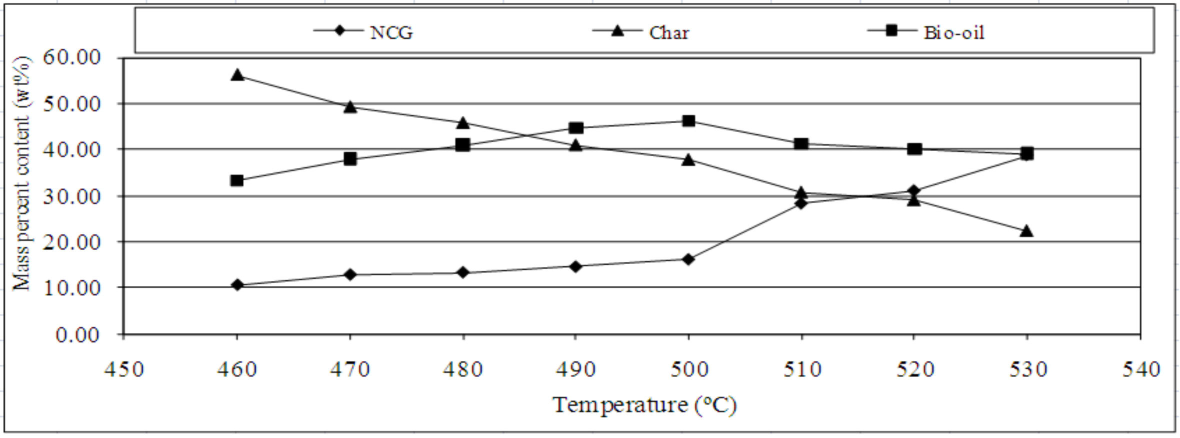

Fig. 3. Relationship between pyrolysis temperature and product yields for air medium at flow-rate of 160 cc.s^{-1} and temperature between 460 °C – 530 °C.

3.2. Effect of flow rate on product distribution.

It is known that sweeping the reactor with N_2 could increase the oil yield because sweeping the environment shortens the residence time of volatiles and reduces their chances of being involved in char and radical forming secondary reactions [6]. Fig. 4 shows the effect of the flow rate of N_2 on the production yield from cane trash pyrolysis. at a temperature of 500 °C. The relationship between the N_2 flow-rate and the production yield shows that: (1) bio-oil yields first increase and then decrease with an increase in flow-rate and the highest yield for cane trash is 31.95 wt% at 160 cc.s^{-1}, (2) NGC yields always decrease with an increase in flow-rate and (3) charcoal yields always increase with the increase in flow-rate. This influence of the N_2 flow-rate is the same as the experimental result of M. F. Parihar et al. [6].

The decrease in bio-oil yields when flow-rate is increased may be due to the very short residence time of the vapors in the condenser and vapors unable to condense due to higher percentage of NGC. Furthermore, the increase in char yields when the flow-rate is increased may be due to un-burned cane trash in the reactor.

3.3. Effect of fluidizing medium gas on the products distribution.

Pyrolysis is a thermal decomposition occurring in the absence or less than 30% theory of air [9]. Bio-oil has a water content as high as 15 - 45 wt% derived from the original moisture in the feedstock and produced by the dehydration of air during the pyrolysis reaction and during storage. The presence of water lowers the heating value and the flame temperature, but on the other hand, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine. Furthermore, the presence of oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content leads to an energy density lower than that of conventional fuel by 50% and also an immiscibility with hydrocarbon fuels. In addition, the strong acidity of bio-oils makes them extremely unstable. Therefore, the use of air as the fluidizing medium has an effect on the yield and properties of the bio-oil.

From the bio-oil production experiment using a different fluidizing medium, either air or N_2, the result showed that using air medium can produce a higher yield of bio-oil than that with N_2 medium, about 9.25 %wt at pyrolysis temperature of 500 ºC and a flow rate of 160 $cc.s^{-1}$. In addition, the bio-oil production from air medium had a high moisture content of 81.11 %wt while the bio-oil production from N_2 medium had a moisture content of 52.14 %wt. This result revealed that the air medium has a higher water content which has the advantage of reducing the viscosity of the bio-oil, but also the disadvantage of causing a lower heating value.

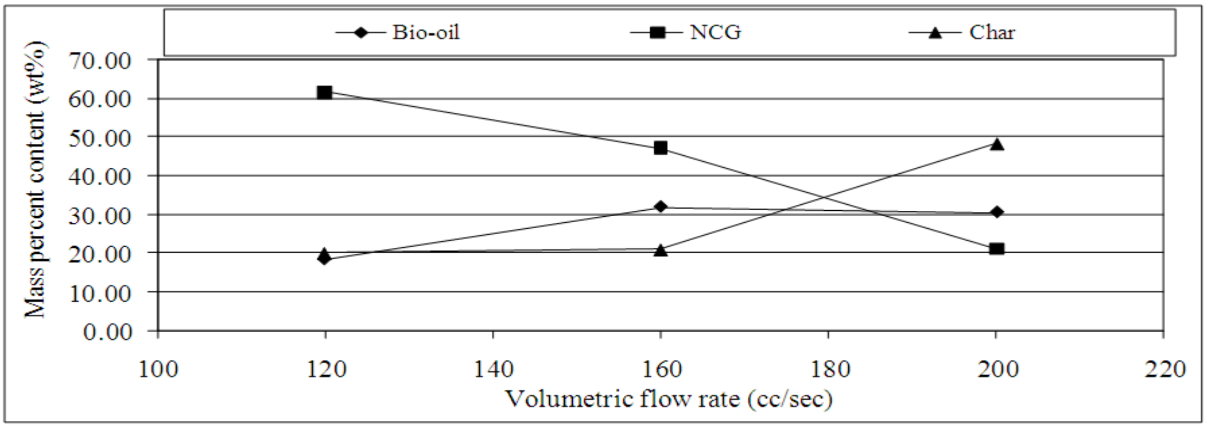

Fig. 4. Effect of flow rate on product yields from cane trash pyrolysis at temperature of 500 ºC and varying flow-rate of 120 $cc.s^{-1}$,160 $cc.s^{-1}$ and 200 $cc.s^{-1}$

3.4. Properties of the bio-oil.

The main properties of the bio-oil from cane trash are shown in Table 4. The low heating value (LHV) of bio-oil production from N_2 medium is higher than that from air medium because the air has a higher quantity of water content. Furthermore, the density, viscosity and pH of bio-oil production from N_2 medium and air medium are very comparable. To increase the heating value of the bio-oil, the water content in the bio-oil was dehydrated. The properties of the bio-oil after dehydration are shown in Table 5. The heating value, density and viscosity were increased while the pH was decreased for both N_2 and air medium.

Table 4. Main properties of bio-oil from cane trash.

Physical properties	Nitrogen medium	Air medium
Heating value ($MJ.kg^{-1}$)	15.48	1.36
Density ($kg.m^{-3}$)	1019.20	1010.12
Water content (wt%)	52.14	81.11
Viscosity (cSt) at 40 ºC	2.31	Similar to water
pH	3	3

Table 5. Main properties of bio-oil after dehydration.

Physical properties	Nitrogen medium	Air medium
Heating value ($MJ.kg^{-1}$)	19.81	16.55
Density ($kg.m^{-3}$)	1260	1230
Viscosity (cSt) at 40 ºC	57.66	-
pH	2	2

3.5. The energy consumption of the pyrolysis process.

The energy consumption of the bio-oil production using both N_2 and air as a medium was analyzed, and the results are shown in Table 6. The energy consumption was divided into two time periods which are during the pre-heating process and during the combustion process. During the pre-heating process, the reactor and fluidizing medium were heated by using a 6 kW heater and the fluidizing medium was transported by using an 15 hp air compressor. During the combustion process, the additional energy consumption was obtained from the use of two 120 W screw feeders for transporting the cane trash. To determine the energy consumption, the electric power was measured by watt meter and the working time of the process was recorded. The electric energy consumption $(MJ.kg^{-1}_{sugarcane\ trash})$ was calculated by multiplication of the electric power (kW) by the number of working hours (h). From the calculation, the energy consumption of the bio-oil production was 131.14 $MJ.kg^{-1}_{sugarcane\ trash}$ and 143.52 $MJ.kg^{-1}_{sugarcane\ trash}$ for N_2 and air medium, respectively. The energy consumption when using N_2 medium was less than that when using air medium because the air compressor was not used when using N_2 as a medium. It was noted that the total energy consumption of bio-oil production from N_2 medium was 12.38 $MJ.kg^{-1}_{sugarcane\ trash}$ less than that when using air medium.

Table 6. The energy consumption of the pyrolysis process.

Energy consumption ($MJ.kg^{-1}_{sugarcane\ trash}$)	N_2 medium	Air medium
Electric energy from heater during pre-heating process	64.15	64.15
Electric energy from feeder during pre-heating process	0.97	0.97
Electric energy from air compressor during pre-heating process	55.58	55.58
Electric energy from heater during combustion process	10.15	10.15
Electric energy from feeder during combustion process	0.29	0.29
Electric energy from air compressor during combustion process	-	12.38
Total energy	131.14	143.52

4. Conclusion

Bio-oil production from sugar cane trash by a pyrolysis process was conducted in a fluidized bed reactor. The effects of the pyrolysis temperature, flow rate, different fluidizing medium on the yield of bio-oil production were investigated. The properties of the bio-oil and the energy consumption were also studied. The experiments were performed by varying the temperature from 460 ºC – 540 ºC and at flow rates of 120 cc.s^{-1}, 160 cc.s^{-1} and 200 cc.s^{-1} under air and N_2 atmosphere. From the experiment, sugar cane trash can be pyrolyzed into bio-oil. The experimental result showed that the maximum yields of bio-oil were 46.2 wt% and 31.95 wt% obtained at 500 ºC and 160 cc.$s^{-1}$for air and N_2 medium, respectively. The bio-oil yield obtained from using air as a medium was higher than that when using N_2 as a medium because of the presence of water content in the air. The result also revealed that the yield of bio-oil varied with the combustion temperature and volumetric flow-rate of the fluidizing medium.

The properties of the obtained bio-oil were determined. It was found that the heating value of bio-oil using N_2 medium was higher than that using air medium because air had a higher water content. Furthermore, the density and pH of the bio-oil production from both N_2 and air medium are very comparable. The heating value, viscosity and density of the bio-oil obtained from both N_2 and air medium, were increased by dehydration. The energy consumption of the bio-oil production was 131.14 $MJ.kg^{-1}_{cane\ trash}$ and 143.52 $MJ.kg^{-1}_{cane\ trash}$ for N_2 and air medium, respectively. This was indicated that the energy consumption for bio-oil production was more than the energy obtained from the bio-oil. Considering the equipment that consumed the energy, it was found that the electric heater and air compressor consumed the most energy with 83.43 - 91.12% of the total energy consumption. However, the energy consumption can be reduced by using 2 hp of high pressure blower instead of the 15 hp of air compressor and adding heat recovery system to heat the medium gas before entering to the reactor. According to the energy saving measure, the energy cost will be lower and worthwhile for investment. From the above results, the obtained bio-oil can be used as a fuel oil for combustion in a boiler or a furnace without any modification.

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Combustion of some Thai agricultural and wood residues in a pilot swirling fluidized-bed combustor

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Abstract: This paper reports a comparative study of burning Thai rice husk, sunflower shells and fine rubberwood sawdust as well as co-firing of the sawdust and shredded eucalyptus bark in the swirling fluidized-bed combustor (SFBC). All experiments for firing individual fuels were performed for the combustor heat input of ~300 kW_{th}. However, in the co-firing tests, the fuel mixture was delivered at a fixed feedrate, while ranging mass fraction of the blended fuels. For each fuel option, excess air was varied from 20% to 80%, while a flowrate of secondary air was constant. Temperature and gas concentrations (O_2, CO and NO) were measured in axial directions in the reactor, as well as at stack. Axial profiles of these variables were compared between the fuel options for selected operating conditions. The axial temperature profiles were weakly dependent on operating conditions, whereas the axial gas concentration profiles were apparently affected by fuel properties, excess air and secondary air injection. The behavior of CO and NO indicated the occurrence of three (or four) specific regions along the combustor height. As revealed by the experimental results, CO and NO emissions from the combustor can be controlled meeting the national emission standard, via maintaining excess air at ~55%, for all the fuel options. At this excess air, high, 99.1–99.9%, combustion efficiency is achievable when burning these fuels in the SFBC. However, the best combustion and emission performance for the co-firing of rubberwood sawdust and eucalyptus bark can be ensured at 85% sawdust contribution to the combustor heat input.

Keywords: *Biomass Residues, Swirling Fluidized-Bed Combustor, Emissions, Combustion Efficiency*

1. Introduction

Biomass is an important source of energy in Thailand. Some agricultural and forest-related residues collected on a large scale (such as rice husk, sugar cane bagasse, wood sawdust and chips) are widely used in this country as biomass fuels for heat and power generation. However, the domestic agricultural and industrial sectors generate a variety of residues and/or byproducts potentially considered as fuels due to their excellent combustion properties.

The fluidized bed-combustion technology is proven to be effective for conversion of energy from biomass. A large number of studies have been devoted to bubbling, vortexing and circulating fluidized-bed combustion systems firing conventional biomass fuels [1–4]. Some authors pointed out difficulties in achieving high combustion efficiency when firing high-ash biomass fuels [1,2], while the others highlighted ash-related operational problems caused by alkali-based compounds in biomass ashes [1,5]. These studies revealed that the combustion of most conventional biomass fuels is accompanied by substantial gaseous emissions [1–4].

During the past decade, a growing attention has been paid to the feasibility of effective utilization of various unconventional biomass fuels (from fibrous fuels to fruit stones and shells), basically, through their burning in bubbling and circulating fluidized-bed combustion systems. As shown in relevant pioneering works, combustion efficiency of these systems firing unconventional fuels is comparatively low and strongly affected by fuel properties, whereas gaseous emissions can be controlled at levels typical for conventional fuels [6–8].

Due to some specific hydrodynamic features, an innovative swirling fluidized-bed combustor (SFBC) with a cone-shaped bed seems to be a promising multi-fuel combustion technique for effective firing of various biomass fuels with significantly different fuel properties and characteristics. A swirling gas–solid fluidized bed is reported to ensure the flexibility in fuel particle size and shape, and, also, prevent the growth of large bubbles in the bed [9].

This work was aimed at comparing the combustion and emission performance of the SFBC between different fuel options: (1) individual burning of Thai rice husk, sunflower shells and fine rubberwood sawdust, and (2) co-firing of the sawdust and eucalyptus bark. Effects of fuel properties and operating conditions on major (CO and NO) emissions, as well as on combustion efficiency of the SFBC, were the main focus of this study.

2. Materials and Methods

2.1. Experimental set-up

Fig. 1 depicts the schematic diagram of an experimental set-up with the SFBC. The combustor consisted of six refractory-lined steel modules: a conical section with a 40° cone angle and an inner diameter of d_0 = 0.25 m at the bottom plane, and five cylindrical sections of 0.5 m height and 0.9 m inner diameter. Quartz sand of 0.5–0.6 mm particle size and 30 cm static bed height was used as the inert bed material to ensure stable swirling fluidized-bed regime [9].

An annular spiral air distributor arranged at the bottom of the conical section was used as the swirler of the bed. A 25-horsepower blower delivered primary air to the combustor. For firing

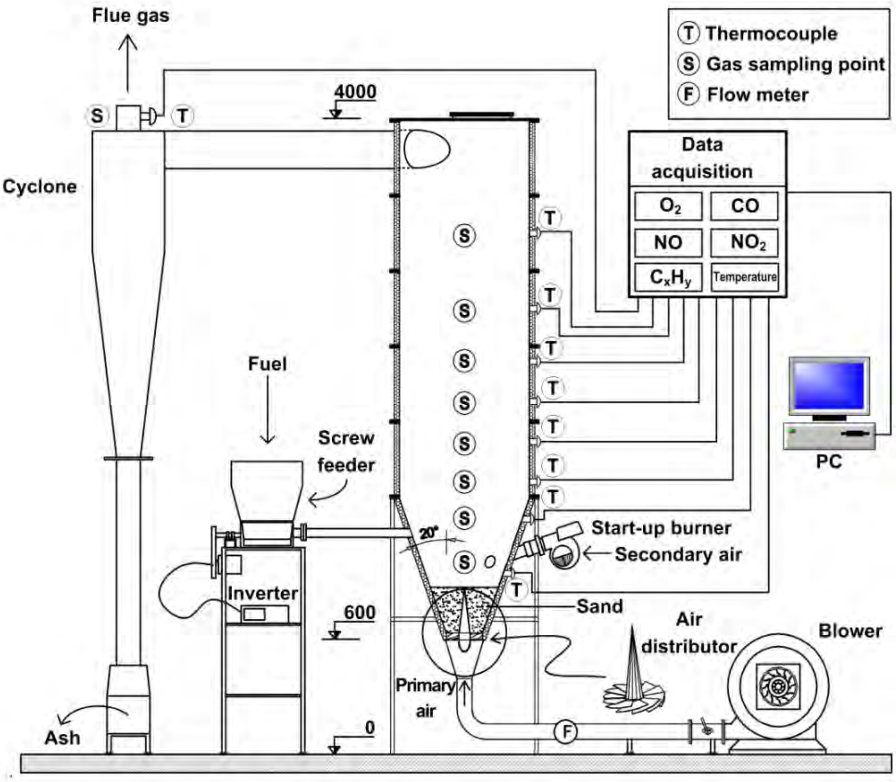

Fig. 1. Schematic diagram of the experimental set-up with the swirling fluidized-bed combustor.

rice husk and sunflower shells, the air distributor was made up of 11 straight steel vanes, each vane being with a length of L = 0.09 m and a swirl angle of $\beta = 76°$ (or 14° to the horizontal). However, for the (co-)firing tests with rubberwood sawdust, the SFBC was equipped with a 22-vane air distributor assembled from the straight steel vanes with L = 0.085 m and $\beta = 79°$. The swirl number of both axial-flow swirlers used in this study was estimated by Ref. [10]:

$$S = \frac{2}{3}\left[\frac{1-(d_\mathrm{h}/d_0)^3}{1-(d_\mathrm{h}/d_0)^2}\right]\tan\beta \qquad (1)$$

where d_h is the hub diameter of the swirler: $d_\mathrm{h} = d_0 - 2L$.

A diesel-fired burner (model “Press G24” from Riello Burners Co.) was used to preheat sand during the combustor start-up. This start-up burner was fixed at a 0.5 m level above the air distributor and inclined at a –30° angle to the horizon. When the bed temperature attained ~700 °C, a diesel pump of the burner was turned off, and the combustor load was sustained by feeding biomass fuel. A screw-type feeder delivered the fuel over the bed at a 0.6 m level above the air distributor. During the combustion tests, the burner fan remained to operate injecting secondary air tangentially into the bed splash zone at a constant flowrate of Q_ba = 0.024 Nm^3/s required to protect the burner head against overheating and impacts from solids.

A “Testo-350XL” gas analyzer was used to measure temperature and gas concentrations (O_2, CO and NO) along the axial direction (Z) in the reactor space, as well as at the cyclone exit.

2.2. The fuels

Table 1 shows the ultimate and proximate analyses as well as lower heating value (LHV) of rice husk, sunflower shells, rubberwood sawdust and eucalyptus bark used in this study. Except eucalyptus bark with its high moisture content (W), the biomass residues were, in effect, high-volatile (VM), low-S fuels. Meanwhile, rice husk included an elevated proportion of fuel ash (A) affecting LHV and fuel devolatilization rate. The average dimensions of rice husk particles were (on average) 2 mm wide, 0.5 mm thick and 10 mm long. On the contrary, sunflower shells were characterized by rather low fuel-ash but medium fuel-N contents, and individual particles of this biomass fuel were a width of 6 mm, a thickness of 0.7 mm, and a length of 10 mm (on average). The main features of rubberwood sawdust were elevated fuel-N but rather low fuel-ash, as well as small particle size (of ~200 μm dominant size). Eucalyptus bark had significant fuel moisture but rather low contents of fixed carbon (FC), fuel-N, fuel-S and fuel-ash. Note that the large size and hard structure of eucalyptus bark particles caused significant problems with fuel feeding when using the above screw-type feeder. It was therefore decided to burn the bark as shredded fuel co-fired with fine rubberwood sawdust.

Table 1. Properties of biomass fuels used in the combustion tests

Biomass fuel	Ultimate analysis (wt.%, as-received basis)					Proximate analysis (wt.%, as-received basis)				
	C	H	O	N	S	W	A	VM	FC	LHV (kJ/kg)
Rice husk	40.5	4.1	28.7	0.3	0.03	8.4	18.0	58.0	15.6	14,620
Sunflower shells	52.2	5.6	29.7	0.6	0.10	9.1	2.7	65.6	22.6	17,150
Rubberwood sawdust	46.7	5.7	33.5	1.8	0.04	6.6	5.7	61.5	26.2	17,070
Eucalyptus bark	25.8	2.9	19.2	0.2	0.02	47.5	4.4	41.5	6.6	8 320

2.3. Experimental planning

Two test series were carried out on the conical SFBC: (1) for firing rice husk and sunflower shells using an 11-vane swirler, and (2) for firing rubberwood sawdust, and also its co-firing with eucalyptus bark using a 22-vane swirler. In the first test series, to ensure similar heat inputs to the combustor (~300 kW_{th}), the fuel feedrate was different: 80 kg/h for firing rice husk, and 60 kg/h for firing sunflower shells. For these two fuel options, axial temperature and gas concentration profiles were compared between two values of excess air (EA): 40% and 80%. However, in the second test series, when a priority was given to the effects of fuel properties, the axial profiles were compared between the energy fractions of the sawdust in the fuel blend (EF_{sd}), while maintaining the fuel feedrate and excess air to be constant: 60 kg/h and 40%, respectively. The trials of the second test series were therefore performed for three sawdust energy fractions: $EF_{sd} = 1$ (firing pure sawdust at heat input of ~300 kW_{th}), $EF_{sd} = 0.85$ and $EF_{sd} = 0.75$.

For all the fuel options, CO and NO emissions and combustion efficiency of the SFBC were quantified for four values of EA: 20%, 40%, 60% and 80%. For each test run, excess air and heat losses (due to unburned carbon and incomplete combustion) were predicted together with combustion efficiency by Ref. [10]. The unburned carbon content in fly ash was determined by laboratory analysis with the aim to estimate associated heat loss (when it was sensible).

3. Results and Discussion

3.1. Axial temperature and gas concentration profiles in the SFBC

Fig. 2 shows the axial temperature as well as O_2, CO and NO concentration profiles in the SFBC firing rice husk and sunflower shells for two EA values: ~ 40% and ~80%. The

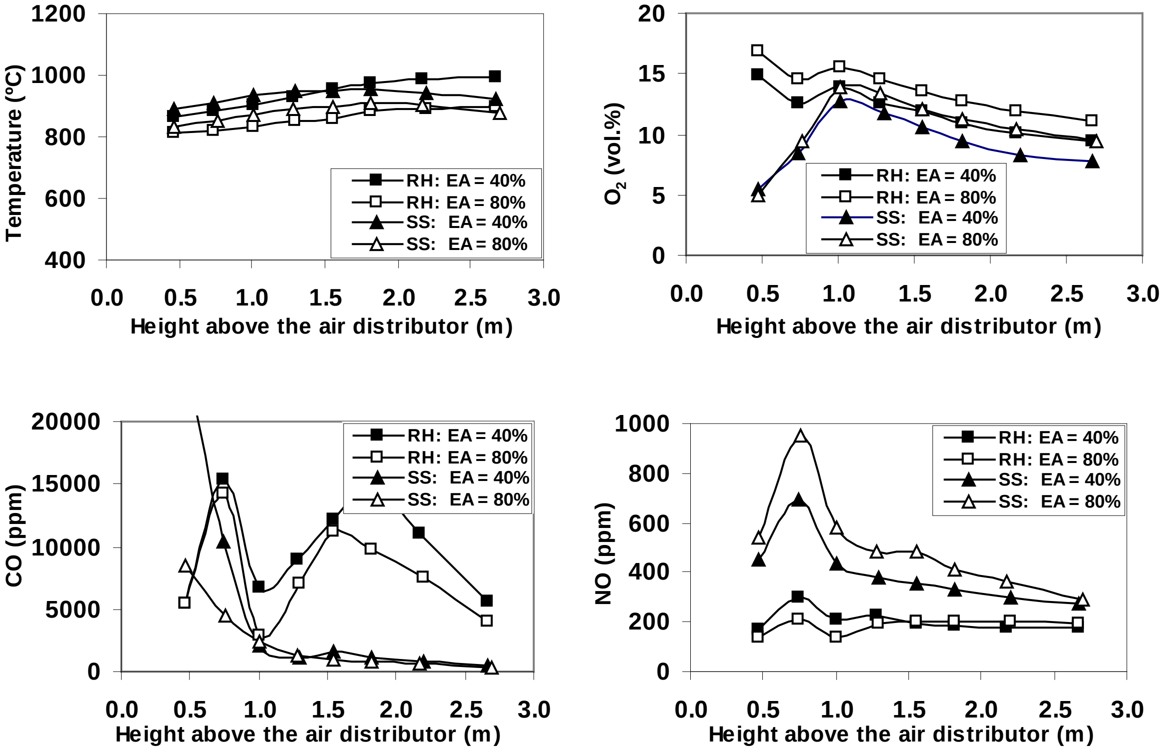

Fig. 2. Effects of excess air on the axial temperature as well as O_2, CO and NO concentration profiles in the conical SFBC firing rice husk (RH) and sunflower shells (SS) at similar heat inputs of ~300 kW_{th}.

temperature profiles were rather uniform, indicating the highly intensive heat-and-mass transfer in the reactor. For both fuels fired at similar EA, the temperatures at different points in the reactor were nearly the same due to similar heat inputs. An increase in EA resulted in some reduction of temperature at any given point, mainly, because of the air dilution effects. However, the axial gas concentration profiles in Fig. 2 exhibit strong effects of fuel properties and secondary air injection as well as the noticeable influence of excess air. In the dense bed region ($0 < Z < 0.5$ m), the rate of O_2 consumption for firing sunflower shells was significantly greater than that for rice husk, mainly, due to the coarser particles, higher VM and lower ash content in sunflower shells. In the next region (up to $Z = 1$ m), O_2 increased along the reactor centerline due to the injection of secondary air. In the combustor freeboard ($Z > 1$ m), O_2 gradually diminished along the centerline showing an apparent influence of excess air.

Like O_2, the CO behavior along the combustor height was quite different in various regions. When firing high-ash rice husk, CO formation in the dense bed occurred at a moderate rate, since some amounts of fuel-C and VM retained in the chars were carried over from this region. However, for firing sunflower shells with higher VM and substantially lower fuel-ash contents, CO formed in the dense bed at a quite significant rate, resulting in higher CO at all points along the reactor axis. In the upper region, up to $Z = 1$ m, CO was characterized by a significant negative gradient along the axial distance caused by the secondary air injection. When burning rice husk, due to the carryover of char-C and VM, CO exhibited a substantial axial increase in the region of $1.0 \text{ m} < Z < 1.8$ m due to oxidation of combustibles, followed by rapid decomposition of CO at the reactor top. However, CO was much lower at all locations in the freeboard when firing sunflower shells for the range of EA (see Fig. 2).

The axial NO concentration profiles in the combustor were found to exhibit four regions. At the combustor bottom, the rate of NO formation from nitrogenous volatile species (mainly, NH_3 [1]) prevailed the rate of NO decomposition. At $Z \approx 0.8$ m, NO attained the maximum, which was quite different for rice husk and sunflower shells, and affected by EA. Due to higher fuel-N, the NO maximum for firing sunflower shells was substantially greater than that for burning rice husk at similar EA. At $0.8 \text{ m} < Z < 1$ m, due to (i) catalytic reduction of NO by CO and (ii) reactions of NO with NH_3 and C_xH_y [1], NO exhibited some reduction in the axial direction. In the freeboard, the rates of NO formation and decomposition were quite low. For firing rice husk, these rates were nearly the same, resulting in rather stable values of NO along the centerline. However, for burning sunflower shells, the NO decomposition rate at the combustor top was greater than that of NO formation, which led to diminishing of NO along the combustor height. Effects of EA on the behavior of NO in the axial direction were rather weak for firing rice husk; however, the effects were substantial for burning sunflower shells.

Attempts to burn fine rubberwood sawdust in this combustor with the 11-vane air distributor, characterized by a swirl number of $S = 2.9$ (as estimated by Eq. (1)), failed in preliminary tests because of the dramatic carryover of light fuel/char particles from the combustor into the cyclone. To increase the residence time of the sawdust char particles in the reactor space, the SFBC was equipped with the 22-vane air distributor with a greater swirl number, $S = 3.6$.

Fig. 3 depicts the axial temperature as well as O_2, CO and NO concentration profiles in the SFBC for (co-)firing fine rubberwood sawdust and eucalyptus bark at different energy fractions of sawdust in the fuel blend at similar EA (of ~40%). Despite the substantial difference in S, the profiles in Fig. 3 exhibit the behaviors and trends similar to those of respective dependencies in Fig. 2. Thus, the axial temperatures for firing sawdust seen to be nearly the same as those for firing rice husk and sunflower shells, and this fact can be explained by similar heat inputs to the

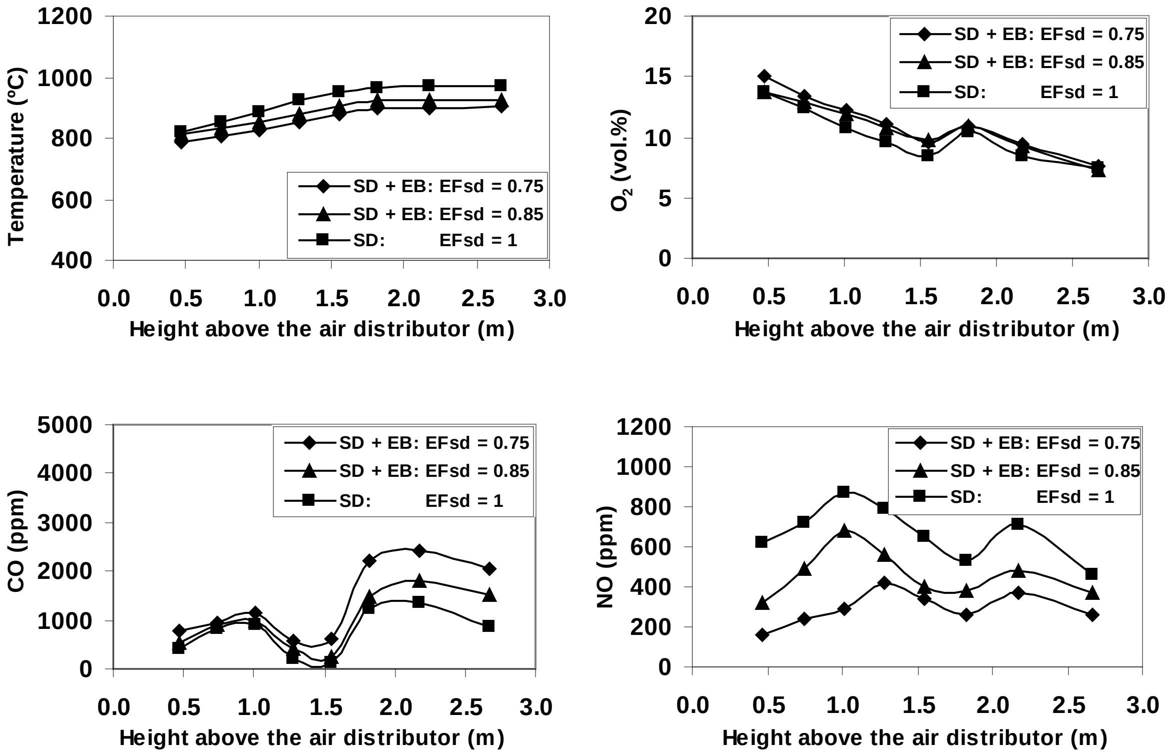

Fig. 3. Effects of the sawdust energy fraction in the fuel mixture on the axial temperature as well as O_2, CO and NO concentration profiles in the conical SFBC firing fine rubberwood sawdust (SD) or co-firing its mixture with eucalyptus bark (SD + EB) at similar excess air value of ~40%.

combustor. However, for the co-firing tests at $EF_{sd} = 0.85$ (corresponding to the sawdust mass fraction of $MF_{sd} \approx 0.73$) and $EF_{sd} = 0.75$ (at $MF_{sd} \approx 0.60$), the temperatures at all locations in the combustor volume where somewhat lower, mainly, due to increased moisture content in the blend. It can be seen in Fig. 3 that the effects of secondary air on the axial gas concentration profiles were shifted upward, as compared to the results for firing rice husk and sunflower shells. The carryover of light fuel/char particles of sawdust (or fuel blend) led to the elevated CO and NO concentrations in the freeboard, exhibiting secondary peaks of CO and NO at $Z \approx 2.2$ m. In the meantime, an increase in the mass fraction of eucalyptus bark in the mixture resulted in the higher concentration of CO at all locations along the centerline, mainly, due to the enhanced rate of carbon-C "wet" oxidation despite the reduction in temperature. Elevated CO, together with the reduction in fuel-N and combustion temperature, led to the lower NO concentrations with increasing the mass/energy fraction of eucalyptus bark in the fuel blend.

3.2. Emissions

Fig. 4 shows the CO and NO emissions from the SFBC firing rice husk and sunflower shells for the range of EA compared in the graphs with the Thai emission standards for biomass-fuelled industrial applications [11], all on 6% O_2 dry gas basis. As seen in Fig. 4, at EA of ~20%, the CO emission from the combustor was very high: ~4200 ppm for rice husk, and ~2700 ppm for sunflower shells. By increasing EA, the CO emission can be significantly reduced to a quite low level. However, with higher excess air, the NO emission was found to be increased, thus, indicating the fuel-NO formation mechanism [1]. An excess air of ~55% seems to be the best option at which both CO and NO emissions from this SFBC firing rice husk and sunflower shells comply with the corresponding national emission standards. Fig. 5

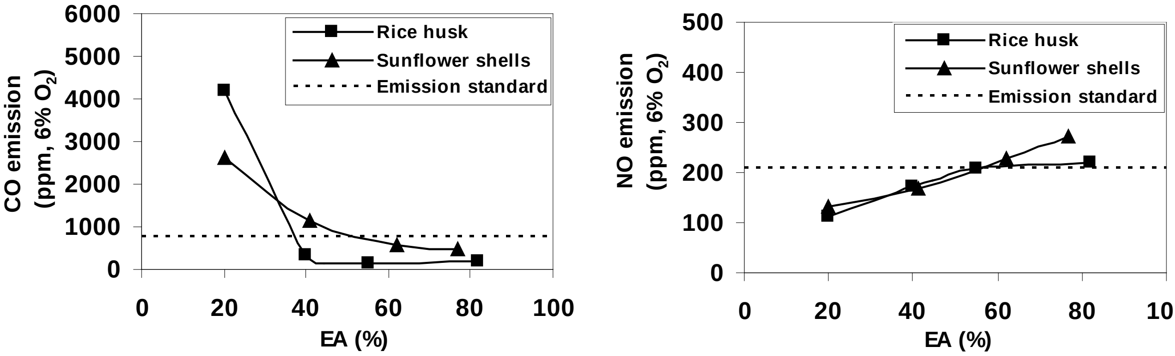

Fig. 4. Effects of excess air on the CO and NO emissions from the conical SFBC firing rice husk and sunflower shells at similar heat inputs of ~300 kW$_{th}$.

depicts the CO and NO emissions versus EA for (co-)firing rubberwood sawdust and eucalyptus bark for variable EF$_{sd}$. As seen in Fig. 5, to meet the emission standards, the SFBC should be fired at EF$_{sd}$ ≈ 0.85 (or SD/EB ≈ 73/27, by weight) maintaining excess air at ~55%.

3.3. Combustion efficiency

For all the fuel options, heat loss due to unburned carbon was found to be weakly dependent on EA and estimated as quite low (0.49–0.74% for firing rice husk, and ~0.15% for firing sunflower shells) or negligible (for firing rubberwood sawdust or its co-firing with eucalyptus bark). In the meantime, heat loss due to incomplete combustion was at a rather low level as well (<1%, for excess air of 40–80%). As the result, at 40–80% excess air values, the total combustion heat losses were estimated to be below 1%, which resulted in the high magnitudes of combustion efficiency, 99.1–99.9%, for all the fuels used. At excess air of ~55% ensuring best emission performance of the SFBC, the combustion efficiency was: 99.4% for rice husk, 99.5% for sunflower shells, 99.9% for rubberwood sawdust, 99.6% for the sawdust–bark mixture at EF$_{sd}$ = 0.85, and 99.1% for the sawdust–bark mixture at EF$_{sd}$ = 0.75.

4. Conclusions

In this comparative study, a swirling fluidized-bed combustor have been successfully tested for different fuel options: firing rice husk, sunflower shells and fine rubberwood sawdust, as

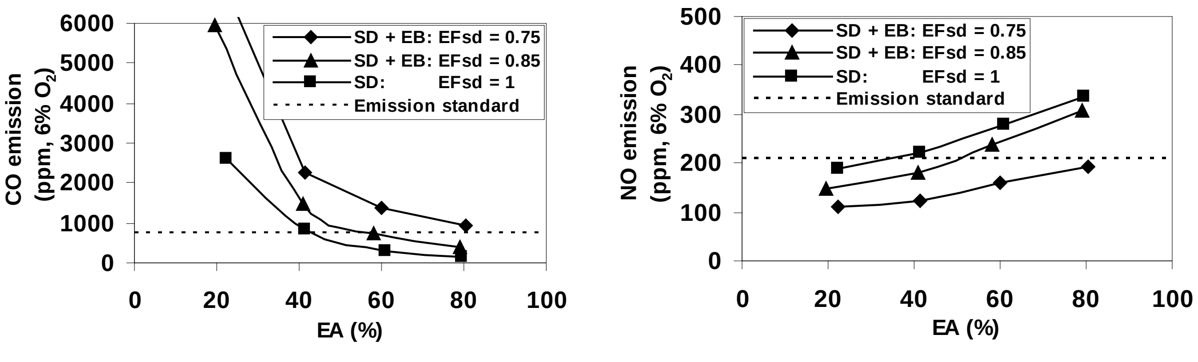

Fig. 5. Effects of excess air and sawdust energy fraction on the CO and NO emissions from the SFBC firing fine rubberwood sawdust (SD) or co-firing its mixture with eucalyptus bark (SD + EB).

well as co-firing the sawdust and eucalyptus bark at variable energy fraction of sawdust in the fuel blend. Substantial differences in properties of the selected fuels/blends (especially, in volatile matter, fuel-N and fuel-ash contents), as well as in the fuel particle size, affect significantly formation and decomposition of CO and NO in various regions of the combustor. For all the fuel options, CO emission can be effectively controlled by tangential injection of secondary air into the bed splash zone of the reactor. With higher excess air, NO emission from the combustor increases substantially in accordance with the fuel-NO formation mechanism. Through co-firing of rubberwood sawdust and high-moisture eucalyptus bark, NO emission from the combustor can be noticeably reduced, which is, however, accompanied by an increase in CO emission. Excess air of ~55% seems to be an optimal value ensuring high, 99.1–99.9%, combustion efficiency for the fuel range. At this excess air, CO and NO emissions can be controlled meeting corresponding national emission standards. For the co-firing, the best result is achievable when the sawdust energy fraction in the fuel blend is ~0.85.

Acknowledgement

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Bioethanol production from cotton stalks or corn stover? A comparative study of their sustainability performance

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Abstract. The production of second generation biofuels (ones produced from lignocellulosic materials) has not yet been developed in a full commercial scale. However, a considerable number of pilot and demonstration plants have been announced or set up in recent years, with research activities taking place mainly in North America, Europe and a few other countries (e.g. Brazil, China, India etc). At the same time their environmental and economic performance are under examination. These performance issues are very sensitive on a variety of parameters such as feedstock material, production technology, logistics involved etc. In this study the sustainability performance of two alternative bioethanol's production systems, namely, one using cotton stalks and a second one using corn stover feedstock, are examined and compared using the Analytic Hierarchy Process method. Life Cycle Impact Assessment is used in order to evaluate each alternative's environmental performance. For this purpose, a modern powerful and state of the art software (SimaPro) is used. The systems' economic performance is based on cost/ benefit calculations.

Keywords: *Bioethanol, Analytical Hierarchy Process, Life Cycle Impact Assessment*

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1. Introduction

Lignocellulosic materials, particularly agricultural residues, seem to be a very attractive source for bio-fuels' production (second generation biofuels) as indicated in recent literature [1],[2],[3]. The reasons for this are, first, they have a big potential, second, they have no adverse effect on food production, and, third, they have the least negative impacts (economic, environmental and social) to human systems compared to energy plant cultivations. Although the production of such biofuels has not yet been developed in a full commercial scale, several pilot and demonstration plants have been announced or set up. Relevant research activities, including performance issues such as environmental and economic ones, are taking place, mainly in North America, Europe and a few other countries [4],[5]. In general, the performance of such materials when used for the production and supply of biofuels depends on a variety of parameters such as kind of feedstock material, production technology, logistics involved etc. The evaluation of such performance is not straightforward, particularly in cases where multiple unrelated objectives or attributes have to be taken into account in the decision making process. In such cases, Operational Research methodologies have to be employed in order to arrive at safe conclusions. In this study the sustainability performance of two candidate alternative bioethanol's production systems, namely, one using cotton stalks and a second one using corn stover feedstock, are examined and compared using the Analytic Hierarchy Process method. Sustainability is meant to be composed of two criteria, namely the economic and the environmental ones, which have been taken into account for the final evaluation. Life Cycle Impact Assessment and, more specifically, the Eco-Indicator 99 method is used in order to evaluate each alternative's environmental performance. For this purpose, a modern powerful and state of the art software (SimaPro) is employed, while cost/ benefit calculations are used for the evaluation of the systems' economic performance. The result in the present case study is that corn stover is always preferable as a feedstock material.

2. Methodology

The methodology employed in this case study is as follows:
The sustainability performance of each bioethanol production system is expressed as a performance index combining the environmental and economic criteria and is calculated using the Analytic Hierarchy Process [6]. Cost/ benefit calculations are used for the evaluation of the systems' economic performance, while the environmental performance is evaluated by the Eco-Indicator 99 (EI 99) method. The combined performance index is then used for the selection of the best scenario from a sustainability perspective. A popular and state of the art software (SimaPro-Version 7.1) is used to determine the environmental performance of each scenario. SimaPro is a professional tool for collecting, analyzing and monitoring the environmental performance of products and services, following the ISO 14040 series recommendations. Amongst the Life Cycle Impact Assessment methods used by this software EI 99 is selected, since it is used extensively in similar evaluations and, in addition, it includes the land use impact category, which is important in agricultural production systems (as in the case of cotton and corn cultivation). The 2002 National Renewable Energy Laboratory's (NREL) report, referring to the design of the ethanol production system based on corn stover biomass, was used as a standard for the description of the production systems under evaluation [7]. Also data concerning the unit processes describing each production system were gathered by field research in Greece. Where no data were available proper assumptions were made. The economic performance of each alternative was measured in terms of total supply chain cost, in particular operational cost from field to distillery as the other costs are the same for both alternatives. The plant is assumed to be situated in the district of Thessaly since it can provide either the whole needed biomass quantity (in the case of corn stover) or the major part of it (in the cotton stalks case). The selected unit basis is 1 Kg EtOH (95% in water) at the distillery.

3. The alternative systems

Both alternative systems are evaluated in respect to the "field to distillery" bioethanol production, which includes the following stages: feedstock harvesting from fields; transport and feedstock storage & handling (size reduction etc); pretreatment and hydrolyzate conditioning process; saccharification and co-fermentation process; product, solids and water recovery stage (distillation, dehydration, evaporation and solid-liquid separation); wastewater treatment; product storage; power co-generation (by-product combustion for steam and electricity generation).

Alternative system A: Ethanol production from corn stover

The system is fed with corn stover harvested in Greece (Thessaly district). Key figures of the production system are presented in Table 1.

Table 1: Key figures for ethanol production from corn stover

	Value	**Note**
Feedstock quantity (t corn stover on a dry basis/yr)	750,000	
Harvested area (ha)	125,000	
Average distance for feedstock transportation (km)	70	5 km by tractor+ rail and 65 Km by lorry 28t
Capacity (t ethanol/yr)	213,300	
Power co-generated (Mwh/yr)	160.000	2.28 KWh/gal EtOH according to NREL report

The total feedstock quantity needed comes from Thessaly. The industrial process yield in the distillery is 284.4 g/Kg of dry feedstock. This value is 80% of the theoretical yield based on the chemical composition of corn stover as provided by NREL measurements [7] (measurements refer to the US). Corn stover is composed of glucan (37.4%), xylan (21.1%), lignin (18.0%) arabinan (2.9%), galactan (2.0%), mannan (1.6%), ash (5.2%), acetate (2.9%), protein (3.1%), extractives (4.7%) and unknown soluble solids (1.1%) (composition in % w/w on a dry basis). Since similar data for Greek corn stover are not available, we assume that their composition, and thus the yield of the industrial process, is identical to those of the US case.

Alternative system B: Ethanol production from cotton stalks

The system is fed with cotton stalks harvested in Greece (Thessaly and Macedonia districts). Key figures of the system are presented in Table 2.

Table 2: Key figures for ethanol production from cotton stalks

	Value	**Note**
Feedstock quantity (t cotton stalks on a dry basis/yr)	750,000	
Harvested area (ha)	300,000	
Average distance for feedstock transportation (km)	226	*16 km by tractor+ rail and 210 Km by lorry 28t*
Capacity (t ethanol/yr)	134,025	
By-product electricity (Mwh/yr)	269,000	*Proportional to lignin concentration of feedstock*

60% of needed feedstock is assumed to come from Thessaly and the rest from Macedonia. The industrial process yield in the distillery is assumed to be 80% of the theoretical yield based on cotton stalks chemical composition as in the case of corn stover ethanol production. Since chemical composition data for the Greek cotton stalks are not available, data from the literature were used [8]. Cotton stalks are composed of glucan (31,1%), xylan (8,3%), lignin (30.1%) arabinan (1.3%), galactan (1.1%), ash (6.0%), extractives (9.0%), and others (13.1%) (composition in % w/w on a dry basis). The aforementioned yield is based on the chemical composition mentioned above and is 178.7 g/kg of dry feedstock.

4. Results

4.1. Environmental criteria

The environmental performance of each of the alternatives was assessed using Life Cycle Impacts Analysis (realized by Sima-Pro). The following impact categories are selected as environmental criteria: Carcinogens, Respiratory organics effects, Respiratory inorganics effects, Climate change, Radiation effects, Ozone layer depletion, Ecotoxicity, Acidification / eutrophication, Land use, Minerals and Fossil fuels. No uncertainty evaluation was performed in this study.

4.1.1. Alternative's A Environmental Performance

For the evaluation of the environmental impacts, data from the Ecoinvent Report n.17 [9] about the inventory and the emissions, in addition to those of the NREL report [7], and data collected through field research were used. Some indicative emissions, in terms of volume produced per unit, are presented in Table 3.

Table 3: Indicative emissions from the corn stover ethanol production system

	Value	**Note**
CO_2 biogenic (Kg/Kg EtOH)	2.93	Emissions to air
Heat waste emissions (MJ/kg EtOH)	25.85	Emissions to air
CO (Kg/Kg EtOH)	0.000497	Emissions to air
Methane biogenic (Kg/Kg EtOH)	$3.0*10^{-5}$	Emissions to air
Mineral oil (Kg/Kg EtOH)	0.000426	Disposal

The resultant value for EI 99 of alternative A is 0.157. The system's performance per impact category is presented in Table 4. For reasons of comparison, the performance of the system "ethanol 95% in water from wood in distillery, CH'' (which describes the ethanol production system from residual wood in Switzerland and is included in the Ecoinvent Database [10]), is given in the same Table.

Table 4: Environmental Performance of the production systems under evaluation

	EtOH(*) from corn stover	**EtOH(*) from cotton stalks**	**EtOH(*) from wood**
Carcinogens	0.00449	0.00766	0.00252
Respir. Organics effects	$2.89*10^{-5}$	$7.51*10^{-5}$	$1.89*10^{-5}$
Respir. Inorganics effects	0.0266	0.0629	0.012
Climate change	0.0122	0.0333	-0.00557
Radiation	$3.49*10^{-5}$	$8.5*10^{-5}$	$1.78*10^{-5}$
Ozone layer depletion	$1.42*10^{-6}$	$3.81*10^{-6}$	$1.11*10^{-6}$
Ecotoxicity	0.00667	0.0122	0.00251
Acidification/Eutrophication	0.00548	0.0106	0.00186
Land use	0.0639	0.126	0.0423
Minerals	0.00138	0.00446	0.00083
Fossil fuels	0.00138	0.0967	0.0293
Environmental Index 99 (EI 99)	0.157	0.354	0.0858

(*): 1 Kg EtOH 95% in water in distillery

4.1.2. Alternative's B Environmental Performance

Data from field research and data from the Ecoinvent Report n.17 were used for the evaluation of the environmental impacts of this system. Where data were not available, reasonable assumptions were made in order to calculate the missing inventory data or emissions. Some indicative emissions, in terms of volume produced per unit, are presented in Table 5. The resultant value Eco-Indicator 99 of alternative A is 0.354. The system's performance per impact category is presented in Table 4.

Table 5: Indicative emissions from the cotton stalks ethanol production system

	Value	**Note**
CO_2 biogenic (Kg/Kg EtOH)	5.93362	Emissions to air
Heat waste emissions (MJ/kg EtOH)	45,36	Emissions to air
CO (Kg/Kg EtOH)	0.000833	Emissions to air
Methane biogenic (Kg/Kg EtOH)	$5.1*10^{-5}$	Emissions to air
Mineral oil (Kg/Kh EtOH)	0.000426	Disposal

4.2. Economic Performance

The criterion used for assessing the economic performance of each alternative is the economic performance (net economic benefit) of each alternative. A measure of the economic performance is the operation cost of each production system, including costs for feedstock, labour, maintenance, insurance & taxes, depreciations and secondary materials. The income from the excess electricity produced is also taken into account (negative cost). The income from ethanol produced is not taken into account for the economic performance evaluation since the calculation basis is 1 Kg EtOH and thus is the same for both alternatives. The operation cost of each of the alternatives is presented in Table 6. As the excess electricity generated by the cotton stalks' ethanol system is greater in relation to the corn stover ethanol system, this leads to a decreased operational cost in the former case.

Table 6: Alternatives' operation cost

	Cost of EtOH from corn stover production system (€/Kg EtOH)	**Cost of EtOH from cotton stalks production system (€/Kg EtOH)**
Feedstock	0.1232	0.1958
Other variable cost (cost for other raw and secondary materials)	0.0889	0.1415
Labor	0.0105	0.0168
Maintenance	0.0115	0.0183
Insurance & Taxes	0.0850	0.0135
Depreciations	0.0041	0.0651
Excess electricity sales	-0.1312	-0.3510
Total	0.1155	0.1000

4.3. Sustainability Performance

According to the preceding analysis, the corn stover ethanol production system is preferable from an environmental performance perspective while the cotton stalks' ethanol system is preferable from an economic perspective. AHP may be used for the purpose of selecting the best alternative based on both criteria, by aggregating the performance of each of the alternatives in terms of both criteria and thus determining an overall index U for each of the alternatives. Making the best choice is then straightforward. Table 7 summarizes the performance of each alternative in terms of both criteria. These performance values are the inverse absolute values of the EI 99 index and the total operation cost, respectively (values in parentheses). This adjustment is necessary in order for the following condition to be fulfilled:

Alternative A is preferable than B iff $x_{Aj} > x_{Bj}$, j=1,2 (x_{Aj} denotes the performance of alternative A in respect to criterion j)

Table 7: Alternatives' performance on environmental an economic criteria

Alternative	**Environmental criterion (EI 99)**	**Economic criterion (operation cost)**
EtOH from corn stover (alternative A)	$X_{A1:}$ 6.37(0.157)	$X_{A2:}$ 8.66 (0.1155)
EtOH from cotton stalks (alternative B)	$X_{B1:}$ 2.82 (0.354)	$X_{B1:}$ 10 (0.1000)

Following the AHP method, two pair-wise comparison matrices must be constructed (one for each criterion) for the determination of each alternative's score against each criterion. The values in these matrices show the decision maker's strength of preference between the two alternatives if only one criterion is taken into consideration. Based on the values presented in Table 7 the matrices are as in Table 8.

Table 8: Pairwise comparison matrices for score determination

	Environmental performance		**Economic benefit**	
	ALTERNATIVE A	ALTERNATIVE B	ALTERNATIVE A	ALTERNATIVE B
ALTERNATIVE A	1	5	1	1/3
ALTERNATIVE B	1/5	1	3	1

The calculated score values of each alternative on the selected criteria are shown in Table 9.

Table 9: Alternative scenarios' performance values

	Criteria	
Scenarios	Environmental Performance	Economic benefit
ALTERNATIVE A	0.83	0.25
ALTERNATIVE B	0.17	0.75

The pairwise comparison matrix for the determination of criteria weights is presented in Table 10. It is assumed that the environmental performance is "weekly more important" than the economic benefit criterion. This is a reasonable assumption, since biofuels come to serve environmental issues at least as much as economics considerations.

Table 10: Pairwise comparison matrix for criteria weights determination

	Environmental performance	Economic benefit
Environmental performance	1	2
Economic benefit	1/2	1

Thus the calculated weights for the environmental performance criterion w_1 and for the economic benefit criterion w_2 are 0.66 and 0.34, respectively. The resulting overall performance (sustainability index) of each alternative is:

$$U_A=0.66*0.83+0.34*0.25=0.6328$$

$$U_B=0.66*0.17+0.34*0.75=0.3672.$$

Thus alternative A must be chosen.

5. Discussion and Conclusions

In the present study the sustainability of two ethanol production systems was evaluated. The systems chosen will be located in Greece and use corn stover (alternative A) or cotton stalks (alternative B) as a raw material. The technology used (introduced by NREL, USA) includes prehydrolysis of raw material, simultaneous saccharification and co-fermentation process, and product, solids and water recovery stages. In addition, power is generated which is used for covering systems' needs and the excess is sold in the grid. For the sustainability evaluation, the environmental and economic performances of the alternatives were determined. It has been shown that ethanol made of corn stover has a better environmental performance than ethanol made of the cotton stalks. This is mainly due to the former's higher process production yield (in the plant) and to higher raw material yield (in the field). On the other hand, the cotton stalks ethanol system has a better economic performance than the corn stover one, due to the bigger excess electricity produced by the former, which is sold to the grid, providing more income. The Analytic Hierarchy Process method was used in order to aggregate the environmental and economic performances of each of the alternatives into an overall (sustainability) index. The analysis has shown that, conditioned to the assumptions made, the corn stover ethanol system is preferable. In the study no uncertainty analysis was performed. It is worthy noting that:

- Ethanol production systems from lignocellulosic materials are a promising technology which is getting more mature nowadays. In Greece there exists adequate biomass potential for the development of such systems.
- The environmental performance of both corn stover and cotton stalks ethanol systems is generally good but it is worse in comparison to ethanol produced from wood.
- The cotton stalks ethanol system has a poorer environmental performance (especially regarding the land use impact category) in relation with the corn stover one, because of its low production yield in ethanol (as a consequence of cotton stalks' low concentration in cellulose) and its low raw material production yield in cotton fields.

Further research in the area of this study must cover:

- uncertainty issues in order for the critical values for a confident decision making process to be determined
- the way the plant's production capacity affects the sustainability of the system
- the exact determination of the chemical composition of Greek agricultural residues.

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Assessing the Environmental Performance of Integrated Ethanol and Biogas Production

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Abstract: As the production of biofuels continues to expand worldwide, criticism about, e.g. the energy output versus input and the competition with food has been questioned. However, biofuels may be optimized to increase the environmental performance through the concepts of industrial symbiosis. This paper offers a quantification of the environmental performance of industrial symbiosis in the biofuel industry through integration of biogas and ethanol processes using a life cycle approach. Results show that although increasing integration is assumed to produce environmental benefits in industrial symbiosis, not all impact categories have achieved this and the results depend upon the allocation methods chosen.

Keywords: *Ethanol, Biogas, Industrial symbiosis, Environmental impacts, Biofuel*

1. Introduction

The production of biofuels for transport has seen a large increase in the past few years to meet the onset of policies for increased production and use worldwide. However, with this onset, biofuels have met much criticism [1,2] which ranges from debates about the competition with food to the energy used to produce the biofuels [3]. Dissimilarities and criticism result primarily from different assumptions made, system boundaries used, technologies and the reference energy systems used in life cycle assessment of biofuel systems [4]. However, biofuel production encompasses large quantities of inputs and outputs and therefore, consideration must be made for the efficient use of resources for biofuel production industries [2] for which the environmental performance may be bettered and the flows of material and energy optimized [5]. One approach to do this is by employing concepts from industrial symbiosis.

Industrial symbiosis is a branch of industrial ecology focusing upon the inter-firm interactions aiming to engage traditionally separate industries to cooperate in a collective approach to create competitive advantages through resource exchanges and synergistic possibilities [6]. However in industrial symbiosis, benefits have rarely been quantified in the literature [7].

On the island of Händelö in Norrköping, Sweden, a unique bioenergy complex of symbiotic activities between the ethanol, biogas and energy system takes place [5]. However, using the concept of industrial symbiosis, these symbiotic activities could be further improved and more synergies could occur [5]. Could these synergies therefore lead to improved environmental performance and can they be quantified?

The aim of this research paper is to outline and present the environmental impacts and performance of several symbiotic activities, i.e. integrated scenarios, between the biogas and bioethanol facilities located on the island of Händelö, Norrköping. Using exchanges (i.e. synergies) between the biogas and bioethanol facilities, the environmental performance will be quantified using a life cycle approach of the synergies for different scenarios with increasing degrees of integration.

2. Methodology

The environmental performance, i.e. environmental impacts, of symbiotic activities between biogas and ethanol production plants will be assessed by comparing different scenarios. Different degrees of integration will be tested from no integration at all (default) to all by-product residues from the ethanol plant used in the biogas plant, as described in the subsequent section entitled, *The Scenarios.*

2.1. System Description

The production of biofuels takes place on the island of Händelö in Norrköping, Sweden. Ethanol is produced from a combination of wheat, barley and rye resulting in a number of by-products such as Dried Distillers Grains with Solubles (DDGS), syrup and impurities. Biogas is produced through the anaerobic digestion of organic matter, in the scenarios e.g. wheat and barley and by-products of the ethanol facility. Conversion technologies and performance for the anaerobic digestion and fermentation processes have been obtained from the companies, along with material and energy flows [5,8-10].

The assessment takes the ethanol plant as starting point and keeps the ethanol fuel output static whereas all of the other inputs and outputs for that plant and the biogas plant are allowed to vary in accordance with the scenarios described below. This approach was chosen in order to reflect upon the importance of size differences between the plants but also of the potential implications of larger by-product exchanges between the two plants.

2.2. Tools and Impact Categories

A life cycle approach is applied to each scenario separately from a cradle-to-gate perspective. All life cycle assessment calculations of environmental impacts have been performed using the software package SimaPro v. 7.2. The life cycle impact assessments have been conducted using the EPD 2007 [11] method. This method was chosen due to its recommendation by the Swedish Environmental Management Council and providing a wide array of environmental impact categories, e.g. global warming potential (GWP), acidification, eutrophication and the use of non-renewable resources.

2.3. Allocation Procedures

By-products and the energy and emissions associated with their use have been taken care of by the use of two separate methods in this paper, including energy allocation and system expansion [4,8]. The energy content of these by-products has been computed for the lower heating value of the DM contained in each fraction. Energy allocation figures used for each scenario can be seen in Tables 1-2.

Table 1: Ethanol Production Allocation for Major Products and By-Products [8]

Product/ By-Product	DM Content (%)	Default Scenario	Existing Scenario	Scenario 1	Scenario 2	Scenario 3
Ethanol	-	70,7%	70,7%	70,7%	60,3%	60,3%
DDGS	90	21,7%	21,7%	21,7%	-	-
Syrup	27	5,6%	5,6%	5,6%	-	-
Impurities	86	2,0%	2,0%	2,0%	-	-
Stillage	16	-	-	-	39,7%	39,7%

Table 2: Biogas Production Allocation for Major Products and By-Products [8]

Product/ By-Product	Default Scenario	Existing Scenario	Scenario 1	Scenario 2	Scenario 3
Biogas	31,3%	35,7%	35,7	35,7%	33,7%
Biogas to Ethanol	-	-	-	-	2,0 %
Biofertilzer	68,7%	64,3%	64,3	64,3%	64,3%

System expansion, also known as substitution, has also been conducted to account for the replacement of by-products produced [4]. System expansion for the default and existing scenarios of the ethanol plant include the use of stillage products for fertilizers and animal fodder applications. Fodder replacement by DDGS and syrup in dry matter content (DM) has been assumed to replace Brazilian soy meal and European barley in the amounts of 0,4 kg DM and 0,6 kg DM [2]. Fertilizer nutrients replaced by biogas digestate per ton is assumed to replace 8 kg N, 5 kg NH_4, 1 kg P and 1,5 kg K per ton of produced digestate [8]. Furthermore, the lower heating value (LHV) for dried stillage has been assumed to be the same as that for the digestate [3] due to limited data availability.

2.4. *The Scenarios*

Scenarios have been produced to test and quantify the environmental performance of several different material and energy exchanges between the bioethanol and biogas production plants as aforementioned. Each scenario is tested using both the energy allocation and system expansion methods to account for energy and replacement of processes from the by-products [12,13]. The outputs have been expressed using the LHV for both biogas and ethanol, 50MJ/kg and 28,87 MJ/kg respectively.

2.4.1. *Default Scenario*

The default scenario will show the impacts of two stand alone plants with no integration. The two plants use respective inputs of wheat, barley and triticale for their production processes. In terms of biofuel production output, the main products are 17 TJ of biogas and 1 314 TJ of ethanol. All inputs and outputs of raw material, by-products, etc. are based on the aforementioned biofuel outputs [8]. The default scenario has been used to compare to the existing scenario in order to compare the environmental impacts of current practice with that of a stand alone system.

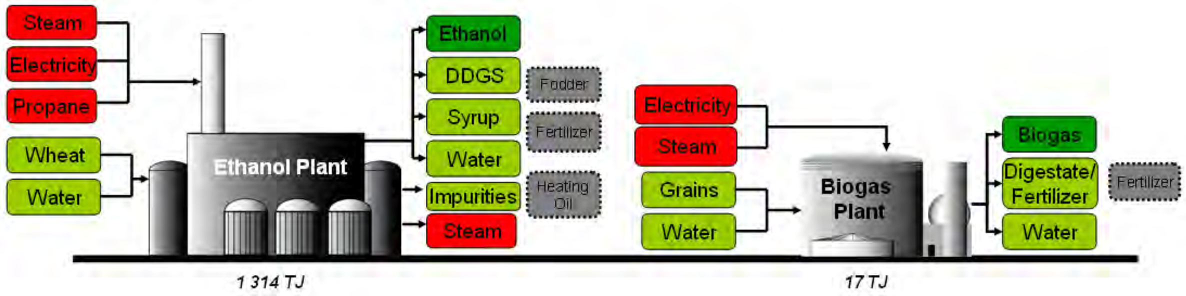

Fig. 1: Default Scenario. Note the avoidance of fodder and fertilizers from the ethanol and biogas plants for the system expansion have been included [8].

2.4.2. Existing Scenario and Scenario 1

The existing scenario is similar to the production process used pre-2009 on the island of Händelö. The exchange of thin stillage is used to produce biogas at the neighboring biogas plant. Furthermore, as the thin stillage is sent to the biogas plant at a temperature of around 70°C, it must be cooled to around 38°C for anaerobic digestion and thus electrical fans are used to cool the substrate and no external process heat is required [14,15]. The output of the system in biofuel is again 17 TJ of biogas and 1 314 MJ of ethanol for which all inputs and outputs are based [8]. Scenario 1 is similar to the existing scenario, however in Scenario 1 the impurities (consisting primarily of husks and filtered grains) are also sent to produce biogas. This therefore raises the output of biogas production and digestate, requiring more electricity and water for the digestion and upgrading processes respectively (ibid.).

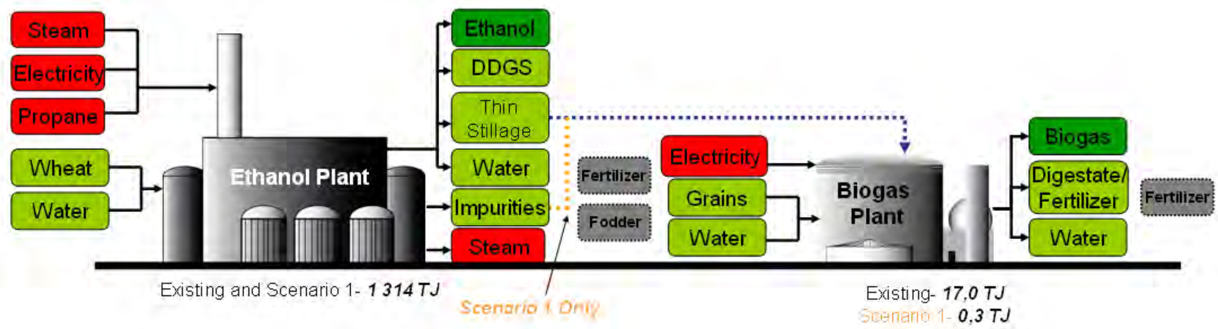

Fig. 2: Existing Scenario and Scenario 1. Note the avoidance of fodder and fertilizers for the system expansion have been included [8].

2.4.3. Scenarios 2 and 3

In Scenarios 2 and 3, it is assumed that all the stillage is sent to the biogas plant for anaerobic digestion. By doing so the ethanol plant can save a large input of energy, roughly 35% less energy [16] from the dryers and handling equipment for fodder production. Scenario 2 and 3 are similar, in that they both use stillage for biogas production. However, Scenario 3 differs in the fact that biogas replaces propane in the ethanol production plant for odor control [14]. Similar to the existing scenario, the stillage is sent to the biogas plant at a higher temperature than necessary for the process and electrical fans are used to cool the substrate, requiring no external process heat. The production of biogas has now been increased to 464 TJ in Scenario 2 and 438 TJ in Scenario 3 (accounting for the use of 26 TJ of biogas for ethanol production) while the production of ethanol remains the same as in the default and existing scenarios [8].

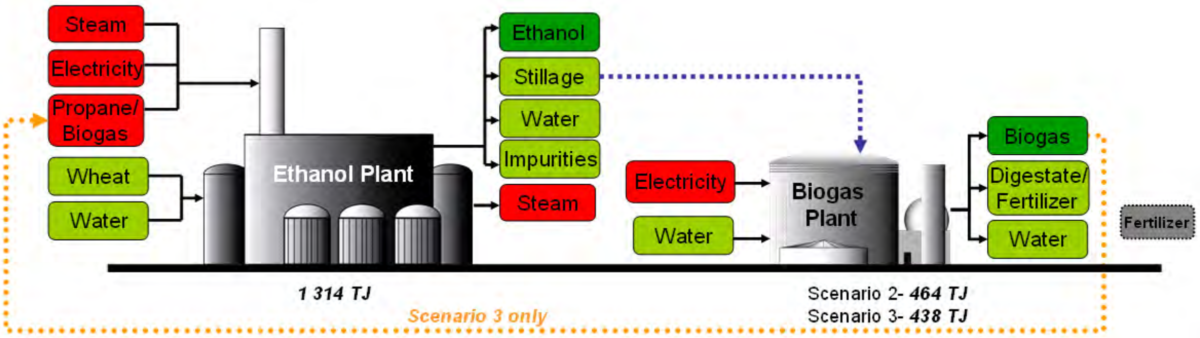

Fig. 3: Scenarios 2 & 3. Note that in Scenario 3, the biogas is used in place of propane (denoted by an orange dashed line). The figure also includes avoided fertilizers for the system expansion method [8].

2.5. Data Inventory

Data has been obtained from the biofuel production firms of Händelö, Norrköping in Sweden. Production figures are relevant for pre-2009 conditions for the default and existing scenarios [8-10,14,15]. When data has been limited or unavailable, comparable data from the Ecoinvent database v. 2.1 has been used for e.g. specific cultivation, fertilizers and transportation data. Energy for the system is provided from the Swedish electricity production system based primarily upon hydropower and nuclear power [17]. Process heat, in the form of steam is provided from a neighboring combined heat and power plant fueled by biomass [8,9,18]. Grains are transported within the Östergötland County to the island of Händelö, with an average distance of 100 km. Transportation of the various raw materials between the neighboring biogas and ethanol production firms is assumed to have an average distance of 5 km. The biofertilzer transport has been assumed to be on average 33 km [8].

3. Results and Discussion

The environmental performance of the integrated systems from the aforementioned scenarios can be seen in Figs. 4-6. These figures show the global warming potential, impacts from acidification and eutrophication as well as the use of non-renewable fuel. A discussion of the results will follow each figure in the subsequent sections. Further details can be found in Martin et al. [8]. The following notation has been used to describe each scenario in the figures:

D-EA: Default Scenario (Energy Allocation)
D-SE: Default Scenario (System Expansion)
E-EA: Existing Scenario (Energy Allocation)
E-SE: Existing Scenario (System Expansion)
1-EA: Scenario 1 (Energy Allocation)
1-SE: Scenario 1 (System Expansion)
2-EA: Scenario 2 (Energy Allocation)
2-SE: Scenario 2 (System Expansion)
3-EA: Scenario 3 (Energy Allocation)
3-SE: Scenario 3 (System Expansion)

3.1. Global Warming Potential

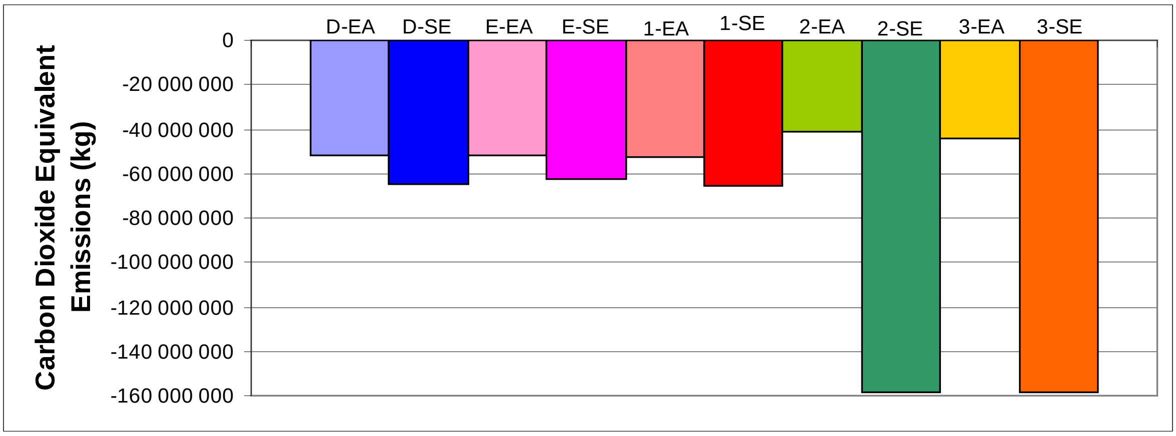

Fig. 4: Global Warming Potential of the different Scenarios measured in kg of CO_2-equivalent. [8]

From Fig. 4 it is apparent that there are some differences between each scenario, with the system expansion method producing the largest variations. The benefits related to the global warming potential from the energy allocation method do not to follow the trend found in the system expansion method with increasing integration of the biogas and ethanol systems, i.e. increased benefits with increasing integration. It can be seen that the systems with the largest integration also have a lower share of the impacts and benefits associated with their outputs based on how the energy is allocated between the products and by-products. This means that while the systems may be increasingly integrated, the outputs receive a lower share of the benefits [8]. Furthermore, when all stillage is used for biogas production this increases the production of biogas thus increasing the use of electricity, water and transportation of biofertilizer and the stillage to and from the biogas facility. These increases therefore lead to reduced benefits for Scenarios 2 and 3 in the energy allocation. With increasing integration of the systems there are also larger impacts associated with increased transportation and electricity consumption (ibid.) thus decreased.

In the system expansion method, all benefits and burdens from the systems are allocated to the main outputs, ethanol and biogas. However, the use and substitution of processes associated with the by-products are also taken into account. Increasing integration tends to therefore produce larger benefits to the system with increasing integration, with exception to the existing scenario. This is primarily a result of the increase in biofertilizer replacing conventional fertilizers, though the biofertilizer production is reduced slightly in the existing scenario. When comparing the existing scenario with the default scenario, the default scenario has a larger benefit due to a larger input of grains. With the current system boundaries, cradle-to-gate, the grain thus sequestrates a large amount of carbon dioxide [8]. Consistent with the energy allocation methods, increasing integration of the systems leads to larger impacts associated with increased transportation and electricity consumption. Nonetheless, these increased impacts are consumed by the benefits to the system from the system expansion (ibid.). In Scenarios 2 and 3, by using the stillage and not adding extra heat for e.g. drying for DDGS production, these scenarios gain further benefits from less heat and water use. Scenario 3 can be seen to have slightly higher benefits in both allocation methods due primarily to the replacement of propane with biogas.

3.2. Non-Renewable Energy Consumption

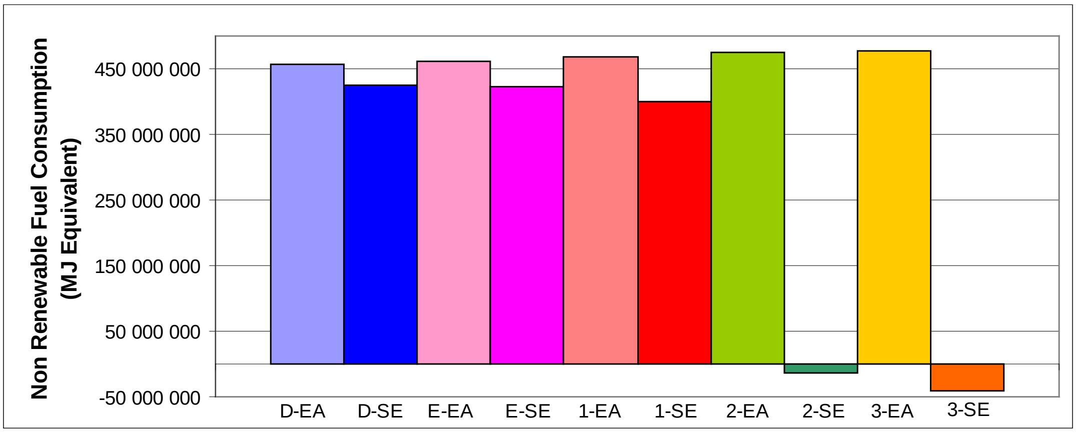

Fig. 5: Consumption of Non-renewable Energy in MJ-equivalent for the different scenarios. [8]

Another important aspect to show is the consumption of nonrenewable energy. The general trend for the consumption of non-renewable fuels for increasing integration is an increase in the energy allocation scenarios and a decrease in the system expansion method. An increase in the energy allocation scenarios is due to increased transportation of stillage and biofertilizer. The decrease of non-renewable fuel consumption with increasing integration in the system expansion scenarios arises from the enhanced quantities of biofertilzer produced, thus replacing conventional fertilizers.

3.3. Acidification and Eutrophication

In order to show an array of local and global impacts, the acidification and eutrophication impacts have also been documented in Fig. 6.

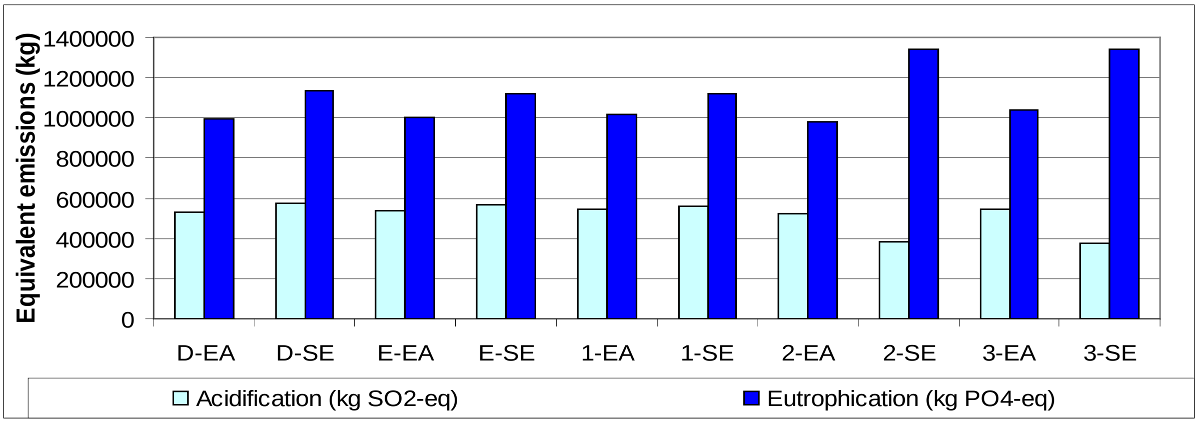

Fig. 6: Impacts in kilograms of equivalent SO_2 and PO_4 for Acidification and Eutrophication. [8]

Fig. 6 shows the Eutrophication potential for the allocation methods of each scenario. The increased integration of biogas and ethanol from the default scenario to the full use of stillage tends to correspond to larger eutrophication impacts in all cases except for the energy allocation method in Scenario 2 and when accounting for the use of biogas instead of propane in the system expansion method for Scenario 3. Once again this is primarily a result of the increase in transportation required with increased integration [8].

Correspondingly the impacts from acidification tend to increase slightly using energy allocation, with exception to Scenario 2. This stems from a slightly reduced impact from the transportation and cultivation of grains in this scenario while Scenario 3 thereafter increases. There is a general decrease in emissions of equivalent SO_2 for the system expansion method due to the reduction of fertilizer by increasing integration, and correspondingly increasing biofertilizer production, replacing conventional fertilizers [8].

4. Conclusions

The integration of biogas and ethanol production can be seen from this paper as a complex system. Although the CO_2-equivalent emissions may be further reduced by increasing the integration of the biofuel plants in the system expansion case, the energy allocation method proves opposite results. Furthermore local impacts such as acidification and eutrophication should be considered, which may increase with increasing integration. Therefore the allocation method chosen is crucial for taking into account energy and impacts embodied in by-products and replaced processes and may lead to converse results. The removal and addition of processes, materials and energy can have both improvements and rebound effects for the system. These impacts could possibly be resolved in the biogas plant by more efficient upgrading processes, transportation of stillage by pipeline and a more efficient cooling system for the incoming stillage as well as internal optimization at the ethanol plant.

This report thus shows that there is a need to understand the impacts produced from biofuel production and industrial symbiosis activities. Symbiotic activities may lead to environmental performance benefits, though the choice of impact category and allocation method is crucial when comparing local vs. global impacts. Nonetheless, this study may open for further work on the quantification of integrated biofuel production processes and other symbiotic activities.

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Evaluation of bamboo as a feedstock for bioethanols in Taiwan

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Abstract: The bamboo covers 152,300 ha in Taiwan, roughly of 7.2 % the overall forest area. This study evaluated Ma bamboo (*Dendrocalamus latiflorus* Munro) as a feedstock for bioethanols in Taiwan. Acidic steam explosion was employed to prepare Ma bamboo chips, as well as alkaline steam explosion, bleached and unbleached kraft pulps. For the saccharification of pretreated bamboo biomaterials, cellulase formulations were applied with three dosages: 2, 6, 12 percents weights to dried pulps. For acidic exploded pulp, the optimal yields were 348.92 ± 39.76 mg/ g o. d. pulp, 68% of pulp alpha cellulose contents. The hydrolysis efficiencies were negatively impacted by lignin and xylan contents of pretreated bamboo biomaterials. Simultaneous saccharification and fermentation (SSF) were also conducted using *Saccharomyces cerevisiae* D5A under 38°C and pH 5 at shake flask level. After 96 hours, 91.8 mg ethanol per g of α-cellulose was obtained for acid exploded pulp; 176.3 mg ethanol per g of α-cellulose was obtained for alkaline exploded pulp; 537.6 mg ethanol per g of α-cellulose was obtained for bleached bamboo pulp. Based on the experimental data, up to 10,700 tons of bioethanols could be produced annually by acidic steam explosion.

Keywords: *Bamboo, Bioethanol, Simultaneous hydrolysis and fermentation, Steam explosion*

1. Introduction

Bamboo stands cover 152,300 hecacres, roughly of 7.2 % the overall forest area in Taiwan [1]. Bamboos are endemic in south and east Asia. Bamboo biomass is accumulating daily, but little of them has been used (edible bamboo shoots and inedible part as materials) and most of them are wasted without utilizing. Its accumulation is about 26.1 tons/ha, with annual growth around 13.84 tons/ha under 5 year rotation cutting. Its fast growth and adaptability toward various soil and climate conditions make the bamboo a good candidate for a renewable resource. Bamboo had been conventionally used as the raw materials for producing artefacts, utensils, plywood, fiberboard, and decorated multi-layered panels in Taiwan and many Asian countries. Recently, more attention was paid for bamboo biomass as biofuel feedstock, *e. g.*, steam-exploded bamboo was employed for methane production [2].

Simultaneous saccharification and fermentation (SSF) processes were firstly described by Takagi *et al.* [3]: it combined enzymatic hydrolysis of cellulose and simultaneous fermentation of the fermentable sugars together to obtain ethanol. In the SSF process, the conditions are nearly the same as in separate hydrolysis and fermentation systems (SHF), just one different is that saccharification and fermentation are performed in the same reactor. Thus, put the yeast and the cellulolytic enzyme complex together reduces the accumulation and inhibition of sugars in the reactor which increasing ethanol yield and hydrolysis rate with respect to separate hydrolysis and fermentation [4]. Another advantage of SSF is that used one fermenter throughout the whole process reducing the facilities costs. This study evaluated Ma bamboo (*Dendrocalamus latiflorus* Munro) as a feedstock for bioethanols in Taiwan. Acidic and alkaline steam exploded bamboo biomass, as well as unbleached and bleached kraft bamboo pulps, were employed as raw materials to investigate the impact of lignin on SSF efficiencies.

2. Methodology

2.1. Materials

The Ma Bamboo (*Dendrocalamus latiflorus* Munro) sample, approx. 4-year-old Ma Bamboo culms, was collected from the Experimental Forest of National Taiwan University. The stem was chopped into 6 × 3 cm (length × width), then air dried for a mouth.

2.2. Steam-explosion

Air-dried bamboo sample was soaked into 1.5% H_2SO_4 solution or 1.5% NaOH & Na_2SO_3 solution for a week. Steam explosion conditions were: solid/liquid ratio=1:7; temperature and pressure of alkali-treated samples were held at 180, 190 and 200°C from 10 to 20 minutes. Acid-treated sampled were held at 190°C for 10 minutes. Samples were then washed by tap water on 200 mesh screen until neutral, then kept in 4 °C.

2.3. Kraft pulping and bleaching

Ma bamboo air-dried kraft pulp was cooked by M/K digester with wood to liquid ratio = 1/4 (w/v), 25% sulfidity and 17% active alkali. H-factor is about 650, with temperature raised at 1.5°C/min to 160 °C in 90 min, then kept at 160 °C for another 90 min. After washing and screening, then keep in 4 °C refrigerator. Bleached pulps were prepared by a commercial DEDD bleaching sequence [5], and then washed and kept in 4 °C refrigerator. "D" and "E" stand for chlorine dioxide and alkali extraction stages.

2.4. Enzyme hydrolysis

Acid and alkali steam-exploded bamboo pulps (biomass) were hydrolyzed with cellulases complex 50010 and 50013 (containing xylanase) from Novozymes®. Three enzyme loadings were equivalent to 1.5, 4.5, 9 IU endoglucanase (CMCase)/mL, 0.15, 0.44, 0.89 IU cellobiohydrolases/mL, and 1.2, 2.4, 7.1 IU xylanase/mL in reaction solutions. Hydrolysis was conducted in a total volume of 200 mL liquid with 0.05 M citrate buffer (pH 5), 2.5% (w/v) samples in a 250mL conical flask. The flasks was water bathed at 50°C, shaken at 100 rpm for 96 h, and the samples were analyzed every 12h.

2.5. Simultaneous saccharification and fermentation (SSF)

100 mL reaction solution, with 5% (w/v) steam-exploded bamboo, 1 % (w/v) yeast extract and 2 % (w/v) peptone, was subject to 38°C and pH 5 in a 250 mL conical flask. The sterilized reaction solution was inoculated with 5% (v/v) *Saccharomyces cerevisiae* D5A culture solutions with optical density at 0.1. The culture solution was prepared by was cultivated with yeast extract 10 g/L, peptone 20 g/L, dextrose 20 g/L for 18 h at 100 rpm, 38 °C on a rotary shaker. The enzymes were added into reaction solutions with endoglucanase 9 IU/mL, cellobiohydrolases 0.89 IU/mL and xylanase 7 IU/mL at 38°C for 96 h, then the samples were analyzed every 12h.

2.6. Analytical methods

Ma bamboo chip and steam exploded samples oven-dried and hand-kneaded, screened to 40-60 mesh before the compositional analyses: ash (TAPPI T211 om-07), acid-insoluble lignin (TAPPI T222 om-06), cellulose and α-cellulose (TAPPI T203 cm-09). Enzymatic hydrolysate and SSF samples were analyzed by high performance liquid chromatography (HPLC) using a ICSep ION-300 column and a RI detector for identifying organic acids, alcohols and mono sugars at 70 °C; mobile phase was 0.0085 N sulfuric acid at flow rate 0.4 mL / min. Error bars indicates the standard deviations from triplicate experiments.

3. Results and discussion

3.1. Compositional analysis

Various yields from pretreatment were obtained (on dried bamboo basis): 57 % for acid steam explosion, 58 % (200°C-10min) to 83% (180°C-10min) for acid steam explosion, 40 % for kraft pulping and 39.8% for bleaching.

Table 1. Compositional analysis of Ma bamboo samples. Units are mg/g dried wood.

Composition	ash	lignin	holocellulose	α-cellulose
Raw Ma bamboo	17±4.36	227.7±39.6	722±66.4	427.7±41.2
Alkali steam-explosion*				
180°C-10min	65±11	160±14.1	703±44	480±20.5
190°C-5min	54±13	148±21.8	820±81.7	598±69.7
190°C-10min	70±18.5	175±31.9	644±98.6	473±117.4
190°C-20min	46±8.1	171±44.1	702±35.2	550±49.1
200°C-10min	63±8.5	180±29.8	690±22.5	525.5±44.1
Acidic steam-explosion*	7.6±0.5	339±44.7	526±82.9	260±63.3
Kraft pulp	6.4±1.7	25.5±3.6	928±36.8	847±41.2
Bleached pulp	9±2.1	<2	966±28.9	869±43.5

** acid steam-exploded: 190°C held for 10 mins at 1.26 MPa*
** alkali steam-exploded: 180°C to 200°C and 0.99 MPa to 1.53 MPa of 5 samples * N.D.: not detected.*

Compositional analysis of raw material bamboo and pretreated samples were listed in Table 1. Great varieties of holocellulose contents were demonstrated for alkali steam exploded pulps. Generally, the lignin contents of alkali steam exploded pulps were lower then the ones of acidic steam exploded pulps. Holocellulose contents were highest for kraft pulp and bleached pulps. Acidic conditions might oxidize the cellulosic components and reduced the holocellulose of the pulps. In addition, the greater incomplete closure of compositional analysis for acidic steam exploded pulps, with its greater lignin content, was consistent to the above assumption. Lignin contents of alkali exploded pulps were increased with increasing treatment times. Although alkali would soften lignin in higher temperatures, soften lignin might melt onto cellulose fibrils; and lignin condensation [2] would contribute the increasing lignin contents among alkali steam exploded pulps.

3.2. Enzyme hydrolysis

Enzyme hydrolysis for pretreated samples was depicted in Fig.1. Enzyme loading was 9 IU endoglucanase/mL, 0.89 IU cellobiohydrolases/mL, and 7.1 IU xylanase/mL in reaction solutions. Conversions for sugar were based on dried weight of samples. 190°C-10min was chosen for alkali steam-exploded bamboo in Figure 1.

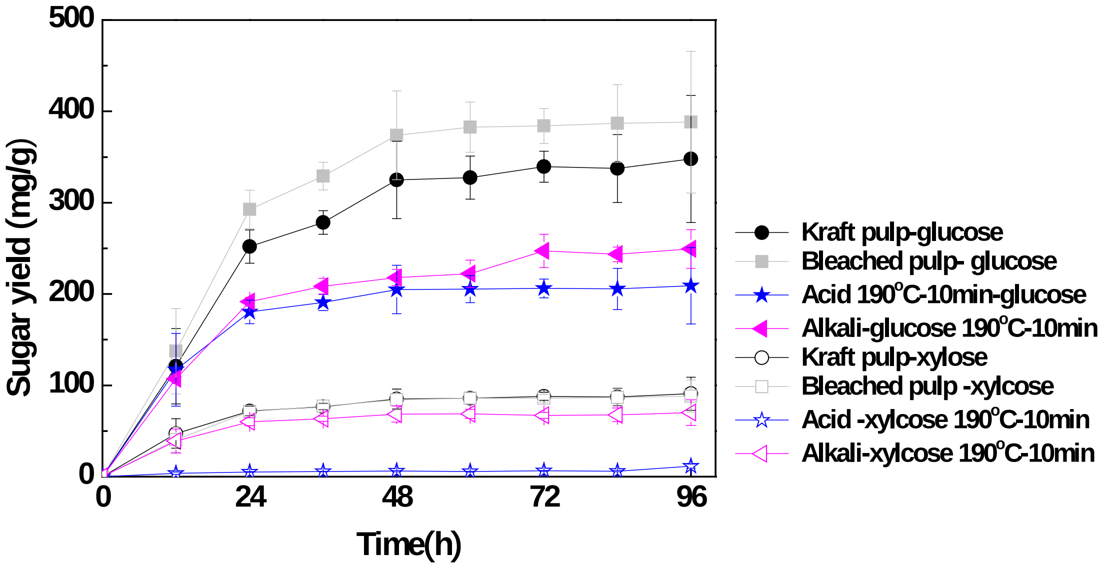

Figure 1. Enzyme hydrolysis to sugar conversion of pretreated bamboo samples with respect to time.

Glucose and xylose increased steadily prior to the first 24 h for all pulps, and the saturation was then reached at approx. 48 hours. At 96 h, the bleached pulp showed a optimal y 388.2 ± 69 mg/g, kraft pulp 347.8 ± 77 mg/g, alkali steam-exploded (190°C-10min) 249.3 ± 21 mg/g and acid steam-exploded 209.1±41 mg/g.

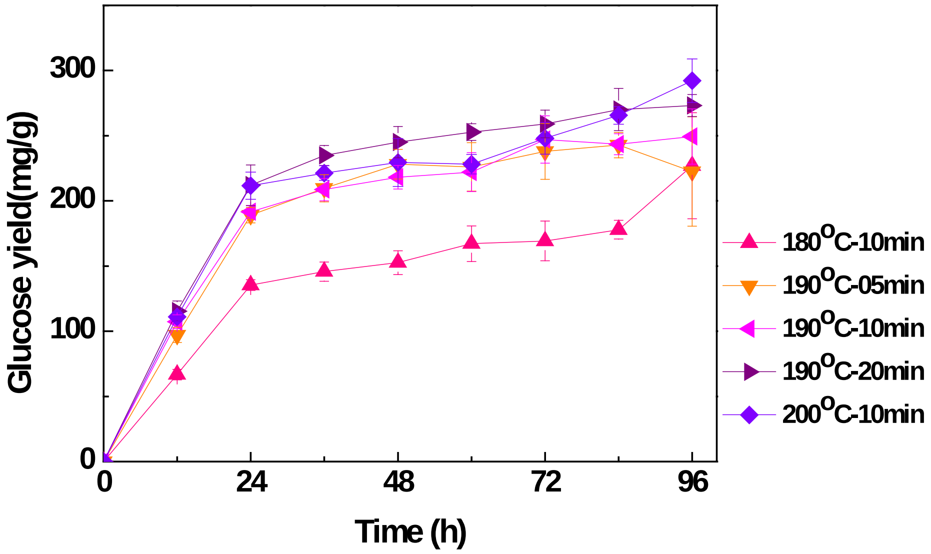

Figure 2. Enzyme hydrolysis to sugar conversion of alkali steam-exploded bamboo samples with respect to time.

Fig. 2 showed hydrolysis for 5 alkali steam-exploded samples, with other conditions as same as Figure 1. Except for the pulp for 180°C-10min, the other pulps have similar glucose yields at around 250 mg glucose per gram dried bamboo. Interestingly, the yields of 200°C-10min pulp were still slightly growing after 48 hours.

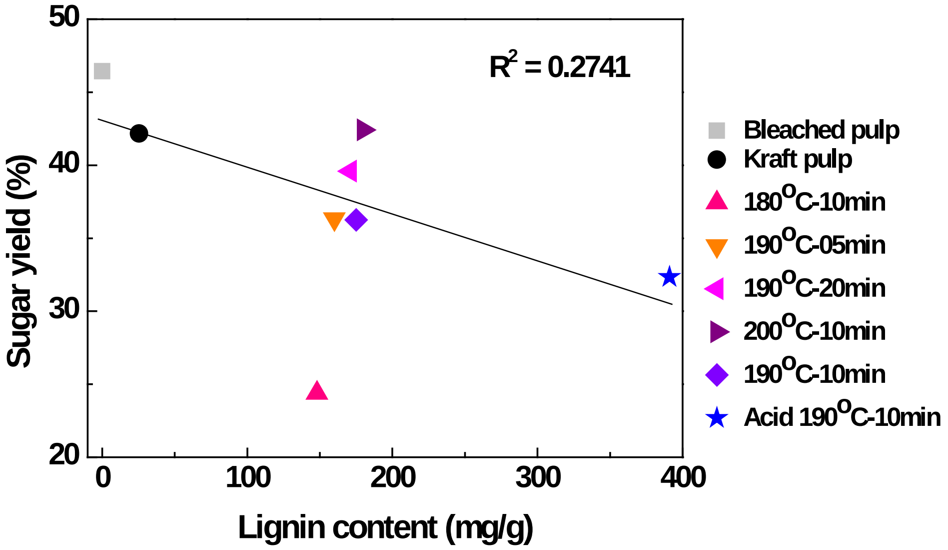

Figure 3. Correlation between pulp lignin contents and sugar yield during enzyme hydrolysis.

Effects of lignin contents on sugar yield during enzyme hydrolysis were shown by Figure 3. The trend was clearly shown, although the correlation was not clear. If the 180°C-10min pulp were removed, the correlation would be more obvious. There was almost no correlation for lignin contents and sugar yield among all alkali steam-exploded samples. The lowest sugar yield of 180°C-10min pulp suggested that other factors, like fiber dimensions, might also play important roles during enzyme hydrolysis. Since the mechanical separation of 180°C-10min pulp during alkali steam explosion should be the least.

3.3. Simultaneous saccharification and fermentation (SSF)

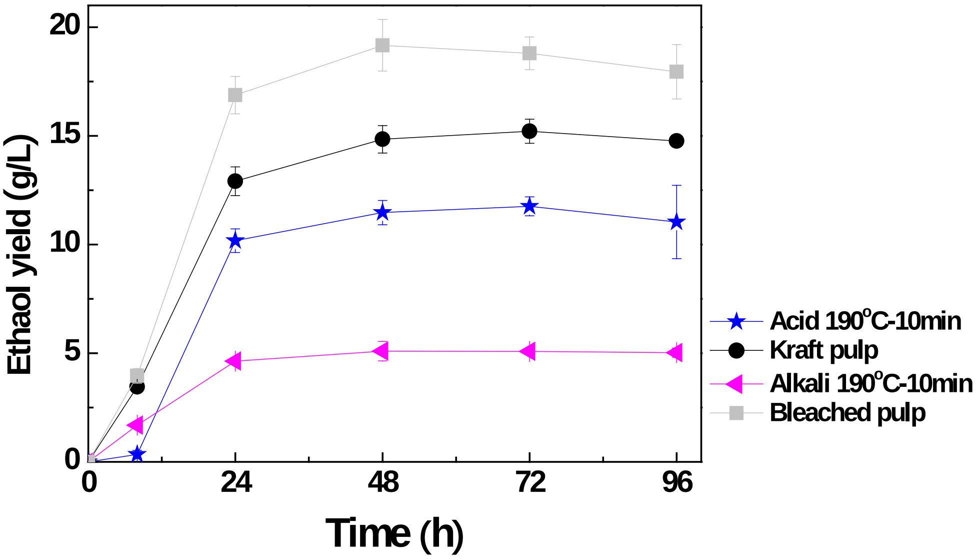

Figure 4. Ethanol yields for acid, alkali (190°C-10min) steam-exploded pulp, kraft and bleached pulps by SSF.

Ethanol yields for acid, alkali steam-exploded pulp, kraft and bleached pulps by SSF were shown by Figure 4. As expected, the ethanol yields of bleached and kraft pulps were higher than the values of acid and alkaline (190°C-10min) steam exploded pulps. Although the lignin content of alkaline 190°C-10min pulp was lower than the value of acid steam exploded pulps, melted lignin in alkali conditions might further hamper enzyme hydrolysis and fermentation.

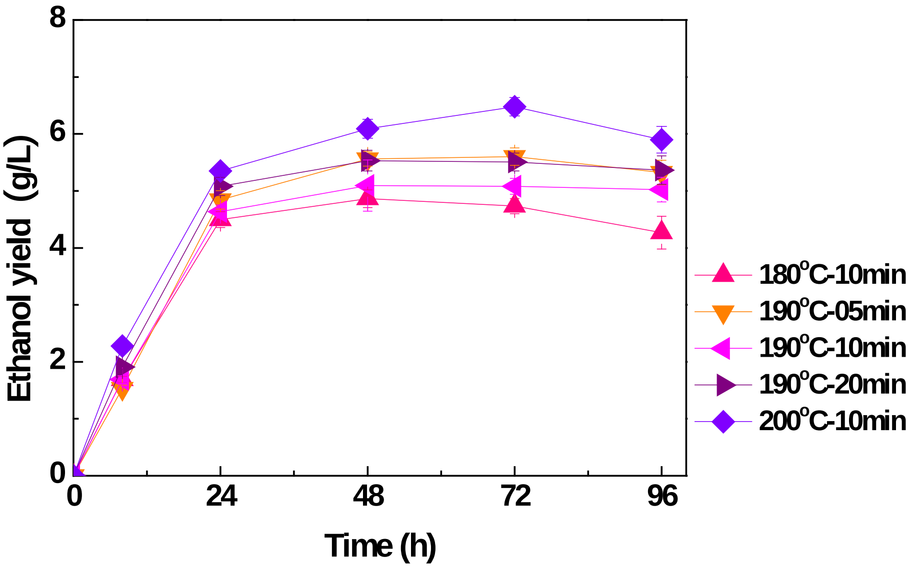

Figure 5. Ethanol yields for five alkali steam-exploded pulps by SSF.

Ethanol yields for five alkali steam-exploded pulps by SSF were shown by Figure 5. The yields increased steadily for the first 24 hours; then the optimal yields were reached after the next 48 hours. The yield from 200 °C-10min pulp was the most, and the yield from 180 °C-10min pulp was the least. With the respect of results from Table 1, lignin contents were not the deciding factor for the above observation.

3.4. Estimated of ethanol yields from bamboo in Taiwan

The bamboo covers 152,300 ha, with overall volume of 535,000 m^3 in Taiwan [1]. Its mass growth were estimated at 10~25 %. Assuming 160,000 m^3 (80,000 ton) of bamboo were harvested annually, Table 2 lists annual ethanol production from bamboo estimated by SSF following different pretreatments.

Table 2. Annual ethanol production from bamboo estimated by SSF following different pretreatments.

	Pretreatment yield (%)	Ethanol yield (g EtOH / g pulp)	Raw material to ethanol (%)	Estimate yield (10^4 tons/Yr)
Acid	57	0.23	13.40	1.07
180°C -10 min	83	0.10	8.07	0.64
190°C-05 min	80	0.11	8.96	0.72
190°C-10 min	76	0.10	7.73	0.61
190°C-20 min	63	0.11	6.97	0.55
200°C-10 min	58	0.13	7.51	0.60
Kraft pulp	40	0.30	12.16	0.97
Bleached pulp	39.8	0.38	15.25	1.22

3.5. Energy balance estimation

Energy balance estimation for bamboo ethanol, expressed by MJ per liter ethanol, were listed in Table 3. Energy consumption analyses for production of fuel ethanol from lignocellulosic biomass [6] and pulp/paper processing [7] were followed by this study. Table 3 showed that the net energy gains could be achieved for the processes with greater ethanol yields: acid steam explosion and fully bleached pulps. But net energy gains must include the utilization for combustion of the fermented waste, lignin.

Table 3. Energy balance estimation for bamboo ethanol (MJ per liter ethanol produced)

Process	Energy Input					Energy Output		Net
	Stock preparation	Pretreatment	SSF	Distillation, dehydration, purification	Total input	Lignin power	Ethanol	Energy gain
Acid explo.	2.483	35.16	13.93	13.7	65.27	48.7	21.2	4.62
180 °C -10 min	4.124	60.84	15.62	28	108.6	60.9	21.2	-26.49
190 °C -05 min	3.714	52.80	15.43	27.4	99.54	60.1	21.2	-17.33
Bleached pulp	2.182	34.64	11.73	11	59.55	40.6	21.2	2.24

4. Conclusions

Biomass derived by photosynthesis has strong potentials from bioethanol production. The present study demonstrated bamboo in Taiwan was a source couldn't be ignored for bioethanol production. Bamboos are some of the fastest growing plants in the world. Planned harvesting for will maximize its carbon sequestration potential without ecological damage. As much as 10,700 tons of bioethanols could be produced annually by acidic steam explosion.

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Production of microalgae biomass and biohydrogen in solar bioreactors

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Abstract: Only water hydrolysis with renewable energies is a sustainable process for hydrogen production. Biohydrogen production is an interesting alternative that is being explored at the scientific level. The microalgae *Chlamydomonas reinhardtii* has been extensively studied and used as a model for the photo-production of H_2. The aim of this proposal is to develop a sustainable bioprocess for the production of H_2 from *C. reinhardtii* and just preliminary results are shown here. For the first step, solar bioreactors have been tested. The biomass is recovered and suspended in another culture media with restricted concentrations of sulphur. The culture is maintained in a closed photobioreactor with magnetic stirring and 24-h illumination with fluorescent lamps. Hydrogen is produced continuously reaching maximal durations of about 20 days. Solar light should be tested in order to avoid energy requirements from artificial illumination during hydrogen production. Coupling the production system to a hybrid electric station, the process would be more sustainable. However, a lot of research must be developed before this technology would allow scale the hydrogen production to a pilot plant in order to be used in rural communities as a source of energy and as an alternative economic activity.

Keywords: *Microalgae, Chlamydomonas reinhardti, Biohydrogen, Photobioreactor, Sustainability*

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1. Introduction

At this moment, none of the sustainable ways to produce energy can completely replace fossil fuels [1]. Nuclear and hydroelectric processes have been proposed some decades ago to solve some energetic demands, but they are controversial regarding sustainability. Alternatively, solar and wind systems are starting to offer technologic solutions at different energy consumption levels. In addition, biofuels are intended to slowly replace fossil fuels, but our knowledge still requires an improvement in the massive methods to produce them. On the other hand, hydrogen (H_2) has been proposed as an alternative fuel with a number of advantages [2]. Being a gas, molecular hydrogen is an attractive substance since it can be transformed to mechanical, thermal or electrical energies involving free-carbon processes. A clean combustion is possible with hydrogen, which involves environmental advantages over the common fossil fuels and even the biofuels. Moreover, future technologies for nuclear fusion could transform hydrogen to clean energy, emulating the processes in the Sun and the other stars.

Hydrogen is the most abundant element in the Universe; in the Earth, water and organic matter include hydrogen as a part of their composition [2]. Nevertheless, molecular hydrogen is not present in Nature and all its commercial production is not only more expensive than fossil fuels but also produce more pollution [3-5]. More than 90 % of the hydrogen production in the world depends on carbon compounds, principally fossil fuels, and its use as energy carrier is only justified in some applications as fuel for spaceships or demonstrative buses or cars. Renewable energies are being proposed to produce sustainable hydrogen in commercial processes: electrolysis units coupled to wind turbines, photovoltaic modules or hydropower systems [6]. Nevertheless, biohydrogen production is also an interesting alternative that is being explored at the scientific level, focusing on three microbial systems: bacterial fermentation, nitrogen fixation in photosynthetic cyanobacteria and photoproduction in green microalgae [7]. Another interesting bioprocess is the use of *in vitro* enzymatic cocktails [8].

The microalgae *Chlamydomonas reinhardtii* have been extensively studied and used as a model for the photo-production of H_2. Light is used through the photosynthesis as the primary energy source for biomass and bio-hydrogen production. The biomass is normally produced in aerobic systems through the well-known photosynthetic pathway. However, after a period of anaerobiosis, the electrons normally generated in the photosystem II are redirected to produce molecular hydrogen in a step catalyzed by a Fe-hydrogenase. Both the genetic expression of the enzyme and its activity are importantly inhibited with small quantities of oxygen [9]. However, only experiments with temperature control and fluorescent illumination are reported for these processes, resting sustainability to the hydrogen production.

The aim of this work is to develop a sustainable bioprocess to produce H_2 from *C. reinhardtii*. The process is separated in three steps: (i) aerobic cultures for biomass production, (ii) recuperation of the biomass and (iii) anaerobic systems for biohydrogen production. The production of biomass and biohydrogen should be performed in bioreactors with natural solar illumination and at environmental temperature. The integration of these steps with a hybrid electric station is planned in order to add sustainability to the process. However, it should be noted that only preliminary results are shown in this work, since more research is being performed before proposing energy balances or economical feasibility.

2. Methodology

2.1. Algal cultures

The strain CC-124 of *Chlamydomonas reinhardtii* (Chlamydomonas Center, USA) was used in this work. Three culture media have been tested for biomass production [10]: (i) Sueoka's High Salt (SHS) medium, as recommended by the strain provider, (ii) Tris-Acetate-Phosphate (TAP) medium, commonly used for hydrogen bioproduction [9], and (iii) a modified TAP medium without acetates (TP) in order to avoid bacterial contaminations during algae growth. The media were sterilized by vacuum filtration (Whatman, GFC, 0.2 μm) but the containers were only washed with household bleach (commercial sodium hypochlorite solution) and distilled water. Stocks are maintained with the SHS medium in Roux bottles with 24-h fluorescent illumination. Pre-cultures for inoculation in reactors were prepared with the corresponding medium during three to five days in Roux cultures with continuous artificial illumination and with bubbling from small air pumps.

2.2. Biomass characterization

Cellular counts were performed with an optical microscope (Olympus, CH-2) and correlated with optical density and with dry weight. Optical density was measured through a portable spectrophotometer (StellarNet, EPP2000) at 640 nm of wavelength. Dry weight was obtained with vacuum filtration of 10 ml of culture sample through membranes (Whatman, GFC 0.2 μm) and the same volume of culture medium to wash. Before and after filtration, the membranes were dried in a microwave oven (15 min, 10 W) and stabilized in a dissicator for 30 min in order to quantify the mass with an analytical balance (Ohaus Adventurer, ARx). Chlorophyll *a* was quantified directly on cellular samples with a fluorometer (Varian, CARY Eclipse), with an excitation wavelength at 432 nm and an emission wavelength at 668 nm. Calibration was previously performed with stock chlorophyll solutions at different concentrations.

2.3. Biomass production

2.3.1. Reactors

Two designs were tested for production of biomass in solar photobioreactors (Fig. 1). Vertical tubular reactors (VTR) were made on acrylic tubes (wall-thick: 25 mm, height: 90 cm) of different internal diameters: 70, 95 and 120 mm. The low part of the tubes was sealed with acrylic, allowing the air inlet through small holes (~1 mm i.d.). The operation volumes of the VTR were 3, 6 and 9 L, respectively. A flat panel reactor (FPR) was also made with acrylic walls (thick: 50 mm), and dimensions of 50 cm length, 50 cm height and 10 cm thick. The operation volume of the FPR was 20 L with air inlet in the low part of the box through porous stones. Both VTR and FPR have acrylic taps with an air outlet. The air inlet comes from a blower and it is passed through a humidifier before going into the reactors; air flux is controlled at 1 $L \cdot min^{-1}$ per liter of culture. Natural illumination was used, with solar radiation marked by days and nights. At least 14 batch experiments were performed with the VTR and two with the FPR.

Fig 1. Pictures showing two different types of solar photobioreactors for the production of microalgal biomass at external conditions: flat panel reactor and vertical tube reactors.

2.3.2. Off-line and on-line monitoring

Daily samples were analyzed with optical density, dry weight and fluorometry. Dry weight was used to evaluate the biomass growth kinetics and the maximal cellular density. Automatic measurements of temperature and illuminance were performed with programmable data loggers (Onset, HOBO Pendant UA-002-64). In addition, on-line monitoring of the pH and pO_2 was possible in the FPR with the corresponding probes (Sensorex) connected to a power supply and an interface (National Instruments, cDAQ-1972 chassis, NI9203 and NI9205 modules). The interface is connected to a personal computer in which data are automatically registered with the Signal Express (National Instruments) software.

2.3.3. Batch algae growth experiments

A number of 12 experiments were performed in the VTR with different conditions: two culture media (SHS and TP), three tube diameters (70, 95 and 120 mm) and two annual seasons (Winter and Spring). Later, one experiment was performed in two VTR with the same diameter (95 mm) and the same meteorological conditions, but with two culture media (SHS and TP). Finally, one experiment more was performed with three VTR at the same conditions (SHS, 95 mm) in order to verify the reproducibility of the growth. Two more experiments were performed with the FPR and the HSS medium at similar meteorological conditions. Other experiments are planned with different concentrations of CO_2 mixed with air.

2.4. Biomass separation

In order to change the culture medium of the microalgae, two low-cost processes have been tested. A separation column with packed cotton wool showed good results with the retention of the biomass. A number of packing densities and designs were essayed in order to optimize the biomass separation. After being washed with the new medium TAP-S (TAP with minimal concentrations of sulphur), the cotton wool is pressed in order to recover the biomass, which is re-suspended in the TAP-S medium at a defined cellular density. The second process uses the same VTR in which the biomass is grown. Polymeric hydrogel is added to the culture with air bubbling and the medium is absorbed and retained in the hydrogel structure. The concentrated culture is re-suspended in the TAP-S medium at a defined cellular density. The hydrogel does not absorb algal cells, it can be dried in a solar system and reused for subsequent culture absorption processes.

2.5. Biohydrogen production

Just preliminary experiments have been performed to test the production of hydrogen from microalgae in VTR with 24-h fluorescent illumination (~100 μE) in a laboratory with controlled temperature (298-300 K) and constant magnetic stirring (Fig. 2). The VTR are made in acrylic tubes (70 mm i.d.) as described previously, with a high of 30 cm and an operation volume of 1 L. The base of the tube is sealed in acrylic and the tap is made in Teflon with an o-ring to seal the system and with a gas outlet. This outlet is connected to a hydrogen PEM-FC (Polymeric Electrochemical Membrane Fuel Cell), which uses oxygen from air to produce water and electricity. The pH and the voltage of the fuel cell are registered on-line with the interface described in section *2.3.2.* and related with the production of hydrogen in the system. The temperature and the illuminance in the reactor are automatically registered with the data logger described in the same section. At the moment, four experiments have been performed with different biomass concentrations: 48, 71, 164 and 248 mg/L. Experiments with light/dark cycles and with natural solar illumination are planned.

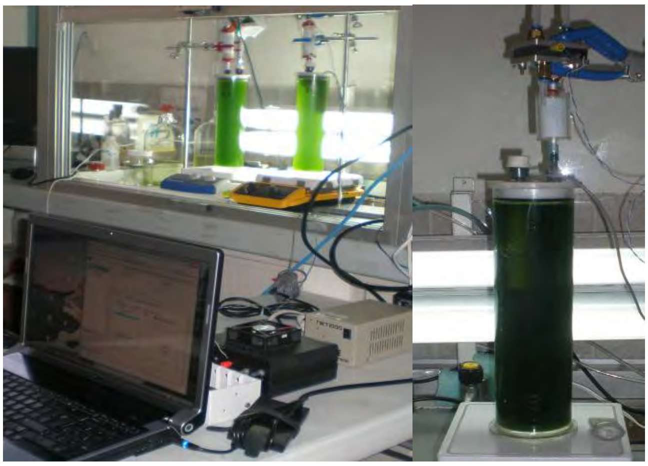

Fig. 2. Pictures showing the reactors for biohydrogen production with microalgae under laboratory conditions.

2.6. Hybrid electric station

The electrical requirements to perform the three processes, basically for air bubbling in the biomass production and separation, and for mixing in the biohydrogen production, may be obtained from a hybrid electric station. At the moment (Fig. 3), four polycrystalline photovoltaic panels (Yingli Solar, 110 W) and one wind turbine (Whisper 200, 1000 W) are installed with four acid lead batteries (Rolls Surette, 6 V) and an electrical inverter (Xantrex, DR1524) from DC (24 V) to AC (120 V). This installation is placed in the Cinvestav Marine

Station at Telchac Port, Yucatan (5 m AMSL, LAT: 21º20’28” N, LONG: 89º18’21” W). Electricity production from the hybrid station will be correlated with the meteorological conditions. The meteorological system (Davis, Vantage Pro 2 Plus) is installed in the Marine Station and has an automatic data registration every 10 min. Wind speed and orientation, solar radiation and temperature are some of the data which are obtained. The energetic fluxes in the hybrid plant will be registered in real time through and interface (National Instruments, Field Point).

Fig. 3. Pictures showing the hybrid electric station installed in Telchac Port, Yucatan, Mexico

3. Results

A typical biomass growth curve for the microalgae in the solar photobioreactors is shown in Fig. 4. The kinetics of the growth does not fit the Monod model; actually, the Gompertz model fits better with the experimental results (Fig. 5) [11,12]. In Table 1, 12 experiments in the VTR are compared in relation with the maximal cellular density, the specific growth rate and the residence time as a function of the medium (SHS or TP), the reactor diameter (70, 95 or 120 mm) and the annual season (winter or spring). The specific growth rate was computed as the slope from a linear correlation with the corresponding Gompertz equation as a function of the time; the lineal correlation had always a value $r^2 > 0.9$. The residence time was calculated as the surface below the curve in a graphic with the inverse of the instant growth rate *versus* the biomass concentration for everyday during the experiments [13]. Experiments 1 to 6 were performed during the Winter, the coolest season in Yucatan (Mexico), with an average temperature of 298 K and illuminance average values below 10 klux. In contrast, the experiments 7 to 12 were performed during the Spring, the hottest period in the year, with an average temperature of 303 K and illuminance averages values over 10 klux. Similar results were obtained in other experiments with both VTR and FPR. In addition, pH and pO_2 do not change importantly during the biomass growth.

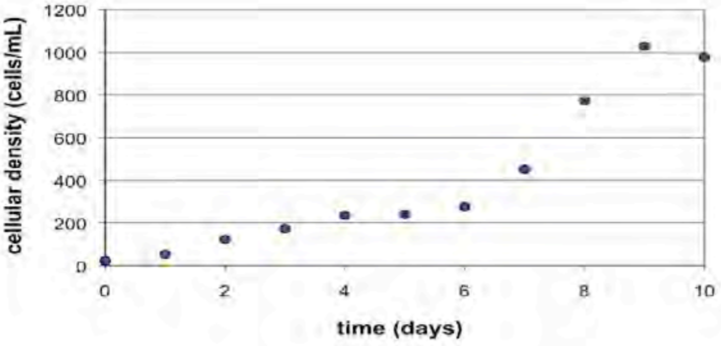

Fig. 4. Typical biomass growth of the microalgae in solar photobioreactors as followed by optical density.

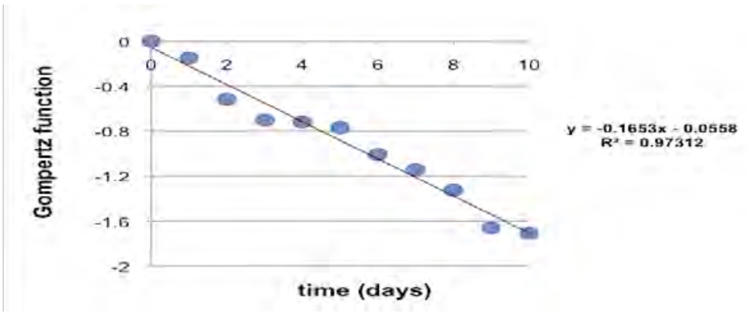

Fig. 5. Fit of the Gompertz model to the experimental cellular growth followed with dry biomass.

Table 1. The compared results for 12 experiments in vertical tubular reactors with three different diameters (d), two culture media and two annual seasons. Maximal cellular density as dry weight (D), specific growth rate (μ) and residence time (T) are reported.

Experiment number	Annual season	Culture medium	d (mm)	D (g/L) ±0.01	μ (day^{-1})	T (day) ±1.0
1	Winter	SHS	70	0.63	0.22 ± 0.02	8.5
2	Winter	SHS	95	0.64	0.30 ± 0.02	7.8
3	Winter	SHS	120	0.60	0.21 ± 0.01	9.8
4	Winter	TP	70	0.31	0.42 ± 0.05	5.2
5	Winter	TP	95	0.47	0.49 ± 0.03	3.4
6	Winter	TP	120	0.45	0.41 ± 0.04	4.1
7	Spring	SHS	70	0.34	0.09 ± 0.01	9.2
8	Spring	SHS	95	0.52	0.17 ± 0.01	7.2
9	Spring	SHS	120	0.44	0.16 ± 0.01	8.0
10	Spring	TP	70	0.33	0.49 ± 0.03	5.0
11	Spring	TP	95	0.39	0.48 ± 0.01	3.8
12	Spring	TP	120	0.35	0.41 ± 0.03	4.5

For the hydrogen production, the calibration of the fuel cell is being performed, where the voltage change is related with the hydrogen produced by the microalgae. In a graphic of measured voltage *versus* time, the surface below the curve is proportional to the total hydrogen production in the experiments. It is possible to see some preliminary results in Table 2 at different initial biomass concentrations. In general, the hydrogen production rate grows gradually during the first 30 hours and then it is maintained more or less constant for a certain period before going down to the base line. The length of this stationary production is directly related with the concentration of the initial biomass concentration with a maximal duration of 20 days for the biggest value of biomass. However, the production rate does not change between 71 and 439 mg/L of initial biomass concentration. The pH neither does change importantly during the experiments. However, the culture illuminances inside the reactor were found to decrease with time, and temperatures were found to be always lower than room temperature, principally at the beginning of the experiments when the biomass concentration is minimal.

Table 2. Biohydrogen production as a function of initial biomass concentration, at T = 298 K and atmospheric pressure. The maximal hydrogen production rate (ΔV_{max}) and the total hydrogen production (THP) are reported. The experiment with initial biomass concentration of 164 mg/L was cut before finishing the hydrogen production.

Initial biomass concentration (mg/L)	Final biomass concentration (mg/L)	ΔV_{max} (mV)	THP (V.h)
48	79	134	10,166
71	219	210	195,524
164	-	197	-
349	835	220	614,030

4. Discussion

The maximal concentration biomass has been obtained after 6 to 12 days of external cultures in solar photobioreactors. The VTR are easy to construct and manipulate, allowing to compare different culture conditions; they are very useful for research work. In general, for the experiments reported in Table 1, the reactor with 95 mm of internal diameter show a better performance for the production of biomass. The meteorological conditions influence significantly on this production, being Winter much better than Spring. Finally, it is possible to see that the TP medium gives the biggest values of the specific growth rate and the lowest values of the residence time, while the SHS medium gives the biggest cellular yields. These results show that the composition in the medium is important to regulate both the kinetics and the maximal biomass production. In particular, the SHS medium has important limitations of calcium and manganese, while the phosphate concentration is extremely low in the TP medium.

On the other hand, the FPR allow bigger production volumes and can soften temperature variations or extreme illuminances. A previous work reports that the raise of the temperature inside the FPR can be diminished when the biggest walls of the reactor are not exposed directly to solar radiation [11]. In general, both VTR and FPR show similar results for the biomass growth. This biomass production must be increased in order to find the economical feasibility and the sustainability of the process. This can be reached improving different operation conditions. By instance, a better system for gas/liquid interchanges, a different air bubbling flux or adding carbon dioxide to the air, could increase the yield of the production [12]. Additionally, it is necessary to reduce costs of the culture media and new compositions should be tested using alternative sources as wastewaters. With respect to the reactors, cheaper materials, as plastic bags, should be used instead of acrylic. It was also found that carbon dioxide in the air is minimally used when bubbled and the height of the reactors may be considerably increased. It is also important to test with a continuous or semi-continuous operation instead of the batch reactors.

For the biomass separation, the filtration with cotton wool is technically complicated and the risk of contamination is important. The medium absorption with hydrogel is much easier and cleaner, although the kinetics of the process should be standardized. The recycling of both hydrogel and medium is important to gain sustainability in the process. In relation with the biohydrogen production, much more work should be performed. It is very important to calibrate the performance of the fuel cell in order to have a true representation of the hydrogen production in the systems. The influence of the initial biomass concentration in the hydrogen production should be completely specified, as well the influence of the illuminance and the light/dark cycles, in order to scale the process in a solar photobioreactor.

5. Conclusions

Only partial results are shown here and more work is being performed to complete the project. It has been demonstrated that *Chlamydomonas reinhardtii* can be growth at external conditions in Yucatan (Mexico) using solar photobioreactors, both VTR and FPR. The production of biohydrogen in external reactors with solar illumination and no control of the temperature must be tested. The integration of all the processes with the hybrid electric station would allow knowing the feasibility of the hydrogen production as a sustainable process.

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Improvement of enzymatic hydrolysis of a marine macro-alga by dilute acid hydrolysis pretreatment

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Abstract: The marine macro-alga *Nizimuddinia zanardini* was harvested from Persian Gulf to assess its biomass for fermentable sugar production. Hydrolysis of the macro-alga was investigated in two stages to evaluate the conversion of cellulose and hemicelluloses in biomass to corresponding monomeric sugars. The biomass was first subjected to dilute sulfuric acid pretreatments at 121 °C and then to enzymatic saccharification (45°C, pH 4.8) at different retention times. The results showed the ability of the first stage hydrolysis in depolymerization of xylan to xylose with a maximum yield of 64% (based on total xylose content) at 7% (w/w) acid concentration for 60 min. However, the yield of glucose from glucan was relatively low in the acid hydrolysis with a maximum of 14.4% (based on total glucan content) at 7% (w/w) acid concentration for 60 min. Under these conditions, no hydroxymethyl furfural (HMF) produced. Formation of furfural depended on the retention time and acid concentration, whereas the concentration of acetic acid was almost constant at retention times higher than 45 min and acid concentration of 7 %.The solid residuals were then subjected to enzymatic hydrolysis. The maximum yield of glucose from the macro-alga by enzymatic saccharification (45°C, pH 4.8, 24 h), using cellulase and *β*-glucosidase, was 70.2 g/kg (70.2% yield based on total glucan content).

Keywords: *Enzymatic hydrolysis, Dilute-acid hydrolysis, Macro-alga, Pretreatment.*

1. Introduction

Considering the expected decline in production of crude oil within a few years and growing concerns about enhanced global warming, production of non-fossil fuels that can cover the crude oil deficit is desirable. One such sources of energy are biofuels which can be produced by fermentation of sugar by microorganisms. Raw materials for these processes are usually obtained from agricultural products. However, if the biofuel industry is to expand in a near future, it is widely recognized that nonfood resources should be used [1].

The production of ethanol from feedstock, other than agriculture materials, has been developed in recent years and third generation biofuels are considered to be technically viable alternative bioenergy resource that is devoid of the major drawbacks. Marine resources have played an important role in biotechnology, particularly in the past decade. Previous studies of algal biofuel production have largely focused on microalgae [1], although there are several macro-algae which contain intracellular carbohydrates and have a potential for production of biofuels e.g. bioethanol and bio-oil. Nizimuddinia zanardini is among the macro-algae which contains appreciating amounts of cellulose. However, cellulose is a high molecular weight crystalline polymer which is highly stable and recalcitrant to enzymatic hydrolysis. Therefore, a pretreatment process is typically necessary for efficient conversion of cellulose to sugars. Dilute-acid treatment has been successfully developed for pretreatment of cellulosic materials. The pretreatment can enhance the carbohydrates available for enzymatic hydrolysis and fermentation. Aqueous pre-treatment at elevated temperatures result in an insoluble cellulose-rich fraction and a soluble fraction, containing hemicelluloses sugars and degradation products. It results in enrichment of the hard to digest materials in hydrolysate, and improves the yield of ethanol from the substrate [2].

2. Methodology

2.1. *Nizimuddinia zanardini*

Nizimuddinia zanardini used in all the experiments which was obtained from Persian Gulf (Chabahar Coastline, Iran). It was dried at 45°C for 24 hour and milled in a hammer mill to pass through a 1.27 mm screen. The milled macro-alga was stored at -5°C.

2.2. *Hydrolysis*

Prior to the hydrolysis experiments, 5 gram of the biomass was soaked in 100 ml dilute H_2S0_4 (7%, 3.5%, and 0.5%w/w) and pretreated in an autoclave at 121°C for different retention times (30, 45, and 60 min). It was then cooled and the liquor was drained. The dilute acid treated solid materials were then subjected to enzymatic hydrolysis using commercial cellulase (15 FPU/g dry biomass) and β-glucosidase (45 IU/g dry biomass) in 75 ml citrate buffer (PH=4.8) for 24 and 48 hours.

2.3. *Analysis*

All the liquids were analyzed by high-performance liquid chromatography (HPLC), equipped with UV/VIS and RI detectors (Jasco International Co., Tokyo, Japan). Glucose and xylose were determined by an Supelcogel Pb HPLC column at 80 °C. Deionized water was used as eluent at a flow rate of 0.6 ml/min. Acetic acid, furfural, and HMF were analyzed on an Aminex HPX-87H column (Bio-Rad) at 60 °C with 0.6 ml/min eluent of 0.005M sulfuric acid. Concentrations of glucose, xylose, and acetic acid were determined by RI detector, while furfural and HMF were quantified on UV chromatograms at 210 nm.

The macro-alga was also analyzed for glucan and xylan following the procedure described in NREL Chemical Analysis & Testing Procedure [3] and the results are summarized in (Table 1).

Table 1. Composition of Nizimuddinia zanardini.

Carbohydrate	(g/Kg dry substrate)
Glucan	100
Xylan	30
Galactan	70
Mannitol	150
Fructosan	50
Arabinan	15

3. Results and discussion

There are a few research has been performed on the pretreatment and enzymatic saccharification of marine macro-algae [4]. During pretreatment, it is possible to solubilize the hemicellulose to fermentable sugars [5]. However, depending on the temperature, the pretreatment usually produces sugar degradation products such as furfural and HMF, which known to be sever inhibitors for fermentative microorganisms [6,7]. Dilute acid pretreatment can be used for improvement of enzymatic saccharification beside the hydrolysis of hemicelluloses.

Dilute acid hydrolysis of macro-alga was performed at different acid concentration of 7, 3.5, and 0.5% at 120 °C. The most important results of the acid hydrolysis were summarized in Figs. 1-6.

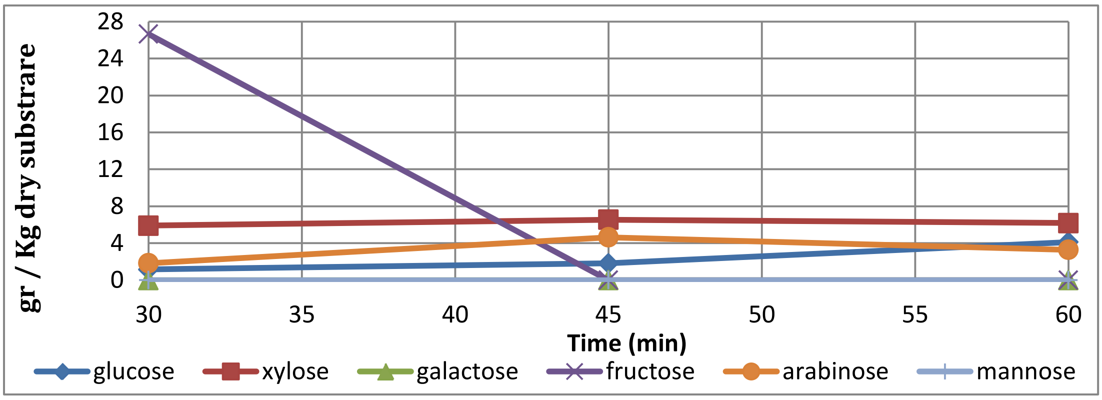

Fig. 1. The effect of retention time on the yields of glucose, xylose, galactose, fructose, arabinose and mannose production with 0.5% H_2SO_4.

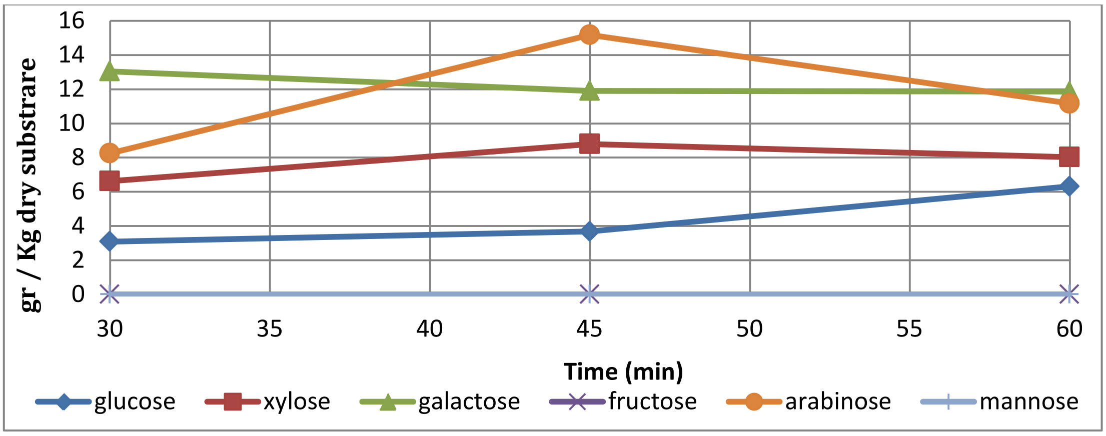

Fig.2. The effect of retention time on the yields of glucose, xylose, galactose, fructose, arabinose, and mannose production with 3.5% H_2SO_4.

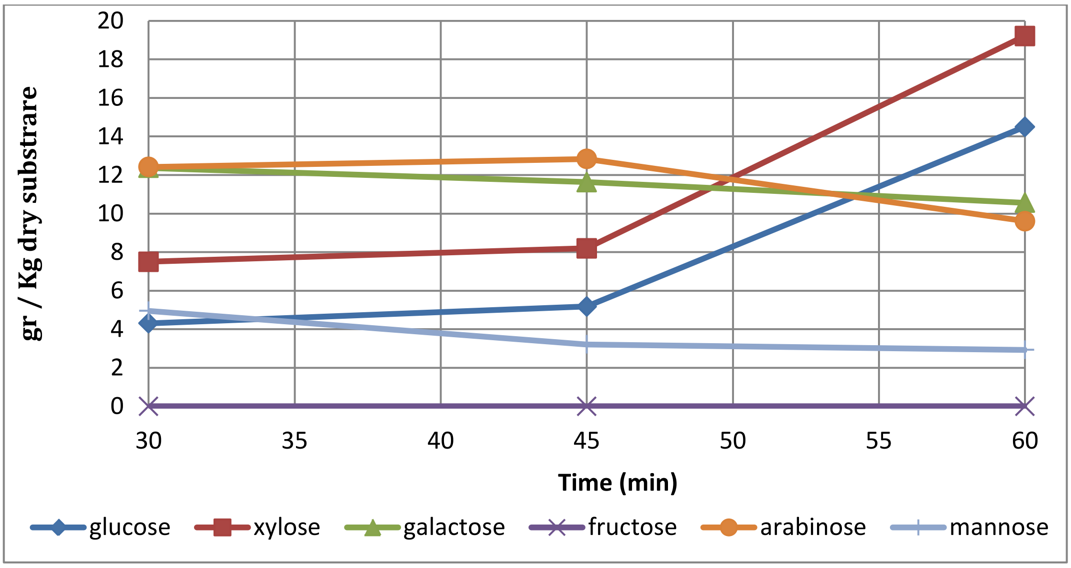

Fig. 3. The effect of retention time on the yields of glucose, xylose, galactose, fructose, arabinose and mannose production with 7% H_2SO_4.

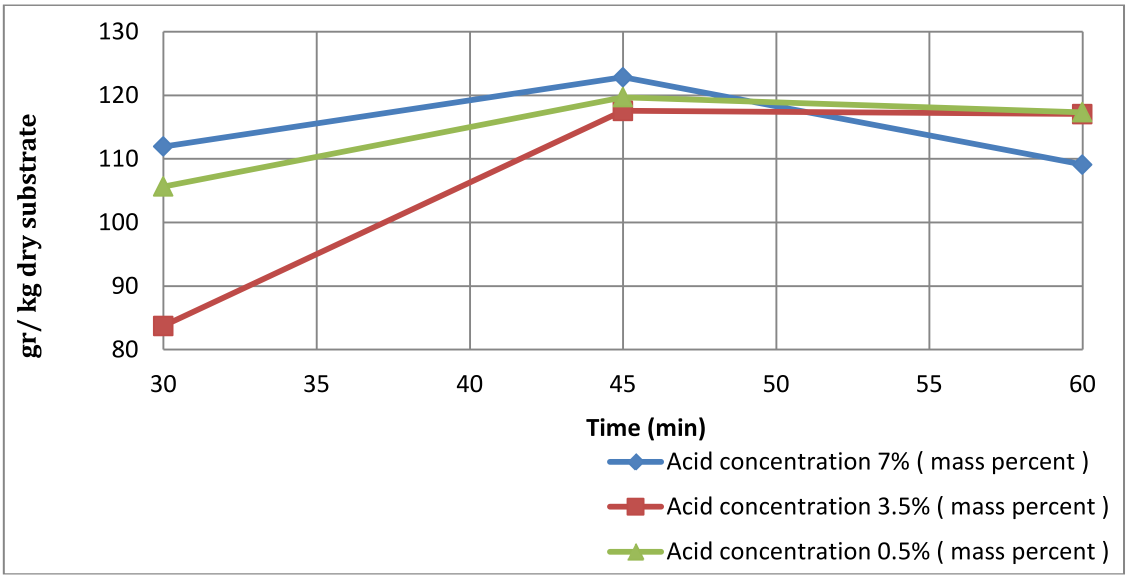

Fig. 4. The effect of retention time on the yields of mannitol by 7%, 3.5% and 0.5% H_2SO_4 .

A comparison of the maximum yields of xylose and glucose (fig. 3) with the xylan and glucan content of the macro-alga (Table. 1) showed the ability of the first stage hydrolysis to depolymerize xylan and glucan to maximum yields of 64% and 14.7% of the theoretical xylan and glucan contents, respectively. Theoretical xylose and glucose yields were calculated based on the total content of xylan and glucan in the macro-alga.

Increasing the retention time of hydrolysis from 30 to 45 min showed negligible effects on formation of glucose, but the yields of xylose, mannitol, galactose, furfural, and acetic acid were significantly affected (Fig. 1-6). It indicated that 30 min hydrolysis at 0.5-7% acid concentration is not enough to depolymerize the hemicelluloses of the biomass. On the other hand, since the concentration of acetic acid reached the maximum concentration (31.8 g/kg) in 60 min hydrolysis at 7% acid concentration, it in dicated complete hydrolysis of the hemicellulose within 60 min, and the optimum retention time should be sometimes between 45 and 60 min (Fig. 5).

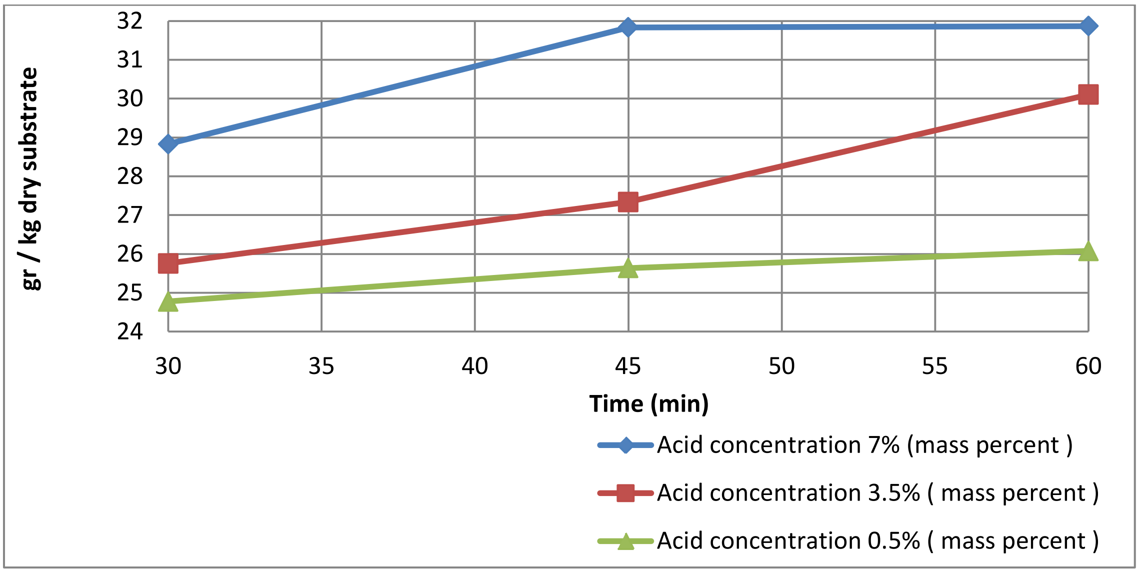

Fig. 5. The effect of retention time on the yields of acetic acid production with 7% , 3.5% and 0.5% H_2SO_4.

Furans, i.e. furfural and hydroxymethyl furfural (HMF), have inhibitory effect on ethanol production yields by fermentation. In this work, maximum yield of furfural was observed at 7% acid concentration and 60 min retention time, while HMF was not detected during all experiments (Fig. 6).

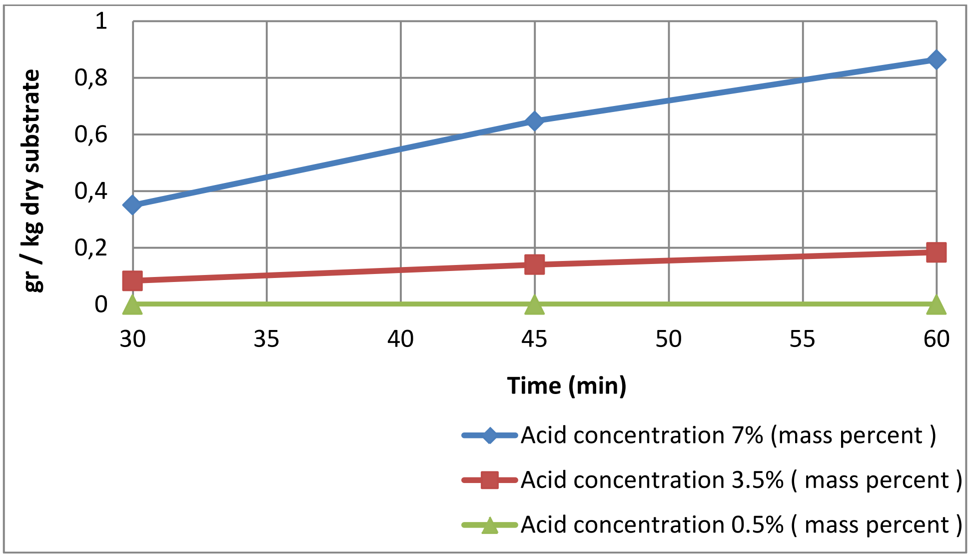

Fig. 6. The effect of retention time on the yield of furfural formation with 7%, 3.5% and 0.5% H_2SO_4.

At the second stage hydrolysis, the residual solids (Table. 2) subjected to enzymatic scarification by cellulase and β-glucosidase.

Table 2. The residual solids remaining after dilute acid hydrolysis.

Test case	Mass of substrate (g)
7%, 60 min	0.8043
7%, 45 min	1.2497
7%, 30min	1.2509
3.5%, 60 min	0.8135
3.5%, 45 min	0.9158
3.5%, 30min	1.2326
0.5%, 60 min	1.1850
0.5%, 45 min	1.2627
0.5%, 30min	1.4077

The yield of substrate without pretreatment for glucose after 24 hour incubation was only 2.98% of the dry substrate (Table. 3).

Table 3. Enzymatic hydrolysis results without pretreatment

Sugar	yield (g / kg of dry substrate)
Glucose	29.8
Xylose	10.05
Galactos	4.72
Mannitol	38.4
Mannose	1.0
Fructose	0
Arabinose	3.51

Among the all experiments, pretreatment with 7% sulfuric acid for 45 min and 24 hours enzymatic hydrolysis yielded the highest glucose in the enzymatic hydrolysates (Fig 7).

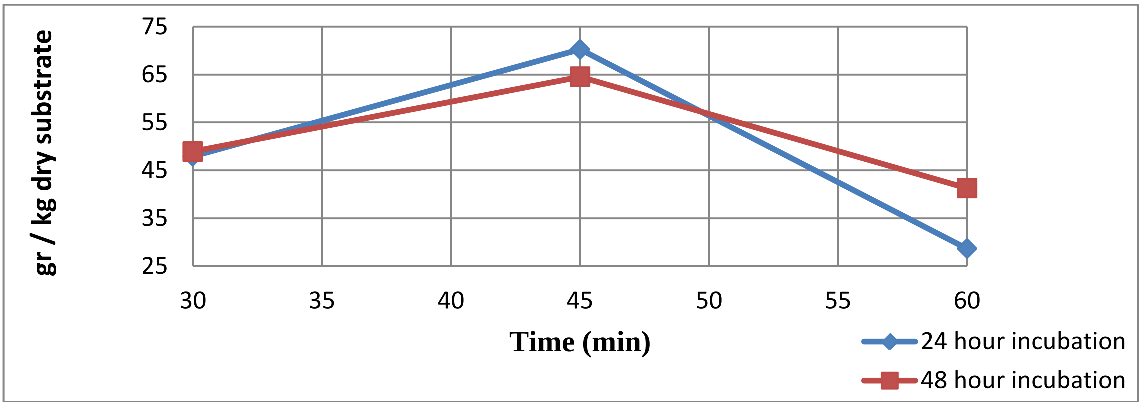

Fig. 7.The effect of retention time on the yields of glucose by enzymatic hydrolysis after pretreatment with 7% dilute acid for 30, 45, 60 min retention times.

4. Conclusions

It is possible to solubilize the hemicellulose to fermentable sugars by dilute acid hydrolysis. The results of this study indicated that 7% (w/w) H_2SO_4 is a promising pretreatment in order to obtain high yields of sugars without sugar degradation products formation.

It is possible to obtain a saccharification yield of 70.2% (70.2 g/kg), based on the glucose content, by using 7% (w/w) acid at 120°C for 45 min and saccharification with two commercial enzymes, where the yield was only 29.8% without pretreatment.

The hydrolyzate of 7% (w/w) acid pretreatment at 120°C for 45 min contains mainly mannitol, which can be a suitable source for ethanol production. The hydrolyzates contains very low concentration of fermentation inhibitors.

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Biodiesel from Microalgae as a solution of third world energy crisis

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Abstract: The world is heading towards the crisis of petro fuel. The excessive use of petrofuel is causing global warming. Now it is high time to search for alternative fuel source that will be environment friendly. The crisis for energy is more acute in Bangladesh, as there is no petrofuel source but only natural gas, the reserve has also dropped down to an alarming level. Again the global warming is threatening Bangladesh to be climate change victim. So there is no alternative for Bangladesh rather than renewable energy sources. Biofuel from microalgae can be a solution of this problem. Oil from the algae lipid can be turned into biodegradable and carbon neutral Biodiesel. Use of this diesel can reduce air pollution at remarkable level. This study focuses on algae cultivation in Bangladesh. A lab scale production of *Chlorella* and B*otroyococcus braunii* was executed in open pond and bioreactor system. Then diesel was produced by transesterification from collected algae oil. Later data was collected from this experiment. Cost analysis was prepared to get a clear concept of the actual scenario of algae fuel probability. This study indicates high potentiality of algae based fuel to be used in Bangladesh replacing diesel for energy production. It can be a model for any third world country to mitigate the energy crisis with a greener solution.

Keywords: *Transesterification, Biofuel, Microalgae ,Lipid*

1. Introduction

Our world is heading towards a severe dilemma of petrofuel usage for the next decades. The price of petrofuel is hiking up rapidly. On the other hand, the supply of fossil fuel will come to an end by 2050 considering a 5% flat increase in demand. Even though, if we can get, we cannot use those because excessive use of fossil fuel causes CO_2 increase in atmosphere and we are already facing tremendous effect of this, vicious change of climate. With the rapid growth of technology and civilization spreading over the world, from 1955 to 2005 the emission of CO_2 at atmosphere simply got twice from 3 billion tons of Carbon to 6 billion tons of Carbon, which certainly results in temperature increase, sea level hike, deviation of biodiversity and ecological imbalance. Most of the CO_2 emission is caused by USA, China and EU countries, but the high risked counties of the impact of this phenomenon are underdeveloped countries like Bangladesh, where Bangladesh causes less than 0.1 tons of Carbon emission/Person compared to almost 6 tons of Carbon emission/Person of USA. The production of natural gas is 100% domestic and the oil supply totally depends on import in Bangladesh. Major of 1961 MMCFD gas produced locally is consumed for power generation and rapidly growing industries. 96.7% of its 5271 MW power generation depends upon fossil fuels. The requirement of natural gas in Bangladesh is 1.5 times higher than the actual production.

Biodiesel can be a strong and ultimate solution to overcome this problem for Bangladesh. This carbon neutral fuel stops CO_2 increase rate in atmosphere and lowers pressure on fossil fuel. Microalgae are one of the sources of biodiesel that can be a major source of energy for future rather than Soya bean and Sugarcane. Microalgae are rich in lipid which can be used for producing Biodiesel.

The paper studies the probability of algae oil as an alternative of fossil fuel in Bangladesh. In particular, different species of algae were investigated for cultivation in different suitable process, diesel was produced from algae lipid by transesterification, their fuel and chemical properties were analyzed. Also we analyzed data for productivity, practicality and potentiality to gain a cost benefit analysis for the commercialization of algae oil production in Bangladesh perspective.

2. Methodology

2.1. Potentiality of microalgae biodiesel in Bangladesh

The amount of diesel run Power plant in Bangladesh is 4% of its Total 5271 MW generation. to replace this by biodiesel of different sources, the amount of land required is shown in Table-1. From the table we can see, microalgae give us highest amount of oil. If we go for harvesting other oilseeds like soyabean, mustard oil and others these will occupy almost 30% of our available land for harvesting. Suppose, to get biodiesel from mustard oil it will require 1.28 M Ha land which is 3.6 times of the available land for mustard oil seed being harvested at present. So, this type of biodiesel production will create an immense pressure on the land available for harvesting in Bangladesh to mitigate its food crop demand.

Table 1: Comparison of sources of Biodiesel in Bangladesh for diesel supply of 230 MW power generations:

Crop	Percentage of Oil %	Oil yield (L/Ha)	Land required (Million Hectare)	Land at present (Million Hectare)
Mustard Oil	39-44	91.5	1.28	0.35
Ground Nut	48-50	156.0	0.75	0.087
Sesame	42-44	55.2	2.13	0.076
Soyabean	19-20	52.0	2.26	0.530
Sunflower	42-44	91.0	1.25	0.042
Microalgae	70	136900	0.00086	-
Microalgae	50	58700	0.002	

Source: Bangladesh Oilseed Harvesting Instruction, DAE and FAO/UNDP Project

This scarcity can be mitigated dramatically if we think of microalgae. These can contain up to 70% of their weight as lipid oil and the oil yield per Hectare is extremely high compared to other oil sources. Oil content of microalgae varies according to the species but most of them contain enough lipid oil to produce biodiesel from it. From Table -2 we can get an idea of the lipid oil content of different microalgae. Again microalgae grow almost twice in amount in every 24 hour in Bangladesh climate. So, thinking microalgae as a source of alternative fuel for Bangladesh can mitigate its continuous fuel crisis.

Table 2: Oil contents of microalgae species:

Microalgae species	Oil content(% of Dry Mass)
Botroyococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cilindrotheca sp.	16-37

Source: (Chisti, 2007; Mathew, 2008)

Producing microalgae in an expensive method compared to general crop production. The basic requirements for microalgae production are light, CO_2, water and nutrients. Nutrients include Nitrogen (N), Phosphorus (P), Iron and Silicon. These growth nutrients are relatively less expensive. The Carbon that is contained in dry Biomass of algae (almost 50% of total weight) is collected from atmosphere by the following reaction:

$$6CO_2 + H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 + 6H_20$$

Producing 1 Ton of algae biomass requires 1.83 ton of CO_2. It can be incorporated with the power plant flue gas. This will reduce air pollution and also will minimize the cost of the algae production. Thus the algae production is carbon neutral, can retain the amount of carbon from the atmosphere.

The water required for microalgae can be used from any source, even the wastewater from our industrial or domestic use. The waste water already contains N or P for algae. Thus this can minimize the production cost as well as mitigates the environment pollution.

Adequate light is another requirement for high rate of Microalgae production. Throughout the year, except some cloudy days in rainy season, sunlight is quite sufficient in Bangladesh for microalgae production.

Space is another requirement for algae production which is largely available in Bangladesh. At present there are 0.73 million Hectare of (Table-3) land those are not suitable for any crop production and instantly can be used for algae production. Also the saline lands can be used for algae production.

Table 3: Type of land in Bangladesh

Type of Land	Amount (Million Hectare)
Dry land	0.73
Ponds	0.31
Low marshy land	3.16
Coastal saline land	0.218

Source: 1. DAE and Agriculture Ministry, 2004 2.Fisheries Department, 2007

The only two practical methods that we have applied for microalgae production in lab is raceway pond and photo bioreactor. We have produced *Chlorella* and *Botroyococcus braunii* in natural environment of Bangladesh to expedite our experiment.

2.2. Raceway Pond

It is made of closed loop water channel. The material may be anything like concrete, plastic or compacted earth with a paddlewheel for proper mixing and circulation of water. During daylight, the culture must be fed in front of the paddlewheel. CO_2 generally collected from the environment, but for better production rate CO_2 can be circulated against the flow of water for the photo biosynthesis. Temperature control of the water totally depends on nature by evaporation. For better production temperature must be maintained from 20^o C to 30^o C.

Figure1: Raceway pond setup

Figure2: Raceway pond setup (Top view)

In our experiment we constructed a low cost raceway pond system. The base body was constructed with 3 inch radius PVC pipe, bends are PVC bends jointed to liner section of pipes together. We put a simple paddlewheel electrically operated for circulation of water. The total amount of water contained in the raceway is 1.5 ft^3. Nutrients are fed into the pond at regular interval manually.CO_2 is naturally taken from air. The setup was successful to produce algae at a satisfactory level.

2.3. Photobioreactor

Tubular photobioreactor consists of solar collectors, where algae collect energy from the Sun. (Figure 3)

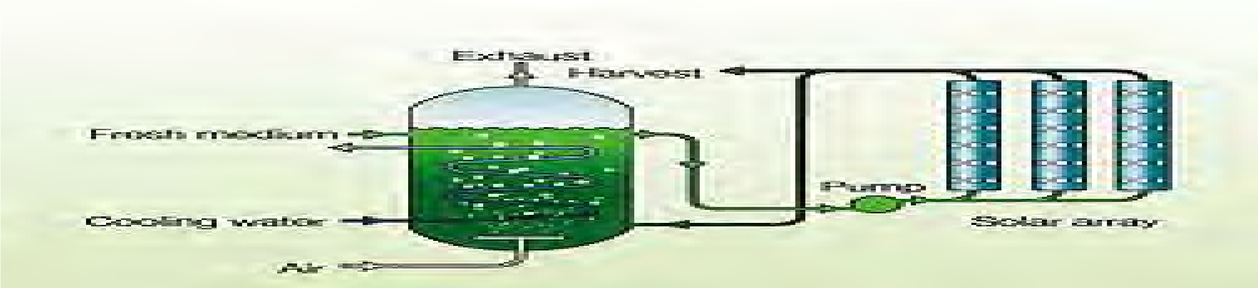


Figure 3: Conventinal PhotoBioreactor

This is generally made of plastic or glass. Tube diameter is limited to maintain proper penetration of sunlight. From the feeding vessel the flow progresses through a mechanical or diaphragm pump. Algae are collected from the vessel. The remaining algae pass through the closed loop. The solar collectors are oriented parallel to each other and flat above the ground to maximize the sunlight availability. The ground may be white painted or Alu foils may be used to maximize the sunlight capture. Biomass sedimentation can be prevented by using mechanical pump, airlift pump, diaphragm pump or peristaltic pump. To minimize higher concentration of O_2, at feeding vessel air is purged through the bottom. The cooling of the system can be maintained by heat exchanger at the feeding vessel.

Figure 4 and 5 shows the setup of low cost photobioreactor that we made at our Lab. Each of the three solar collectors is 9 inch long and diameter is 1.5 inch. Unit capacity is 0.0276ft^3 .Surface area is 0.88 ft^2 . The solar collectors are made of plastic tubes. The feeding vessel is 2 L HDP container. A small scale peristaltic pump is used for flow turbulence .There are three tubes fed into the feeding vessel, outlet and inlet from solar collectors and other for supplying air and CO_2 at the bottom of the vessel.

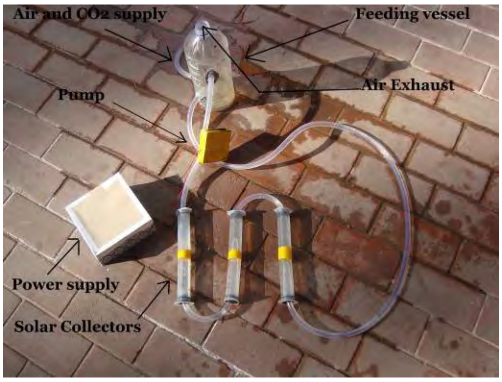
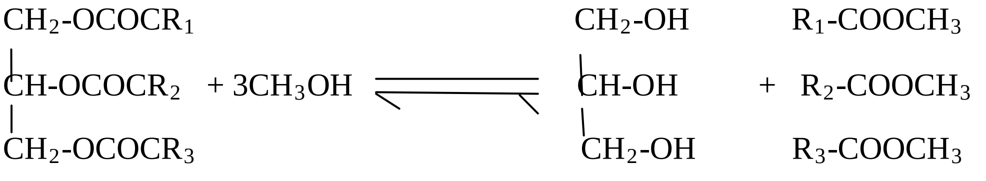


Figure 4: Details of PBR set up

Figure 5: Side view of PBR set up

2.4. Biodiesel Production

We collected set samples of Algae *(Chlorella 30 gm* and *Botroyococcus braunii 28 gm)* from and carried out the experiment at Chemistry Lab, Islamic University Of technology (IUT), Dhaka. Algae were ground by hand motor and pestle. The oil was extracted from the dry mass by drying the algae for 30 Minutes in 80^{o}C. Ether solution and Hexane was mixed to algae and the mixture was kept 24 hours for settling. Then by filtration the biomass was collected and oil was evaporated. A mixture of NaOH (0.25 gm) and 25 ml methanol was poured into a conical flask with the algae oil. The process than converts the algae oil into Biodiesel is called transesterification. It requires 3 mol of alcohol for each mole of triglyceride to produce 1 mol of glycerol and 3 mol of methyl esters. The conical flask is shaken for 4 hours at electric shakers.



$$\begin{array}{llll} CH_2\text{-}OCOCR_1 & & CH_2\text{-}OH & R_1\text{-}COOCH_3 \\ | & & | & \\ CH\text{-}OCOCR_2 \ + 3CH_3OH & \rightleftharpoons & CH\text{-}OH \quad + & R_2\text{-}COOCH_3 \\ | & & | & \\ CH_2\text{-}OCOCR_3 & & CH_2\text{-}OH & R_3\text{-}COOCH_3 \end{array}$$

Triglyceride Methanol Glycerol Methyl Ester (Biodiesel)

After this reaction the solution was given time in idle for 20 Hours to settle the sediment layer to pour out the biodiesel. Then it is washed by 5% Water and dried under fan for 18 hours.

3. Results ad Discussions

3.1. Comparison between Raceway pond and Photobioreactor system lab experiment

Considering the productivity both by volume and area our experimental algae production from the PBR and raceway pond shows that (table 4), raceway pond system's productivity is lower than the PBR productivity by 11 times. But CO_2 consumption for both systems is almost same. It is possible to obtain more oil/ Hectare from PBR system rather than raceway pond. As the biomass concentration is higher in PBR (21.97 times), so we can extract more biomass in the same time from PBR and less from Raceway pond.

Table 4: Lab experiment result of algae production scaled up to 100000 kg production:

Parameters	Raceway Pond	Photobioreactor
Annual biomass production(kg)	100000	100000
Volumetric productivity($kgm^{-3}d^{-1}$)	0.103	1.1
Areal Productivity($kgm^{-2}d^{-1}$)	0.029	0.034
Biomass concentration($kgm^{-3}\ d^{-1}$)	0.137	3.01
Dilution Rate(per day)	0.22	0.275
Oil yield(L/H)	99400	136900
Annual CO_2 consumption(Kg)	183300	183300

3.2. Comparison of Oil extracted from Chlorella and Botroyococcus braunii

Table 5: Measurement of gross and dry weight, extracted oil and biomass of algae:

Specimens	Gross wt(g)	Dry Weight(g)	Oil(g)	Biomass(g)
Chlorella	30	9	1.86	4.05
		30%	6.2%	45%
Botroyococcus braunii	28	12.6	7.56	5.29
		45%	27%	41.9%

Source: Author’s Lab Experiment

Percentage of dry weight algae is higher in *Botroyoccus braunii* than in *Chlorella* (Table -5). Oil extracted from *Botroyoccus braunii* also at higher percentage rate as we found in table 2. After extraction Biomass was found lower in *Botroyoccus braunii* than *Chlorella*

3.3. Properties of Microalgae Biodiesel over Diesel

Table 6:

Properties	[1]Microalgae Biodiesel	[2]Diesel
Density	0.864kg/L	0.838Kg/L
Viscosity	$5\ x10^{-4}$ Pa s at 40^oC	$1.9\ x\ 10^{-4}$ Pa s at 40^oC
Flash Point	75^oC	$75\ ^oC$
Heating value	0.35 MJ kg^{-1}	0.5 MJ kg^{-1}

Source: 1.Author’s Lab experiment 2.PetroBangla Ltd

3.4. Cost Analysis of a project to run the 480 KW diesel generator of IUT (Islamic University of Technology, Dhaka) with biodiesel:

*Required diesel per hour at full load=120 L
*Total diesel required for 171 working days@ 6 hours time= 171 x 120 x 6=123120 L
*Total biodiesel B20 (20% Biodeisel-80 % Petrodiesel) = 24624 L=21275 Kg (table 6)
*Algae production required/day at 70 % oil Content=30390 Kg/year
*CO_2 produced by generator =278 Ton, CO_2 is fed into the algae production.
*CO_2 Consumed /year by the algae=30390 x 1.83 kg =55613.7 kg =55.6137 Ton
*Daily production required =83 Kg of Algae

*Required land=3000 Sqm at raceway pond system, productivity rate 0.103 $kg/m^3/day$ and raceway depth 0.3 m.Total land with open spaces between the ponds=6000 Sqm.
*At a rate 560 Taka/Sqm (pipe, bends, cement, adhesive, paddlewheel, motor and other materials, labor and electricity) the total cost (fixed and variable) for 6000 Sqm stands =3360000 Taka=46666 USD. 1 Liter Oil price= (46666/24624) USD=1.88 USD

The cost for per Liter micro algae oil goes up to 136 taka or 1.88 USD at our project. The price is higher than diesel price (55 taka/L). The price can be reduced by attaining better efficiency and algae concentration in production. Also the pricing of microalgae oil can be bring in a relation with the crude oil price, so that it can be affordable to the limit of diesel price:
$C_{\text{algae oil}}=6.9 \times 10^{-3}\, C_{\text{petroleum}}$

4. Conclusion

As discussed here, we see that, microalgae oil is technically compatible like diesel. From Table -6 we find the properties are quite similar to diesel properties. So, similar engines or machines can be driven by microalgae oil instead of diesel .From Table-4, a comparative statement of both raceway pond and PBR is clear to us and surely this will encourage us for more diversified research on PBR in Bangladesh. From table-5, we understand which species of microalgae should be emphasized for biodiesel production at lower cost and higher efficiency. From earlier discussions it is clear that Bangladesh has a huge potentiality to produce microalgae as we still have available land and cheap labor for this. Both raceway pond and photobioreactor is possible in Bangladesh, but raceway pond can be introduced by mass level people in villages as the cost is lower and a huge supply of microalgae can be made available from this source and thus a revolution in energy sector can be ignited. Now we are working to find out the suitable, efficient and cost effective way for replacing the diesel that is being used in national energy production by scaling up the pilot work of microalgae oil use in IUT power generation. The most challenging part of this will be to reduce the price as lower as diesel or. Extensive researches need to be carried out for this work. Thinking of a better and greener Bangladesh, we must now rush towards this research more deeply and establish microalgae oil as a substitute of conventional diesel. This research can be implemented for third world countries to produce large scale microalgae oil and lessen the load from petrofuel.

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Preliminary study of hydrogen production from local arid area algae in a bubble column

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Abstract: Fighting climate change and ensuring sustainable development is one of the greatest concerns nowadays. In this regard, energy production from biomass is already a reality and presents tremendous possibilities of use as an alternative source. Among the various technologies, hydrogen production from microalgae is a promising clean energy alternative. Indeed, some unicellular green algae have the ability to produce hydrogen simply in the presence of water and light. However, an important factor governing the efficiency of hydrogen production by microalgae depends on the method of production. Designing a suitable bioreactor is therefore very important in order to control the main production parameters. Hence, a suitable bubble agitation system, with proper bubble size, that keeps algal cells in suspension is proposed.

The present work foresees a tentative method of hydrogen production from *Chlamydomonas sp*, a local alga from the arid area of Adrar (southern Algeria). This is performed in a photobioreactor of the type of a bubble column. It should be noted that a hydrodynamic study of the bubble column has been previously conducted. This has led to a proper choice of the diffuser and an approximate assessment of microalgae culture parameters. Moreover, various process parameters were monitored under a given light intensity, namely: pH, temperature, dissolved oxygen, etc. The observations show massive growth of the algae biomass which indicates a good adaptation of this type of photobioreactors for microalgae production, and subsequently hydrogen production as long as low rates are required.

Keywords: *Renewable Energy, Hydrogen, Microalgae, Photobioreactor, Bubble column.*

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1. Introduction

World energy consumption can only grow given the accelerated growth of the population. It is largely dominated by fossil fuels (oil, natural gas and coal) as the sole energy source. Moreover, their massive use exposes the planet to two major problems: a devastating pollution caused by the emission of greenhouse gases and the depletion of fossil fuel reserves. The growing awareness about the risks of climate change and the conditions for sustainable development of the planet led to the search for alternative energy sources more environmentally friendly as substitute for fossil fuels. Ultimately, renewable energies are the best alternative. However, they have the disadvantage of not being competitive yet for many applications. More specifically, hydrogen appears to be the ideal alternative energy source and represents a serious hope to achieve an industrial era with considerably lower carbon dioxide emission. Indeed, it is considered as a viable alternative and as "the energy carrier of the future. Biologically produced hydrogen is a promising alternative to produce clean energy as it shares both advantages of being renewable and nonpolluting. In fact, from just water and solar energy, some unicellular green algae or cyanobacteria are known for their ability to provide hydrogen by photosynthesis [1]. However, for purely economic reasons, it is difficult to accept that biologically produced hydrogen may compete with other modes of production [2]. Bubble column reactors are mainly used in various industries such as: chemical, petrochemical, biological, bioenergetic…etc, due to their simple construction and their low operating costs. The gas holdup and the bubble size constitute important parameters for the study of the flow patterns in a bubble column. In addition, bubble size distribution, as well as the gas holdup depends on some parameters such as: column geometry, operating conditions, physicochemical properties of the two phases put in contact and the type of gas sparger [3]. The liquid is assumed to be mixed by the motion of gas bubbles in it. However, the use of a gas sparger which generates small bubbles distributed with homogeneous way throughout the column ensures a better mixture [4].

The aim of the present work is to undertake preliminary test of photobiological production of hydrogen from microalgae strains isolated locally in Algeria. A Pyrex made bubble column type photobioreactor has been designed for this purpose with the possibility of controlling some of the culture parameters such as light intensity, thus allowing the optimization of certain operating conditions. To the dispersion of the gas phase, the total gas holdup , the bubble size distribution within the column are studied. So, the bubble diameter was measured by using a photographic method, with the help of a millimetre.

2. Methodology

2.1. Material and methods

2.1.1. Strain and culture medium used

Microalgae used in this study were isolated from freshwater samples collected from southern Algeria. The microalgal species used is a locally isolated *Chlamydomonas sp*. The culture medium used is tri-acetate phosphate (TAP) which is adjusted to pH 7.2. This medium is widely used for cultivation of microalgae for the purpose of hydrogen production.

2.1.2. Experimental set-up

The experimental set-up used in this study is a cylindrical Pyrex column of 0.04m internal diameter and 0.86m height, provided with several lateral pipes (Figure 1). Stirring provided by injecting air through a porous sintered glass diffuser of porosity 40µm, which is placed at the bottom of the column. The airflow is controlled by a flowmeter. It should be noted that a preculture is first prepared and inoculated in the column in 900 ml of culture medium. Bubbling with nitrogen is recommended to create anoxia (low dissolved oxygen) and counteract the inhibition of hydrogen production.

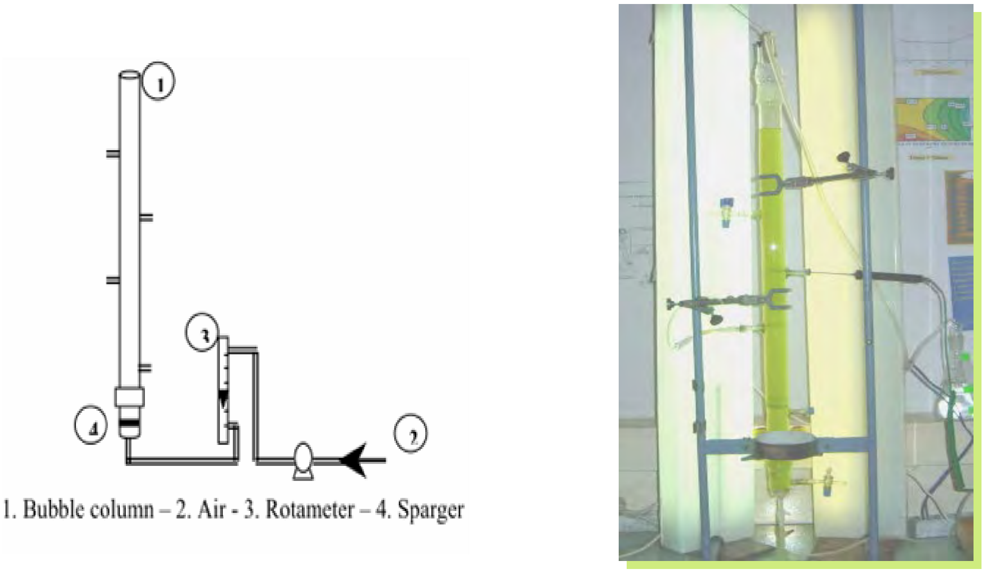

Fig. 1. Experimental set-up

2.1.3. Microalgae growth

The growth of microalgae is favorable in the presence of a culture medium rich in nutrients and exposed to sufficient luminous intensity. Different factors may influence the growth and the production of hydrogen from microalgae [5]. The experiments were performed in the bubble column inoculated with a preculture of *Chlamydomonas sp*, which allowed us to follow the temporal evolution of biophysical parameters such as: dissolved oxygen, pH and Temperature, etc. Microalgal cell count was performed using a microscope. The count is carried out with a cell count, which allows us to check any contamination present in the medium. An average of three samples is performed for each test.

2.1.4. Gas retention

The gas retention is given according to superficial gas velocity and the type of the sparger. For bubble columns the gas holdup, ε_g, is given by the following relation:

$$\varepsilon_G = \frac{\Delta H}{\Delta H + H_L} \qquad (1)$$

Where:

H_L: Height of the liquid before injection of gas.
ΔH: Increase in the level of the liquid after gas expansion.

2.1.5. Bubble diameter

The average diameter of the bubbles is measured by a photographic method. The pictures of the bubbles were taken at a certain distance to the bottom of the column where the distribution of the bubbles is uniform with a using numerical photograph (SONY). Then, the photographs are treated and the diameter of the bubble is calculated using the software Matlab 6.5. The shape of the bubbles is generally ellipsoidal.

The local bubble diameter was calculated using the following relationship:

$$d_i = \sqrt[3]{a^2\,b} \qquad (2)$$

Where a and b are the diameter and the width of the ellipsoid respectively.

For each gas velocity, the average Sauter diameter is calculated from the following relation:

$$d_{32} = \frac{\sum_i n_i . d_u^3}{\sum_i n_i . d_i^2} \qquad (3)$$

n_i : the number of the bubbles with an individual diameter d_i.

2.1.6. Axial dispersion

The model employed is the one used to characterize flows in tubular engines. It takes into account two effects: convection, which represents the flow in block, and dispersion, which results from the molecular and turbulent diffusion. There are two types of contributions to dispersion: radial and axial [6]. The radial effect is negligible compared to the axial effect when the ratio L/D is greater than 4. With these considerations, the transient matter assessment in the tracer is written as:

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \tag{4}$$

Where C is the concentration of the tracer, u the speed of the fluid, D_Z the axial dispersion coefficient, z the axial co-ordinate and t, the time

The solution of equation (4) is then:

$$\frac{c(t,z)}{c_E} = 1 + \frac{2L}{\pi\beta} \sum_{n=1}^{\infty} \left\{ \frac{1}{n} \sin\left(\frac{n\pi}{L}\beta\right) \cos\left(\frac{n\pi}{L}z\right) \exp\left[-\left(\frac{n\pi}{L}\right)^2 D_z t\right] \right\} \tag{5}$$

3. Results and discussions

3.1. Gas retention

The mixing of the liquid phase is ensured by the injection of gas. The study of the dispersion of the gas phase can bring information on the flow within the column. The gas retention εg, which is one of the most important parameters characterising the hydrodynamics of the bubble column reactors, depends mainly on the superficial gas velocity and the type of gas sparger. According to M.S. Michaud, 2001 [4], there is no significant difference in the value of gas retention according to the type of sparger used.

Our results, presented in figure 2, show clearly the influence of the type of sparger on the gas holdup. According to this figure, we observe that for superficial gas velocity lower than 0.03 m/s, the gas retention is similar for the two spargers. For high superficial gas velocity, however, the gas holdup obtained for sparger 1 is higher than that obtained in sparger 2. So the type of sparger does influence the gas holdup for high gas regimes. Indeed, sparger 1 (150 µm) generates large bubbles and thus increases the gas retention in the whole column. Moreover, the gas retention increases with increasing gas velocity, which is in agreement with the observations of Thomas et al. (1989) [7].

The dependence of the gas holdup on the superficial gas velocity v_g , can be written as:

$\varepsilon_g = C. (v_g)^{\alpha}$

The experimental values of C and α obtained in this work are: C=12.091 and α=0.747 for the sparger 1(150µm), which is in agreement with the work of Shah and al, 1982 [9]. According to this author, the exponent α varies usually from 0.7 to 1.2 for bubbly flow. As for sparger 2 (40µm), the constant C was 7.1511 and α was 0.6775 which corresponds to a heterogeneous flow where the exponent α ranged from 0.4 to 0.7 according to the same author. Figure 3 illustrates the experimental results compared to those found in the literature. For low superficial gas velocities our experimental results are in good agreement with those from the literature. However, for high gas velocities, the results diverge due mainly to the operating conditions and to the type of spargers used.

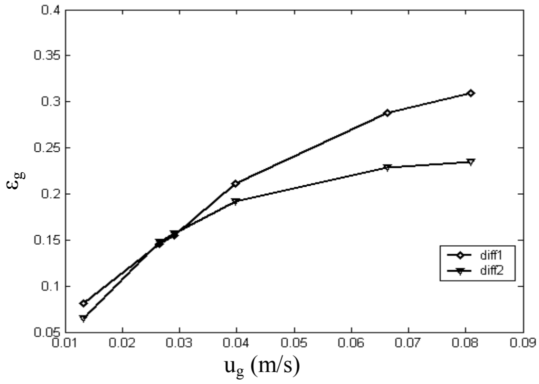

Fig. 2. Gas retention vs superficial gas velocity

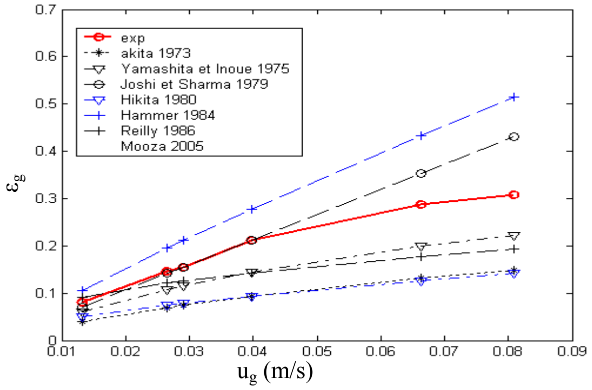

Fig. 3. Gas retention vs superficial velocity compared with the literature data

3.2. Bubble diameter

Bubble size is a very significant parameter for better understanding the gas dispersion within the column. In bubble column reactors, the variations of the average diameter of the bubbles depends on the type of gas sparger [8], and the Sauter diameter increases slightly with the increase of superficial gas velocity. For our study, the variation of the bubble size according to the superficial gas velocity is represented in figure 4, we notice that the average diameter of the bubbles increases with increasing gas velocity. We also observe a coalescence of the bubbles beyond a gas velocity of 0.033 m/s; at which point, the size of the bubbles becomes difficult to determine. The bubbles are generally ellipsoidal and for the porous spargers used, the bubble diameter ranges from 2,5 mm to 8,5 mm. For the two spargers, The Sauter diameter varies similarly according to the superficial gas velocity (Figure 5). However, for sparger 1, the Sauter diameter is about 5mm, while for sparger 2, the Sauter diameter is 7.5mm.

We also represent in the figure 4 and 5 the Sauter diameter and the average diameter for the two spargers. We note that the variation follows the same increasing pattern. However, sparger 1 presents larger bubbles than those generated by sparger 2.

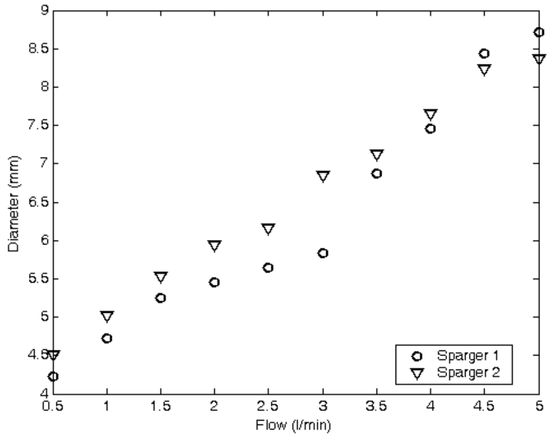

Fig. 4. Mean bubble diameter versus the injection gas velocity.

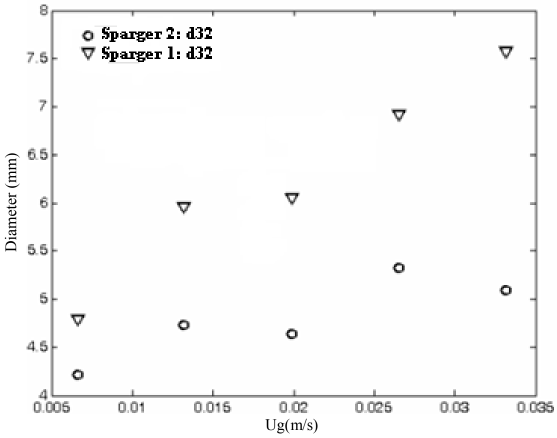

Fig. 5. Sauter diameter vs superficial gas velocity

3.3. Modelling of the column

The computed curves are generated using a model with axial dispersion. The results obtained are represented in figure 6 and 7 for each flow and each type of diffuser. The experimental data points are represented and compared with the model of axial dispersion. The parameters of the model are adjusted in order to obtain a good adjustment of the model to the experimental data using MATLAB 6.5. We note that for a bubble column in batch mode, the SDR fits the model of axial dispersion almost perfectly. The expression used is that of Eq. 5 and the results of this model seem to be in agreement with the experimental data. Figure 7 represent the exit of the tracer for diffuser 1 (150µm) for flow gas of Q_G =3l/min.

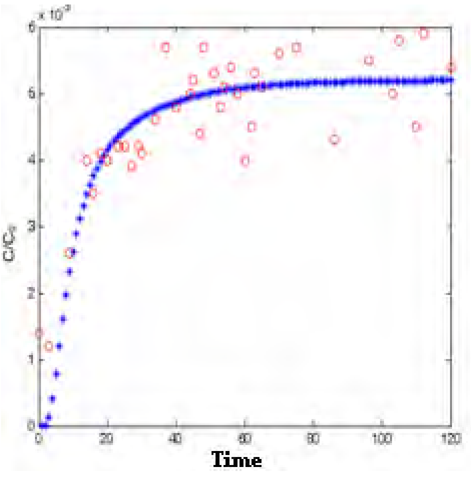

Fig. 6. Exit-tracer concentration in batch mode (D=150µm , Q_G =1 l/min)

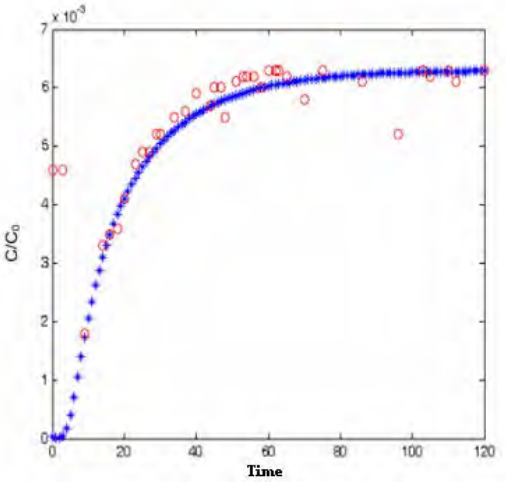

Fig. 7. Exit- tracer concentration in batch mode (D= 150µm, Q_G=3l/min)

3.4. Microalgae growth

For a light intensity of 7800 lux, a considerable evolution of microalgal biomass is observed over time. Figure 8 shows the change in optical density vs. time and informs us about the temporal evolution of the growth of microalgae. It is noted that this curve actually reflects the growth kinetics of the *Chlamydomonas sp*. Strain, reaching a maximum after 98 hours of cultivation, then a stationary phase where the concentration of biomass is stable

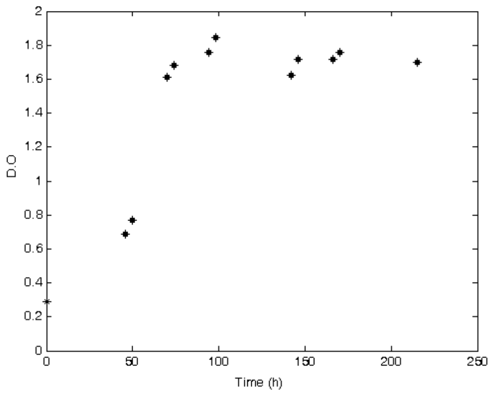

Fig . 8. Evolution of optical density vs Time

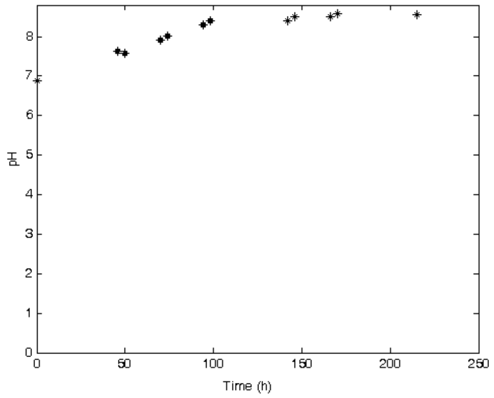

Fig. 9. pH vs time in growth algae

An increase of pH, while remaining within the range of 6.9 and 8.5, is also observed during growth (Figure 9). This increase reflects the growth of microorganisms. The pH increase is due to the microalgae photosynthetic activity. Given the fact that microalgae absorb CO_2 very rapidly, the pH of the medium moves to values above 7.5 in the case where CO_2 demand of microalgae is higher than its supply to the middle. The variation of dry matter is shown in Figure 10 an increase in dry matter over time is observed, reflecting the concentration in the cell culture medium. However, a decrease of dry matter towards the end of growth is noted. The evolution of dissolved oxygen during growth is also monitored. Overall, dissolved oxygen increases over time during the period of illumination.

This also reflects the photosynthetic activity and hence the growth of microalgae (Fig. 11). The measured dissolved oxygen concentrations are in the range of 2.9 to 11.7mg/L.

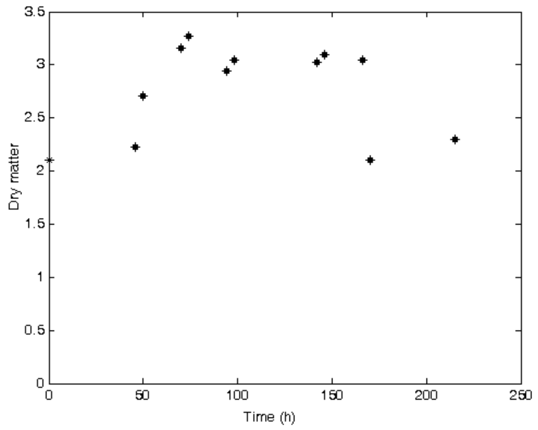

Fig. 10. Dry matter vs time

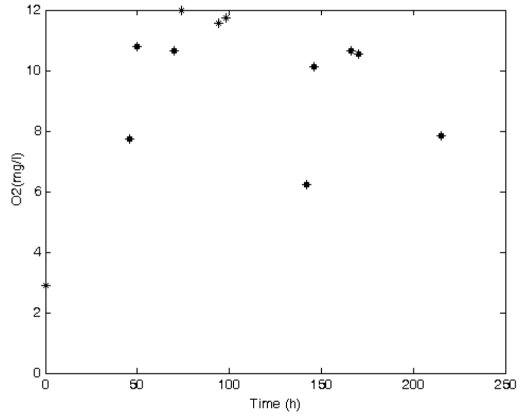

Fig. 11. Dissolved oxygen vs time

Preliminary tests of hydrogen production by the ***Chlamydomonas sp***. strain are undertaken in the bubble column serving as a photobioreactor. The column is equipped with a mechanical agitation system to keep algal cells in suspension and prevent them from settling. It is noteworthy that during the hydrogen production testing, nitrogen bubbling is performed to achieve anoxia and induce the production of hydrogen [9, 10]. At the beginning of culture, the dissolved oxygen content is relatively constant. Beyond 20 minutes, it increases due to photosynthesis (O_2 release). However, a short period after the cultivation initiation, we note the formation of small bubbles through the capillary tube leaving the bubble column type photobioreactor (gas trapping system). This can be explained by the fact that culture was in anoxia which favored the production of hydrogen (transcription of the Fe-hydrogenase). This is followed by an increase of oxygen dissolved in the medium which inhibits the production since bubbles are no longer observed. These observations are consistent with those reported by [11].

4. Conclusion

Bubble columns equipped with porous spargers offer a greater gas-liquid contact area as bubbles created by this type of spargers are numerous and far smaller. The use of porous spargers seems to be advantageous compared to the other types because of the multiple points of injection. According to the experimental results obtained, the type of sparger influences the gas retention for high superficial gas velocities. Moreover, the diameter of the bubbles increases with increasing gas velocity. We also note that the gas holdup and the Sauter diameter agree well with results reported in the literature. In the present study, the culture of locally isolated microalgae in a bubble column type photobioreactor is tested; followed by a preliminary investigation of hydrogen production.

The growth and massive evolution of algal biomass in this reactor type demonstrate the suitability of this type of reactor for the cultivation of microalgae. Subsequently, preliminary tests of the biological production of hydrogen by microalgae show that anoxia is achieved by nitrogen bubbling in the culture medium; which allowed observation a hydrogen production but for a short period of time only.

Thus, the preliminary tests of photobiological production of hydrogen by an algal strain and in a bubble column remain conclusive despite its transient character under the present conditions. The question that arises is how to maintain the conditions of the onset of hydrogen production for longer periods of time so to make it economically viable.
In order to elucidate a number of phenomena hitherto unexplained, this work is to be pursued and deepened to address these questions and more particularly in regard to the implementation of more adapted micro algal strains for hydrogen production in photobioreactors

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Short Rotation Coppice in Italy: a model to asses economic, energetic and environmental performances of different crop systems

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Abstract: In the near future, the role that renewable energies can play in order to achieve the ambitious objectives fixed by the European Union is decisive. Besides economic aspect also energetic and environmental issues of agro-energy chains must be carefully evaluated. We developed a software tool able to assess economic, energetic and environmental performance of renewable energy from biomass. The aim of this paper is present the software and its application about one of the most promising energy crop in Italy: Short Rotation Coppice (SRC) based on poplar clones.

SRC, subdivided into SRF – plantation with a short cutting frequency (1 or 2 yrs) and in MRF – plantation with a medium cutting time (5 yrs), takes up about 7,000 hectares in Italy. Twenty years after their introduction, in bibliography the information concerning this crop is not always clear and unanimous. On the basis of the cultivation technique carried out in Northern Italy, an economic, energetic and environmental (EEE) evaluation of the poplar SRC (SRF and MRF) has been carried out. The analysis is focused on field and transport phases of the agro-energy chain.

Keywords: *Short Rotation Coppice (SRC), Poplar, Energy Crops, Energy balance, Sustainability,* CO_2 *balance*

1. Introduction

In Italy, the contribution of agro-energy to national energy demand is still moderate; nevertheless, even if slowly contributing, its relevance has increased in recent years. Agro-energy seems like a possible and, theoretically, interesting alternative to traditional crops, allowing a diversification of income sources. Compared with other energy sources, the dedicated crops offer the advantage of extremely intense field management that ensures the highest yield as well as the shortest wait time. Cultivation of biomass crops on arable lands allows for increased energy production and should be quite profitable for the environment (groundwater protection, ecological planning, phyto-remediation, and Green House Gases absorption, among other options). This is especially true in the case of woody crops, including Short Rotation Coppice (SRC). Over the last 20 years in Italy, supported by favorable public grant programs, SRC has grown to comprise about 6,500 ha, mainly in the Po Valley area. Leaders in the Lombardy and Veneto Regions have been the first to give subsidies for SRC, and the planting areas in these regions now account for almost all the Italian land area dedicated to this energy crop, 4,000 and 1,300 ha, respectively.

In Italy, the woody species suitable for SRC are *Populus* spp, *Salix* spp, black locust, and eucalyptus; however, most plantations consist of specific poplar clones. This arboreus species is historically well-known by Italian farmers and has proven the most adaptable for bio-fuel production. Over the years, the development of new specific clones for biomass production (at the moment, the most important are AF2, Monviso, and Pegaso) and improvement in cultivation techniques have made it possible to obtain remarkable yield increases. Regarding the crop management, several systems with different cutting times have been used: first 1-year, and later, 2-year and 5- to 6-year. Different cutting times require different plant densities and different lane widths. The SRC thus can be subdivided into Short Rotation Forestry SRF – plantations with short cutting frequency (1 or 2 years) and (Medium Rotation Forestry) MRF – plantations with medium cutting frequency (> 5 years). Planting systems are different, too, with highly variable plant density: 10,000 to 14,000 plants/ha (annual plantation with twin rows), 5,000 to 6,000 plants/ha (biennial plantation with single rows) and 1,000 - 1,800 plants/ha (in MRF). In plantations with medium cutting times, the distance between stumps in the row is quite similar to the width of lanes.

At present, even if the best quality bio-fuel comes from 5-year plantations, the larger part of Italian SRC is based on 2-years cuts. In the near future, MRF plantations will be more widespread because of the better quality of chips (mainly due to lower ash content).

Wood chips produced from SRC are a raw material with a low market value (sale prices range from 60 to 110 €/ t_{dm}); the economic sustainability of this crop is highly dependent on reduction of production costs. This aim can be reached through high yields as well as through the complete mechanization of all field operations. Among the field operations the harvest is the most difficult because of new, sophisticated equipment with high operating costs. The need for high yield requires high input during the crop cycle that can lessen both energetic and environmental sustainability.

In addition to economic sustainability, energetic and environmental aspects must be considered. Taking into account the considerable public grants given to the main agro-energy chains, researchers should evaluate not only economic sustainability (often achieved by means of public subsidies) but also energetic and environmental sustainability. In this way, a Comprehensive Sustainability could be estimated. Nevertheless, though experts in provide information about this wood-crop, the information is not always clear and unanimous. Regarding SRC energy performances, several values of woody biomass production have been reported [3, 6, 8, 12, 14] . Discrepancies in results can be attributed mainly to differences in the following factors: species cultivated, calculation methodology, cultivation techniques (i.e., field operations, type, and rate of fertilizers/herbicides), biomass yield, selection of agro-energy chain phases/operations (i.e., storage, transport, drying, conversion process).

Few studies have been conducted to investigate the environmental aspects of energy-crop cultivations, but a number of software tools to assess economic and energy performance of bio-energy production recently have been developed. Nevertheless, most of these tools lack flexibility; their analysis often is restricted to a single type of bio-energy chain or only the main operations of a chain. This makes application of them difficult for the several agro-energy chains actually in use.

Moreover in the future, evaluating the energy-environmental sustainability of each bio-energy chain will become more and more important. Already, before allowing public subsidies, leaders in several Italian regions are calling for energy and environmental evaluations of some bio-energy chains.

In order to overcome the above-mentioned limitations, we have developed a specific tool to assess the comprehensive sustainability of renewable energy produced by farms and easily are able to compare different agro-technical solutions. The software is capable of providing unbiased information on these three aspects (economic, energetic and environmental) of “Comprehensive Sustainability” of this bio-energy chain.

The aim of this work is to show the software tool and present an application regarding Short Rotation Coppice in Italy in order to clarify, 20 years after their introduction, the economic, energetic, and environmental sustainability of SRF and MRF with poplar in northern Italy.

2. Methodology

The software tool works on a farm scale, and the boundaries of the system analyzed are - at the moment - limited to the farm and transport phase of the chain and does not take into account the conversion process. The functional unit is 1 t_{dm} of biomass. Input required by the software are details of: (a) farm (area, agricultural machinery fleet, crop system); (b) cultivation technique (mechanization operations and sequence; input rate and market prices, energetic and carbon equivalent); and (c) the characteristics of products and byproducts (yields, market prices, lower heating value, and moisture content).

For the economic evaluation, the method of *fixed and variable costs* [11] is used, while for energy balance computation, the software uses the *Gross Energy Requirement* (GER) methodology [13]. The environmental analysis takes into account the same input considered in the energy evaluation and assesses the amount of GHG emitted according to guidelines of IPCC [9]. The mass and energy flow between the different operations of the supply chain are converted in economic, energetic, and environmental values, respectively, by using, for each used production factor, the price (P, €/kg or €/m^3), the energy equivalent (EE, MJ/kg or MJ/m^3), and the emission factor (FE, kg CO_2equivalent/kg or kgCO_2eq/m^3) [10].

For *direct input*, the economic, energetic, and environmental load of the production factors is accomplished easily by multiplying the quantity used (Q; kg or m^3) during the chain as showed in the following equations:

$$C_{ECO} = Q \cdot P \qquad [€]$$

$$C_{ENE} = Q \cdot EE \qquad [MJ]$$

$$C_{ENV} = Q \cdot EF \qquad [kgCO_2eq]$$

where C_{ECO}, C_{ENE}, C_{ENV} are, respectively, the economic, energetic, and environmental costs linked to the different production factors.

In addition to direct input during the cycles of production, others goods are required in order to allow the production of the biomass. These goods are not consumed completely when employed and can be used for several cycles of production. For these production factors, called *indirect input*, the economic, energetic and environmental cost (EEE cost) (C_{ECO}, C_{ENE}, C_{ENV}) is assessed using the same equations adopted for direct input but subdividing their value, the energy, and the greenhouse gases embedded for the overall hours of use and taking into account their economic life (years) and the annual employment (hours).

Therefore, for each production factor, the software computes an EEE cost that summarizes the "load" on the three levels of the analysis. The sum of all the EEE costs allows us to calculate the overall EEE cost for the produced biomass.

To calculate economic net income, the software considers chip-wood selling as well as public subsidies coming from the Rural Development Program (RDP) and Common Agricultural Policy (CAP). Regarding energy aspects, the Lower Heating Value (LHV) of biomass harvested is taken into account to assess the output of these phases of the agro-energy chain. Because the carbon absorbed and stored in the biomass will be oxidized when it will be utilized for energy purposes, this amount cannot be counted as one environmental output. Regarding the C cycle, the agro-energy chain is supposed to be neutral. The environmental output for the GHG issue must be assessed by comparing the emissions for the energy produced with the agro-energy chain with the emissions of a proper reference system (for example, energy produced by a fossil fuel chain). Since at the moment, the software has not yet been implemented with the last phase of the chains, the environmental output cannot be calculated, and the analysis shows just the environmental production cost of the biomass ($kgCO_2eq/t_{dm}$). For the functional unit, the software assesses economic, energetic, and environmental cost (EEE Cost), economic and energetic revenues and gains, and the economic and energy ratios (between revenue and cost economic and between output and input energetic, respectively).

By means of the integration of the three EEE costs, the software computes a synthetic index, the Global Sustainability Index (GSI), which summarizes the results achieved on the three levels of the analysis.

3. Case Studies

In order to show its applicability, the software was used to evaluate the economic, energetic, and environmental performances of Short Rotation Coppice with poplar in Northern Italy. Two case studies are reported and compared: Short Rotation Forestry (SRF) with 2 years' cutting time and Medium Rotation Forestry (MRF) with 5 years' cutting time.

In both the cases, the crop duration is 10 years, with 2- and 5-year harvests for SRF and MRF, respectively. With respect to the operating conditions of the Po Valley area, the results concerning the conversion from cereals (maize) to poplar for biomass of 40 ha (50% of total farm AUA – Agricultural Used Area) are reported.

Table 1 shows the operations required during the entire SRF and MRF poplar cultivation-cycle. Table 2 shows the rates for the various production factors. Market prices and energy and environmental equivalents are deduced by bibliography [1, 2, 4, 5, 6, 7, 10].

In the study case, the software tool considers the following: (a) a biomass yield of 40 t_{wb}/ha·yr for SRF and equal to 40 t_{wb}/ha·yr for MRF (moisture content = 55%, LHV = 18.5 GJ/t_{dm} or 6.9 GJ/t_{wb}); (b) a chip-wood sale price of 35 €/t_{wb}; and for public grants: the decoupling cap (400 €/ha·yr) and the planting subsidy provided by leaders in the Lombardy Region (1000 €/ha).

The transport of the chip wood is carried out by a lorry (load volume: 96 m^3, 54000 km/year, 3 km/kg of gasoline, bulk density of the chips = 0,3 t/m^3, carriage price = 1,7 €/km). The lorry never travels empty, so the global coefficient of load for a round trip is equal to 100%. We considered two different transport distances of 70 and 450 km in order to take into account both small- to medium-sized plants in which the biomass supply is prevalently local and large-sized plants in which biomass is collected in a larger area.

4. Results

Table 3 shows the EEE Cost for the field phase of the agro-energy chain, with an overall price (selling price is more than public grants) equal to 109.5 and 105.6 €/t_{dm}, respectively, for SRF and MRF, and the energy crop allows the farmer a gain of 18,84 €/t_{dm} (265 €/ha·year) for poplar plantations with 2-year cutting times and of 46.1 €/t_{dm} (829 €/ha·year) for those with 5-year cutting time. Consequently, the ratio between economic cost and revenue is equal to 1,18 for SRF and 1,77 for MRF. The energetic aspect of the production cost represents approximately the 6.6% (for SRF) and the 4.3% (for MRF) of the LHV (MJ/kg_{wb}) of the biomass.

Table 1: Machines and mechanization planning on surface intended for SRC (SRF and MRF) and for traditional crops [4, 5]

OPERATION	MACHINE		COOPLING TYPE, MACHINE SIZE	WORKING YEARS [TIMES PER YEAR]		
				SRF	MRF	MAIZE
Pre-planting Fertilization	Manure Spreader	Agricultural Machinery Fleet	TP, 10 t, 10 m^3	1 [1]	1 [1]	From 1 to 10 [1]
Primary soil cultivation	Plough	Agricultural Machinery Fleet	P, double-shovel	1 [1]	1 [1]	From 1 to 10 [1]
Secondary soil cultivation	Rotary harrow	Agricultural Machinery Fleet	PP, 2,40 m	1 [1]	1 [1]	From 1 to 10 [1]
Transplanting	Planting Machine	Contractor	T, bifilar	1 [1]	1 [1]	-
Chemical Weed Control	Spraying machine	Agricultural Machinery Fleet	PP, 15 m, 1000 dm^3	1-3-5-7-9 [1]	1-6 [2] 2-7 [1]	From 1 to 10 [1]
Pests and Diseases Management	Spraying machine	Agricultural Machinery Fleet	PP, 15 m, 1000 dm^3	1-3-5-7-9 [1]	1-2-6-7 [1]	
Cover Fertilization	Fertilizer Spreader	Agricultural Machinery Fleet	PP, 1500 dm^3	3-5-7-9 [1]	6 [1]	From 1 to 10 [1]
Mechanical Weed Control	Rotary harrow	Agricultural Machinery Fleet	PP, 2,40 m	1-3-5-7-9 [1]	1-2-6-7 [2] 3-8 [1]	-
Harvest Operations	Harvester, Chipper, Trailer	Contractor	SPM, T, PP	2-4-6-8-10 [1]	5-10 [1]	-
Soil Final Restoration	Hoeing Machine	Contractor	P, 1,2 m	10 [1]	10 [1]	-

Table 4 shows the EEE cost for transport phase of the chain. Since the characteristics of the biomass are supposed to be unvaried for chips from both SRF and from MRF, the EEE cost for this phase is the same for both types of poplar plantations.

Summing the EEE cost for field and transport phase is possible to calculate the EEE cost for the biomass at the plant mouth of energetic conversion. This cost depends on the cutting time of the plantation as well as on the transport distance between the farm and the conversion plant.

After the field and transport phase, the EEE cost for the SRF plantations is equal to 96.8 €/t$_{dm}$, 499.1 MJ/t$_{dm}$, and 65.5 kg CO$_2$eq/t$_{dm}$ if the distance between the farm and the conversion plant is 70 km, while for longer distances (450 km), this cost is significantly higher and reaches 151.7 €/t$_{dm}$, 1058.9 MJ/t$_{dm}$, and 120.8 kgCO$_2$eq/t$_{dm}$. In the case of medium rotation forestry, for the shorter distance, the EEE cost is 63.3 €/t$_{dm}$, 343,1 MJ/t$_{dm}$, and 44.2 kgCO$_2$eq/t$_{dm}$ and equal to 118.5 €/t$_{dm}$, 902.9 MJ/t$_{dm}$, 99.4 kgCO$_2$eq/t$_{dm}$ when the distance is 450 km. At the end of the transport operations, the energetic cost represents a variable share of the LHV (MJ/kg$_{wb}$) of the biomass: 15,3% for SRF in which the biomass is transported for a long distance, 7.2% for SRF when the product is destined to supply small plants, and 13.0% (d = 450 km) and 4.9% (d = 70 km) if the wood chips come from MRF.

Table 2: Production factors utilized within simulation on SRF and MRF [4, 5]

PRODUCTION FACTORS	**QUANTITY**		
	Unit	**SRF**	**MRF**
Planting material	cuttings/ha plant rod/ha	5560	1150
Organic Manure	t/ha	50	50
N fertilizer (covering)	kg/ha	320	200
Herbicide	kg/ha	20	12
Pesticide (pyrethroid)	kg/ha	10	4
Water	m^3/ha	2000	1600

Table 3: Field phase; EEE costs for two different cutting time

EEE COSTS FIELD PHASE	**Unit**	**SRF**	**MRF**
Economic	€/t_{dm}	92,4	59,5
Energetic	MJ/t_{dm}	456	301
Environmental	kg CO_2eq/t_{dm}	61,5	40,1

Table 4: Transport phase; EEE costs for two different distances

EEE COSTS TRANSPORT PHASE	**Unit**	**Chip Wood**	
		d = 70 km	d = 450 km
Economic	€/t_{dm}	4,13	59,0
Energetic	MJ/t_{dm}	42,1	601,9
Environmental	kg CO_2eq/t_{dm}	4,15	59,1

Comprehensive Sustainability is expressed by all 3 results obtained by the simulation. The smaller the area of the triangle identified by the three costs (economic, energetic, and environmental), the higher the energy-crop sustainability. Figure 1 shows the EEE cost for the different technical solutions studied; in blue are the results for SRF, while MRF results are shown in orange. Regarding the two different transport distances, on the left are shown the results for d = 70 km, and on the right are shown the results for d = 450 km.

The *Global Sustainability Index*, represented by the triangular area, can be calculated by means of Heron's formula. The highest is the GSI, and the lower is the global sustainability of the solution studied. The GSI is 348 and 838 for SRF, while it reaches 617 and 191 for MRF, for short and long transport distances, respectively.

5. Discussion and Conclusions

In the near future, the role that renewable energies can play in order to achieve the ambitious objectives fixed by the European Union is decisive; among the renewable energies, the agro-energy chains appear to be one of the most promising. On the other hand, the development of energy production in agriculture is linked strongly to the possibility that farmers can obtain satisfactory economic results. For this reason, in recent years, several kinds of public grants have been foreseen in order to induce farmers to plant energy crops. In addition to the economic aspects, the energetic and environmental issues also must be taken into account in order to avoid the diffusion of agro-energy chains that are effective from a monetary point of view but not functional regarding the others two topics that determine the Global Sustainability of the chain.

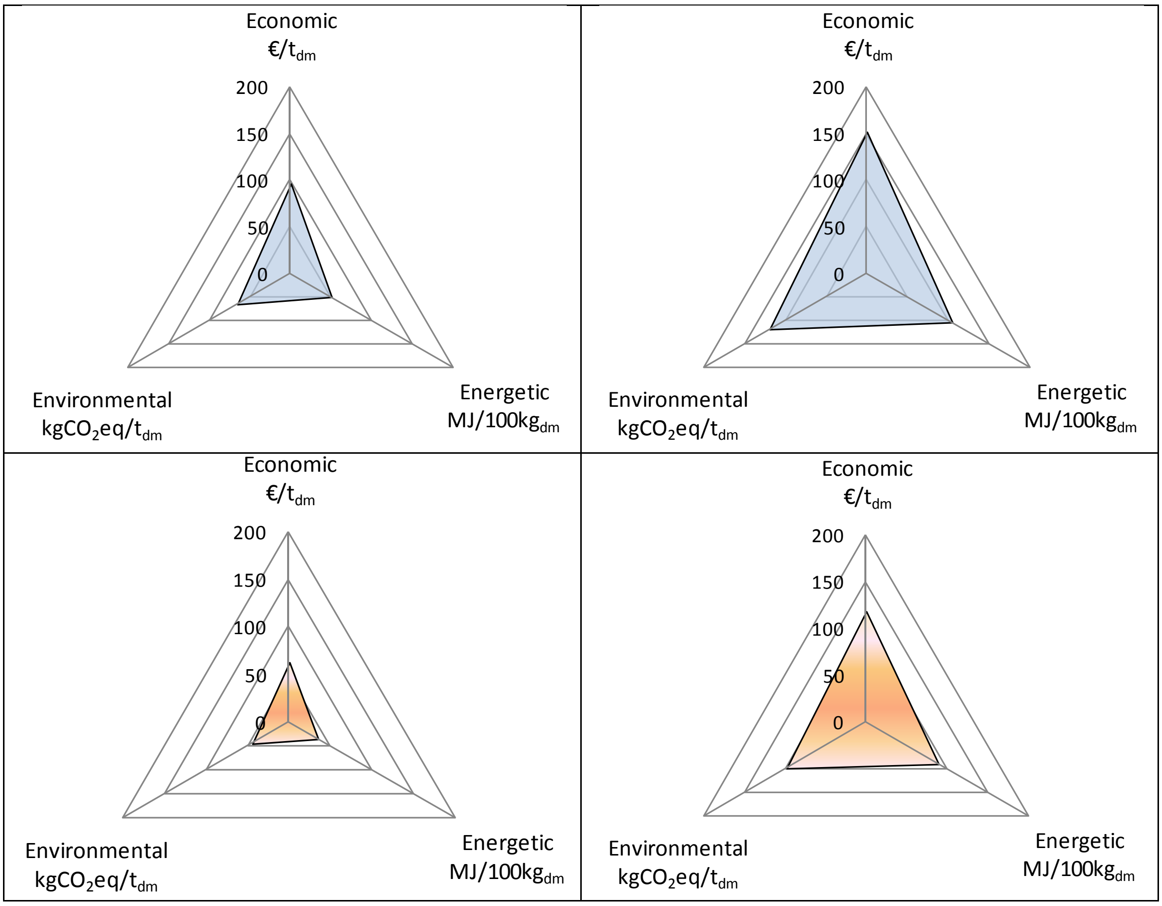

Figure 1 – EEE cost at plant mouth for the different scenarios analyzed

In Italy, good results have been achieved for wood energy crops, and today, a large area of SRC is cultivated. Nevertheless, two different kinds of poplar plantations are still practiced: SRF with short intervals between two harvests and MRF in which the harvests are separated by at least 4 to 5 years. Considering that the production and the transport to the conversion plants are the more energy intensive operations of the agro-energy chains, the present work is focused on the analysis of the economic, energetic, and environmental performances of these phases of the chains, comparing the results between SRF and MRF.

The analysis has been carried out to show that MRF, as compared with SRF, allows farmers to reach better results on all three levels studied. For the MRF, the higher yield and the lower level of input used during the crop cycle (such as nitrogen fertilization) allow the farmer to obtain a better EEE Cost and, consequently, a higher global sustainability.

Regarding transport, the distance between farm and conversion plant must be evaluated carefully; the EEE cost at plant mouth is significantly higher if the biomass transformation takes place in big plants far from the production area. In this analysis, we supposed that the lorry never travels empty, thus the reduction of the transport cost can be achieved only by the reduction of the distance. Accordingly, the development of several small and medium plants is preferable as opposed to the growth of a few large plants with a very large supply area.

The developed software is a useful tool in order to assess the EEE performances of the different agro-energy chains. Implementation of the last phase of the chains (conversion operations) will allow us to determine not only the agro-energy chain costs but also the output and benefits for the three levels considered.

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Integral analysis of feedstocks and technologies for Biodiesel production in tropical and subtropical countries

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Abstract: In this work different methodologies from process engineering based on conceptual design and process simulation with ASPEN PLUS, life cycle assessment and waste reduction algorithm are used for energy, and environmental impact assessment of 5 different feedstocks (Palm, Jatropha, Microalgae, Tallow, Waste Cooking Oil) using 3 different technological configurations from industry, such processes with acid catalysis, basic catalysis and cogeneration, at Colombian and Peruvian context. It was found how productivities for process catalyzed with NaOH are comparatively higher (1.007-1.014 kg of Biodiesel per kg of Crude Oil), than those catalyzed with H_2SO_4 (0.845-0.949 kg of Biodiesel per kg of Crude Oil). The Production costs for basic catalyzed processes (USD/L 0.408-0.505) were higher than those for acid catalyzed processes (USD/L 0.219-0.257). The PEI (Potential Environmental Impact) generated for basic catalyzed, had a PEI per kg between -0.078 and -0.033, while acid catalyzed -0.031 and -0.025. Finally LCA for jatropha and palm oil process, evidence Ecosystem Quality damage, a Resources damage, a Human Health damage lower for Jatropha oil in comparison to Palm oil. The Jatropha oil, in a basic catalyzed configuration with energy cogeneration is the best alternative of process, environmental and economics by biodiesel production.

Keywords: *Integral Analysis, Biodiesel, WAR algorithm, LCA, Economic Evaluation*

1. Introduction

Biodiesel is produced from various fat and oils with vegetable, animal or algae origin. These Feedstocks (mainly composed by triglycerides), through transesterification reaction with short chain alcohols and in presence of catalyst, yields to fatty alkyl esters and glycerol as byproduct [1]. Almost 95% of vegetable oils used in biodiesel production are edible (palm, soybean, rapeseed oils). Different positive characteristics are related to Biodiesel: improvement of the environment, reduction of foreign oil imports, increase in rural job and energy self-sufficiency in rural areas. However, not all the above mentioned advantages are reached for all biodiesel feedstocks. Edible crops have food competition; possibly leading to food shortages and increase in their prices. Moreover, an expansion of these crops could require monoculture plantation, affecting water resources and biodiversity. Tropical and subtropical countries are called to be the future world suppliers of feedstocks and biodiesel given the high productivity in crops and algae. Most of these countries are involved in a difficult decision of what kind of feedstock should be used, and then the policies to be developed for encouraging new projects, with new feedstocks. Non-edible oils (jatropha and microalgae oil), allows the employment at massive scale of agricultural/degraded/waste lands, preserving most productive lands for food production. Animal fat (tallow oil) and waste cooking oil are valuable alternatives due their low market prices and availability. Additionally, aiming to increase competitiveness of oilseed based biodiesel plants is an actual trend to use cogeneration plants. Last allows the satisfaction of local heat and power requirements, while surplus electricity is sold to central grid [2]. In this work different methodologies from conceptual design and process simulation with ASPEN PLUS, life cycle assessment and waste reduction algorithm are used for energy, and environmental impact investigation of 5 different feedstocks using 3 different technological configurations from industry, such as process with acid catalysis, basic catalysis and cogeneration. The study was developed in the framework of two countries Colombia and Peru. As a result, two feedstocks and one technological configuration are defined as the more convenient for biodiesel production in these countries.

2. Feedstocks for biodiesel production

In this work five feedstocks for biodiesel production, are analyzed, which can be potentially used in tropical and subtropical countries. i) **Oil Palm,** is one of the largest supply of edible oil in the world, extended throughout tropics, among major producers are Malaysia, Indonesia and Colombia with 83% of global production [3]. It is a high yield crop that requires small areas to be cultivated. ii) **Jatropha Curcas**, a Native American tropical crop, is a small tree belonging to the family of *Euphorbiaceae*. This crop is highly resistant plant capable of surviving in fallowed agricultural lands and low to high rainfall areas, being easily cultivated with little effort to sustain [4]. iii) **Microalgae**, is a promising feedstock, due to its ability to accumulate lipids and their high photosynthetic yields. Those used in biodiesel production are comprised by up to 40% of overall mass by fatty acids, among its representative species are: *Chlorella*, *Spirulina maxima,* and *Nannochloropsis sp.* They are fast growers in aquatic habitats, under autotrophic and heterotrophic conditions [5]. iv) **Waste oil**, includes residues from frying oils, soap stocks, yellow and brown greases, obtained from restaurants, hotels and industries; Their Free fatty acid content range between 10 and 25%, as result of frying process where heating in presence of air and light increase viscosity and specific heat, also changing surface tension, color and tendency to fat formation. This feature makes necessary a pretreatment stage before be converted in biodiesel [6]. Finally, v) **Tallow oil**, is a term referred to those fat and greases obtained in slaughter processing facilities from animals. Human consumption of tallow oil is low due its effect on health, finding its main use in the soap industry. However, when its market is overloaded, this oil is incinerated or disposed in landfills [7]. Because of that its use as biodiesel feedstock, is an attractive alternative due its easy availability and historical low prices.

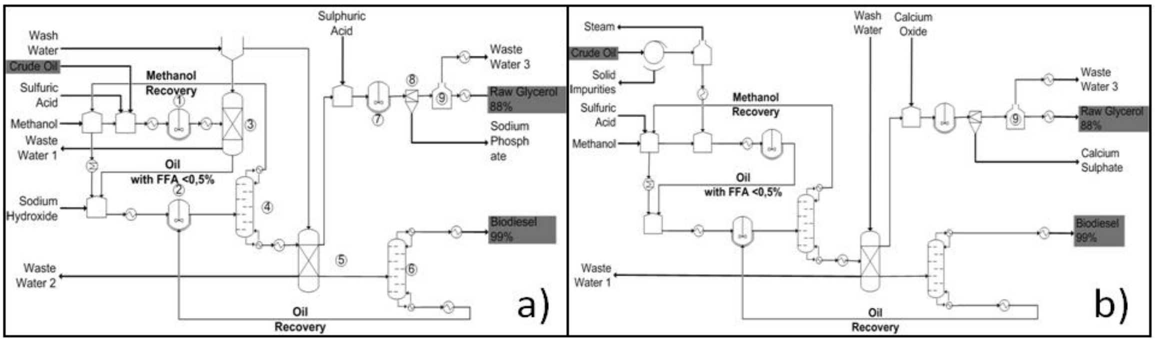

Fig. 1. Process flow diagram for Biodiesel production Using: a) Acid Catalysis; b) Basic Catalysis.

3. Technologies for Biodiesel Production

Biodiesel production can be described, in a general way, by three main sequential stages: i) **Pretreatment,** where undesired elements content in feedstock oil are withdraw. Particles, colloidal mater, pigment, extraction residues and other impurities can be removed using filtration. When water content (>0,06%) and free fatty acid (FFA) content (>4%), a saponification reaction can be induced, generating a gel soap instead of biodiesel. To avoid this is necessary dry the oil, and eliminate free fatty acids, using: Presterification or neutralization. ii) **Reaction,** in this stage, the oils suffer a transesterification reaction. Methanol is the most extensively used alcohol because its low cost and physical and chemical properties. The main catalysts, employed in transesterification process are: acids (sulphuric, phosphoric) or bases (sodium and potassium hydroxide) [8]. iii) **Separation and Purification**

stage is employed to produce biodiesel with high quality requirements. Biodiesel purification is performed by either of two main routes: 1) separating first esters and glycerin, before recover non c onverted alcohol or 2) using vacuum distillation to separate non c onverted alcohol, using then a decanter to separate glycerin and biodiesel [8]. Obtained biodiesel is then purified, removing excess of alcohol, catalyst, neutralization salts and possible soaps formed. The Selected technology for biodiesel production determines main process variables, such as: reaction time, phase, catalyst, as well as energy consumption (see Fig 1).

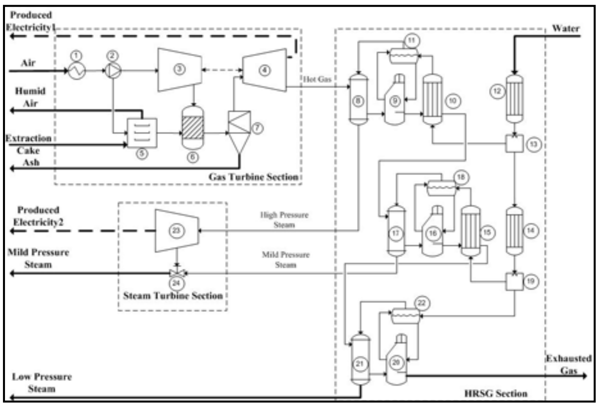

Fig. 2. Process flow diagram for Cogeneration system based on extraction cake residues

Cogeneration plants integrated to biodiesel production facilities usually employs extraction cakes and other biomass residues as fuel in a configuration called biomass fired cogeneration. Combined production of mechanical and thermal energy has remarkable cost and energy savings. Among available technologies for biomass fired cogeneration, the combined cycle gas turbine (CCGT), is considered as the most energy efficient. CCGT configurations are composed by: Gas Turbine, Heat steam recovery generator (HSRG) and Steam Turbine (see Fig. 2) [9].

4. Methodology

The simulations of biodiesel production and heat and power cogeneration were carried out in Aspen Plus 2006.5 (Aspen Technologies Inc., USA). This scheme allows obtaining data of mass and energy balances; as well as, basic engineering estimations of equipment size and its energy consumption. Feedstocks (Palm, Jatropha, Microalgae, Tallow and Waste cooking oils) for biodiesel production, were modeled as a sort of pseudocomponents, created to represent triglycerides and methyl esters; according to Chang and Liu methodology [10]. Conversely, Palm oil cake, jatropha oil cake and microalgae paste were introduced to simulator database as non conventional components according to its elemental and immediate analysis. Physicochemical properties for pseudocomponents, were estimated using the Marrero and Gani Method [11]. UNIFAC Dortmund for liquid phase, Soave Redlich Kwong with the Bosto Mathias modification for the vapor phase; water enthalpy calculated with NBS steam tables, were used as base methods. The Kinetic model for acid and basic catalysis, employed in this work, was reported by Granjo et al. [12], as first order and second order expressions, respectively. Biodiesel simulated process use a same flow rate input of 1000 kg/h, to make a comparison among yields for all processes. Additionally, from these values, was calculated a residue flow rate for palm oil cake, jatropha oil cake and microalgae paste; using it as input for the biomass fired cogeneration system. The economic analysis was performed using Aspen Icarus Process Evaluator package (Aspen Technology, Inc., USA), to calculate a mean cost in US dollar per liter for biodiesel produced with the selected feedstocks. This analysis was performed using the design information provided by Aspen

Plus, under the economic conditions of Colombia (annual interest rate of 17% and tax rate of 33%) and Peru (annual interest rate of 18% and tax rate of 30%). A straight Line depreciation method, at 12 year of analysis period, was considered. For feedstock prices, were employed the international reports from ICIS pricing; while, operative charges such operator and supervisor labor cost were defined for both countries at USD 2.14/h and USD 4.29/h, respectively. Electricity, potable water, low and high steam pressure costs were USD 0.0304/kWh, USD 1.25/m^3, USD 8.18/ton. The environmental impact was assessed with WAR, Waste Reduction algorithm (EPA, USA), to estimate the potential environmental impact (PEI) generated in the biodiesel production process. Considering eight environmental impact categories: Human toxicity potential by ingestion (HTPI), Human toxicity potential by exposure both dermal and inhalation (HTPE), Terrestrial toxicity potential (TTP), Aquatic toxicity potential (ATP), Global warming potential (GWP), Ozone depletion potential (ODP), Photochemical oxidation potential (PCOP), and Acidification potential (AP). The mass flow rate of each component in the process streams is multiplied by its chemical potency; determining its contribution to the potential environmental impact categories [13]. To compare the environmental profiles for all process, total PEI was determined by the sum of all (eight) potential environmental impact categories as follows: $\sum_{i=1}^{n} \propto_i \varphi_i$, where α_i is the weighting factor for potential environmental impact category i, and φ_i represents the potential environmental impact for category i. In this work all of the weighting factors were set equal to 1. Finally, Life cycle assessment was performed for those process with a potential impact in land change use (LCU), such palm and jatropha; using a demo version of SimaPro 7, with Eco-indicator 99 (E) as base method. The LCA study consists of four steps: Defining the goal and scope of the study; making a model of the product life cycle with all the environmental inflows and outflows; understanding the environmental relevance of all the inflows and outflows and finally the interpretation of the study [14].

Table 1. Simulation Results for Biodiesel Production using Basic or Acid Catalysis

	Basic Catalysis			**Acid Catalysis**	
	Palm Oil	**Jatropha Oil**	**Microalgae Oil**	**Tallow Oil**	**Waste Cooking Oil**
Materials (kg/h)					
Crude Oil	1000.00	1000.00	1000.000	1000.00	1000.00
FFA content (% wt)	6%	4%	4%	15%	10%
Water content (% wt)	0%	0%	0%	8%	12%
Methanol	160.21	214.75	207.77	1579.07	1772.44
NaOH	9.40	9.60	9.29	-	-
Water	1400.00	1400.00	1400.00	1250.00	1400.00
H_2SO_4	21.00	21.45	20.75	35.00	41.20
CaO	-	-	-	30.00	29.60
Products (kg/h)					
Biodiesel @>99% wt	1007.46	1009.69	1014.62	949.85	847.63
Glycerol @>88% wt	113.05	117.34	127.33	81.95	82.07
Waste Water	1010.95	942.77	1062.20	2163.03	1836.84
$CaSO_4$	-	-	-	104.51	95.27
Na_2SO_4	10.64	17.03	17.03	-	-

5. Results

In the simulation of biodiesel production for acid and basic catalyzed processes using palm, jatropha, microalgae, tallow and waste cooking oils, as feedstocks (see Table 1), was found how productivities for process catalyzed with NaOH are comparatively higher (1.007-1.014 kg of Biodiesel/kg of Crude Oil), than those catalyzed with H_2SO_4 (0.848-0.949 kg of Biodiesel/kg of Crude Oil). Otherwise, Methanol consumption as well as global energy consumption (heating and electricity) is higher for acid catalyzed process, requiring 1.579-1.772 kg of Methanol/kg of crude oil and heating of 53.389 - 69.112 MW respectively. About process residues, acid catalyzed processes also have higher production rates for waste water (1.863-2.163 kg of Water/kg of crude oil). Simulation results for the biomass fired cogeneration plant using palm oil cake, jatropha oil cake and microalgae paste as fuels (see Table 2), reveals how heating energy production from jatropha cake (31.34 MW) is higher than produced with Microalgae paste (33.82 MW) and palm oil cake (20.61 MW). Consequently, only heating requirements for biodiesel production from jatropha (26.59 MW) are fully satisfied. Biodiesel from palm oil and microalgae oil meet only 68.13% and 74.15%, respectively of its Heating requirements. Regard to electricity, all cogeneration processes cover at 100% biodiesel plant requirements, with a surplus able to be sold. However, among three residues consider, was microalgae paste who cogenerates more electricity (8.34 MW) than jatropha oil cake (7.06 MW) and Palm Oil Cake (4.88 MW).

Table 2. Cogeneration Results for Extraction residues Based Biomass fired cogeneration system

	Jatropha Oil Cake	**Palm Oil Cake**	**Microalgae Oil Paste**
Available Residue [kg/h]	3092	2304	3964
Calorific Value [MJ/kg]	15.77	12.32	14.21
Total Cogenerated Heating [MW]	31.34	20.61	33.83
Total Cogenerated Electricity [MW]	7.66	4.88	8.34

Table 3. Economic Evaluation Results for Biodiesel Production using Basic Catalysis

	Jatropha Oil	**Palm Oil**	**Microalgae Oil**	**Waste Cooking Oil**	**Tallow Oil**
	USD/L	USD/L	USD/L	USD/L	USD/L
Raw material Cost	0.325	0.426	4.646	0.139	0.186
Total utilities Cost	0.022	0.021	0.022	0.052	0.044
Operating Labor	0.008	0.008	0.008	0.009	0.008
Maintenance	0.005	0.004	0.005	0.002	0.002
Operating Charges	0.002	0.002	0.002	0.002	0.002
Plant Overhead	0.006	0.006	0.006	0.006	0.005
General and Administrative Cost	0.039	0.037	0.038	0.008	0.010
Subtotal Cost	0.408	0.505	4.727	0.219	0.257
Credit by electricity selling	- 0.252	- 0.168	- 0.278	0.000	0.000
Total Cost with Cogeneration	0.157	0.337	4.449	0.219	0.257

Results of economic evaluation for biodiesel production under Colombian and Peruvian contexts were quite similar and because of that, in table 3, average results are presented. As highlights results, Raw material cost for basic catalyzed processes (USD 0.325-4.646/L) were higher than those for acid catalyzed processes (USD 0.139-0.186/L). Otherwise, Utilities costs for acid catalyzed processes (USD 0.044-0.052/L) were higher than basic catalyzed process (USD 0.021-0.022/L). Remaining cost, for both processes were similar. As result, Production costs for basic catalyzed processes (USD 0.408-0.505/L) were higher than those for acid catalyzed processes (USD 0.219-0.257/L). However, considering Potential income for electricity selling at average price between Colombia and Peru, can be seen how total production cost for jatropha, palm and microalgae biodiesels were reduced to 0.157 USD/L, 0.337 USD/L and 4.449 USD/L, respectively.

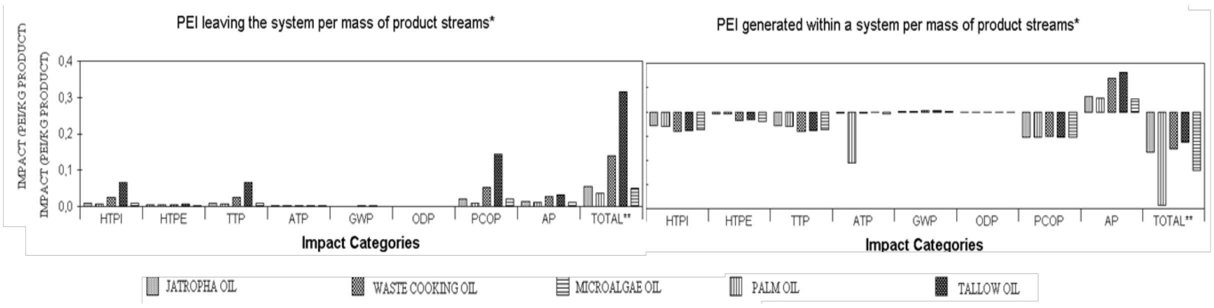

Fig. 3. PEI (Potential Environmental Impact) Analysis for Biodiesel Production from different feedstocks.

Regarding to environmental analysis; WAR analysis results of 5 biodiesel feedstocks, stated analyzing by process, how basic catalyzed had a PEI per kg of product ranging between 0.037 and 5.518e-2, while acid catalyzed catalysis between 0.139 and 0.317 for emissions output. Furthermore, when these feedstocks were analyzed by emission generation, basic catalyzed raw materials, had a PEI per kg between -0.078 and -0.033, while acid catalyzed -0.031 and -0.025 (see Fig. 3). Finally LCA analysis performed with SimaPro 7, for jatropha and palm oil process, evidence a Ecosystem Quality damage of 0.062 and 0.087 PDF*m^2*yr. Besides of a Resources damage of 1.07 and 1.49 MJ surplus, while Human Health damage was of 1.96e-6 y 2.73e-6 Daly, respectively.

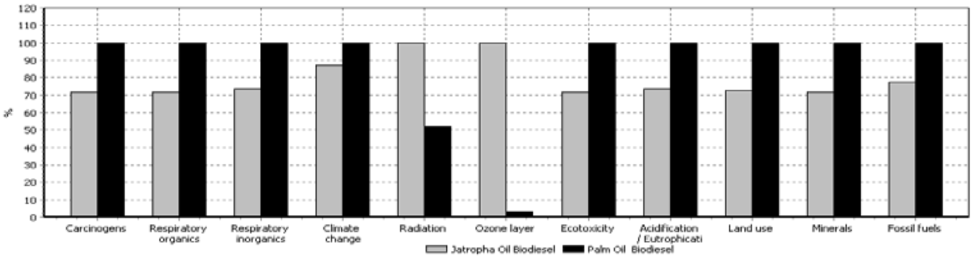

Fig. 4. LCA for Biodiesel Production from Jatropha oil and Palm oil

6. Discussion and Conclusions

In this work, the obtained results reveal how with selected five feedstocks is possible to obtain high quality biodiesel (>99 wt); besides, raw glycerol (88%wt). Among results for chemical processes simulation, can be seen how basic catalyzed processes have higher biodiesel yields (74-78%), than acid catalyzed ones (54-63%), with the consequent reduction in the total biodiesel produced. These results are lower compared with values between 90-95% reported from biodiesel simulations, on literature [15]. This fact can be explained by the lower quality of feedstocks considered, especially tallow and waste cooking oil, where a high FFA content and impurities presence; which, although increase the simulation quality, reduces the amount of initial reactant available for transesterification reaction, reducing also biodiesel produced.

Regard to cogeneration results, these gave an advantage to basic catalyzed processes due to the possibility of employ its extraction residues to generate heat and power. The bigger amount of heating potential was released by jatropha oil cake; while the higher power potential by microalgae oil paste. This result can be partially explained by the high calorific value and available flow of these residues, which increase its potential to generate steam and consequently produce heat and power (see Table 2). Jatropha oil cake results were the best, due its capacity to meet heating requirements of the biodiesel plant generating also an important amount of electricity able to be selling to central grid.

Economic evaluation of biodiesel production process, without cogeneration, shows how production cost for basic catalyzed processes initially were higher than acid catalyzed, despite high methanol consumption of this last. These results were agreed with those reported on literature where biodiesel production cost range between USD $ 0.30 – 0.6/L [16]. The main component of this production cost was the raw material price, which is higher for vegetable oils (jatropha and palm) than for residual oils (waste cooking and tallow), explaining their lower production cost. However, when a cogeneration scheme is included for processes based on vegetable oils, which can employs its extraction residues as fuel in a biomass fired scheme, the total production cost of basic catalyzed process is reduced (see Table 3). Apart mention, deserves microalgae oil, which price as feedstock still today is higher, mainly due the high energy consumption in its processing, either in open pounds or bioreactors; in the future is expected is expected a reduction in its price using better microalgae oil production technologies.

The Environmental analysis results, reveals with WAR algorithm, how despite all processes had a positive PEI, still all of them can generate acid rain because its positive acidification potential produced by the sulphuric acid. In these sense, acid catalyzed processes had more polluting waste streams than basic catalyzed. Particularly, output emissions from process waste streams for waste cooking oil, had the more positive PEI among all simulated processes. This effect could be explained by the substances contained in its process residues, which had a high degree of potential PCOP influenced by acid catalysis, increasing the total values. Otherwise, palm and jatropha oils had the comparatively lesser PEI, revealing them as environmentally friendly feedstocks; because, they are converted to high value products in a cleaner process (basic catalysis) being more environmentally favorable, reducing significantly the aquatic toxicity potential. Regard to LCA analysis performed to jatropha and palm oils as best WAR results, was found that most promising feedstock was the jatropha oil because its comparatively low land use than the palm and its possibility of growth in fallow agricultural lands. Also, its impact on climate change and emissions were lower than palm at every stage, from cultivation to waste scenarios.

In conclusion, the more convenient configuration for biodiesel production in tropical and subtropical countries is employ jatropha oil in a basic catalyzed scheme, integrated to a cogeneration plant fired with jatropha oil cake. This configuration is able to produce high rates of biodiesel with the lower production cost, improved by electricity selling. Also, this configuration proves, be the most environmentally friendly with lesser potential emissions and climate change effect, as well as reduced land use by its ability to be growth in marginal lands.

Acknowledgements

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Evaluation of the factors that affect the lignin content in the reed canarygrass (*Phalaris arundinacea* L.) in Latvia

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Abstract: In the production of granules from plants the cohesive substance lignin has a great importance, as it holds the granule together and does not allow it to disintegrate. The objective of this research was to evaluate the influencing factors of lignin content in reed canarygrass (*Phalaris arundinacea* L.) crop yield. In this research the varieties of reed canarygrass 'Marathon' and 'Bamse' were analysed for yields of first and second year. The lignin content of the samples was established by Classon's method. Arsenic (As), Cadmium (Cd), and Lead (Pb) and other chemical elements were established in the reed canarygrass samples with the spectrometer Optima 2100DV. The reed canarygrass second year crop yield was 3-4 times greater than the first year crop yield. A significantly correlation ($p<0.05$) was established in the first crop yield October samples between lignin and natrium (Na). Some correlation relationships are contradictory, which confirms that within the plant growth period the meteorological conditions are of great importance. Analysing the determining factors of lignin content it can be seen that they were influenced by the interaction of various factors - the sowing and growing period, the variety and the N-fertilizer rate application.

Keywords: *Ashes, Heavy Metal, Lignin, N-fertilizer Rate, Phalaris arundinacea L., Yield*

Nomenclature

A	*area of the plots*	m^2
R	*rainfall*	*mm*
H	*plant height*	*m*
L	*lignin content*	$g \cdot kg^{-1}$
T	*mean temperature*	*K*
DM	*dry matter*	$t \cdot ha^{-1}$
N	*nitrogen fertilizer rate*	$kg \cdot ha^{-1}$
Hv	*heating value*	$MJ \cdot kg^{-1} DM$

1. Introduction

The most common natural polymer is cellulose, which with lignin and hemicellulose are the main components of plants (Gosselink et al., 2004; Lignin…, 2009). Cellulose pulp is considered as the first depositary of the sun's energy (Gosselink et al., 2004). In nature lignin is very resistant to degradation, as it has strong chemical bonds (McCrady, 1991).

Lignin first appeared hundreds of millions years ago, when plants started to grow vertically upwards. Lignin can be found in all caulescent plants, mainly in the cells and cellwalls. It regulates the transportation of liquid in plant cells (partly strengthening the cell walls, partly regulating the flow of liquid) also it a llows plants to grow longer to better compete for sunlight (McCrady,1991; Rouhi, 2000; Lignin…, 2009).

Lignin which is found in a natural state (protolignin) is of various types, which are common to deciduous trees, conifer trees and stemgrasses. Each type has a lot of variations; lignin can vary with each variety, each plant group, and at the same time even within one cell, and also according to the age of the plant (McCrady, 1991; Zaķis, 2008; Lignin…, 2009).

The technical lignin is used as a bonding material, a surfactant, growth enhancer, a supplementary substance for composite materials and other uses (Skudra et al., 2010). Up to now only 2% of lignin had been used in cellulose and paper production (Gosselink et al., 2004). Products from lignin could be used to replace fossil resources (Gosselink et al., 2004). Also it must be noted, that low lignin content helps animals digest fodder. If the biosynthesis of lignin is complete, then the cell dies (Rouhi, 2000).

Today there are many studies concerning lignin as a by-product of wood-pulp processing. In Latvia it is traditional to produce energy from forestry products, but due to the sharp increase in price for fossil energy, it has become profitable to produce energy from agricultural biomass production. Reed canary grass is suitable for the Latvian agricultural climatic and growth conditions and can be used as a local resource for obtaining renewable energy.

Lignin is used variously, for instance in the production of materials (polymer, glue) and specific chemical substances (concrete additives, emulsifiers, binding materials) (Gosselink et al., 2004). In granule production chemical additives are not desirable (glue, lacquer, etc.) therefore the binding material lignin is important, which holds the granule together and does not allow it to disintegrate. Lignin improves the thermochemical energy transformation effectiveness (Boateng et al., 2006).

The objective of this research: to evaluate the influencing factors of lignin content in reed canarygrass (*Phalaris arundinacea* L.) crop yield.

2. Methodology

2.1. Field trials

The object of the research is reed canarygrass (*Phalaris arundinacea* L.). Three repeat experiments in the field with reed canarygrass varieties 'Marathon' and 'Bamse' were carried out in sod-podzolic loamy soil (the organic content of the soil - 5.2%, pH KCl - 5.8, P_2O_5 - 20 $mg \cdot kg^{-1}$, and K_2O - 90 $mg \cdot kg^{-1}$ of the soil).

The area of the plots was 16 m^2, the location of the plots was randomised. The reed canarygrass was sown after bare follow. Before sowing a complex fertiliser was applied N:P:K - 5:10:25 - 400 $kg \cdot ha^{-1}$. The nitrogen supplementary fertiliser rates: N0 - control, treatments - N30, N60, N90 $kg \cdot ha^{-1}$. Reed canarygrass variety 'Marathon' was sown on the 12th August in 2008 (henceforth 'Marathon' 08) and varieties "Marathon' and 'Bamse' - on 29th April in 2009 (henceforth 'Marathon' 09 and 'Bamse' 09). Nitrogen (N) supplementary fertiliser was given to 'Marathon' 08 on the 20th May 2009, and on the 22nd July 2009 for 'Marathon' 09 and 'Bamse' 09. On the 13th April 2010 the reed canarygrass plant growth was renewed. N fertiliser (ammonium nitrate) was applied at 21st April 2010.

The plant length was determined for five plants on each repeat occasion (for all plant stalks). The reed canarygrass samples were taken on the 12th October 2009 and the 4th April, 7th September, 6th October, 7th November 2010. The dry matter (DM) samples were taken from 0.25 m^2 areas on three occasions on the 12th October 2009, and the 4th April, 6th October 2010.

2.2. Laboratory work

Arsenic (As), cadmium (Cd), lead (Pb), titanium (Ti), potassium (K), calcium (Ca), magnesium (Mg), sodium (Na) and silicon (Si) concentrations in the reed canarygrass samples were established with the inductively coupled plasma optical emission spectrometer Perkin Elmer Optima 2100 DV. The heating value in the samples was established with the calorimeter IKA C 5003. The ash content (three replications) was established with the accelerated standard method. Lignin content (three replications) in samples was determined using the method of Classon (Zaķis, 2008).

2.3. Meteorological conditions

The meteorological conditions were different in both trial years (Fig. 1.) The meteorological conditions for agriculture during 2009 the plant growth period had a significant deficit in rainfall. The temperature was in compliance with the long term yearly long-term average. In the winter of 2009/2010 snow was observed to be greater and the temperature was lower than the long term yearly long-term average.

On the 23rd and 24th of April 2010 there was snow and hail. The plant growth period in 2010 was characterized by higher temperatures and a lack of precipitation in April, July, August and September.

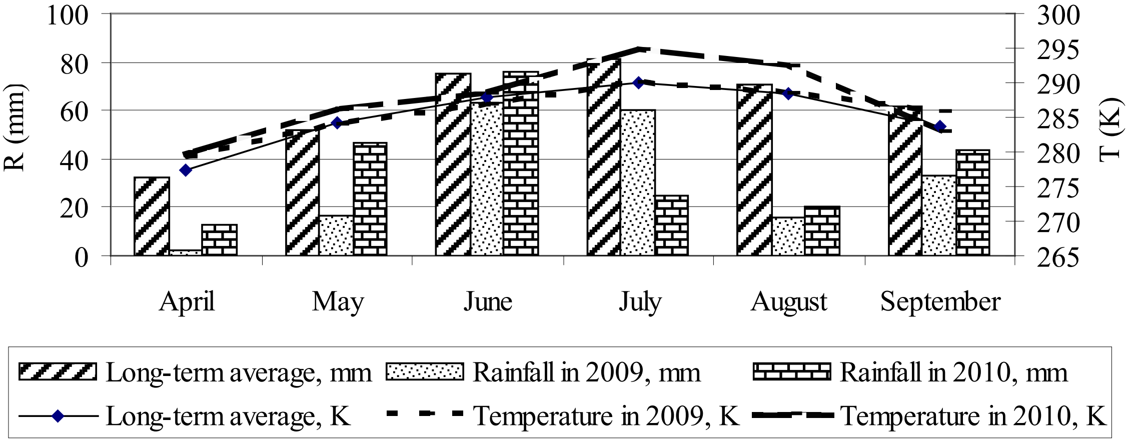

Fig. 1. Mean air temperature and sum of precipitation in 2009 and 2010 growing period.

2.4. Data analysis

The trial data were processed using correlation and variance analyses of two and three factors (ANOVA) and descriptive statistics. The means are presented with their LSD test. Representative average samples of the indicators were used in the calculations.

3. Results

The reed canary grass varieties sown in 2009, had a crop yield 3 - 4 times greater in the following year compared to the first year crop, but the 2008 sowing only produced a 2 times greater yield (Table 1). Two two-factor variance calculations showed, that the variety 'Marathon' had its crop yield for October 2010 influenced ($p<0.05$) by the sowing period ($\eta=62.5\%$) and N fertiliser rates($\eta=19.8\%$), but for both varieties 'Marathon' and 'Bamse' a significantly influence ($p<0.05$) was established for the variety($\eta=70.7\%$) and N fertiliser rates($\eta=10.8\%$). 'Marathon' 09 in the 2010 plant growth period grew three times longer compared to the year 2009, which was most influenced by N fertiliser rates ($p<0.05$).

Table 1. Reed canarygrass dry matter yield and plant length in the second crop year.

Varieties Sowing time	Fertilizer rate ($kg \cdot ha^{-1}$)	Dry matter, ($t \cdot ha^{-1}$)	Increase in comparison to the 2009 October crop yield (%)	Increase in comparison to the 2009 April crop yield (%)	Plant height (m)
‘Bamse’	N0	9.80	437	456	1.548
29th April in 2009	N30	10.25	420	465	1.515
	N60	10.27	370	465	1.533
	N90	11.79	390	546	1.452
‘Marathon’	N0	8.61	424	620	1.453
29th April in 2009	N30	8.94	422	493	1.566
	N60	8.87	394	406	1.527
	N90	8.57	371	384	1.485
‘Marathon’	N0	8.98	196	201	1.443
12th August in 2008	N30	10.18	218	220	1.566
	N60	10.77	227	230	1.590
	N90	10.45	216	232	1.578
$\text{LSD}_{0.05\text{varieties}}$		0.19			0.024
$\text{LSD}_{0.05\text{sowing time}}$		0.18			0.036

A fundamental correlation ($p<0.05$) was established for the samples from the October first year crop between lignin and natrium (Na) (Fig. 2). During the investigation the significantly relationship ($p<0.05$) between the content of lignin and content of heavy metals in the reed canary grass plants was not established. Revealed a few trends ($p>0.05$), when increase lignin content in plants, decreases amount of Ca, Cd, but the amount of Si increase in plants.

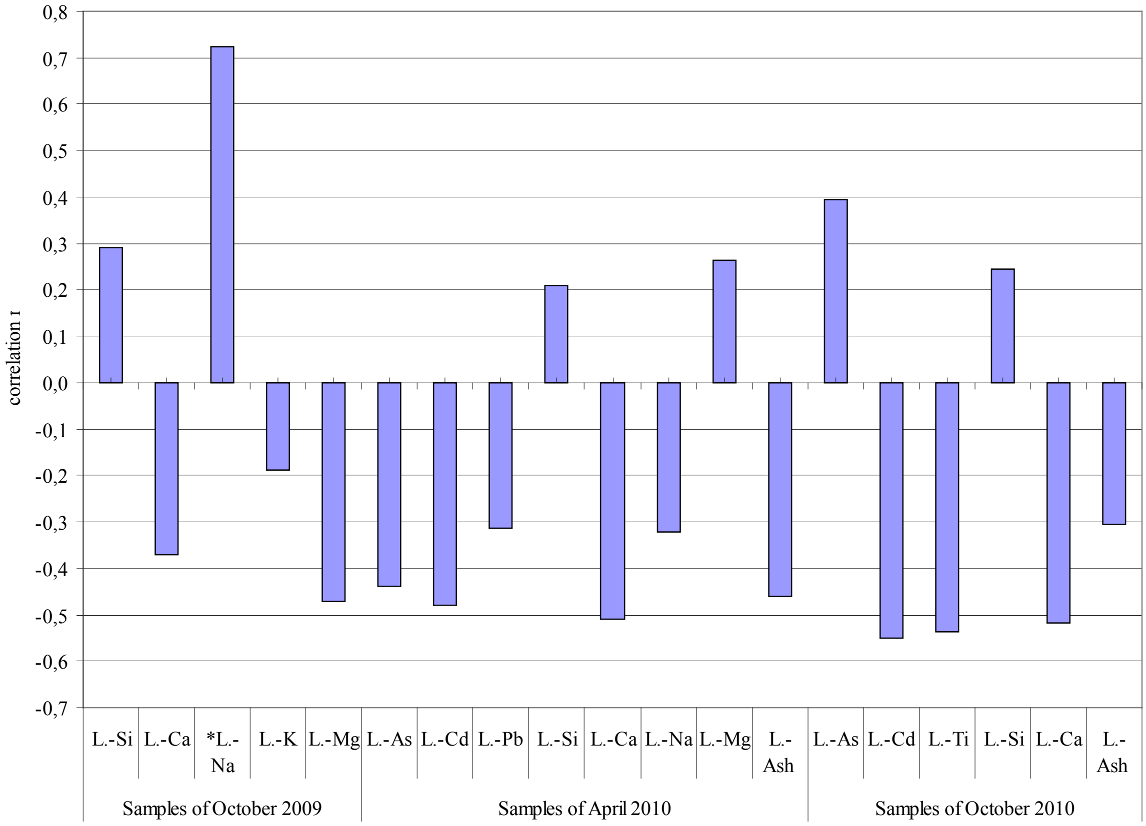

*Fig. 2. Relationship between lignin content (L.) and content of the metals in reed canary grass plants: *(p<0.05).*

Regression analysis for the samples taken in autumn 2010 shows that between lignin (y) and ash (x) content there is a significant connection ($n=36$; $p=0.0036<0.05$) which means, that between these indicators there is a linear connection.

The lignin content in the October samples from the 1st year crop yield was 140 - 210 $g \cdot kg^{-1}$, for the April samples it was 200 - 270 $g \cdot kg^{-1}$, but in the 2nd year crop yield it was from 179 $g \cdot kg^{-1}$ to 269 $g \cdot kg^{-1}$ (Fig. 3). Taking two 3-factor dispersion calculations, it can be seen, that the period when the samples are taken ($\eta=70.1\%$) and the amount of the N fertiliser rate ($\eta=14.7\%$) are of significant importance ($p<0.05$), but the sowing period ($\eta=0.6\%$) and the chosen variety ($\eta=3.9\%$) have no significant importance. The research has brought up contradictory results; in the 2009 sown varieties had the smallest lignin content using N fertiliser rate N30 $kg \cdot ha^{-1}$, but the lignin content was the largest for the 2008 sown variety 'Marathon', using N fertiliser rate N30 $kg \cdot ha^{-1}$. The polynomial equation shows lignin content depending on the sampling time (Fig. 3).

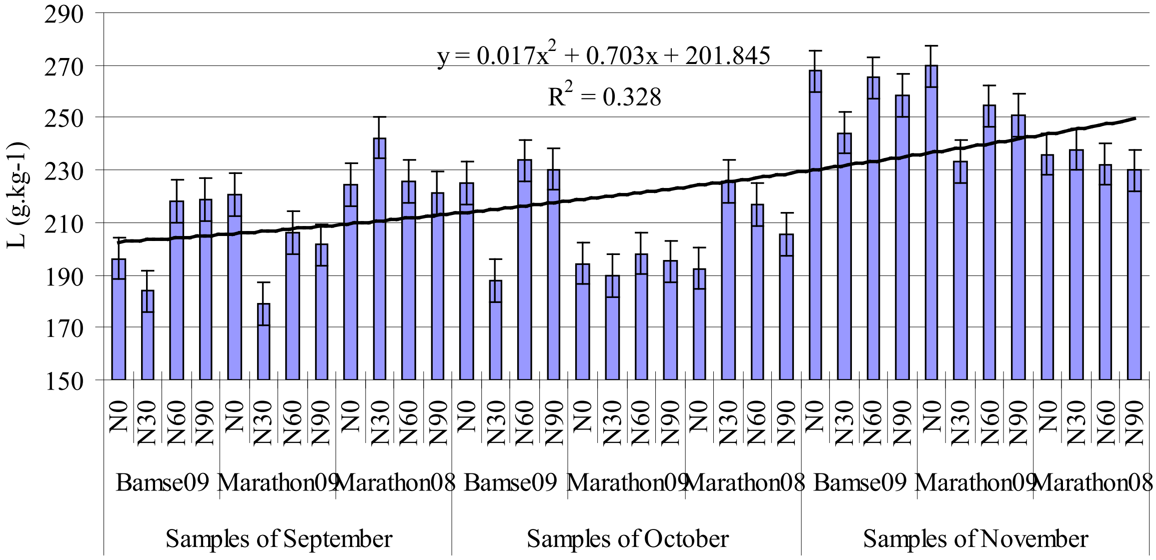

Fig. 3. Lignin content in reed canary grass 2^{nd} year swards in 2010 (g·kg^{-1}).

Heating value for the reed canary grass samples for the variable N90 varied from 17.16 to 18.13 MJ·ha^{-1} DM (Fig.4). A significant correlation between reed canary grass lignin content and the heating value was not established.

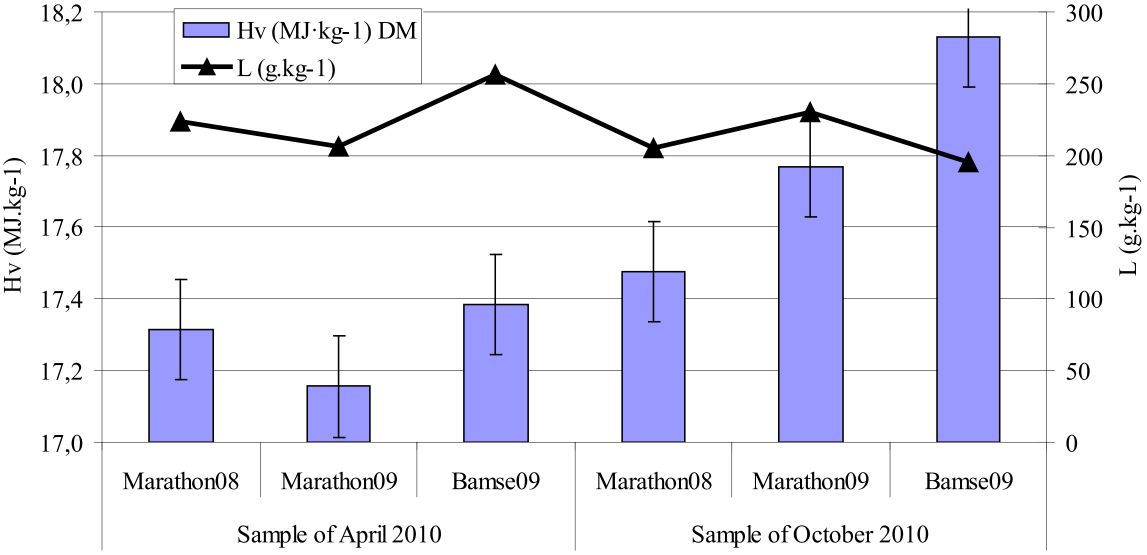

Fig. 4. Reed canary grass sample heating value and lignin content (N 90 kg·ha^{-1}).

The study will continue, because in this article is only the first and the second year yields lignin content analysis, which can vary when reed canarygrass seed get older, because now there are differences in quality indicators between the first and the second year samples.

4. Discussion and conclusion

An extended period with a precipitation deficit and air temperature above the yearly long-term average, get a negative impact on reed canarygrass productiveness during the 2010 plant growth period. Comparing lignin content correlations in relationship with various indicators for the reed canarygrass crop yield for the 1st year, it can be seen, that for the samples these relationships are not fundamental. Data show, that great importance should be attached to the chemical composition of the plant, which can be manifested also in the genetic characteristics. A few correlative connections are contradictory, which confirms that within the plant growth period the meteorological conditions are of great importance.

Analysing the determining factor of lignin content it can be seen that they were influenced by the interaction of various factors-when the samples were taken, the sowing period, the variety and the N-fertilizer rate application. That is confirmed by other researchers, that the genetic biomass plant background, the period when samples are taken and the growing environment, influence the lignin content in plants (Boateng et al., 2006). The lignin content is significantly influenced by the age of reed canarygrass (McCrady, 1991; Zaķis, 2008; Lignin…, 2009). That means that for lignin extraction reed canary grass harvesting needs to take place as far as possible at the later stages of growth.

In the conclusion of study concluded that on the lignin content in reed canarygrass samples affect the agronomic factors - time of sowing, N fertilizer rate and harvest time. On the lignin content does not affect amount of heavy metals and other chemicals elements in plants. In study was not found that the lignin content affect on the solid fuel parameters such as ash content and heating value.

Acknowledgements

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Integrated Research on *Jatropha curcas* Plantation Management

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Abstract: This paper will present the interactive research of expert team on *Jatropha curcas* plantation management to obtain high productivity in terms of dry seed weight per cultivation area. Set of experiments were designed and performed on randomize central block design and triplicate data were collected. The spacing was the important factor along with the cutting management program for long time cultivation. Therefore, the 3 different spacing (2x2, 2x3 and 3x3) were tested. The results show that 2x3 and 3x3 m spacing gave high yield of 129.2 and 127.1 kg/rai for the first cultivation year. In addition, types of insect and pest were surveyed in the Jatropha plantations and the ranking of the most found insect and pest was proposed. Mealy bug, Aphids and coccus were the most found insects in the Jatropha plantation. In the mean time, leaf spot, fungus infection, was the most sever in many areas in Thailand. Then the harmless chemical and biological treatments were tested to control those insects. The harmless chemical such as sodium lauryl sulphate and consumable products (tooth paste, shampoo etc) were used. In case of biological control, the natural predator, green lace wing, of the first top three insects was introduced and tested in the field. On the other hand, the number of insect pollinator was recorded at the Jatropha plantation responding to the Sun direction and time of the day. Interestingly, pollen germination also depends on the Sun direction. On the other hand, Box-Behnken design was used to optimize the transesterification of Jatropha oil to obtain the high fatty acid methyl ester (FAME) percentage. The results show that at the mole ratio of methanol and oil of 9:1, catalyze of 1.5%, reaction time of 72 min and temperature of 60 ^{o}C was the optimum condition and 99.0% of FAME was obtained. For the seed cake utilization, different rates of the seed cake (1,600, 800, 400 kg/rai) were applied to the cultivation of Chinese kale, tomato and potato. It was understandable that the mix of chemical fertilizer and Jatropha seed cake (1,600 kg/rai) gave the highest plant performance and no phorbol ester residue left in the cultivation soil and harvested vegetable.

Keywords: *Jatropha curcas, Plantation management, Jatropha insect and pest, Jatropha polinator*

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1. Introduction

Jatropha curcas Linn. is perennial shrub belongs to Euphorbiaceae family same as rubber tree and cassava [1]. Originally, *Jatropha curcas* was native tree in South America and was induced to Thailand about 200 years ago by Portuguese who produced soap from Jatropha oil. Generally, Jatropha tree is 3-5 meter tall, smooth grey bark, having latex and heart green leaf. The flowers are small in size, white color and much more male flowers than female ones. Flowering occurs at the branch terminal. The fruit is green at the beginning and then turns to yellow and dark brown at the ripen stage. The fruit composes of 2-3 seeds. The seed is black, oval shape and one white point at the top. Oil content in the seed is about 30-40% [2, 3]. However, without the seed coat the oil content increases to 50-54%. Oil is non-edible, high unsaturated fatty acid with the same heating value as other vegetable oil. Jatropha can grow in many types of soil including marginal land which is not suitable land for food crop cultivation. This reduces the conflict of food/feed/fuel issue in some countries. Nevertheless, many products can be produced from Jatropha residues such as fertilizer from the seed cake (this work), pesticides and medical bio-active compounds from Jatropha extract [4, 5].

Jatropha curcas has great potential as energy crop as above mentioned. However, low yield seed is the burden and challenging for the researchers to overcome. Therefore, there have been many findings conducting to improve yield of Jatropha. As a wild crop the knowledge of Jatopha plantation management is little known and slowly developed. To accelerate the research investigation under limited human resources and budget, the integrated research at the plantation level is desired. This paper shows how different discipline approaches to one goal of Jatropha yield improvement.

2. Methodology

This content will be divided to 5 sections according to the discipline and experimental set up. The five sections are agronomy, plant pathology, entomology, engineering and seed cake utilization.

2.1. Agronomy

To obtain the objective of Jatropha high yield, the optimum spacing and level of fertilizer was investigated. This experiment has been taken at 2 plantations. The first plantation aimed to conduct the investigation of the spacing (2x2; 2x3; 3x3 m) and the second plantation was to observe the effect of fertilizer (high, medium, low and none inputs) to the Jatropha performance. Note that high input means chemical (15-15-15 and 50 kg/rai) and organic fertilizer (500 kg/rai), medium means only chemical fertilizer (50 kg/rai), low means only organic fertilizer (500 kg/rai) and none is no fertilizer. Note that 6.5 rais equal 1 hectare. There is only 1 variety, TH1 (plant form seed) reported in this paper. The collected data are the seed yield, number of fruit, weight of 100 seed, plant height, and canopy width during one year cultivation time.

2.2. Plant pathology

The survey has been conducted across the Kingdom of Thailand to collect the specimen such as leaf or stem or confected part of Jatropha tree. The severity of pest was ranking and the specimens were then taken from the plantation to the laboratory for the biological assay. The symptom finally was identified.

2.3. Entomology

There are three investigations in this area namely insect, nature predator of Jatropha insects and pollinator. Each investigation was separately carried on by different researcher. For the insect, mealy bug, was controlled by household chemical and natural predator (green lace wing). In fact, green lace wing is effective natural predator not only for mealy bug but also aphids and coccus. This paper did the mass cultivation of green lace wings and their eggs were packed in the capsules and tested in the Jatropha plantation. Concerning the pollinator, the percentage of pollinator visiting to 1,500 flowers was recorded during the dry and wet season at different time of the day. Then the pollen was collected from the Jatropha canopy and germinated in the laboratory to check germination percentage.

2.4. Engineering (biodiesel production)

After the Jatropha seeds were collected from the field, the shells have been cracked by machine and oil was expelled using the oil expeller. The expelled oil was filtered to remove the solid residue and oil was used for biodiesel production using transestification technique and KOH was used as catalyst. The condition of biodiesel production namely mole ratio of methanol to oil (3-9), catalyst concentration (0.5-1.5%), reaction time (60-120 min) and reaction temperature (30-60 ^{o}C) was optimized by experimental Box-Behnken design. Then percentage of fatty acid methyl ester (%FAME) was analyzed by gas chromatography.

2.5. Seed cake Utilization

As known that one liter of Jatropha oil comes from about 4 kg of seed which will give about 3 kg of the seed cake. The objective of this section was to utilize the seed cake as fresh fertilizer to the vegetable cultivation. The experiment was conducted and applied to three types of vegetables namely Chinese kale, tomato and potato which represented the fresh consumed vegetables, fruit plants and root plants. Three level of seed cake was applied to those plants as high (1,600 kg/rai: 6.5 rais = 1 ha), medium (800 kg/rai) and low rates (400 kg/rai). Nevertheless, sole chemical fertilizer (recommended rate), sole organic fertilizer and half mixed of the seed cake (three doses) and chemical fertilizer or organic fertilizer were applied. Twelve treatments in total were carried out including the control (without fertilizer). The growth of plants was recorded. However, in this paper only the results of Chinese kale were reported. Samples were taken from the leaf and cultivation soil to check the phorbol ester residue. HPLC and LC-MS/MS were used to analyze phorbol ester content using TPA as external standard.

3. Result and Discussion

The results and discussion are divided into 5 parts according to the methodology as following.

3.1. Agronomy

As can be seen in Table 1, 2x2 and 2x3 spacing gave the high seed yield of 129.2 and 127.1 kg/rai respectively. Number of fruit and 100 seed weight responded directly to the seed yield. Even though the plant height is the same but the canopy width clearly relates to the spacing. The larger spacing of 3x3 comparing to the narrower ones gives the wider canopy width.

Table 1. Effect of spacing on Jatropha performance of TH1 variety.

Spacing	Seed yield (kg/rai)	number Fruit/rai	100 seed weight (g)	Plant height (m)	Canopy width (m)
2x2	129.2	55,804	86.3a	2.7	1.6b
2x3	127.1	56,698	84.4b	2.7	1.9a
3x3	97.9	44,498	84.2b	2.7	2.0a
F-test (a)	ns	ns	**	ns	**
LSD (0.05a)	-	-	0.6	-	2.7

Table 2. Effect of fertilizer on Jatropha performance of TH1 variety.

Input	Seed yield (kg/rai)	number Fruit/rai	100 seed weight (g)	Plant height (m)	Canopy width (m)
High	182.3a	80,455a	85.5	276.0a	187.5a
Medium	132.1b	58,826b	85.1	276.5a	188.6a
Low	98.6c	43,530c	85.2	264.1ab	183.6a
None	59.1d	26,524d	84.1	256.6b	163.5b
F-test (b)	**	**	ns	*	*
LSD (0.05b)	29.5	12892	-	13.3	17.8
Spacing x fertilizer	ns	ns	ns	ns	ns
CV (%)	25.3	24.9	3.6	5.0	9.9

3.2. Plant pathogen

The specimens (Fig 1.1) from the plantation were assayed for the microbial type. Leaf spot was the top ranking severity in the plantation as shown in Table 3. Fungal infection was the most found particularly at the moderate temperature and high humidity. Fig. 1 shows the fascicles of conidiospores and conidium of *Pseudocercospora* sp. causing leaf spot.

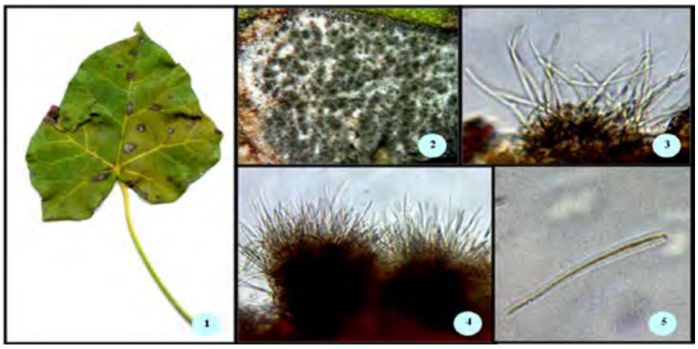


Fig.1. Leaf spot infected by Pseudocercospora sp. 1) disease symptom on leaf; 2) fungal fruiting structure under stero-microscope; 3, 4) fascicles of conidiophores; 5) conidium

Table 3. Diseases and severity in the Jatropha plantation.

Diseases	Severity
Leaf spot (*Pseudocercospora* sp.)	++++
Leaf spot (*Pestalotiopsis* sp.)	++
Leaf spot (*Phoma* sp.)	++
Leaf spot (*Alternaria brassicicola*)	+

3.3. Entomology

There are three different investigation in entomology namely Jatropha insect, natural predator and pollinator.

3.3.1. Jatropha Insect

From the field survey, it was obvious that mealy bug was the most found insect in many areas of Thailand. The second and third populations of insect found were aphids and coccus. Fig. 2 shows the mealy bug before and after the treatment of sodium lauryl sulfate (SLS). As can be seen in Fig.2b SLS dissolve wax on the mealy bug’s body.

Fig. 2. Mealy bug on the Jatropha tree a) before b) after treating with SLS

3.3.2. Natural predator

The survey of prime natural predators of Jatropha insect particularly mealy bug, aphids and coccus has been done intensively. Green lace wing was found to be the effective natural predator of those insects. This natural predator has potential for mass production. Therefore, it was selected for further study. Table 4 shows the longevity and number of egg collecting from the laboratory. Comparing of different starting egg numbers of 50, 100 and 200 eggs, starting with 50 eggs give the highest ratio of egg/longevity and reasonable daily egg number. As the result this number is used for finding the suitable food composition for egg production (Table

5). Bee pollen and honey food mixed was selected as it gave the highest ratio of egg/longevity and daily egg obtained.

Table 4. Number of eggs of Plesichrysa ramburi and its adult longevity from various number of starting adults at 27 °C and 70% RH.

No of starting	Ratio of egg/longevity	Mean longevity (day)	Daily obtained egg
50	2,080a	22.33c	94.12
100	3,590b	20.67b	180.40
200	4,565c	14.67a	323.78
CV (%)	2.98	3.11	-

Table 5. Number of eggs obtained from 50 starting aduls in different food composition.

Food composition	Ratio of egg/longevity	Mean longevity (day)	Daily obtained egg
Yeast & honey	1,708	14.00	122.00
Bee pollen & honey	1,891	13.67	138.37
CV (%)	5.25	14.95	-

After eggs were mass produced in the laboratory, 300 eggs were packed in the plastic tube and tested at the field sites for 1, 2 and 3 weeks including the control (no egg pack). Unfortunately, during the experiment, there were not many insects as expected. Therefore, we could not observe the different numbers of the predator and insects before and after treatment. This field experiment is needed to re-perform later.

3.3.3. *Pollinator*

The number of pollinator during the dry and wet seasons was recorded as shown in Fig 3. As can be seen in Fig 3, it is noticeable that the female flower is more preferable as the number of pollinator visiting is higher than male flower particularly in the morning. Fig 4 shows the percentage of pollen germination at different direction and time of the day. In the morning the high percentage of pollen germination is found in the direction exposing to the Sun. Correspondingly, in the late afternoon the higher percentage of pollen germination is found in the Southern west where the Sun is.

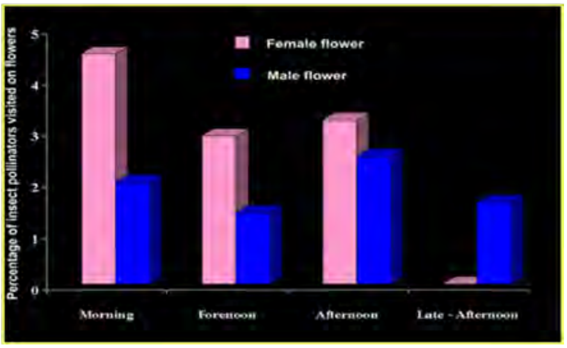


Fig. 3. The percentage of pollinator visiting female (first) and male flower (second) in the morning, late morning, afternoon and late afternoon

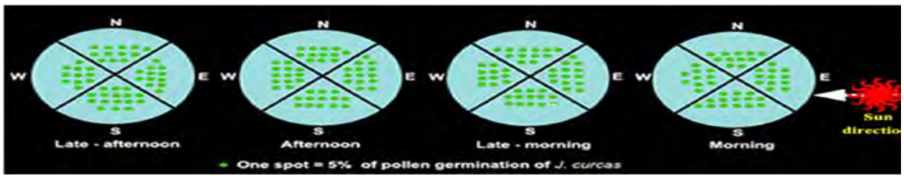
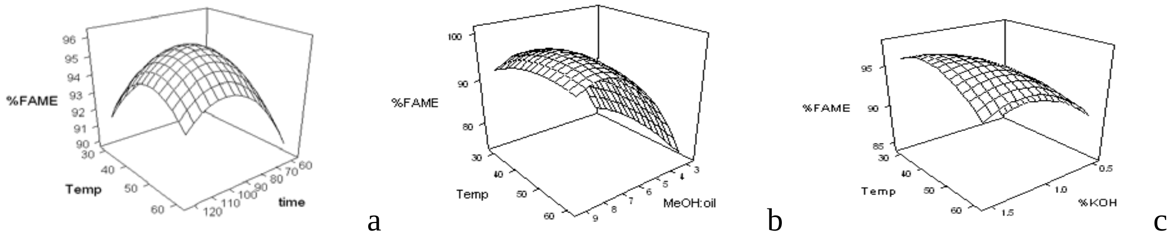


Fig. 4. The percentage of pollen germination according to the direction

3.4. Engineering

From the Box-Behnken design of experiment with three levels, 35 experiment runs were designed. The data was analyzed using Minitab software to construct the contour as in Fig 5. As can be seen in Fig 5, the effect of reaction temperature and time has more influence on % fatty acid methyl ester (FAME) (Fig 5a). While the effect of mole ratio of methanol to oil, and %KOH has greater effect than reaction temperature (Fig 5b & 5c). The optimum condition for transesterification from Jatropha oil suggested by the model was 9:1 mole ratio, 1.5% KOH, 72 min reaction time and 60 °C reaction temperature and 99.0% FAME was obtained at this optimum condition.



a b c

Fig. 5. Surface plot of %FAME and a)reaction temperature and time b) reaction temperature and mole ratio c) reaction temperature and %KOH (catalyst).

3.5. Seed cake utilization

Table 6 shows the growth performance of Chinese kale of twelve fertilizer treatments. Pure chemical fertilizer and half dose of chemical fertilizer plus high rate of Jatropha seed cake give the highest Chinese kale yield of 9.87 and 9.08 t/ha. Note that 4 kg of Jatropha seed will give approximately 1 kg of oil and 3 kg of seed cake. From the phorbol ester analysis, the residue of phorbol ester both in the Chinese kale and cultivation soil was not found.

Table 6. Average growth characteristic of Chinese kale (a, b, c show statistical significant).

Treatment	Leaf length (cm)	Leaf width (cm)	Plant height (cm)	Canopy height (cm)	Canopy width (cm)	Total yield (t/ha)
Without fertilizer	10.87c	8.70b	7.39b	19.83c	13.27cd	4.12c
CF	14.83a	12.26a	15.83a	29.27a	21.27a	9.87a
OF	11.18c	8.58b	7.73b	20.47c	17.00bc	2.02e
SF (400 kg/rai: H)	9.75c	7.05b	7.26b	18.37c	13.57cd	1.77e
SF (800 kg/rai: M)	9.63c	7.04b	7.83 b	17.60c	12.33d	4.08c
SF (1,600 kg/rai: L)	11.35bc	9.63ab	9.06b	22.91bc	14.42cd	3.77cd
0.5CF + SF (H)	12.10abc	10.03ab	10.13b	20.90c	14.23cd	7.07b
0.5CF + SF (M)	9.76c	8.00b	8.33b	19.07c	12.60cd	4.55c
0.5CF + SF (L)	14.23ab	12.40a	10.57b	27.87ab	19.67ab	9.08a
0.5OF + SF (H)	10.43ac	7.63b	8.05b	20.77c	15.40cd	2.60de
0.5OF + SF (M)	12.07abc	8.267b	9.60b	23.27bc	15.23cd	4.12c
0.5OF + SF (L)	11.50bc	9.16b	8.85b	23.30bc	15.20cd	3.99c

Please note that CF is the chemical fertilizer, OF is organic fertilizer and SF is Jatropha seed cake fertilizer,

4. Conclusion

This paper shows the multidisciplinary research work of Jatropha in the plantation level. The results of this preliminary investigation are the important basic knowledge to increase the Jatropha yield. The actual work has been done intensively in the plantation level to make sure that the developed technology is practical and useful for the future users. It is clear that Jatropha yield improvement is the challenge and it needs the integrated research of agriculture, engineering and science.

5. Acknowledgement

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Biomass waste – a source of raw materials and new energy source

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Abstract: Agricultural crop residues, such as straw, corn stover and wood wastes such as leftovers from timber cutting, broken furniture, sawdust, residues from paper mills etc. contain appreciable quantities of cellulose, hemicelluloses and lignin. Much effort has been devoted to convert these types of biomass into useful industrial and commercially viable products.

During liquefaction, lignocellulosic components are depolymerised to low molecular mass compounds with high reactivity and high hydroxyl group content. We have used a high energy ultrasound as an energy source to speed up the liquefaction process in our research. The liquefied biomass was used as a feedstock in synthesis of polyesters, polyurethane foams and adhesives. Adhesives for the wood particle boards with incorporated liquefied lignocellulosic materials emit less formaldehyde and products have the same or even better mechanical and physical properties.

A special attention was given to the utilization of the liquefied lignocellulosic materials as a new energy source with high heating value. It was found that the combustion efficiency of lignocellulosic liquid fuel is comparable to the combustion efficiency of Diesel fuel although it has much higher content of cyclic hydrocarbons. The emissions are within the range of the European emission regulations.

The utilization of liquefied lignocellulosic materials can at least partially reduce the crude oil consumption, thus increasing the use of the renewable resources in large extent.

Keywords: *biomass liquefaction, polyester synthesis, adhesives, fuel*

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1. Introduction

Biomass based materials and wood in particular are among the most abundant renewable resources. Much effort has been devoted to convert these types of biomass into useful industrial and commercially viable products. One of the possible routes to achieving this is through **liquefaction** where wood or lignocellulosic materials, such as waste paper, starch, etc. reacts with phenol or multifunctional alcohols to yield low molecular mass, liquid products that can be used for polymer synthesis [1,2,3,].

In our research native hardwood and softwood as well as paper and different wood based waste materials were liquefied with different glycols and with a minor addition of p-toluene sulphonic acid as catalyst.

However, a novel approach to a very efficient energy input during the thermochemically conversion of lignocellulosic biomass into liquefied depolymerized products is the use of ultrasound power. Sonochemistry is nowadays an excellent tool in chemical, physical and biological processes. The irradiation with ultrasound can be regarded as a special type of energy input into the system. The range from 20 kHz to 1MHz is used in chemistry while higher frequencies are used in medical and diagnostic applications. The high frequency mechanical vibrations are transferred into the medium by titanium made horn, in different sizes and shapes. Ultrasound is transmitted through a medium via pressure waves and the main advantage is directly related to the physical effect of acoustic cavitation. Acoustic waves can break the cohesion of a liquid and create micro cavities. The cavity is actually a micro bubble which corresponds to the sound wave by growing till becoming unstable. At that point bubbles collapse violently creating drastic conditions inside the medium for a very short time: temperatures of 2000-5000K and pressures up to 1800 atm inside the collapsing cavity. Consequently, under such extreme conditions volatile molecules vaporize and form free radicals as was proved in extensive studies of the sonification of water. Radicals cause fragmentation of large molecules, stripping off the ligands and oxidation. Shaw and Lee [6] exposed the effluent from pulp and paper kraft mill to power ultrasound and efficiently reduced the chemical oxygen demand (COD) and effluent turbidity. Shock waves, generated at the collapse of cavities induce mechanical effects, such as splitting large molecules to smaller fragments, particle size reduction, surface cleaning and intensive mixing and heating. The later are used for the formation of stable emulsions in liquid-liquid systems.

Sonochemical methods are used also in carbohydrate chemistry [7]. Hydrolysis and clevage of di- and polysaccharides were quantitatively proved with starch, dextran, cellulose derivatives and other polysaccharides. In our research we have utilized high energy ultrasound for depolymerization and liquefaction of different lignocellulosic materials. It was found, that the reaction yield was in all experiments almost 100% and the reaction time grossly reduced.

Liquefied wood can be considered to be a polyhydric alcohol. After the liquefaction process, the presence of hydroxyl group-containing species in the wood components can be used as polyols for several different purposes. The hydroxyl value of the liquefied wood has been determined to be between 500 and 1000 mg of KOH/g. This high number means that the products can be used as the hydroxyl component in complex polyester synthesis [4]. Some benefits could be expected from such systems. These include the incorporation of the biomass components into the polymeric compositions and consequently, the provision of a certain degree of biodegradability. Esterification of a proportion of the hydroxyl groups reduces the reactivity of the liquid wood, a feature that is sometimes desired in polyurethane synthesis.

It was found during initial experiments that a mixture of liquefied wood with melamine-formaldehyde or melamine-urea-formaldehyde resin can react at elevated temperatures forming a solid crosslinked product that was suitable for the use in wood furniture industry. Such an adhesive has lower formaldehyde content than the standard melamine-formaldehyde or melamine-urea formaldehyde adhesives [5]. In the condensation – elimination reaction, the methylol groups of the melamine-formaldehyde resins precursors react with the hydroxyl groups on the liquefied wood, eliminating water or methanol. The acid catalyst which is present in the liquefied wood additionally speeds up the reaction.

In our research we have utilized high energy ultrasound for depolymerisation and liquefaction of different lignocellulosic materials, wood wastes in particular. A town with 350.000 inhabitants generate 5.700 tons of different wood waste materials per year, mainly broken furniture and packaging materials. Besides that, 2.300 tons of forest residues are deposited, manly tree branches, bark and larger pieces of timber. The aim of this study was to find a highly efficient way to transform this biomass waste into valuable chemicals and as a new energy source. It was found, that the reaction yield in all experiments was almost 100% and the reaction time grossly reduced.

The first objective of this study was to synthesize a liquefied wood that contained high hydroxyl group content, with a good yield in the liquefaction reaction. The second goal was to achieve the utilization of liquefied wood in the synthesis of polyester-polyols. These polyols were successfully utilized in polyurethane foam production. The third goal was to establish the criteria for creating a melamin-fomaldehyde or a m elamine-urea-formaldehyde resin precursor that would react at elevated temperature with liquefied wood and could be used as an adhesive. The fourth objective was to utilize the liquefied wood as an energy source with high heating value. Most of liquefied products have a heating value higher than 22 KJ/kg, that is in the range of pure ethanol and higher than brown coal. Initial tests have indicated that these products could also be used as a motor fuel. Since the production of such liquid fuel utilizes a huge variety of lignocellulosic wastes and takes place under very mild reaction conditions, an overall energy output is high. Several possible applications in energy production were identified and explored by our group.

The utilization of liquefied lignocellulosic materials can at least partially reduce the crude oil consumption, thus increasing the use of the renewable resources in large extent.

2. Materials And Methods

The most common wood waste materials such as medium density fibreboard (MDF), veneered particleboard, particleboard, oriented strand board (OSB), plywood and wheat straw were milled on ROTSCH SM-2000 mill. All meals (flours) including spruce (*Picea spp.*) sawdust were sieved through a 2 mm screens and dried at room temperature to constant water content.

All chemicals were of synthesis grade (Merck) and were used without further purification.

2.1. Experimental setup

The liquefaction was carried out in a 1000mL three-neck glass reactor, equipped with the mechanical stirrer and condenser.

The ultrasonic device was UP400S processor, produced by Hielscher Ultrasonics GmbH, Warthestrasse 21, 14513 Teltow, Germany. The high frequency (24 kHz) power output can be regulated by adjustment of amplitude from 20% to 100% of the nominal power of 400W. The high frequency output is transferred through titanium cylindrical horn, introduced into the reactor through the side neck and submerged 20mm into the reaction mixture. The horn had diameter of 22 mm, with the calculated power output (at the maximum amplitude) $105 Wcm^{-2}$.

The experimental setup is shown in Figure 1.

2.2. Biomass (wood waste) liquefaction

The reactor was charged with 140g of biomass and 700g of glycol. 21g of p-toluenesulfonic acid was added. The liquefaction of different wood waste materials was governed in diethylene glycol: glycerol = 1:4 mixtures.

The mixture was heated for maximum of 2 hours at 180 °C while being constantly stirred.

The ultrasound was switched on when the temperature of the reaction mixture reached 160^oC. The energy input was controlled by the amplitude of the ultrasound. Ultrasound of amplitude from 20% to 100% was used for waste wood liquefaction.

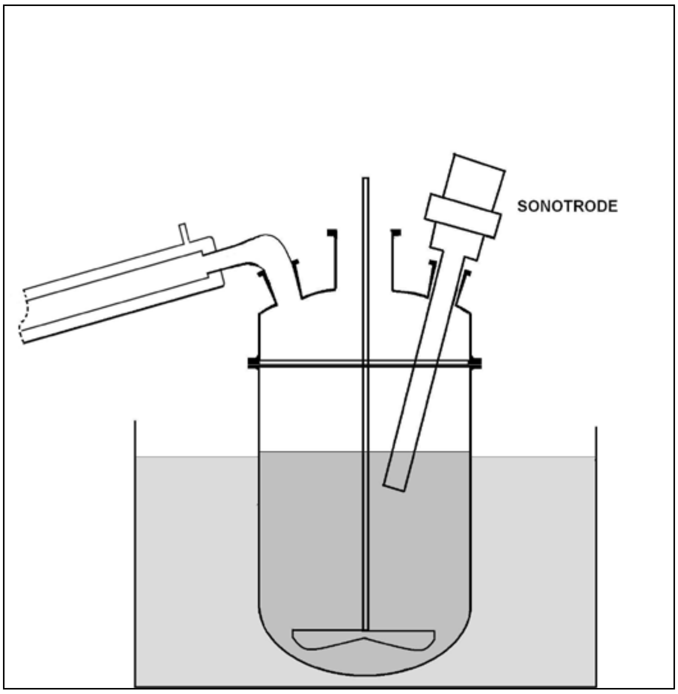

Fig. 1: Glass reactor with external heater, mixer and ultrasound sonotrode

2.3. Polyester polyols from the liquefied wood (LW)

Three different formulations with two different dibasic organic acids were used in order to study the differences in the physical and the chemical properties of the final products. 300 g of liquefied wood were used in combination with 60 g of adipic acid; the resulting polyester was identified as P1. With 60 g of phthalic acid anhydride, the product was identified as P2. With 30 g of adipic acid and 30 g of phthalic acid anhydride, the resulting polyester was identified as P3.

The liquefied wood was introduced into the four-necked 1000 cm^3 glass reactor, equipped with a water condenser and mechanical stirrer. The reactor was placed in an electric jacket heater. Adipic acid and/or phthalic acid anhydride were added when the liquefied wood reached 180°C. Dibutyl tin oxide (0.2% w/w) was added as the sterification/transesterification catalyst. The mixture was heated gradually up to 200°C, under stirring and was held at this temperature. Water was continuously distilled from the reaction system. A slight stream of nitrogen was introduced into the reactor for easier transport of water vapor into a condenser. A sample was withdrawn periodically from the reaction system and its acid value was determined. The total reaction time was between 160 minutes and 180 minutes. After completion of the reaction, when the acid value was reduced to less than 30 mgKOH/g, the reaction mixture was cooled to ambient temperature.

1.1. Product characterization

Hydroxyl values were determined by standard ASTM Standard D4274-05 (2005) method.
The extent of liquefaction was evaluated by determining the residue after the washing out the sample with dioxane and water (4:1 v/v). The residue was dried in an oven at 105°C to constant weight. The conversion yield was calculated as the weight percentage based on the starting wood material.

3. Results and Discussion

3.1. The efficiency of the ultrasound

Initial experiments were dedicated to determining the influence of the ultrasound to the speed of the liquefaction reaction. The increase of the ultrasound amplitude reduces liquefaction time needed to achieve the same liquefaction residue amounts. The efficiency of the ultrasound is illustrated in Figure 2, where the liquefaction process without the use of the ultrasound needs 120 minutes to achieve the total liquefaction while with the ultrasound at the minimal amplitude of 20% only 80 minutes. Accordingly, the use of the ultrasound with 60% amplitude completes liquefaction in 60 minutes that represents only half of the time which is consumed in order to achieve the same liquefaction extent without ultrasound.

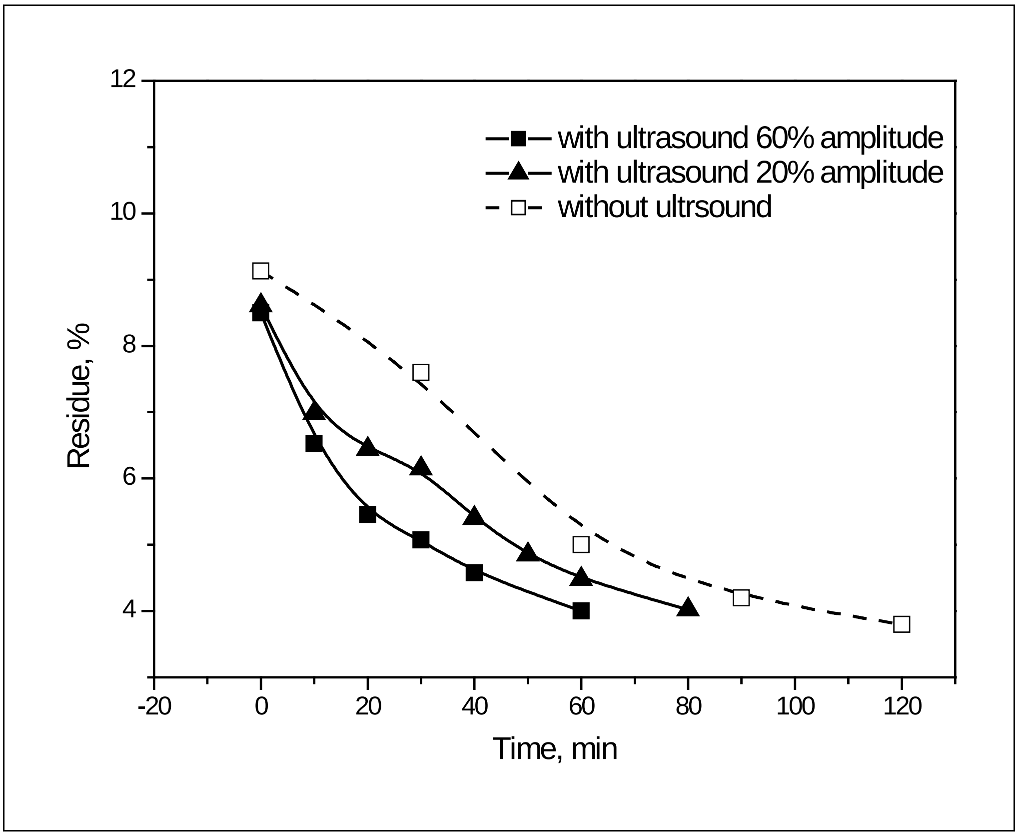

Fig. 2: The decrease of the wood residue in % during the liquefaction with ultrasound 60% amplitude (squares), 20% amplitude (triangles) and without ultrasound (empty squares). (Values at 0 min represent residue % of the samples taken after the reaction mixture achieved 160 °C and in case of ultrasonically assisted liquefaction - when the ultrasound was switched on.)

The powerful energy input through the cavitation effect is demonstrated in the reduction of the biomass particles size and through the depolymerization of the large biopolymers. The size reduction is visible by naked eye since after initial few minutes the reaction mixture becomes homogeneous dispersion. The process continues till all the biomass is completely dissolved and a dark brown liquid is formed with particles sizes less than 1μm.

3.2. Polyester polyols from liquefied wood

Liquefied wood was used as a component in polyester synthesis due to the large number of hydroxyl groups that are available in the liquefied wood. The liquefied wood was used as a substitute for part of the polyhydroxy alcohols that are standard raw material in polyester formulation. Polyester polyols were prepared by using adipic acid and/or phthalic acid anhydride in a high temperature polycondensation/esterification reaction. The polyesters were prepared under the standard high temperature polycondensation conditions, confirming the use of the liquefied wood as a raw material in polyester synthesis. The products were characterized using FTIR, GPC/SEC and viscosity measurements showing similar properties to those possessed by equivalent commercial polyesters. The characteristic data are presented in Table 1.

Table 1: Characteristic data of polyesters and the initial liquefied wood

	Mn(Av.) g/mol	MW(Av.) g/mol	PDI	OH value mgKOH/g	Viscosity kPa.s	% of wood (w/w)
LW	4790	19400	4.0	1043	2.8	28
P-1	10300	39900	3.9	798	1.9	22
P-2	4590	60000	13.1	378	1.9	23
P-3	7980	79500	10.0	437	2.2	23

A rise of the average molar mass was achieved together with a reduction of the hydroxyl group content. Such a modification of the polyester reactivity and complexity is favorable for further utilization in polyurethane synthesis. The final OH values of the polyesters were in the range of saturated polyesters that are used in polyurethane production. The viscosity is grossly dependent on the type of the glycol used for the liquefaction and on the wood glycol ratio. The use of wood in these experiments replaced up to 23% of polyhydroxy alcohols in polyester formulations. This amount varies according to product requirements and can be increased significantly.

3.3. Liquefied Wood As A New Particle Board Adhesive System

The OH groups in the liquefied wood, including those of the remaining unreacted glycols were available for the condensation reactions with different melamine-formaldehyde and melamine-urea-formaldehyde resin precursors. By measuring the mechanical properties of selected particle boards and by measuring the formaldehyde release, it was found, that a 50% addition of the liquefied wood met the European standard quality demands for particle boards. Formaldehyde release was lower than 8mg/100g in all experiments due to the positive influence of the liquefied wood components. It can be concluded that the products of the liquefied lignin with their aromatic character behaved as a formaldehyde scavenger. Lower formaldehyde emissions from particle boards due to the use of the liquefied wood, are extremely important in the provision of better quality of life. The properties of particle boards made with the mixture of the liquefied spruce wood and the melamine-urea-formaldehyde resin precursor Meldur H97 and melamine-formaldehyde resin precursor MS-1 were within the European standard EN 312 (2003), type P2 limitations..

On the basis of the presented values one can conclude that liquefied woods can be used as a substitute for synthetic resin precursors in adhesives that are used for particle board production.

3.4. Liquefied biomass as a fuel

A special attention was given to the utilization of the liquefied lignocellulosic materials as a new energy source with high heating value. Most of liquefied products have a heating value higher than 22 KJ/kg, that is in the range of pure ethanol and higher than brown coal. Initial tests have indicated that these products could also be used as a motor fuel. Since the production of such liquid fuel utilizes a huge variety of lignocellulosic wastes and takes place under very mild reaction conditions, an overall energy output is high. The viscosity of the liquefied biomass depends on the biomass content in the formulation and can be between 149 kPa.s to 2 kPa.s. However, if it is applied at higher temperatures, the viscosity is reduced to 100 Pa.s and can be directly introduced into the burner. The sulphur content is less than 0.3%. The carbon monoxide, nitrogen oxides and solid particles emission were within the range of the European emission regulations for heavy duty diesel engines.

Preliminary test were carried out in a prototype gas turbine, where efficiency, power output, exhaust emissions as well as wear and durability of components were examined. These results were compared to the results obtained during the tests with Diesel fuel. Due to high viscosity of the lignocellulosic liquid fuel, a new fuel injection system was designed and manufactured to allow injection of heated and pressurized fuel.

It was found that the combustion efficiency of lignocellulosic liquid fuel is comparable to the combustion efficiency of Diesel fuel although it has much higher content of cyclic hydrocarbons. It was also proven that utilization of lignocellulosic liquid fuel in the prototype gas turbine complies with current emission regulations for electric power generation. Differences in exhaust emissions while utilizing lignocellulosic liquid fuel and Diesel fuel were analyzed and interpreted. It was found that total hydrocarbon emissions are higher than those of Diesel fuel; however the difference diminishes for high air-fuel ratios, high combustion chamber air inlet temperature, and high fuel temperatures. All effects enhance evaporation of fuel with high viscosity thereby additionally enabling higher conversion rate of cyclic hydrocarbons. It was also found that NO_x emission increased slightly at the same enthalpy of exhaust gasses while using lignocellulosic liquid fuel, which could be attributed to high oxygen content of the fuel. Influence of utilizing lignocellulosic liquid fuel on wear and durability of components of the gas turbine and its fuel injection system is currently examined.

4. Conclusions

Different lignocellulosic materials were liquefied with yields higher than 95% and with additional use of the ultrasound the reaction times could be reduced for more than 50%.

Polyesters were synthesized using liquefied wood and other lignocellulosic materials as a replacement for a certain amount of polyhydric alcohols – produced from crude oil. The chemical and physical properties of such polyesters are favorable for their use in polyurethane synthesis. The use of wood in these experiments replaced up to 23% of polyhydroxy alcohols in polyester formulations.

Liquefied lignocellulosic materials were also used as adhesives for particle boards production – with reduced formaldehyde emission and excellent mechanical properties. By measuring the mechanical properties of selected particle boards and by measuring the formaldehyde release, it was found, that a 50% addition of the liquefied wood met the European standard quality demands for particle boards. It can be concluded that the products of the liquefied lignin with their aromatic character behaved as a formaldehyde scavenger. Lower formaldehyde emissions from particle boards due to the use of the liquefied wood, are extremely important in the provision of better quality of life.

The liquefied biomass has high heating value. The residual particles have low average diameter and the liquefied biomass has low viscosity. These are the properties, favorable to its utilization as the liquid fuel in traditional oil burners and in diesel engines. The emissions are within the range of the European emission regulations. Successfully completed initial test thus pave the way for utilization of a new renewable fuel in gas turbines, which are known for their high efficiency, high power density, high reliability, technology availability and affordability. Overall energy conversion efficiency will be increased by utilizing co- or tri-generation power plants. The key achievement arises from the fact that the fuel is produced from mainly unused renewable source and from the fact that its use has very low carbon footprint.

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Sustainable energy from dairy farm waste using a Microbial Fuel Cell (MFC)

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Abstract: A dairy farm waste which include milk waste, unconverted feed and bedding, cow manure and cow slurry water have been applied as raw materials to produce renewable energy using a continuous flow membrane-less microbial fuel cell (MFC). The COD content decreased with 98% from 33,600 J/L to 558 J/L within 6 days by turning the organic content into electricity and hydrogen. The voltage generated reached a peak of 1.6136mV, which indicating that dairy farm waste can be an appropriate resource for MFC. The total energy of hydrogen gas was 38,338J/L on the sixth day, which suggesting that about 80% of the energy stored in the COD was transferred into hydrogen gas. The nitrogen content of the farm waste slurry also decreased 20% during the first 24 hours indicating that MFC can be used for nitrogen harvesting.

Keywords: *1. Biomass fuel; 2. Renewable energy; 3. Dairy farm; 4. MFC; 5. hydrogen production*

1. Introduction

There are close to 2 million dairy cows in the UK producing an estimate of 70 million m^3 of slurry annually. Since each m^3 of slurry contains 200-250kwh, it can be considered as one of the largest sustainable energy resource in the UK. Due to increasing use of intensive farming methods, agriculture derived wastes will continue to increase, especially within the livestock farming. From 1961 to 1999, there was a 34% increase of the total livestock numbers in UK (BERR & DEFRA, 2003). Farm wastes, such as slurry, dirty water, silage liquor and manure, need to be treated and disposed in an environmentally appropriate way. For dairy farms, most of the slurry wastes are used as fertilizer to grow winter feed crops for the animals. However, there are future logistical and economic constraints, such as for nitrate vulnerable zones were spreading is limited to 170kg/ha (Cinar et al., 2004). The restriction is to stop nutrients run-off into surrounding ground water from manure spread on the fields. Removal of nitrate is an option, but it is not easy to completely remove ammonia and other nitrogen compounds from wastewater or slurry water by conventional wastewater treatment technologies (Jetten et al., 2002). There are significant hazardous environmental impacts of nitrogen. For example, due to bacteria oxidation into nitrate, depletion of dissolved oxygen in receiving streams and promotion of eutrophication that are toxic to most aquatic organisms. Moreover, high concentration of nitrate in groundwater is also harmful to human health, because some diseases could occur, such as gastric cancers and infant methaemoglobinemia (Jetten et al., 2002). Therefore, there is a great potential for nitrate rich dairy farm waste to be used as feedstock in microbial fuel cells. In these processes, the available nutrients can be converted into energy resulting in reduced environmental impact and lowered energy cost for conventional dairy farms could be offset (Young and Pian, 2003).

2. Methodology

The Microbial Fuel Cell is a technology that can be used to generate electricity from waste water or animal slurry water by employing microorganisms to digest inorganic and organic compounds (Liu and Logan, 2004). The catalytic reaction of bacteria produces electrons which are transferred to the anode, i.e. the negative terminal, directly or by electron mediators (Liu and Logan, 2004). The microbes also produce protons that travel from the anode chamber to the cathode chamber. The electrons from the anode travel through an external load and recombine with the protons at the cathode to form electric current and hydrogen.

In this study, a continuous flow membrane-less 1m^3 MFC was used at 25° C temperature with a flow rate of 0.8L/min. The MFC pilot plant was located at the Sutton Bonington campus of the University of Nottingham (Figure 1). The microbial culture available in the liquid cow manure from a 3 million L storage tank at the Sutton Bonington Campus was used as inoculums.. A HACH spectrophotometer DR2500 (Inc.US) was used to conduct COD tests. An HPR-20 MS was used to quantify the hydrogen produced. The total nitrogen removal was been determined by the Kjeldahl method..

Figure 1MFC pilot plant of the University of Nottingham

3. Results

The COD value decreased rapidly during the first 2 days and then slightly decreased until the sixth day, as shown in Figure 2. The initial COD energy level was 33,600 J/L, and finally reached 558 J/L after 6 days. The overall removal of initial COD energy was 98%. This indicates that the microbial fuel cell is very active during the initial stage where nutrients, such as nitrates, are abundant.

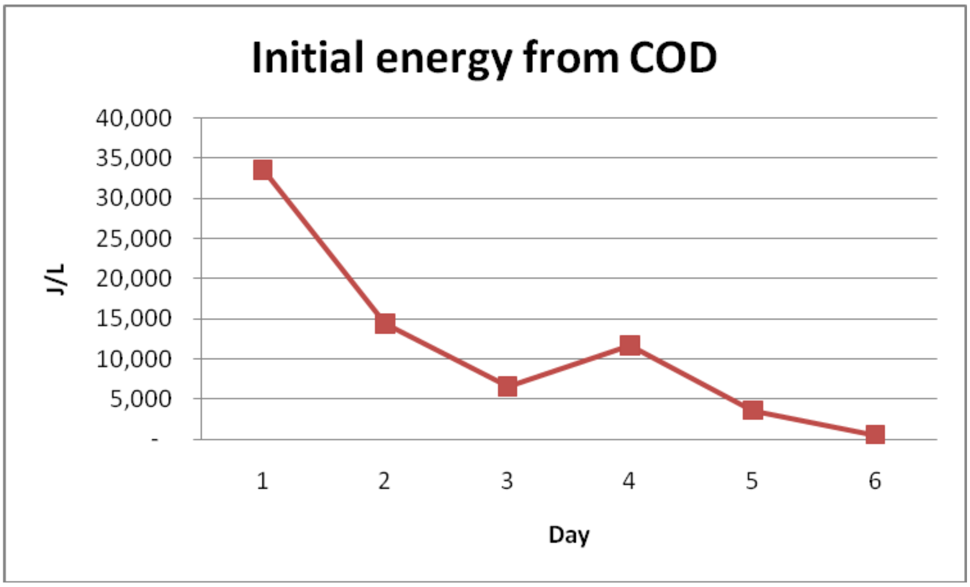

Figure 2 COD removal for MFC

Figure 3 shows the voltage variation between day 1 (0) to day 6 (5). The initial voltage increased from 1.2 mV to 1.6 mW within two days. Correspondingly, the largest amount of COD was removed from the first day to the third day. Therefore, the voltage achieved the highest value (1.6mV) on the third day and stayed stable until the end of forth day. As the COD energy is depleted, the voltage decreases on the sixth day.

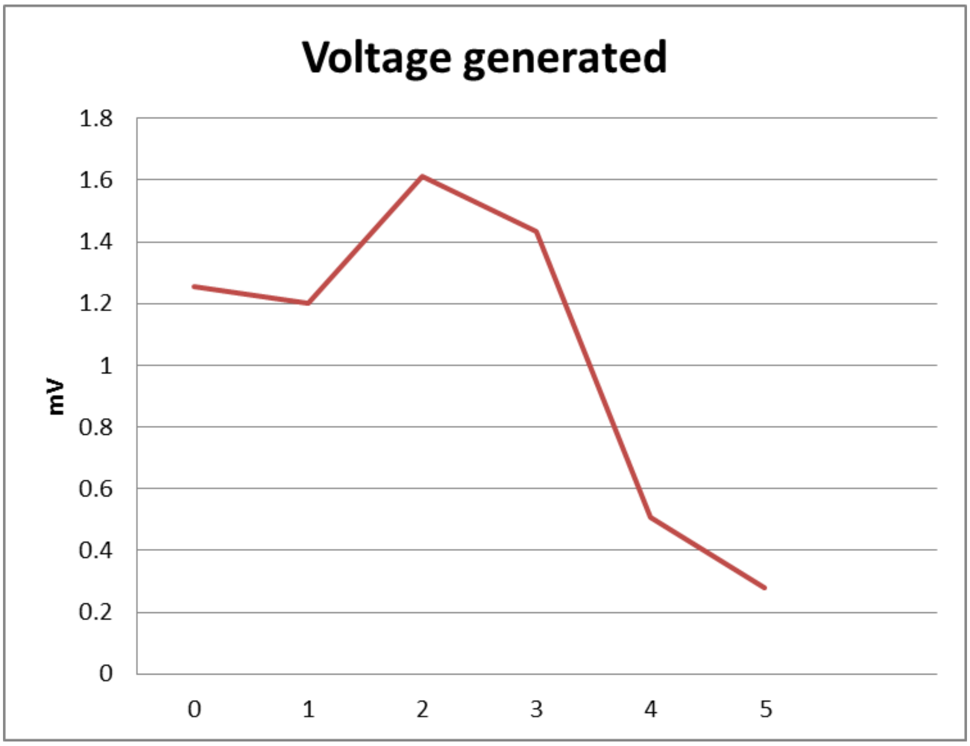

Figure 3 Electricity generated from MFC

Figure 4 shows the hydrogen production variation between day 1 (0) to day 6 (5). There was a rapid increase in the hydrogen produced within the first two days corresponding with the rapid fall in COD and increase in voltage generated. The energy content of hydrogen was increasing continuously and finally achieved 38,333 J/L, which indicated that 80% of the COD energy was transferred to hydrogen gas.

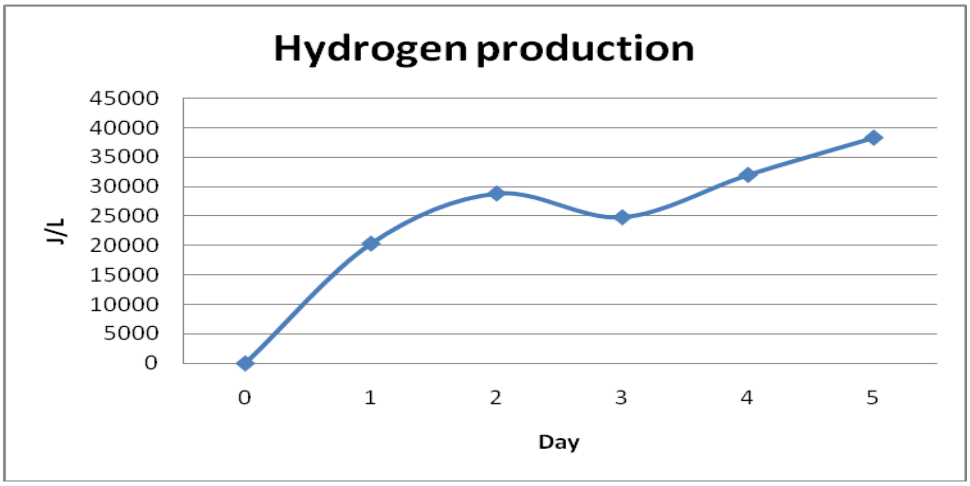

Figure 4 Energy to hydrogen production

According to the analysis, the content of nitrogen was decreasing continuously. There were 20% total nitrogen removals during the first 24 hours. That means organic nitrogen have been removed from liquid manure effectively by MFC, and stored in the MFC micro-organisms. The depletion of nitrate may also result in decreased microbial activity after day 4.

4. Conclusions

The overall COD removal from dairy farm waste using a microbial fuel cell was 98% after 6 days. The highest value of voltage generated was 1.6136mV indicating that dairy farm slurry waste is an appropriate resource for MFC. It could supply certain amount energy for the dairy farm, and also, the carbon emission and the disposal charging could be reduced. There is also bio-hydrogen produced by MFC where 80% of the COD energy has been transferred to hydrogen gas. Moreover, there were 20% nitrogen removals in the MFC during the first 24 hours. The most of nitrogen content of liquid slurry were immobilized in microbes indicating that available nitrate is a key for strong MFC activities.

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Comparison of the combustion behaviors of agricultural wastes under dry air and oxygen

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Abstract: Burning tests of some agricultural waste biomass materials such as sunflower seed shell (SSS), hazelnut shell (HS), rice hull (RH), and olive refuse (OR) were performed in order to compare the combustion reactivities of these materials under dry air and oxygen. For this purpose, these samples were burned in a thermal analyzer to obtain TGA (Thermogravimetric Analysis), DTG (Derivative Thermogravimetry), DTA (Differential Thermal Analysis), and DSC (Differential Scanning Calorimetry) thermograms under both conditions. Initial sample mass was approximately 10 mg for each sample which has a particle size of <0.25 mm, and temperature was raised from ambient to 900°C with a linear heating rate of 40°C/min under gas flow rate of 100 mL/min. No hold time was allowed at the final temperature. The results of this study showed that the thermal reactivities of biomass species change in a wide region, and the type of the oxidative medium plays very important effects on the burning parameters such as the ignition point, maximum rate of combustion and its temperature, as well as the end point of burning. On the other hand, macromolecular ingredients of biomass such as hemicellulosics, celluloses, and lignin have significant effects on the combustion behavior of biomass.

Keywords: *Biomass, Agricultural Wastes, Combustion, Dry Air, Oxygen*

1. Introduction

There are several methods to control CO_2 emissions emitted from power plants including pre-combustion capture, post-combustion capture, and oxy-fuel combustion. Pre-combustion capture is also called as gasification or partial reforming for which fuel is reacted with air, oxygen, or steam to produce gaseous products. Post-combustion techniques are based on scrubbing of CO_2 from the flue gas. In oxy-fuel or O_2/CO_2 recycle combustion method, nitrogen is excluded using pure O_2 instead of air [1,2]. In oxy-fuel technique, the diluting effect of nitrogen in the flue gas does not take place, and the concentration of CO_2 becomes likely high which is suitable for CO_2 capture and storage (CCS) techniques [3]. That is, the concentration of CO_2 in the flue gas from conventional coal-fired boilers typically changes in the range of 4-14 vol % [1], whereas in case of oxy-fuel its concentration increases to 55-65 vol %. Then, cooling and condensing of water vapor leads to increase in the CO_2 concentration to around 96 vol % [4].

On the other hand, high concentrations of CO_2 in the combustion medium alter the combustion properties compared to N_2-rich combustion medium. Ignition temperature, burner stability, flame propagation, gas temperature, the char burnout, the radiating properties of the flame, the efficiency of the boiler, and the evolution of pollutants are closely affected from the high concentration of CO_2 [5]. Some of these alterations are directly associated with the increasing radiative properties and the thermal capacity of the mixture of CO_2 and water vapor compared to N_2. Combustion kinetics also changes considerably under high CO_2 concentration [6]. From this point of view, combustion characteristics of a given fuel species should be evaluated depending on the type of oxidizer.

So the aim of this paper is to investigate the differences in the combustion properties of some agricultural wastes using dry air or pure oxygen. For this purpose, sunflower seed shell, hazelnut shells, rice husks, and olive refuse have been selected as the model biomass species, all of which are abundant in Turkey and they have already been used for energy resources for a long time.

2. Methodology

Agricultural biomass energy resources such as sunflower seed shell (SSS), hazelnut shells (HS), rice husks (RH), and olive refuse from milling (OR) used in this study are Turkish origin. These renewable energy sources were not dried in oven to avoid any modification in their original structure due to rapid drying, and they were kept at laboratory medium for 15 days to allow removal of the free moisture. Then, air-dried samples were milled and screened through a sieve having an opening of 250 µm. The proximate analysis and the gross calorific value measurements of the biomass species were carried out according to ASTM standards, and the ultimate analyses were performed by an elemental analyzer (EuroEA3000 model). These tests were repeated several times to check the reproducibility of the results.

The main ingredients of biomasses such as holocellulose (hemicellulosics + cellulose forms), lignin, and extractive matter were determined by analytical methods according to the following procedures. In order to remove the extractives and to obtain extractives-free samples, benzene-ethyl alcohol extraction procedure was applied according to ASTM D1105 standard.

The extractives-free bulk was then used as feedstock to isolate each of holocellulose and lignin. Isolation of holocellulose was performed with the mixtures of $NaClO_2$, acetic acid, and water. Whereas, the isolation of lignin was carried out by van Soest method in which extractives-free sample was treated with 72 vol % sulphuric acid to hydrolyze the cellulosics and to isolate the lignin [7]. The content of acid insoluble lignin which is called as “Klason Lignin” was determined by drying and ashing of the neutralized bulk.

Combustion tests of the samples were performed using a TA Instruments SDTQ600 model thermogravimetric analyzer with a differential scanning calorimetry detector. TGA (Thermogravimetric Analysis), DTG (Derivative Thermogravimetry), DTA (Differential Thermal Analysis), and DSC (Differential Scanning Calorimetry) thermograms were obtained using dry air or oxygen at flow rates of 100 mL/min, and the initial weights of the samples were around 10 mg. Temperature was increased from ambient to 900°C by a heating rate of 40°C/min, and no hold time was allowed.

3. Results and Discussion

Analysis results of the samples are seen in Table 1. According to data given in Table 1, it can be said that all the biomass species are rich in volatiles and their fixed carbon contents are considerably lower than the contents of volatiles. In fact, such a distribution of the contents of volatile matter and fixed carbon is typical for most biomass species [8]. SSS is the biomass material that contains the highest volatiles among the samples. Ash contents of the samples varies in a so wide range that the ash content of SSS is only 2.7 % while the ash content of RH reaches 23.8 %. Sulfur contents of the biomass species are very low regarding the ash contents of the low rank coals in general. On the other hand, hydrogen and nitrogen contents of all the samples are very close to each other.

Lignin contents of the biomass materials are also very close to each other except for HS. Although, the lignin contents of SSS, RH, and OR changes between 31.4 and 34.8 %, HS which has a woody structure contains higher lignin content as much as 51.5 %. Besides, SSS which gives the highest volatiles yield also contains the highest holocellulose content. In addition, the lowest calorific value belongs to RH that is rich in ash forming mineral matter.

Table 1. Analysis results of the biomass species

		SSS	HS	RH	OR
Proximate Analysis (%, dry basis)	Volatiles	83.7	72.0	66.2	71.2
	Fixed Carbon	13.6	21.0	10.0	14.6
	Ash	2.7	7.0	23.8	14.2
Ultimate Analysis (%, dry-ash-free basis)	C	47.8	54.8	44.8	49.3
	H	6.1	6.7	6.3	6.2
	N	1.2	1.0	0.9	1.7
	S	0.3	0.1	0.1	0.1
	O*	44.6	37.4	47.9	42.7
Structural Analysis (%, dry basis)	Extractives	13.8	6.2	9.8	13.6
	Lignin	31.4	51.5	34.8	34.7
	Holocellulose	62.5	38.6	44.9	40.0
Calorific Analysis	Higher Calorific Value (MJ/kg)	17.7	18.2	13.9	17.2

* calculated by difference

DTG and DSC curves obtained from non-isothermal thermal analyses of the biomass samples under dry air are illustrated in Fig.1.

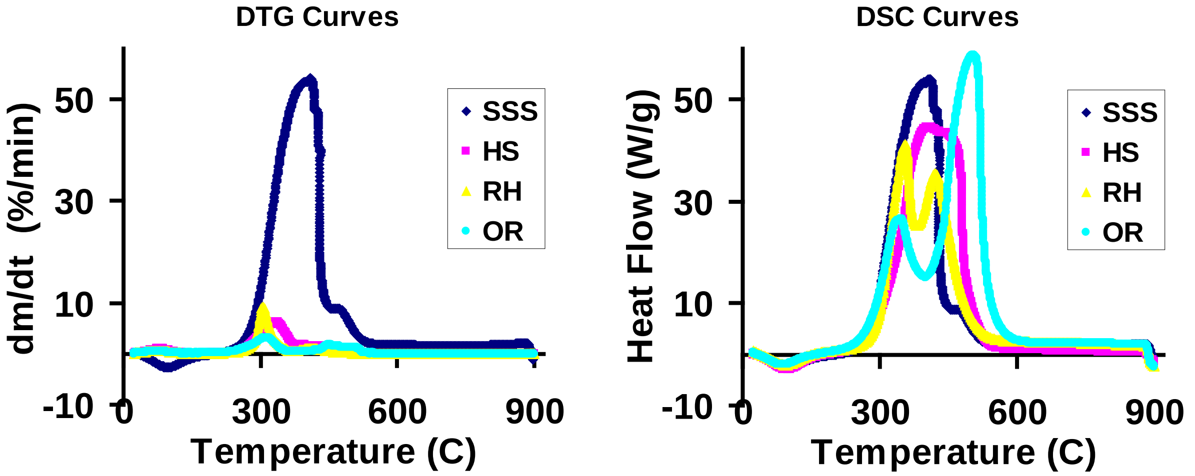

Fig. 1. DTG and DSC curves obtained from burning with dry air.

DTG curves which are seen on the left hand side of Fig.1 show the relation between temperature and the rates of the mass losses from the biomass samples. These curves indicated that the thermal decomposition and the burning of SSS have such a characteristics that it losses the weight so rapidly that its maximum rate of burning reaches 53.6 %/min at

413ºC. Besides, the maximum burning rates for the other samples could not be at this level that they were 8.2 %/min at 320 ºC for RH, 6.3 %/min at 307 ºC for HS, and 3.2 %/min at 314 ºC for OR. Although the mass losses from the samples continued as temperature increases up to the final temperature, they are negligible beyond 600ºC. The high thermal reactivity and the very high rates of mass losses from SSS can be attributed to the high contents of volatiles in this sample. In fact, high contents of holocellulose which is sum of hemicellulosics and cellulosics contribute to the formation of volatiles [9]. These constituents which are rich in weak ether bonds are thermally unstable and they produce volatile species. Of which, combustible volatiles are able to burn in the gaseous phase as homogeneous combustion. Elimination of the volatiles from the solid matrix leads to the formation of porous remnant and then burning of the char takes place firstly on the surface which is followed by diffusion of oxygen into the pores and complete burning of the particles. The latter is generally called as the heterogeneous burning stage [10]. Thus, all the organic part of the samples could be oxidized until the end of the burning experiment since the final temperature was high enough for combustion of most biomass materials.

On the other hand, the heat flows which are shown as DSC curves on the right hand side of Fig.1 predicts that the huge rates of mass losses in the DTG curve for SSS could not contribute to the exothermic performance of this sample at expected level. This is because the most of the mass losses are formed from the elimination of the volatiles such as carbon dioxide which play no important role on the calorific output. The exothermic regions for all the samples either comprised of two different parts or a unique broad peak having a shoulder, representing the effects of both homogeneous combustion of volatiles and char burning.

In order to investigate the individual effects of biomass ingredients on burning, each of the isolated ingredients including holocellulose, lignin, and extractive-free samples were burned under dry air condition. Fig.2 represents the burning characteristics of the ingredients of sunflower seed shell and rice husk, the burning properties of which were highly different in their parent samples.

The ingredients for both samples showed similar trends below 250°C that almost all of the ingredients lost the same weight in this stage. Increasing temperature affected the weight losses in different way that holocellulose and extractives-free sample of SSS rapidly lost weight while higher temperatures necessitated getting the similar decomposition yield for the lignin content of SSS. On the other hand, decompositions of holocellulose and lignin contents for RH exceeded the decomposition of extractives-free sample from 250°C to the end of the experiment. In this context, the high ratio of ash for RH is effective at this point, since most of the ash forming minerals still exist after treatment with benzene-ethyl alcohol. Accordingly, it is possible to conclude that the burning yields for the ingredients of SSS are higher than those for RH. This shows that the complex structure of biomass which is comprised of mainly from the major macromolecular ingredients are closely affected from the individual behaviors of the each ingredient during thermal process.

DTG and DSC curves obtained from the burning experiments in which oxygen were used instead of dry air are given in Fig.3.

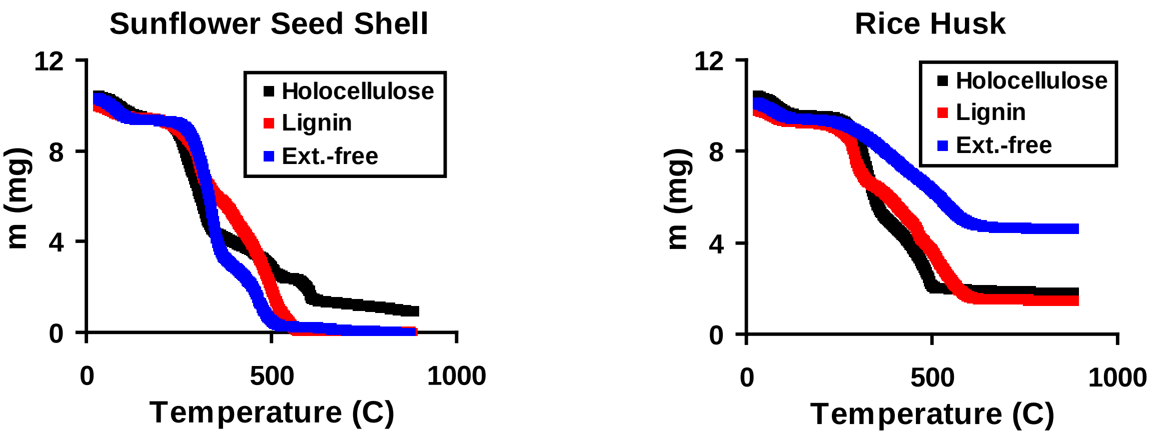

Fig. 2. TGA curves for the Ingredients of SSS and RH under dry air.

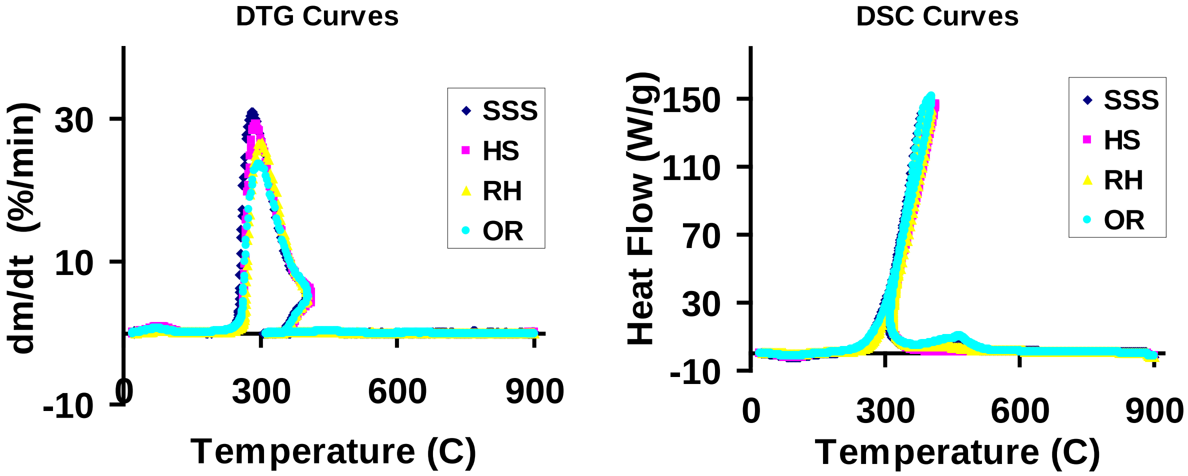

Fig. 3. DTG and DSC curves obtained from burning with oxygen

At the first sight it is likely to conclude that the difference among the DTG curves of the biomass species encountered for burning using dry air wholly disappeared, and the DTG curves almost overlapped in case of oxygen. Also, the burning rates for all the biomass samples except SSS increased more than three-folds when oxidizing gas changed from dry air to oxygen. This shows that usage of pure oxygen during burning of biomass so augmented the thermal reactivity that very different burning profiles could be obtained. Furthermore, the combustion process ended at lower temperatures. These findings can be supported by the results found from the DSC curves. That is, usage of pure oxygen so changed the shapes of the heat flow curves that they almost became very sharp peaks in contrast to the shapes of DSC curves for dry air which had some apparent regions in which heat flows take place. The exothermic heat flows occurred in so narrow temperature intervals that the temperatures of the lower and upper limits of these regions are very close to each other. Therefore, it is very difficult to distinguish the individual DSC curves as well as DTG profiles. These results predict that not only the rates of the mass losses but also the heat flows are seriously influenced from the type of the oxidizer medium. Increase in the concentration of oxygen caused variations in thermal behavior of biomass in the favor of increasing reactivity.

4. Conclusions

Burning characteristics of some agricultural waste biomass species such as sunflower seed shell, hazelnut shell, rice husk, and olive refuse have been tested under dynamic flows of dry air or oxygen under relatively slow heating conditions in a thermal analyzer. These tests indicated that both the rates of the mass losses from the biomass samples and the heat flow properties are obviously different for each biomass material under dry air. For an example, sunflower seed shell showed such a different weight loss character from the other biomass samples under dry air that it is possible to say that its thermal reactivity is extremely higher than that for the other samples under investigated conditions. Despite this big difference in weight loss characteristics of SSS, heat flow properties determined from DSC curves could not monitored at expected level, and all the samples showed similar heat flow characteristics to some extent. The major ingredients of biomass samples including holocellulose and lignin plays a significant role on the thermal reactivity and the exothermic characteristics of the burning process.

On the other hand, a different situation was detected in the DTG and DSC curves obtained under pure oxygen. That is, almost all the DTG curves for the samples overlapped to form a unique peak as well as the DSC curves. This shows that usage of oxygen instead of dry air eliminated the differences in the thermal reactivity and the burning features of the biomass species under investigated conditions. Also, thermal reactivities of biomasses seriously increased in case of oxygen usage.

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Nigeria's Bio-Ethanol: Need for Capacity Building Strategies to prevent Food Crises

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Abstract: This work reviews current bio-ethanol developments in Nigeria and offers recommendations to help sustains this trend of development. The use of staple crops, such as cassava for bio ethanol production is generating mixed reactions among the populace who depend largely on these crops for food due to poor living conditions in the country. This paper reports that while there is a target of 1.27 billion litres of ethanol per year to be blended with petroleum, the government is doing little to increase cassava production and cassava extraction efficiency. The current average yield of Nigeria's cassava stands at 15 tonnes per hectare compared to countries like Brazil with an average of 35 tonnes per hectare. Furthermore agricultural research and development in the country is underfunded, a situation which hampers innovation and growth in the agricultural sector. The need to concentrate efforts on increasing the average yield of cassava is emphasised in this work. This study could not explore the technical aspect of the cellulosic feedstock for bio-ethanol due to the non-standardization of the techniques coupled with the fact that the bio-ethanol industry in Nigeria is still at its infancy. It is obvious that the government lacks comprehensive policies to tackle the challenges that ethanol development will pose to the citizenry. Therefore this paper provides recommendations for policy makers to aid in formulating a sustainable bio-ethanol policy for Nigeria.

Keywords: *Ethanol, Biofuel, Energy crops, Food crise,Cassava*

1. Introduction

Environmental concerns and crude oil price volatility are creating market gaps between conventional and renewable energy sources. The conventional sources of energy are currently being supplemented by renewable energies to reduce and accommodate the high fluctuations in the price of oil in recent years. Bio fuel among other forms of renewable energy is attracting attention globally especially in Brazil and United State of America. It is being touted as the future supply of energy in transportation and electricity generation. Africa, the second largest continent in the world, host 13% of world's populations and 10% of the world crude oil reserves [1]. Africa's energy consumption is less than 5% of global consumption therefore African countries are categorised as poor based on energy consumption, a major developmental index. Bio fuel is not a recent development in a number of African countries like Zimbabwe, Malawi and Kenya as they started blending programmes in the 1980's. In Nigeria, bio-ethanol production is still in its infancy and requires attention from policy makers and financial institutions to develop and build the industry. In many African countries uncertainty exists on the massive utilization of bio-ethanol due to the possible risks of food scarcity. The use of bio-ethanol blend in Nigeria transportation fuel (E10) has triggered sharply polarized views among agricultural scientists, food engineers, policy-makers and the general public. Nigeria in an effort to minimise carbon emissions, energy insecurity and take advantage of renewable energy is investing in bio-ethanol technology in partnership with Brazil. One major concern shared by many on Nigeria's ethanol blend is her capacity to prevent food crises while achieving energy security. Bio-ethanol production in Nigeria adopts the use of cassava (majorly), sweet sorghum and sugarcane as feed stock knowing that these staple crops are the major food crops in Nigeria. Although Nigeria is the largest producer of cassava in the world, but more than 90% of cassava production in Nigeria is used for domestic food consumption. The government's road map for achieving the bio-ethanol target of 1.27 billion litres/year distances itself from how this will not lead to food shortage in Nigeria. It is obvious that the bio-ethanol target of Nigeria is achievable due to the size of useful land available in the country but there is need for capacity building strategies to sustain bio-ethanol production. Nigeria's size and land usage are presented in Table 1.

Table 1: Nigeria's Size and Land use Parameters [2]

Nigeria	Percentage (%)	Quantity (Million ha)
A. SIZE		
Total Area	100.0	92.4
Land area	85.9	79.4
Water bodies	14.1	13.0
B. LAND USE		
Agricultural land	**77.8**	**71.9**
Arable cropland	30.5	28.2
Permanent cropland	2.7	2.5
Pasture land	30.6	28.3
Forest and woodland	11.6	10.9
Fadama	2.2	2.0
Other land	8.1	7.5

There is huge potential for bio-ethanol in Nigeria as can been seen from Table 1. Nigeria's total area is 92.4 million hectares out of which 79.4 million and 13.0 million hectares are occupied by land and water bodies respectively. Agricultural land occupies 71.9 million hectares making Nigeria one of the top bio-fuel potential countries in the world. In Nigeria 94% of households engage in crop farming while about 68% of households engage in livestock farming [3]. This work will attempt to review government's effort to advance bio-ethanol in Nigeria, assess the risk of using food crop for ethanol production and recommend policy to help in safe-guarding food security in the country.

2. Nigeria's Bio-Ethanol Feedstock and Industries

Nigeria bio-ethanol production like most countries in the world comes from first generation feedstock like cassava, sugarcane and sorghum. Cassava is the main feedstock for Nigeria's bio-ethanol because the country imports about 50% of its sugar consumption. The world annual cassava production is estimated at 208 million tones per year with about 60% grown in Africa. Figure 1 shows cassava production in some selected countries with Nigeria leading the production chart. Nigeria produces more than 40 million tonnes of cassava yearly with the average yield of 15 tons/hectare as compared to 25-30 tons/hectare obtainable in other countries. Nigeria has more than a million hectares of land that could support cassava commercial plantation if financial institutions will invest adequately [3]. The key driver's of Nigeria's bio-ethanol are 1) urgent need to reduce energy insecurity 2) increase electricity accessibility 3) need to raise GDP from 3.5% to 8% per annum and 4) maximise the use of available resources. The plan to blend ethanol with petroleum for domestic use is driven by the need to reduce the cost of fuel importation, since Nigeria's refineries are not working at optimum capacity and to respond to climate change. Elijah I. Ohimain stated that, an investment of over $3.86 billion has already been committed to the construction of 19 ethanol bio refineries, 10,000 units of mini-refineries and feedstock plantations for the production of over 2.66 billion litres of fuel grade ethanol per annum. Also an additional 14 new projects are in the offing. Of the 20 pioneer projects, 4 are at the conception phase, 8 are in the planning phase, and 7 are under construction with only 1 operational. Many have argued that a sustainable bio-fuel policy will be needed to regulate sales, use and production [4-6].

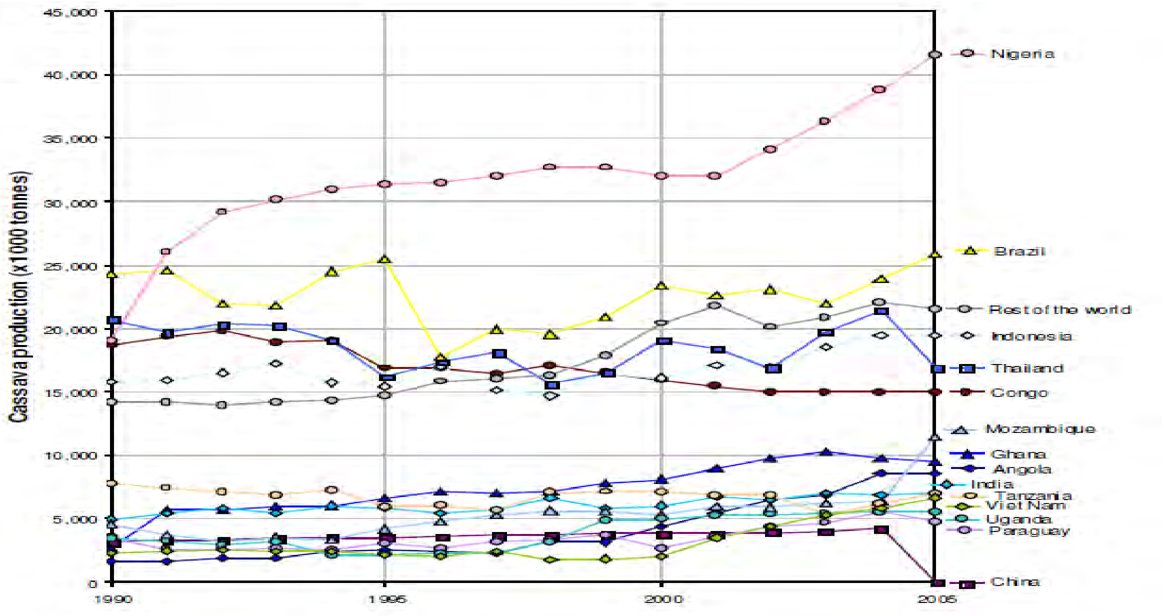

Fig. 1. Cassava production in selected countries 1990- 2005 (Source: F AO, 2007)

Table 2. Some Selected Ethanol Plant in Nigeria

Name of Company	Plant Location	Feed stock	Installed capacity (million litres/year)
Dura Clean	Bacita	Molasses/Cassava	4.4
AADL	Sango Ota	Cassava	10.9
CrowNek	Ekiti	Cassava	64.0
BV Energy Company	Bayelsa	Cassava	75.0
Akoni	Lagos	Cassava	53.0

Table 3. Some Selected Proposed Plants

No	Name of Company	Project information	Budget
1	Jigawa,Benue, Anambra and Ondo State	Integrated bio-ethanol refinaries and sugarcane farm	$4 Billion
2	Nasarawa State	Integrated bio-ethanol refinary and cassava farm	$27 Million
3	Casplex	Ethanol refinary and cassava farm	NA
4	Ekiti State	Integrated bio-ethanol refinary and cassava farm	$100Million
5	Petrobras	Ethanol plant	$200 Million
6	Kogi State	Ethanol plant	$1 Million
7	Taraba state	Ethanol plant	$115 Million
8	Niger State	Ethanol plant	$314 Million
9	lemna	Ethanol plant	$50 Million

Production of bio-ethanol from non-edible crops/oil seed and cellulosic substances are going to create a new window of opportunity for agriculture, mitigate green house emissions and end Fuel-Food debate. The entire supply chain and process of the first generation feedstock (e.g. Cassava) needs to be re-evaluated to derive added value from bio-ethanol. Currently bio-ethanol from energy crops grown for traditional markets is too expensive for use as fuel and this is causing rising cost of food especially in Nigeria where government regulations is ineffective. Table 2&3 shows bio-ethanol plants in Nigeria requiring mostly cassava as feedstock.

3. Cassava: Feedstock versus Staple Food

Nigeria produces more cassava than any other country in the world followed by Brazil. Nigeria's cassava production is almost double the production of Indonesia and Thailand. Cassava is a very versatile commodity with numerous uses and by products. The crop is abundant in 24 of the 36 states, requires minimum labour input, and remains the most important food security crop for millions of Nigerians. The leaves can serve as vegetables; the stem is used for plant propagation and grafting while the roots are typically processed for human and industrial consumption. Cassava flour has applications in the biscuits and confectionary industry, dextrin pre-gelled starch for adhesives, starch and hydrolysates for pharmaceuticals, and seasonings. Table 4 show Cassava production from 1990 -2005.

Nigeria's Cassava is traditionally processed into food products like, gari (roasted cassava granules),cassava chips and pellets, fufu flour, starch, cassava flour (lafun and elubo), etc consumed by the populace. Cassava in Nigeria is consumed mostly as gari in almost every part of the country. In some places the cassava root is a major staple while in other areas (especially in the south west) cassava leaves serve as vegetables. Since the populace is highly dependent on this crop, its use for bio-ethanol will lead to food crises. Already over 60% of the population is poor and survive with less than a dollar per day. The use of cassava for monosodium glutamate, glues/adhesives is also common but in small quantities when compared with its use for food. The ethanol content of cassava root depends on yield per hectare, technology used in the extraction and the variety of the cassava. A conservative average for a ton of cassava will be about 100 litres of ethanol [7-9]. The government target is to blend ethanol with PMS using a ratio of 9:1 meaning the government is adopting E10. Using the 2010 PMS consumption as baseline, total PMS consumption stood at 12.775×10^9 litres where over 60% was imported due to the poor state of the refineries in Nigeria. The drive to produce 1.2775×10^9litres (or 1.2775×10^6 m^3) of ethanol from cassava will require about 12.8 million tones of cassava. The average per capita food consumption in Nigeria is about 600 calories per capita per day where more than 300 calories per capita per day is from cassava in different forms. The consumption of gari may account for more than 70% of cassava consumption in Nigeria [10]. If the same cassava is to be used as feedstock for ethanol, it means that about 30% of total cassava production in Nigeria will not be available for the production of daily calories per capital per day.

Converting 30% of cassava production in Nigeria into ethanol will mean that around 3.83 million tonnes of gari will be lost in circulation thereby increase gari scarcity and threatening food security. The argument is that for every $1m^3$ of ethanol produced for fuel from cassava root, about 3 tones of gari are lost. According to Phillips et al [7] 16% of cassava produced is used in industries (excluding ethanol based industries) as raw materials, a value that must have increased since 2001. Since there is no data on the current percentage, if we assume 25% at the end of 2010 and allowing 10% for post harvest losses and wastes, it means just around

65% of cassava production will be left for other uses including food production and ethanol production).

According to the estimate revealed in this paper about 30% of cassava production is needed by the ethanol plants to deliver the 10% blended needed for the E10 in transportation. It is very obvious that 35% of the remaining cassava production can not feed the Nigeria populace of about 150 million who depend heavily on cassava products for survival due to its low cost availability and traditions. The daily consumption of ethanol in this paper does not include ethanol for cooking, a scheme the government is also seriously considering. This will increase the ethanol need as calculated in this study and will increase the need for cassava. Also the informal exportation of cassava to some neighbouring countries like Niger is not accounted for in this study. It is obvious that there is the danger of food insecurity in the country if she continues to pursue her cassava based ethanol policy without looking into other substitute energy crops.

Furthermore there is the need for second generation feedstock for Nigeria's ethanol needs. This can be obtained from the waste from wood industries, bamboo etc. Table 4 shows the production of cassava and yearly yield in Nigeria. it will be observed that the cassava production yield fluctuates without an trend of definite increment. The current yield stands at 15 tonnes / hectare.

Table 4: Levels of Cassava Production from 1990-2003 (tonnes)

Year	Production	Yield
1990	19,043,008	11.65
1991	26,004,000	10.19
1992	29,184,000	10.59
1993	30,128,000	10.59
1994	31,005,000	10.59
1995	31,404,000	10.68
1996	32,050,000	10.66
1997	32,695,000	11.88
1998	32,698,000	10.75
1999	32,070,000	10.64
2000	32,810,000	10.64
2001	32,586,000	10.80
2002	34,476,000	9.98
2003	33,379,000	10.92
2004	38,211,000	11.60
2005	42,012,000	11.60

Source: FAO (2004) &Authors

4. Capacity Building Strategies

Ethanol production in Nigeria has the potential to radically change the economic condition of the country which presently relies solely on the exportation of crude oil. The Nigerian agricultural sector which is currently dedicated only to food production, will also receive a boost. The construction of Ethanol plants in Nigeria is taking place within a non-consolidated governmental policy framework, though there are efforts to address this situation. The political environment in Nigeria is known to have lots of challenges, and the bio-ethanol industry is no exception. No adequate policy framework exist that directly addresses the challenges and peculiarities of the bio-ethanol industry in Nigeria; however, this work will provide recommendations and capacity building strategies to sustain current developments in the Ethanol industry in Nigeria.

4.1 Research and Development Centres

One key attribute of the success of the Brazilian ethanol industry was the huge investment in agricultural research and development by both the government and the private sector. The results of most of the research carried out by some government owned agencies (like EMBRAPA) together with universities have allowed Brazil to play a major role in Bio-ethanol technology [11, 12]. There is need for Nigeria to learn from countries like Brazil and US on how to efficiently utilize agricultural land for optimum yield. Nigeria produces more than 40 million tonnes of cassava yearly with an average yield of about 15 tons/hectare as compared to 25-30 tons/hectare obtainable in other countries. Increasing efficiency of inputs and processes to optimize output per hectare of feedstock comes only through research. The growth rate in Brazil's efficiency in ethanol production is about 4% per year. Innovations in the industrial process of cassava (saccharification and fermentation) will allow an increase in carbohydrate extraction from the cassava root up to 70 %. The government's budget and policies have not laid emphasis on research and development but more on ethanol plant construction and cassava plantations. There are more than 70 universities in Nigeria and more than 4 of the Universities are Universities of Agriculture, well equipped to carry out research on the second generation feedstock for ethanol, but the government has consistently ignored the role of research institutions in its Bio-ethanol development. The government needs to empower the Universities through its various agencies to carry out substantial research to aid the development of a more sustainable ethanol technology.

4.2 Financial Institutions, Private Investments and government incentives

Nigeria's bio-ethanol feedstock production is government led and has little input from private firms. The industry needs more participation from commercial agricultural firms and support by financial institutions. Government intervention at the initial phase of bio-ethanol production is necessary but access to finance and availability of affordable loans should be encouraged. In Nigeria for instance, no insurance or commercial bank gives soft loans for the cultivation of cassava for bio-ethanol production. The banks are unwilling to provide finance due to market uncertainties and perceived high risks. The lack of adequate data to guide financial institutions and insurance firms in taking decisions are due to gross variations in the data obtained from the government and the private sector. There are a number of incentives the government can deploy to stimulate the Nigeria's bio-ethanol industry [13]. These include:

- **Pioneer Status**: All registered businesses engaged in activities related to biofuels production and/or the production of feedstock for the purpose of biofuel production and co-generation within the country shall be accorded Pioneer Status within the provisions of the Industrial Development (Income Tax Relief) Act.
- **Withholding tax on interest, dividends, etc**.: Biofuel companies shall be exempted from taxation, withholding tax and capital gains tax imposed under sections 78, 79, 80 and 81 of the Companies Income Tax Act in respect of interest on foreign loans, dividends, and services rendered from outside Nigeria to biofuel companies by foreigners
- **Waiver on import and customs duties:** Biofuel companies shall be exempted from the payment of customs duties, taxes and all other charges of a similar nature.

- **Waiver on Value Added Tax: T**his shall also apply to all Biofuel companies operating in Nigeria.
- **Long term preferential loans:** Preferential loan arrangements will be made available to investors in the biofuel industry to aid the development of large scale outgrower schemes and large scale integrated operations, including plantation, plant, and within the gate co-located power generation plants. An Environmental Degradation Tax shall be charged on oil and gas upstream operations to provide a source of funding for preferential loans.

5. Policy Recommendations

The development of bio-ethanol in Nigeria is a welcome idea coupled with the benefit of job employment and increased revenue for the government. The sustainability of bio-ethanol implies that government needs to improve on their present commitment and learn from the success stories of countries like Brazil and inculcate suggestions that will help to sustain the bio-ethanol development in Nigeria. In lieu of that the following recommendations are given:

(i) Effective and robust loan facilities: There is the need for long term loan facilities to motivate farmers into practicing commercialized farming. Agricultural incentives like little or no interest rates on short term loans, low interest on long term loans should be made available to farmers. The recapitalization of banks in Nigeria was to allow cash flow to small business but this is not the case.
(ii) The land use act: There are so many flaws in the land use act that needs to be amended, the land use acts needs to favour land for agriculture purposes.
(iii) Tax exception: Tax incentives should be given to private investors willing to invest in the bio-fuel feedstock.
(iv) Export and import duties: The waiver of duties on imports and exports related to bio-fuel should be considered by the government to kick start her ambition in the bio-ethanol field. Since the government has a poor record in the management of bio-ethanol blend. The management of bio- ethanol blend should be private sector driven
(v) Well equipped R&D: The technology of bio-ethanol in Nigeria should have indigenous perspectives, the government and the private sector should jointly fund research both at home and abroad to validate their outcomes at every point. Bio-fuel industry comes with new technology. The Universities of Agriculture in conjunction with Universities of Technology available in the country should be given the responsibility of pioneering this research.
(vi) Bio-fuel policy and legislature: Nigeria's bio-fuel policy at the moment is still sketchy and need thorough work to establish a frame work and legislature for industry. Clean energy and techniques should be well promoted and the consequences of breaking the law should be severe. The law to govern the bio-fuel industry should be corruption proof.
(vii) Promoting the use of second generation feed stocks: This will reduce the risk and threat to food security especially in Nigeria where the first generation feed stocks are the main source of food.
(ix) Setting up a Bio-fuel Feedstock regulatory body: A body like this will be given the responsibilities to oversee the sale, price and consumption of feedstock for domestic consumption and for the bio-fuel industry
(x) Brazil and the US partnership: The government should involve the two leading countries in bio-fuels to shape its bio-fuel policy and technology.

6. Conclusion

The development of the bio-ethanol industry in Nigeria is an important milestone in achieving energy self-sufficiency and sustainable development, especially in the transportation sector.

This paper has reviewed efforts of the Nigerian government towards bio-ethanol blend in the country, the risks and dangers involved in kick-starting ethanol production without proper policy and developmental frameworks to increase cassava production and yield. Commercial agriculture must play a pivotal role in this development of bio-ethanol without leading to food insecurity. There is need for the government to encourage and give incentive for cassava production in the country. The need for government to involve research institutions in the development of bio-ethanol and cassava cannot be over emphasis. The government also has to design incentives for financial institutions to grant soft loans for the purpose of cassava cultivation on a large scale. The government's ambition to advance bio-ethanol technology in Nigeria poses a threat to its populace of about 150 million if adequate frameworks are not put in place as recommended in this work. If the government wants to continue its bio-ethanol technology the paper recommends that the decision makers should carefully review the policy recommendations in this work.

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Planting sweet sorghum under hot and dry climatic condition for bioethanol production

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Abstract: Plants are the best choice for meeting the projected bio-ethanol demands.For this scope, a comparative analysis of the technological options using different feed stocks should be performed. Sweet sorghum can be used as a feedstock for ethanol production under hot and dry climatic conditions. Because, it has higher tolerance to salt and drought comparing to sugarcane and corn that are currently used for bio-fuel production in the world. In addition, high carbohydrates content of sweet sorghum stalk are similar to sugarcane but its water and fertilizer requirements are much lower than sugarcane. Also, sugarcane is not a salt tolerant plant. On the other hand, high fermentable sugar content in sweet sorghum stalk makes it to be more suitable for fermentation to ethanol.In this work, planting sweet sorghum in hot and dry provinces of Iran generally produced 80 tons stalks, 5 tons grains and 15 tons green leaves per hectare. However comparison among 29 sweet sorghum cultivars and lines showed that Rio had higher biomass (117.14t/ha), stalk yield (95.00t/ha), grain yield (5.00t/ha) and leaves (17.00 t/ha). It is interesting to point out that sweet sorghum could be cultivated in southern parts of Iran 3-4 times per year. Based on these results it is more economical to plant sweet sorghum for bio-ethanol production in hot and dry regions of the world.

Keywords: Sweet sorghum, carbohydrate, bio-ethanol, bio-fuel.

1. Introduction

Due to the diminishing fossil fuel reserves, alternative energy sources need to be renewable, sustainable, efficient, cost effective and safe [1]. Ethanol is one of the best renewable source that has all the above characteristics. Ethanol produced from starch hydrolysis and sugar fermentation from biomass is called bio-ethanol. The raw materials used in the ethanol production by fermentation can be classified into three main types of materials, which are sugars, starches and ligno-cellulose. Sugar can be converted into ethanol directly. Starch could be hydrolyzed to fermentable sugars by enzymes; and lingo-cellulose following pre-treatment by acids or alkali could be hydrolyzed to sugars. Industrial bio-ethanol is produced from various crops like sugarcane or sugar beet molasses, corn starch, sweet sorghum, tapioca etc. Among them sweet sorghum has been considered as one of the most promising crop for energy and industry in hot and dry climates. Sweet sorghum (*Sorghum bicolor* L.Moench) is a C_4 plant characterized by high biomass and sugar –yielding and a high photosynthetic efficiency [2,3]. It also has a rapid growth rate as it has a shorter growing season than sugarcane and therefore suitable to be grown in most parts of the world. It is well adapted to drought [4] and has the capability of remaining dormant during the driest period Sweet sorghum is the only plant that all parts of plant can be used for bio-ethanol production. Its stalk has sucrose, glucose and fructose readily fermented to ethanol. Its grain flowing starch hydrolysis to glucose could be fermented to ethanol. Sweet sorghum leaves and bagasse as lingo-cellulosic feed-stocks have the greatest potential to be used as second generation of biofuel production. The conversion of sweet sorghum leaves and bagasse to bio-ethanol requires pretreatment to break down the lingo-cellulosic structure, remove lignin and hydrolyze the cellulose and hemicellulose components to sugars. Sugars are converted to bio-fuel through fermentation. However conversion of lingo-cellulosic feed-stocks to bio-ethanol is not commercialized yet and it is a renewable energy for the future.Most part of Iran has hot and dry climatic condition and due to this condition, corn and wheat is imported. Sugar beet and sugar cane molasses are not in large quantities so the ethanol produced from these substrates is supplied by industries. The purpose of this study was to plant sweet sorghum under Iran hot and dry climatic condition and produce bio-ethanol to be mixed with fuel.

2. Comparisons among sweet sorghum cultivars and lines

The purpose of this experiment was to determine the most adapted sweet sorghum cultivars and lines under hot and dry condition. 29 sweet sorghum cultivars and lines were compared in a randomized complete block design at the University of Isfahan Experiment Station and University of Isfahan Chemical engineering Lab. Plots consisted of 4 rows, 10 m apart and 0.75m apart. Plots received 300 kg/ha of di-ammonium phosphate and 100 kg/ha of urea disked into the soil before planting. Water was applied as needed. When kernels were at physiological maturity, three meters form two central rows were harvested. Biomass and stripped stalks were determined. The fresh stalk, after removing the leaves was crushed in a sugarcane crusher to extract the juice. After filtration through a sieve to remove the chaff etc. the soluble solids (brix), sucrose (pol%) and the purity of the juice were measured according to Varma [5]. Statistical analyses were performed using Statistical Analysis System (SAS) computer program. The means were compared according to Turkey’s test.

3. Results and Discussion

3.1. Weather Information.

Iran has an arid climate with average annual precipitation of 250 mm or less.There is no summer rain and this low amount of rain precipitates from October to April when sugar crops such as corn, sorghum, sugar beet and sugar cane are not growing. Therefore all these crops should be irrigated from planting to harvest. Optimum temperature for sweet sorghum germination and growth is above 18 oC. Since sweet sorghum is a warm season crop, so its growth will be reduced considerably when temperature falls below 5 degree centigrade. Table 1 shows the planting date of different provinces of Iran. Sweet sorghum duration from planting to harvest is 120-150 days. So in Southern part of Iran when the growing season is long (Table2), sweet sorghum can be planted two to three times per year.

3.2. Comparison among sugarcane, sugar beet and sweet sorghum.

Among sugar and starch crops that is used for ethanol production in other countries, in Iran ethanol only is produced from sugarcane and sugar beet molasses.

In comparison to other two crops, sweet sorghum has the least crop duration, growing season, soil water requirements, water management and crop management (Table 3). Under Iran climatic condition sweet sorghum has similar biomass, sugar content, sugar yield and ethanol production to sugar cane. It should be mentioned that sugar cane can only be grown in the sought where there is no freeze temperature, whereas sweet sorghum is grown in most part of the country. Based on the above results it is recommended to plant sweet sorghum for ethanol production [6].

Table 1. The planting date of different provinces of Iran for sweet sorghum

State	Above 15 ^{o}C	Less than 0 ^{o}C
Bandar Abbas	Feb.	-
Dezful	April	-
Isfahan	May	Dec.
Kerman	June	Nov.
Rasht	May	-
Shiraz	May	Dec.
Uromieh	Apr.	Nov.
Yazd	May	Dec.
Zahedan	Apr.	Dec.

Table 2. Climatic conditions of Kahnooj

Month	T_{max} (^{0}C)	T_{min} (^{0}C)	Relative Humidity (%)
Jan.	21.1	8.7	70.1
Feb.	21.0	11.7	72.0
Mar.	27.3	14.5	60.3
Apr.	32.2	18.7	60.1
May	40.5	24.8	40.0
June	44.4	29.8	38.9
July	45.4	30.0	42.0
Aug.	44.0	30.0	45.9
Sep.	40.7	30.3	46.0
Oct.	38.7	23.5	53.0
Nov.	30.5	17.0	66.0
Dec.	24.0	11.4	64.0

Table 3.Comparison among sugarcane, sugar beet and sweet sorghum [6]

	Sugar cane	**Sugar beet**	**Sweet sorghum**
Crop duration	About 7 months	About 5-6 months	About 4 months
Growing season	Only one season	Only one season	One season in temperate and two or three seasons in tropical areas
Soil requirement	Grows well in drain soil	Grows well in sandy loam; also tolerates alkalinity	All types of drained soil
Water management	36000 m^3/ha	18000 m^3/ha	12000 m^3/ha
Crop management	Requires good management	Greater fertilizer requirement; requires moderate management	Little fertilizer required; less pest disease complex; easy management
Yield per ha	70-80 tons	30-40 tons	54-69 tons
Sugar content on weight basis	10-12%	15-18%	7-12%
Sugar yield	7-8 tons/ha	5-6 tons/ha	6-8 ton/ha
Ethanol production directly from juice	3000-5000 L/ha	5000-6000 L/ha	3000 L/ha
Harvesting	Mechanical harvest	Very simple; normally manual	Very simple; both manual and mechanical

3.3. Energy balance

Among feedstock that currently are used in different countries for bio- ethanol production reported sweet sorghum has the highest energy output/input (Table 4). Wheat in Canada has the lowest energy input/output (1.2) while sweet sorghum in temperate areas has the highest output/input (12-16) [7]. Most parts of Iran have high day and low night temperature. During the day because of high temperature through photosynthesis more carbohydrates will be accumulated. Cool nights cause respiration to be decreased. As a result, higher sweet sorghum biomass and sugar will be produced.

Table 4. Energy output/input for different feedstock

Feed stock	**Energy output/input**
Sugarcane (Brazil)	8.3
Sugar beet (European Union)	1.9
Corn (United States)	1.3-1.8
Wheat (Canada)	1.2
Fossil- fuels	0.8
Sweet sorghum	8(12-16 in temperate ares)

3.4. Comparison among 29 sweet sorghum cultivars and lines for stem yield, brix and sucrose content.

Mean comparisons are presented in Table 5. Since both stem yield and brix has more important role in ethanol production from sweet sorghum, therefore cultivars and lines have that more than 60t/ha stalk yield and brix more than 20% were selected. These cultivars are Vespa, MN1500, Soave, Sofra, SSV108, SSV94, SSV96, Foralco and Rio. A further selection among these cultivars indicated that Rio had the highest stalk yield (95 t/ha) and highest brix (22.36). Although the stem yield of M81-E, Theis and Wray was more than 100 t/ha but their brix was lower than Rio. None of the sweet sorghum lines due to their low stem yield and brix were suitable for ethanol production.[8].

Table 5. Mean comparisons among 29 sweet sorghum cultivars and lines regarding stem yield, °Brix, Sucrose and purity at university of Isfahan, Iran [8].

Genotypes	Stem yield (t/ha)	Brix (%)	Sucrose (%)	Purity (%)
Cultivars				
Roce	39.14	21.96	14.39	66.71
Vespa	84.53	20.99	13.05	74.59
Brandes	77.14	18.72	8.92	46.39
MN1500	83.71	20.71	12.00	57.59
E36-1	48.00	18.26	13.41	76.02
Soave	61.57	20.73	13.46	65.00
M81-E	103.57	16.01	10.26	65.10
Somac	44.43	21.12	12.85	60.10
Sofrah	85.57	19.63	12.61	64.05
SSV-108	62.85	22.25	13.97	62.26
SSV-94	70.14	20.64	11.75	57.12
SSV-96	62.00	22.54	13.71	60.10
Theis	100.14	19.10	7.26	37.59
Foralco	97.71	20.40	12.64	60.83
Rio	95.00	22.36	16.06	71.31
S-35	58.43	19.78	11.58	58.75
Turno	39.86	11.16	6.00	35.86
Satiro	27.86	17.16	10.33	60.02
Wray	126.42	15.84	7.85	49.40
Lines				
IS 686	61.43	16.54	9.00	54.39
IS 16054	51.85	21.07	11.73	55.83
IS 18154	42.14	19.04	12.71	66.71
IS 6962	43.00	23.01	13.61	58.85
IS 9639	54.00	21.77	14.31	65.23
IS 2325	59.57	20.70	14.28	60.18
IS 6973	33.43	22.85	14.21	61.88
IS 4546	56.43	22.03	13.05	60.12
IS 19273	46.28	20.29	15.04	73.69
IS 4354	33.86	17.66	9.80	55.28
W[1]	**2.53**	**6.18**	**5.05**	**23.981**

[1].Tukey's value for 5% level

4. Conclusions

It is clear that fuel ethanol from sweet sorghum is the best choice to be implement under hot and dry climatic conditions regarding both economic and environmental considerations. Because, sweet sorghum has higher tolerance to drought [9], water logging and salt [10, 11], alkali and aluminum soils; It may be harvested 3 - 4 months after planting (Table 1) and planted 1 - 2 times a year (in tropical areas); Its energy output / fossil energy input is higher than sugarcane, sugar beet, corn, wheat and etc… specially in temperate areas; It is more water use efficient (1/3 of water used by sugarcane at equal sugar production); Its production can be completely mechanized and its bagasse has higher nutritional value than the bagasse from sugarcane, when used for animal feeding. Also, by implementing agricultural practices such as adequate water and fertilizers, suitable cultivars or hybrids, crop rotation, pest management and etc… can increase productivity with focus on bio-fuel production [12].

In addition, sweet sorghum has high amount of sucrose [8] and invert sugar [13] which are easily converted to ethanol [14, 15]. Therefore, it seems that sweet sorghum is the most suitable crop for bio-fuel production in arid regions of the world. This awareness should push government of the countries with such climatic conditions to promote the development of projects for fuel ethanol production from sweet sorghum. However, social aspects (including environmental concerns) should play a more significant role in the selection of the most suitable feed-stocks for the alcohol industry. In this way, financial indicators would not be necessarily the decisive factors when new large-impact projects for bio-fuels production are studied and implemented in developing countries.

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Evaluation of greenhouse gas emission by ethanol production from sugarcane (case study of Minas Gerais, Brazil)

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Abstract: The paper presents an evaluation of greenhouse gas emission during the industrial process of ethanol production from sugarcane crops. The production of biofuels is experiencing an increasing trend in most regions of the world, following the need of the optimization of renewable energy from biomass. In Brazil sugarcane is one of the main raw materials for the production of ethanol. The research summarized in this paper was carried out in the period 2008-10 in the State of Minas Gerais, Brazil. The tool *Ecoinvent* has been used for the estimation of the environmental magnitude of the components of bioethanol production. Moreover a field survey has been carried out, which involved the visit to 11 selected distilleries, together with the application of questionnaires related to the whole ethanol production process and to the utilization of chemical components and by-products. The total emission of CO_2eq (representing the whole amount of greenhouse gases: CO_2, CH_4 and N_2O) could be estimated in 1540 kg/ha.year. The key sources of greenhouse gas emissions in the bioethanol production are sugarcane burning and use of fuels, which account for more than 50 % of total emissions. This shows a clear environmental limitation in the process of sugarcane utilization.

Keywords: *Ethanol, Greenhouse Gases Sugarcane*

1. Introduction

The environmental constraints related to the explotation of fossile fuels, together with the current concerns regarding the massive production of hydropower lead to the convenience of searching alternative energy sources. In this sense the production of biofuels is experiencing an increasing trend under a global perspective. Countries like Brazil, which present large agricultural areas, are intensively researching the optimization of renewable energy from biomass. In Brazil sugarcane is one of the main raw materials for the production of ethanol. The fermentation of sugar into ethanol is one of the earliest organic reactions employed by humanity. Sugarcane is a semiperennial grass of the genus *Saccharum*, which is native to warm temperate to tropical regions of Asia. They present stout, jointed, fibrous stalks that are rich in sugar. Two countries (Brazil and India) are together responsible for around 50 % of the world sugarcane production. Sugarcane products include table sugar, molasses, alcoholic beverages (e.g. rum) and ethanol. World's ethanol production forecast for 2012 will pass 20 billion gallons and Brazil will be responsible for one third of this amount [1]. The largest single use of ethanol is as motor fuel and fuel additive. Gasoline sold in Brazil contains at least 20 % anhydrous ethanol, which is blended since 1933. In 2003 the country started a massive production of vehicles flex-fuel, which function with gasoline as well as with ethanol. The cane delivered to the processing plant is called *burned and cropped* and represents 77 % of the mass of the raw cane. The reason for this reduction is that the stalks are separated from the leaves (which are burned and whose ashes are left in the field as fertilizer) and from the roots that remain in the ground to sprout for the next crop. The basic steps for large scale production of ethanol are: microbial fermentation of sugars, distillation and dehydration. Some crops require previous saccharification or hydrolysis of the carbohydrates such as cellulose and starch into sugars. Currently only the sugar (from sugarcane) and starch (from corn) portions can be economically converted to sugars. However there is much activity in the area of cellulosic ethanol, where the cellulose part of a plant is broken down to sugars and subsequently converted to ethanol. Greenhouse gases (CO_2, CH_4 and N_2O) are generated during the agricultural process together with the corresponding inputs manufacturing emissions.

Fig. 1 presents the main steps in conventional ethanol production in Brazil [2].

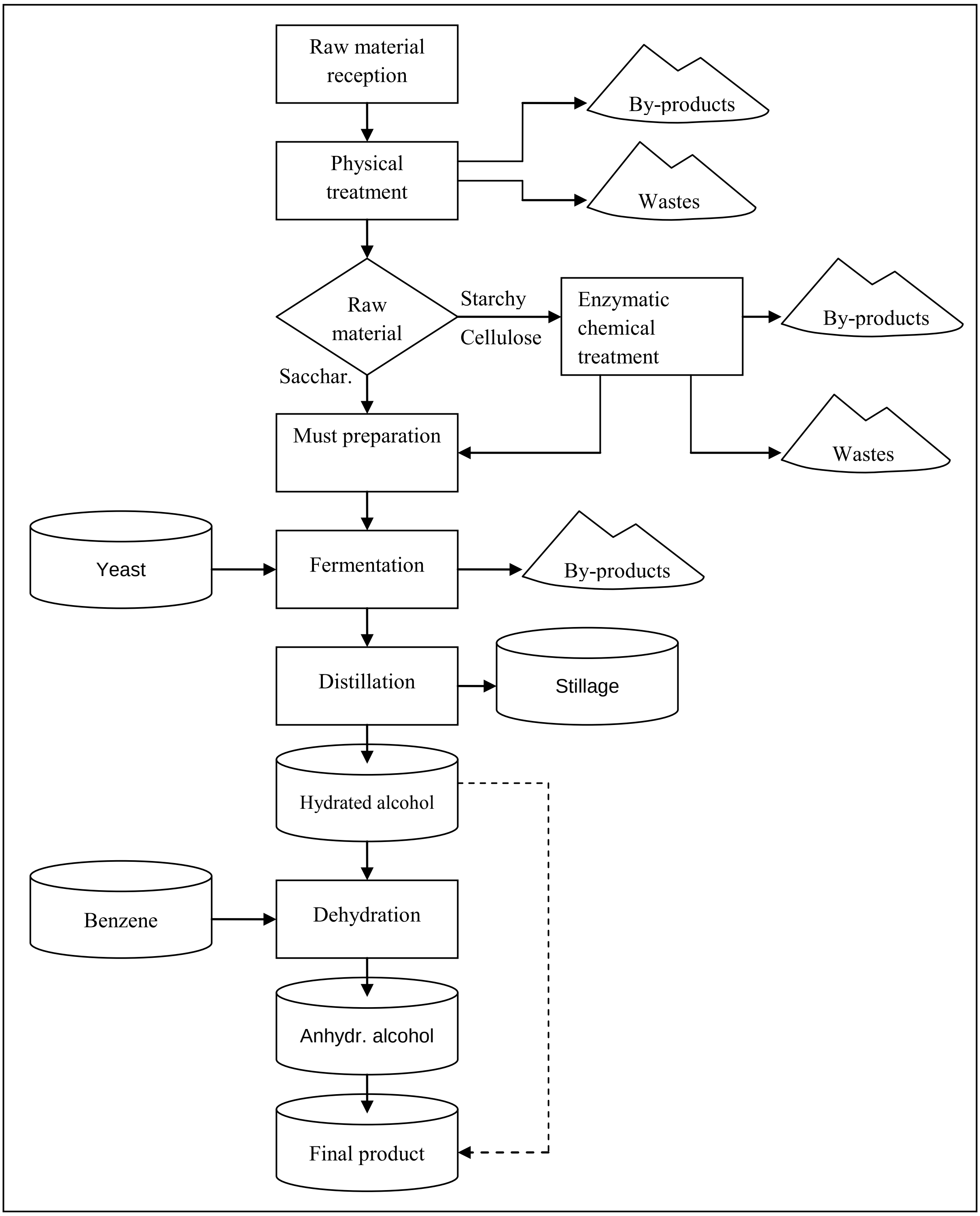

Fig. 1: Technological routes for ethanol production in Brazil

Some international studies [3, 4, 5] have been dedicated to the evaluation of energetic efficiency and the corresponding mitigation of the emission of greenhouse gases. However there is no broad consensus about energetic gains due to ethanol utilization and its impact on generation of greenhouse gases. Major inconsistencies are related to assumptions adopted by the quantification of inputs and outputs in ethanol life cycle [6]. Also technological differences in the local ethanol production process affect the accuracy of the results [7]. Consequently further studies are demanded in order to solve these limitations.

2. Methodology

The research presented in this paper was carried out in the period 2008-10 in the state of Minas Gerais, one of the 27 states which forms the Federative Republic of Brazil. Minas Gerais is currently the second largest sugarcane and ethanol producer state in Brazil, being placed after the state of São Paulo. In order to estimate the environmental magnitude of the components of bioethanol production the tool *Ecoinvent* has been used, which provides data for inputs and outputs of lifecycle of thousands of materials. The field survey involved the visit to 11 selected distilleries in the State of Minas Gerais, together with the application of questionnaires related to the whole ethanol production process and to the utilization of chemical components and by-products.

The first step for the evaluation of greenhouse emission gases in ethanol production was the correct identification of all relevant stages in the agricultural phase and in the sugarcane industrialization. Technological variations in both phases may result in quite different numbers for the emission values. Principles of Life Cycle Evaluation [8] together with IPCC recommendations [9] have been used in this phase. Only the most important greenhouse gases have been considered (CO_2, CH_4 and N_2O) and total emissions are expressed in (kg CO_2eq) as follows: 1 kg CH_4 = 21 kg CO_{2eq} and 1 kg N_2O = 310 kg CO_{2eq} [10]. Emissions estimation assumed 1 ha of cultivated soil as the functional unity. Adopted time span was 6 years, which encompasses seedling application, sugarcane cycle and 4 cycles of agricultural plant resprout. Emissions were calculated using Eq. 1:

$$Ei = \frac{Ij \times nc \times FEj}{6} \tag{1}$$

Where: Ei = greenhouse gas emission corresponding to activity (i) i = fuel consumption in agricultural operations, fuel consumption in seedling transport, fuel consumption in filtercake, ashes and sediments transport, fuel consumption in lime and fertilizers transport, fuel consumption in irrigation, fuel consumption in mechanical harvest, fuel consumption in loading and sugarcane transport, crop burning, N_2O emission from soil, seedling production, consumption of chemical products in the industrial phase; Ij = consumed quantity of raw materials in each category; nc = number of cycles; FEj = emission factor corresponding to raw material Ij; j = fuel, lime, fertilizers, pesticides, burnt sugarcane during crop and chemical products used in industrial stage.

Emission factors were obtained from *Ecoinvent* [11] and, when available, from [9]. *Ecoinvent* is a broad data base which shows environmental loads, including here gaseous emissions associated with lifecycle of agricultural and industrial products. Data about fuel consumption in vehicles and agricultural machines, eventually not available in visited industries, have been extracted from [12].

3. Results and Discussion

The calculated emissions have been obtained by multiplying *activity data* (e.g. liters of diesel in a selected agricultural operation) and *emission factor* (average values found in the Brazilian technical literature).

All researched distilleries send the whole amount of generated filtercake, ashes and sediments to further utilization in sugarcane farming. Average waste generation rates are respectively 2051.63 kg/ha·a, 659.60 kg/ha·a and 1430.02 kg/ha·ano (total = 4141.25 kg/ha·a. Average distance between processing plant and agricultural area is 13 km.

For the calculation of gas emission in transport of lime and fertilizers it was assumed the utilization of a 12 t truck, with fuel consumption of 2,5 km/L and an average distance of 25 km between supplier and farming. In a period of 6 years around 3640 kg load would be transported [12]. All researched farms use wastewater for sugarcane culture irrigation (24 cycles in 6 years). With respect to fertilizers, the emissions have been calculated considering the most frequent chemical inputs used in the country: N in the ammonium form, P_2O_5 and K_2O [13]. Pesticides have been classified according to their active components and the emissions have been calculated based on literature values [9] (Table 1).

Table 1. Emission of greenhouse gases in lime and fertilizers consumption

Inputs	Consumption (kg/ha)	Gas emission (kg CO_2eq/ha)
Lime	1520	228
Fertilizers		
N	84	254
P_2O_5	123	328
K_2O	163	85
Total		895

The gaseous emissions from burning activity in sugarcane plantations have been estimated by the corresponding factors for agricultural wastes recommended by IPCC [9]: 2.7 g CH_4/kg and 0.07 g N_2O/kg of dry mass, which is equivalent to 82.82 g CO_2eq/kg considering a combustion factor of 0.80. CO_2 emissions are here not taken into account since the emitted carbon will be reassimilated in the next crop. Nitrogen addition to the soil through the use of fertilizers intensifies nitrification and denitrification processes and liberates N_2O as a by-product to the atmosphere. N_2O emissions are around 20 g per kg of N used in the soil [9].

In the present case all energy consumed in the researched factories is generated by burning bagasse (crushed sugarcane), therefore no gas emission from fossile fuels are registered. Direct CO_2 emissions, which are associated with bagasse burning and molasse (sugarcane syrup) fermentation, are not considered in these calculations since, as pointed before, carbon will be reassimilated by the vegetation. Consequently only emissions coupled with the use of chemical products take part in the general account for the indudtrial phase of ethanol production.

Productivity variations in irrigated and non irrigated areas have been also taken into account in loading, transport and sugarcane industrialization. Field research showed that average distances were 18 km for trucks of 28 and 45 t and 40 km in the case of heavier trucks (58 t).

Moreover inputs transport from suppliers to the industries are carried out by 15 t trucks which cover an average distance of 400 km.

After computing the emission of greenhouse gases in all the necessary steps for ethanol production, following number could be estimated: 1539 kg/ha.year of CO_2eq (representing the whole amount of greenhouse gases: CO_2, CH_4 and N_2O). Table 1 summarizes the corresponding emissions and percent values in each of the most relevant categories in ethanol production from sugarcane.

Table 2. Emission of greenhouse gases in agriculture and industrialization of sugarcane for ethanol production

Category	**Gas emission (kgCO_2.eq/ha.a)**	**% contribution in total emission**
Fuel consumption	337.18	21.9
Fertilizers consumption	298.38	19.38
Biocides consumption	30.39	1.97
Crop burning	434.31	28.21
N_2O from soil	331.52	21.54
Seedling production	72.81	4.73
Chemical products	35.01	2.27
Total	**1539.6**	**100**

4. Conclusions

It can be seen that the key sources of greenhouse gas emissions in the bioethanol production are sugarcane burning, fuel consumption, N_2O liberation from soil and fertilizers consumption, which account for more than 90 % of total emissions. One of the learning points of this research is that the consideration of other technological scenarios can lead to significant differences in the quantification of greenhouse gases emissions. Moreover, in spite of favourable points in the utilization of ethanol, there are clearly environmental limitations in the process of sugarcane utilization, which are represented by the possibility of the generation of greenhouse gases during the lifecycle of biofuels production.

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An environmental optimization model for bioenergy plant sizes and locations for the case of wood-derived SNG in Switzerland

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Abstract: Bioenergy from woodfuel has a considerable potential to substitute fossil fuels and alleviate global warming. One issue so far not systematically addressed is the question of the optimal size of bioenergy plants with regards to environmental and economic performance. The aim of this work is to fill this gap by modeling the entire production chain of wood and its conversion to bioenergy in a synthetic natural gas plant both with respect to economic and environmental performance. Several spatially explicit submodels for the availability, harvest, transportation and conversion of wood were built and joined in a multi-objective optimization model to determine optimal plant sizes for any desired weighting of environmental impacts and profits.

We find a trade-off between environmental and economic optimal plant sizes. While the economic optima range between 75 – 200 MW, the environmental optima are with 10 – 40 MW significantly smaller. Moreover, the economic optima are highly location specific and tend to be smaller if the biomass resource in the geographic region of the plant is scarcer. The results are similar with regards to the effect on global warming as well as with respect to the aggregated environmental impact assessment methods Ecoindicator '99 and Ecological Scarcity 2006.

Keywords: *Biofuels, Wood energy, SNG, Life cycle assessment, Environmental optimization*

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1. Introduction

Bioenergy from woodfuel has a large potential to substitute fossil fuels and alleviate global warming. At the same time, it is a limited resource, which should be used optimally from the environmental perspective. An important variable determining the sustainability of wood energy production chains, which has not yet been systematically addressed, is the influence of the size of bioenergy plants on the environmental impacts generated along the bioenergy production chain.

The size of a bioenergy plant affects several variables at the plant and production chain levels. At the plant level the size of a bioenergy plant influences the technology choice and configuration and therefore the efficiency of the biomass conversion, the generated environmental impacts as well as production costs. At the production chain level, the size of a bioenergy plant influences mainly the geographical area needed for the biomass supply, which affects the average transport distance and therefore again environmental impacts and costs. If the biomass is more or less equally distributed on a regional scale, the average transport distance could be estimated by a simple radius-surface relationship. However, in countries with large regional differences in biomass availability – either due to geographic factors such as mountains or deserts, or due to variations of regional demand – this relationship may be different.

The aim of our model is to show how these variables affect the environmental and cost performance of bioenergy plants at different plant sizes and locations. We choose the case of the production of synthetic natural gas (SNG) from forest wood (mainly residues from the roundwood production and thinning operations) in Switzerland.

2. Material and Methods

2.1. Overall approach

In order to model the entire production chain of SNG from wood four submodels were designed to model (A) the spatial wood availability, (B) harvest, (C) transport and (D) the conversion to SNG at the bioenergy plant (Fig. 1). Each submodel models the costs as well as environmental impacts based on life cycle assessment (LCA) resulting for its part of the production chain. Data from the submodels is then processed in the optimization model. The latter first chooses optimal technology configurations for the bioenergy plant from a set of potential technologies for each plant size based on a weighting of environmental impacts and profits. Second the environmental and economic performance is calculated for plant sizes from 5 – 200 MW. Third the optimal plant size is determined and the procedure is repeated for plants in different geographic contexts of Switzerland.

Environmental impacts are assessed with the methods global warming potential (GWP) [1], the Ecoindicator '99 (H/A) (EI'99) [2] and the Ecological Scarcity 2006 (ES'06) [3]. Life cycle inventory has been taken from the ecoinvent database [4].

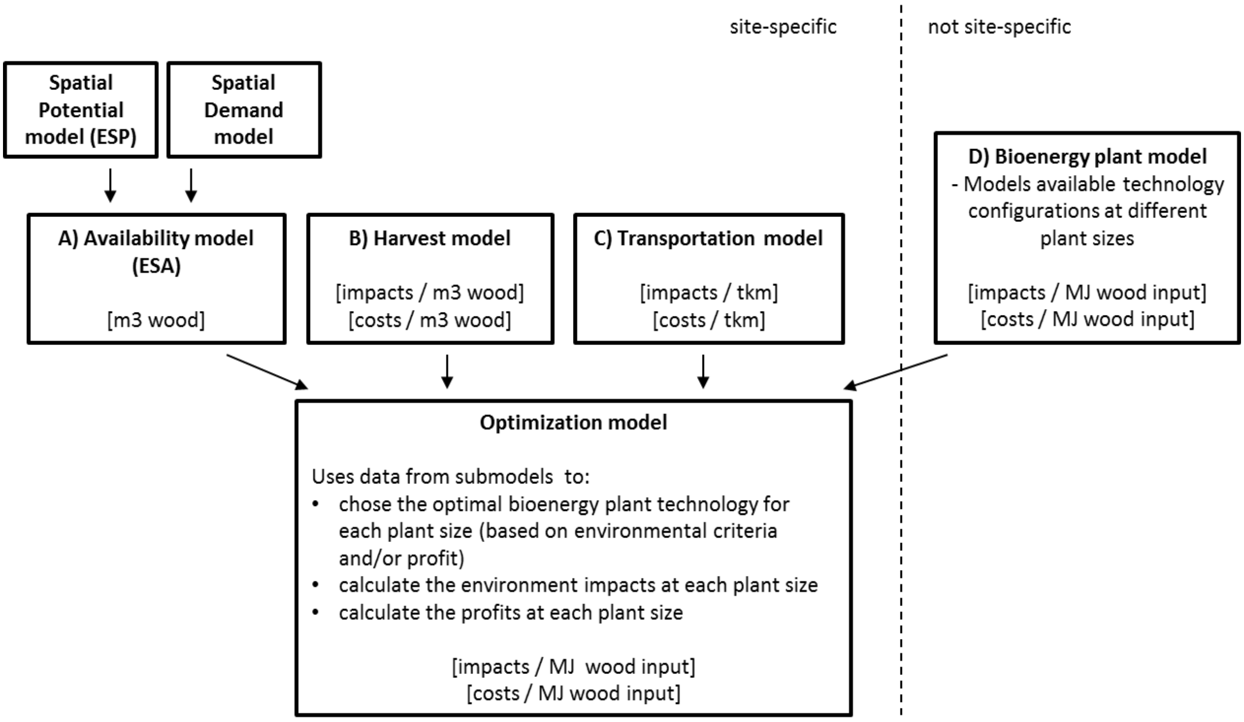

Fig. 1. Methodological approach used

2.2. Submodels

2.2.1. Availability model

The spatial wood availability model consists of two separate models. The first is the *spatial potential model*. It derives the effective spatial potential (ESP) of forest fuel based on data from the Swiss national forest inventory (NFI) as well as sustainability criteria such as biological, societal and economic restrictions [5]. The ESP was calculated for two different harvest scenarios, reflecting on the one hand the current situation where approximately 7 million m^3 are harvested in total and on the other hand a maximum scenario where 12 million

m^3 are harvested. The maximum scenario involves a reduction of the stock which has been built up during recent decades as the growth of approximately 9.5 million m^3 has been higher than the harvested quantities [6]. The maximum scenario could be sustained for about 30 years.

The *spatial wood demand model* [5] is based on the one hand on a database containing spatially explicit information for automated wood energy installations in Switzerland [7] and on the other hand on the overall demand from households [8], which was spatially distributed according to population density.

The *effective spatial availability* (ESA) is yielded by subtracting the spatial wood demand from the spatial wood potential.

2.2.2. Harvest model

The calculation of the environmental impacts of the harvest is based on ecoinvent data, which includes stand development and forest maintenance as well as the felling and chipping of the wood. The price for forest fuel at the SNG plant site is assumed to be 37 CHF / b-m^3 (bulk cubic meters) [9], excluding transport costs.

2.2.3. Transportation model

The transportation model calculates the costs and environmental impacts resulting from the transport of wood chips from the forest to the SNG plant by lorry. Transportation distances from NFI sample points to all plant locations have been calculated along the forest road network and the adjacent street network from Vector25 [10]. The environmental impacts are based on ecoinvent data for a 20-28t lorry. We assume average transportation costs of 6.50 CHF per driven vehicle kilometer[1].

2.2.4. Bioenergy plant model

The conversion of wood to SNG has been comprehensively modeled using different technologies and configurations including directly and indirectly heated fluidized bed gasification systems as well as several alternatives for gas separation [11-13]. Our bioenergy plant model contains the results for these technology configurations with respect to economic and environmental performance. In addition we defined the restriction that more sophisticated technologies, e.g. directly heated oxygen-blown gasification or pressurized indirect gasification may only be chosen for plant sizes greater than 25 MW. The bioenergy plant model therefore represents a set of potential technology options for each plant size from which the optimization model can choose the optimal one given the environmental and economic weighting.

2.3. Optimization model

An optimization model was implemented in Matlab. It first chooses optimal technology configurations from the bioenergy model for each plant size. The choice is based upon weighted environmental and economic performances. To be able to calculate the economic performance (profit), we must also include the revenues from the sale of SNG as well as the co-products electricity and heat. For the revenues we assume the following prices per MWh:

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[1] Own calculation based on data from the ASTAG (Swiss Association for Road Transportation: www.astag.ch)

90 CHF for SNG, 135 CHF for electricity[2] and 60 CHF for heat. To calculate the environmental impacts we assume a substitution of fossil energy. We expect that SNG is used in natural gas cars (Euro 5 emission standard[3]) to replaces petrol driven cars (Euro 5), electricity is used to replace the marginal future Swiss electricity mix which consists of nuclear power (90%) and power from natural gas combined cycle plants (10%), and the excess heat from the SNG production is fed into a district heating network to substitute heat otherwise provided by natural gas boilers. Profit and environmental impacts are calculated according to equations (1) and (2):

$$\text{Profit} = \text{Revenues}_{\text{bioenergy}} - \text{Production Costs}_{\text{bioenergy}} \qquad (1)$$

$$\text{Env.Imp.}_{\text{net}} = \text{Env.Imp.}_{\text{bioenergy}} - \text{Env.Imp.}_{\text{fossil energy}} \qquad (2)$$

Profit and environmental impacts are calculated for each technology option from the bioenergy plant model. Then a weighted score is calculated for each technology choice based on normalized profits and environmental impacts as well as weighting criteria, as in Eq. 3. The technology with the highest score is then chosen for the specific plant size and location.

$$\text{Score}_{\text{technology choice}} = \text{Env.Imp.}_{\text{normalized}} * \text{weight}_{\text{env}} + \text{Profit}_{\text{normalized}} * \text{weight}_{\text{eco}} \qquad (3)$$

Next, the environmental and economic performance is calculated for plant sizes from 5 – 200 MW for different locations in Switzerland. We choose these locations to be close to populated areas to allow for a potential heat use of the plant as well as with the aim to represent the different regions of Switzerland. Sensitivity analysis is performed with regards to weighting criteria as well as wood availability scenarios.

3. Results

Fig. 2 shows the average transport distances that are covered to supply SNG plants with wood for different locations and sizes from 5-200 MW for the maximum effective spatial potential (ESP) and the maximum effective spatial availability (ESA) scenarios. It can be observed that the variation of the transport difference at a given plant size is considerable for different locations, especially for larger plant sizes. This effect becomes even more important in the ESA scenario due to the increased scarcity of wood. It should also be noticed that for some locations a simple radius-surface relationship would not be correct to assume (e.g. St. Gallen).

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[2] Not in all cases electricity is produced. If it is not produced then the same price is paid for the electricity consumption of the plant.

[3] http://europa.eu/legislation_summaries/environment/air_pollution/l28186_en.htm

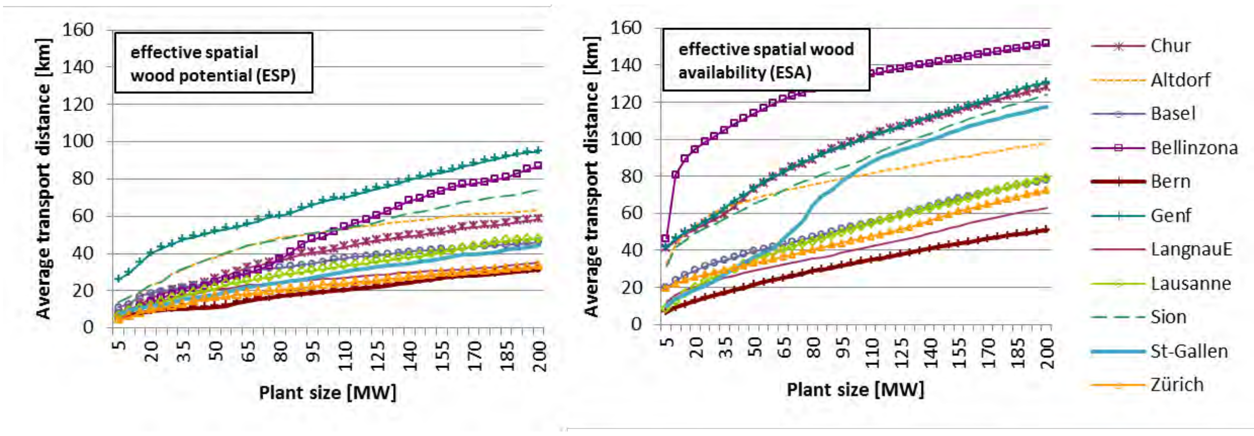

Fig. 2. Average wood transport distances for plant sizes from 5-200 MW for different locations in Switzerland (right: without demand consideration (ESP), left: with demand consideration, both maximum scenario)

Fig. 3 (left and middle) show the economic and environmental performance for a specific SNG plant (Chur) for an equal weighting of profits and environmental performance. First of all, it can be observed that the environmental performance of the system is dominated by the effect of the substitution of fossil fuels through the plant’s products SNG and heat. In other words, what really matters is a high wood-to-fuel conversion efficiency, whereas the impacts of the production of the biofuel are rather small. Nevertheless, the impacts of transportation are responsible for the general slope of the environmental performance. Concerning the profits, however, the increased transport distance is more relevant and responsible for the overall decline of profits at large plant sizes. The most important factor for the profits are economies of scale that can be achieved at higher plant sizes due to decreasing production costs. The drastic change at 50 MW is due to a shift in technology with lower production costs as well as a higher SNG efficiency and a lower heat production. As a result of this technology change, profits increase, whereas the environmental performance decreases, which is also due to the fact that the new technology is more sophisticated and more environmental impacts arise during the SNG production. Note that if the wood price (harvest) would increase (or decrease), it would lead to lower (or higher) overall profits and thus influence the plant size at which SNG plants become profitable.

Fig. 3 (right) shows the normalized and weighted performance[4] over the entire range of 5-200 MW. It can be observed that for an equal weighting of environmental performance and profits, the highest weighted performance is achieved between 20-50 MW for this location. For smaller plant sizes it decreases significantly due to considerably lower profits whereas for larger plant sizes it decreases only slightly.

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[4] The environmental curve has the opposite shape as in Fig. 3 (left) since negative environmental impacts are avoided impacts and need therefore to be valued positively

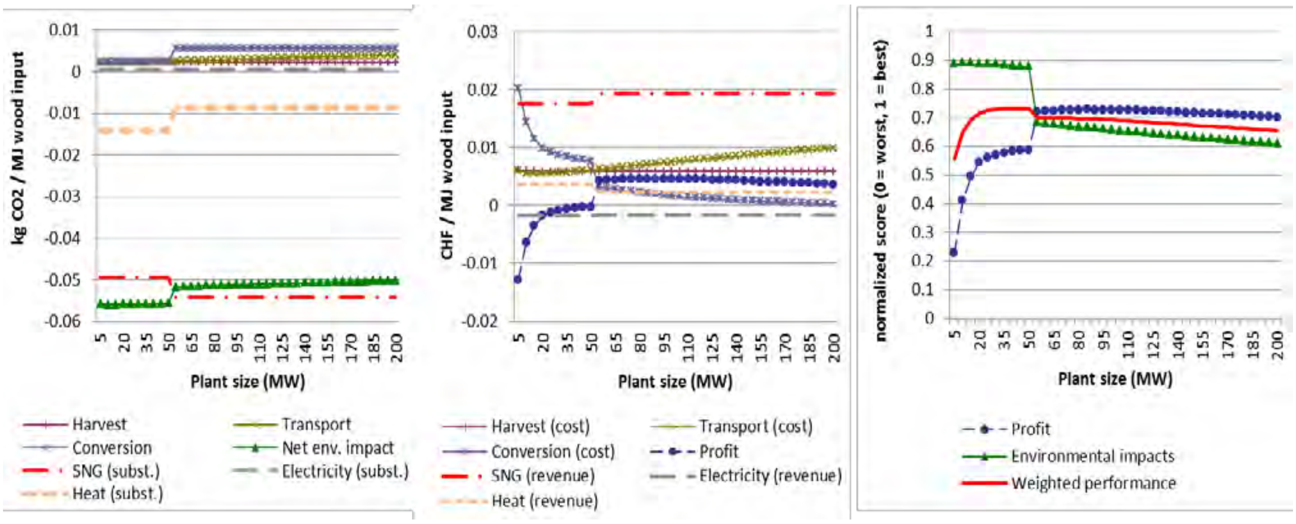

Fig. 3. Environmental impacts, costs and weighted performance for the location of Chur (ESA, equal weighting for profits and environmental performance)[5]

Since weighting between decision parameters is generally a subjective choice, it is important to understand how the weighting parameters influence the results. In our case, weighting strongly affects the optimal sizes for SNG-plants (Fig. 4). This is due to the fact that environmental performance generally decreases for larger plant sizes (economies of scale are too small or outweighed by increased transport distances), whereas profits generally increase with increasing plant sizes (or have a least a maximum at a higher plant size). This holds also true for a change in wood prices (harvest) since the latter only vertically shifts the profits curve but does not change its shape. Fig. 4 also shows that for a pure environmental weighting (GWP) the optimal plant size converges towards 10 MW, while at pure economic weighting the range of optimal plant sizes is large, from 75 – 200 MW, depending strongly on the spatial wood availability. The same results are obtained for an aggregated impact assessment with Ecoindicator'99 and Ecological Scarcity 2006 except that for at a pure environmental weighting plant sizes converge between 20 – 40 MW.

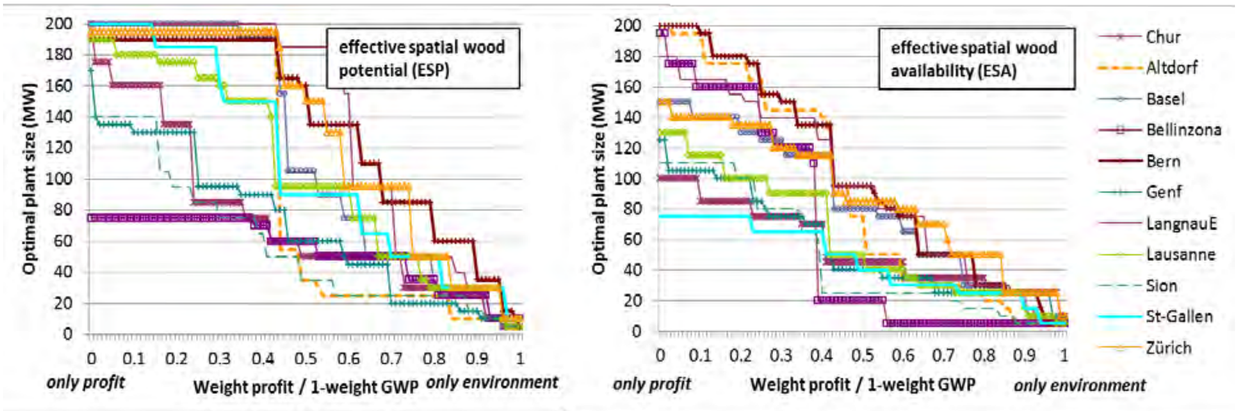

Fig. 4. Relationship of optimal SNG plant scales and weighting of environmental performance (GWP) and profits for different locations

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[5] At the state of writing 1 CHF was worth 0.78 Euro or 1.04 USD

4. Discussion

The sensitivity analysis for the weighting parameters suggests that the final decision must be based on a subjective choice since environmental and economic criteria lead to different optima regarding the plant size (trade-off situation). Even though this conclusion seems to be robust at least for three different environmental evaluation methods, more sensitivity analysis needs to be performed for other model parameters. These include the wood price, sale prices of SNG, electricity and heat (revenues), transport costs, substitution choices (which fossil energy SNG, electricity and heat replace), the heat utilization ratio throughout the year and wood availability. This analysis would also help to understand which factors are the most relevant and need therefore be considered when building SNG plants.

More research is also needed concerning the question whether the results presented here can be generalized for other types of bioenergy plants, e.g. conventional wood district heating systems or combined heat and power plants. An important step missing so far to proceed into this direction is a quantification of the relationships between environmental impacts and plant size for these applications. A recent study however produces empirical evidence that power-law relationships could be used for the scaling of environmental impacts at different plant sizes [14].

5. Conclusions

We conclude that there seems to be a trade-off between environmental performance and profits regarding optimal plant sizes. While the environmentally optimal plant sizes were found to be between 10 – 40 MW, the economically optimal plant sizes range between 75 – 200 MW. The economic optima are highly location-specific and locations with a lower wood availability also lead to smaller plant sizes from the economic perspective. The results are similar with regards to the impact on global warming as well as two aggregated impact assessment methods. The most important drivers for the economic performance are production and wood transportation costs. The most important drivers for the environmental performance are the effect of the substitution of fossil energy as well as the impacts generated during wood transportation and conversion.

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Synergy effects on combining hydrogen and gasification for synthetic biogas

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Abstract: This paper focuses on biogas and suggests methods for strongly increasing its production potential by combining gasification with hydrogen addition. By utilizing hydrogen produced from non-fossil energy sources, synthetic biogas can be obtained. The suggested methods are gasification combined with the Sabatier reaction, and hydrogasification. Both processes utilize hydrogen as a co-feedstock which can be produced via electrolysis from renewable electricity. Hydrogen addition to the gasification enhances the conversion efficiency and this synergy effect leads to higher fuel output compared to separate use of biomass and hydrogen.

The exploitation of renewable sources such as wind- and solar power is rapidly increasing since many countries have introduced incentives for these alternatives to expand. Since these are intermittent sources it would be highly beneficial to use electrolysis for balancing excess power in the grid during e.g. high loads or off-peak periods. Additionally, there would be an economical benefit as well since the price of electricity during these periods often is reduced.

The suggested methods could increase the biogas output by 130 – 150 % from the same amount of biomass as in conventional gasification. Contrary to upcoming fuels and solutions in the transport sector, biogas can be considered as conventional since a developed distribution system and storage capacity exists. It would also be a first step of introducing renewable electricity to the transport sector.

Keywords: *Synthetic biogas, Gasification, Transport sector, Hydrogen, Renewable fuels Introduction*

1. Introduction

The transport sector today poses one of the largest emitting sources of carbon dioxide. In a global perspective CO_2 from transport is responsible for approximately 23 % of the total green-house gas (GHG) emissions [1]. Moreover, the share of fossil energy used in the transport sector amounts to almost 95 %, most of it originating from oil [1]. With such a high share of fossil energy, the global transport sector is highly vulnerable and dependent on the fossil fuel market. Therefore, many regional and intergovernmental goals have been set, aiming for heavy reductions of fossil energy usage in the future as an act of CO_2 mitigation as well as an increased security of supply for their region. However, it is still highly uncertain how these goals could be reached. Many proposed solutions, e.g. the hydrogen economy, electric vehicles; CCS etc. are concepts and technologies still under development which probably cannot be used in any significant magnitude in a near future.

The most noticeable reaction from society towards a more climate neutral transport sector has been an increased usage of biofuels (mainly ethanol) and hybridized vehicles. The use of biofuels has increased quite rapidly during the past decade. However, the potential of biofuels from biomass is quite limited. The topic has been studied by many research groups such as [2, 3, 4] using Sweden (or local regions in Sweden) as an example, which is a particularly rich country in terms of forest (lignocellulosic biomass). Their studies have shown that even a forest rich country like Sweden will only be able to support parts of the total energy needs in the transport sector. Moreover it is shown that it will be necessary to combine different solutions, both for the supply-side and the demand-side in order to reach highly reduced levels of fossil energy in the transport sector [2].

Another renewable fuel that lately has received more and more attention is biogas. Today biogas constitutes only a minor part of the energy usage in transport. Biogas consists mainly of methane and is usually produced through digestion of organic materials. The amount of biogas that could be obtained from each alternative depends on available raw material (waste water sludge, manure and to some extent crops). Among others, [5,6] have studied the biogas potential from waste water sludge and solid municipal waste depending on the amount of inhabitants in a region and have estimated that it is possible to obtain a total of about 0.8 GJ biogas/person/year [5,6].

This paper suggests methods and technologies for strongly increasing the biogas potential by producing synthetic biogas from renewable energy sources. Synthetic biogas is a good alternative in the transport sector, which could contribute to large reductions of fossil fuel related CO_2 emissions. Biogas is in this paper defined as a biofuel containing mostly methane, independent of the route used to produce it.

1.1. Aim and Scope

The aim of the paper is to present possibilities for utilising biomass, mainly lignocellulosic, more efficiently than via conventional gasification. With the suggested methods it is possible to convert larger fractions of the tree into a propellant (in this case methane). It would result in an almost 100 % increase in fuel potential from forest biomass compared to when conventional methods are used. Such increase would have a substantial effect on the total biomass potential as raw material for propellant production. Accordingly, the transport sector would take a leap towards the possibility of achieving a transport sector with no net emissions of greenhouse gases.

The paper suggests implementing:
- Gasification combined with the Sabatier reaction
- Hydrogasification

These methods use the same fundamental principle i.e. thermal degradation of a given material. However, there are some key differences that are presented, discussed and evaluated in this paper. Comparisons are made and suggestions given for where each process should be implemented to make the greatest contribution.

2. The processes

Both suggested processes use biomass and hydrogen as raw materials for producing methane (synthetic biogas). They reach almost the same yield, however the main difference is that the hydrogen is introduced into the process at different stages. To keep the product (i.e synthetic biogas) CO_2 lean the suggested processes are will use hydrogen produced from renewable sources. In such case water electrolysis would be an excellent alternative. Electrolysis could be driven by renewable electricity (which often is intermittent) which gives the possibility of obtaining pure hydrogen at relatively low cost if run at e.g. off-peak periods when electricity is in excess. The two processes are illustrated and more thoroughly described in the following sections.

2.1. Gasification combined with the Sabatier reaction

Gasification is a known application and is commonly used to produce syngas, a mixture of mainly hydrogen and carbon monoxide. CO and H_2 in combination are suitable for production of hydrocarbons e.g. synthetic methane, methanol and Fischer-Tropsch fuels.
Generally, there is a shortage of hydrogen in syngas if the aim is to produce synthetic biogas. Therefore, WGS is used to increase the share of hydrogen before the methane synthesis. However, when applying WGS, carbon dioxide is formed as a by-product which must be separated. It is a target for removal in the upgrading step after the fuel synthesis and vented to the air. The biomass to biogas efficiency in terms of energy is approximately 60 % [7] even though most of the carbon feed (about 65 %) is removed as CO_2 [8]. Table 1 displays the general chemical reaction for methane production via gasification where oxygen is used as the gasification agent.

Table 1. Reaction and energy balance for oxygen gasification based on 1 mole produced methane.

Oxygen gasification					
Reaction	$2.7\ CH_{1.5}O_{0.6}$	$+\ 1.4\ O_2$	$\rightarrow CH_4\ +$	reaction heat	$+1.7CO_2$
Energy	1127	0	676 (60 %)	450	[kJ/mol CH_4]

To increase the methane yield from biomass it would be possible to use the separated CO_2 for additional methane production. This could be done by implementing the Sabatier reaction which is showed in Eq. (1). Due to a very beneficial equilibrium in the Sabatier reaction it would be possible to convert most of the CO_2 to additional methane [9,10]. Hence, in this report it is assumed that 90 % of the input CO_2 is converted and such process would increase the total amount of methane produced, significantly.

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O \qquad \Delta H = -165\ \text{kJ/mol} \qquad (1)$$

As can be seen in Eq. (1), there is need for four hydrogen molecules per carbon dioxide molecule for the reduction of the carbon dioxide to methane according to the Sabatier reaction. As a by-product, two water molecules are produced for every molecule of methane; additionally the reaction is exothermal according to the equation. In Fig. 1 it is illustrated how the Sabatier process could be used to retrofit a gasification process.

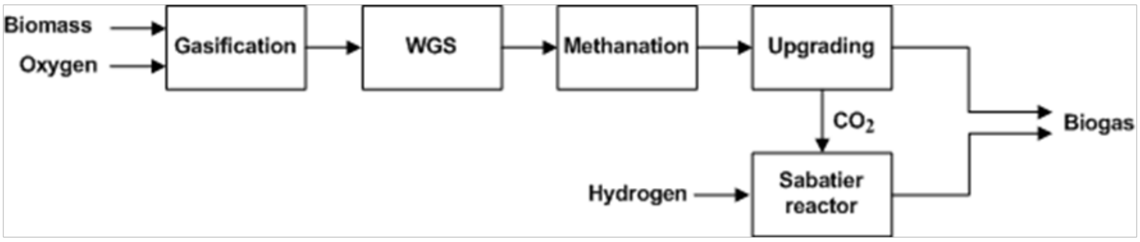

Fig. 1. Oxygen gasification combined with the Sabatier reaction.

After separation from the methane, the CO_2 stream could be directed to an external reactor where the Sabatier reaction takes place. The reaction could be run at atmospheric pressure but needs temperatures between 250 - 400^oC. If running close to equilibrium it would be possible to increase the methane yield significantly, hence about 85 – 90 % of the carbon dioxide would be converted to additional methane [9,10]. To keep the "new" methane CO_2-clean the hydrogen is supposed to originate from electrolysis driven by a renewable source e.g wind power or photovoltaics (PV).

2.2. Hydrogasification

As stated in the previous section, the limiting factor for methane formation in the fuel synthesis is the low proportion of hydrogen in syngas. If WGS is used to obtain hydrogen, carbon dioxide is produced simultaneously and must be removed. By adding hydrogen in an earlier stage, i.e. in the gasifier, WGS can be avoided, moreover less or even no CO_2 removal is necessary. Adding hydrogen to the gasifier also has the positive effect of eliminating the need for oxygen as a gasification agent. Since the produced biogas has a low CO_2 content, the only upgrading that is needed is to remove the water by condensation. The process is illustrated in Fig. 2.

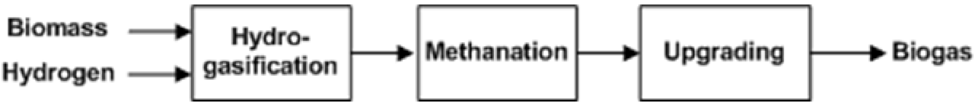

Fig. 2. Hydrogasification process

Table 2 shows the theoretical reaction and energy balance for hydrogasification which may be compared to oxygen gasification in Table 1. As can be seen, less reaction heat is produced and there are no CO_2 in the product (assuming total reaction).

Table 2. Reaction and energy balance for hydrogasification

Hydrogasification							
Reaction	$CH_{1.5}\,O_{0.6}$	+	1.85 H_2	$\rightarrow CH_4$	+	reaction heat	+ $0.6H_2O$
Energy	420		448	676 (78 %)		192	[kJ/mol CH_4]

3. Potential for enhanced methane production

The mentioned processes are suggested as alternatives which significantly can enhance the yield of fuel obtained from biomass compared e.g. with biological processes. One must keep in mind though, that hydrogen is needed for both processes. The needed hydrogen is suggested to be produced through water electrolysis using a renewable energy source e.g. wind power or PV. It has been suggested by many researchers that electricity could be stored as hydrogen (which in turn can be used to produce propellants) through electrolysis [11-13]. This is especially beneficial when considering intermittent power i.e. wind- and solar power. Accordingly, electrolysis could act as stabilizer when electricity production is high and the grid load is low. In the Nordic countries the electricity price varies continuously and depends on supply and demand [14]. When high amounts of electricity are produced with few end users, the price will naturally decrease. Therefore, if running the electrolysis during these periods, the produced hydrogen will be as cheap as possible. It could also be stored for later use which could create possibilities for producing methane in a cost efficient manner.

In Table 3 and Table 4 examples for both processes are presented. The calculations are based on input biomass containing 100 moles of carbon (C). As stated earlier a 90 % conversion rate of the CO_2 is used in the calculations with the Sabatier reaction. It must be noted that in Table 3 the system boundaries for the gasification also includes the WGS reaction i.e. the flow is led in to the gasification and out from the upgrading process.

Table 3. Potential for increased biogas production by using the Sabatier reaction (input data for gasification from [7])

Gasification	Biomass	H_2	CO_2	CH_4
In (mol)	100 (mol C)	-		
Out (mol)		0.7	54	36
Sabatier				
In (mol)		217	54	
Out (mol)		22	5.4	49
Total CH_4 out				85

By using the removed carbon dioxide from the biogas, production can be increased by 136 %. In addition to the produced methane some un-reacted hydrogen is added to the biogas.

Table 4. Potential for increased biogas production by hydrogasification [7]

Hydrogasification	Biomass	H_2	CO_2	CH_4
In (mol)	100 (mol C)	178	12	
Out (mol)		8	8	83
Total CH_4 out				83

The input of CO_2 in the hydrogasifier is used as inert gas in the feeding process to avoid nitrogen in the system. The increase in biogas production can be calculated by comparing with the case of oxygen blown gasifier. In the case of hydrogasification the yield of methane will increase 130% compared to oxygen gasification (without Sabatier).

It is important to consider not only the yield of methane since biogas contains other combustible gases e.g. hydrogen which will increase the total energy output. In Table 5 it is possible to see the total energy balance. There are some facts to consider when reading Table 5 regarding the carbon input and the hydrogen content in the biogas. There is a higher carbon input in the hydrogasification process since carbon dioxide is used as feed, and it will also take part in the reaction and forms methane. Carbon dioxide is also used for feeding the oxygen-blown gasifier, but in that case a part of the produced carbon dioxide is re-circulated, thus no additional carbon source is added. The higher biogas output from the Sabatier reactor, despite the lower carbon input, can be traced to the higher hydrogen content in the produced biogas (20 mol-% from Sabatier and 8 mol-% from hydrogasification).

Table 5. Example of the efficiency of SNG production [7]

SNG production		**Hydrogasification**	**Gasification + Sabatier**	**Oxygen gasification**
Input	Biomass [MW]	100	100	100
	Hydrogen [MW]	94.8	117.7	
Output	Biogas [MW]	154	165.9	66.3
Efficiency		79 %	76.2 %	66.3 %
Hydrogen efficiency[1]		92.5 %	84.6 %	

[1] Hydrogen efficiency refers to the increase in fuel production compared with amount added hydrogen. In the hydrogasification case, 94.8 MW hydrogen is added which increases the output by 87.7 MW compared to the oxygen blown gasifier. The efficiency is obtained by dividing the increase (87.7MW) with added hydrogen (94.8 MW), 87.7/94.8 = 0.925

Adding hydrogen increases the efficiency which gives a high yield based on the LHV of hydrogen, 92 % for the hydrogasification case and 85 % when the Sabatier reactor is used. Table 5 also shows that the suggested methods could increase the biogas output with 130 – 150 % from the same amount of green carbon. Furthermore, the hydrogasification has a positive power balance with the possibility to export 4.5 MW; meanwhile oxygen gasification requires an import of 2.7 MW. If the oxygen is taken from the electrolysis in the case of oxygen gasification, the plant would lower the electric demand by 4 MW resulting in a 1.3 MW power export[7].

4. Discussion

Biogas' corresponding fossil fuel is CNG (compressed natural gas). The main difference between biogas and CNG is that biogas, when upgraded for vehicle usage, contains about 98 % pure methane and the remaining carbon dioxide. Natural gas however, contains mainly methane (about 80-90 %), higher hydrocarbons and carbon dioxide. Today many vehicles are driven by CNG, e.g. private cars, buses, trucks, taxicabs etc. In many urban areas (and to some extent in rural areas), there is a grid for CNG distribution. Hence, existing grids would be suitable for introducing biogas since both gases can be used in the same applications due to similar combustion qualities and energy content.

In both suggested processes small amounts of hydrogen are present in the product flow. Technically, the hydrogen does not need to be separated. According to test runs from 2006 in Malmö, Sweden, natural gas buses have tried driving on hydrogen blended CNG (HCNG) with promising results. The buses used up to 25 vol-% hydrogen with no, or only minor changes, in the system depending on blend [15].

Acquiring the essential hydrogen is one of the key issues for the processes. In this paper, electrolysis has been suggested for hydrogen production. However, electrolysis is energy demanding with an efficiency of about 70 % from electricity to hydrogen (LHV) [16]. Additionally, energy is lost when the actual reaction takes place. On the other hand, using electrolysis opens for possibilities of storing electricity in a manner the does not exist today; especially intermittent power which is growing rapidly. Moreover it is possible to produce a variety of different valuable products from hydrogen. Battery electric vehicles or plug-in hybrids have been suggested as possible electricity depots, however the technology and infrastructure for this kind of usage is still not commercially available.

An important matter regarding synthetic biogas is that it depends on renewable electricity for hydrogen production. Wind power and PV are renewable energy sources that have shown promising future potential. However, these sources produce intermittent power which is entirely controlled by current weather conditions. Hydrogen production through electrolysis would therefore be an effective method to regulate the fluctuations when excess power is produced.

Transporting and storing hydrogen for use as a vehicle fuel are issues that have not been solved yet. In such terms, it would be more favorable to use the hydrogen as a component for further conversion, in this case to produce synthetic biogas. One of the main problems when storing hydrogen is that a significant compression work is needed if stored as compressed gas. Biogas contains over 3 times more energy per volume than hydrogen which makes compression of biogas much more beneficial compared to hydrogen. Additionally, storage and infrastructure for biogas is more developed and the vehicles are available today, both as private cars and buses for public transportation.

As can be seen in the results, both processes show a significant increase in biogas production with the highest hydrogen efficiency when using hydrogen in the gasifier. An advantage of the Sabatier reaction however, is that it is not limited to gasification processes; basically any process with CO_2 emissions would be possible to retrofit. The fact that energy is lost as heat when adding hydrogen to the processes, could be solved (to some extent) by recovering the heat for power production in a steam cycle. Excess heat from the electrolysis could also be integrated in the steam cycle as preheating energy or used in e.g biomass drying.

5. Conclusions

Based on the presented information in this paper, it would be feasible to implement the suggested methods for fuel production. These would increase the capacity of biogas production greatly in areas where sufficient sustainable electricity is available.

It would be an excellent synergy opportunity to use intermittent electricity from renewable power production, to run the electrolysis when loads are high on the grid or during off-peak periods.

In a short time scale, the methods would be feasible options, since gasification and the Sabatier reaction are known technologies and furthermore biogas is used as vehicle fuel commercially.

Acknowledgments

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Economic feasibility of biomass gasification for small-scale electricity generation in Brazil

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Abstract: Although Brazil has a clean energy matrix, factors such as increased electricity consumption forecast for the next 25 years and the peculiarities of the isolated systems of electricity generation in the north of the country could require the inclusion of alternative energy sources that can show competitive production costs. This study aimed to evaluate the feasibility of a 100 kW_e gasification system including an engine generator set, examining the major costs in using this technology and the sensitivity of different factors on the variation of the electricity cost. With a capital cost of 1,100.50 €.kW_e^{-1}, the levelized unit cost of electricity delivered (LUCE) found was 459,83 €.MWh^{-1}, which would make this technology uncompetitive even in places where the generation is done using diesel oil. The parameters that showed to have a greater impact on LUCE were, in decreasing order, the load factor, the gasifier capital cost, the electric conversion efficiency, the capacity utilization factor and the gasifier useful lifetime, but even with variations of 30% within the range considered no parameter alone would allow reducing the LUCE to a competitive level.

Keywords: *Alternative energy sources, Biomass-based power plant, Levelized unit cost of electricity*

Nomenclature

E_O	*annual delivered electricity output*	$kWh.y^{-1}$
P	*rated power output*	*kWh*
CUF	*capacity utilization factor*	*fraction*
α	*generated power consumed by the auxiliaries*	*fraction*
l	*electricity losses in the local distribution network*	*fraction*
AC	*annual cost of BGPP*	€.y^{-1}
R	*capital recovery factor*	*fraction*
c_d	*diesel price*	€.L^{-1}
c_b	*biomass price*	€.kg^{-1}
sc_d	*diesel specific consumption*	$L.kWh^{-1}$
sc_b	*biomass specific consumption*	$kg.kWh^{-1}$
m_l	*manpower wage*	€.$h^{-1}.man^{-1}$
d	*discount rate*	$fraction.y^{-1}$
LUCE	*levelized unit cost of electricity*	€.kWh^{-1}

1. Introduction

Biomass used in a sustainable way has a very important role to reduce the climate changes because it presents a carbon neutral balance, is relatively abundant and also because its forms of energy conversion have been already studied for a long time. Sustainable use of biomass can be defined as an infinite and continuous use which won't pollute and will maintain the natural resources and its benefits to humanity [1].

The energy conversion of biomass can be made by biological processes such as fermentation and digestion, by thermochemical processes such as combustion, pyrolysis and gasification, and also by mechanical extraction processes. Gasification can be defined as the conversion of biomass, or any solid fuel, into a gas fuel by partial oxidation at elevated temperatures [2]. The most common classification of types of gasifiers refers to the bed type, in the fixed bed gasifiers the biomass movement only occurs by gravity and in the fluidized bed gasifiers the fuel is kept in suspension by an intense oxidant medium flow, which can be air, oxygen or steam.

The produced gas has a combination of CO, CO_2, CH_4, H_2, N_2, tar, particulates and water, but its composition is extremely variable depending on the type and characteristics (texture, moisture, ash content and volatile compounds) of fuel used and the type and operating conditions (oxidant medium, temperature, pressure, etc.) of the gasifier [3]. For small-scale electricity generation, fixed bed downdraft gasifiers are generally more suitable due to lower tar levels in the produced gases [4].

Renewable sources, with the exception of hydropower, still have higher costs of electricity conversion [5], however, for small rural communities, their low levels of energy demand and high costs of transmission lines usually restrict the energy supply to these communities by connecting them to the conventional power grid, which can make the use of renewable sources in decentralized systems to become economically viable.

This paper aims to present an economic assessment of small-scale electricity generation from biomass gasification in Brazil. The technology considered for biomass energy conversion was a 100 kW_e downdraft fixed bed gasifier coupled to a diesel engine operation on dual-fuel mode.

2. Characteristics of the Brazilian electrical system

The Brazilian energy matrix can be considered “clean”, renewable sources are responsible for 48.7% of its primary energy [6], it has an installed capacity of 111 GW and nearly 80% of electricity produced in the country comes from a renewable source, 7% from biomass and 72% from hydropower [7], which makes the country's third biggest consumer of hydropower in the world, consuming 391 TWh in 2009 [8]. The country is currently experiencing a good economic period and it is expected an annual growth of 4.53% in electricity consumption for the next 25 years [9].

The Brazilian electrical system is formed by both the National Interconnected System (NIS) and the Isolated Systems (IS). NIS has a transmission network that sum 89,200 km and is responsible for 96.6% of the full capacity of electricity production in the country. The high costs of the national grid expansion in northern region of the country, due to its geographical characteristics and its low population density, makes the IS the major supplier of energy in this region. These systems cover an area equivalent to 45% of the national territory but they supply energy for only 3% of the population, with 8.7 TWh of electricity generated from fossil fuels in 2009. Despite the large subsidies FROM the government (about 1.05 billion Euros in 2007) [11], the average price of electricity paid by the customers in the Northern region is the country´s most expensive, 105 $€.MWh^{-1}$ [7], currently, some isolated communities in the Amazon region use diesel generators at an average generating cost ranging between 143 and 205 $€.MWh^{-1}$, whereas in the interconnected system the generating cost is around 22 $€.MWh^{-1}$ [12].

3. BGPP-based decentralized electricity generation

Decentralized systems are designed to meet the demands and needs of a small local population [13], often in areas previously without access to electricity. The use of biomass gasification for energy supply in this kind of community is a reality as demonstrated in countries such as India and China [14,15]. The most suitable technology for small-scale electricity generation (lower than $1MW_e$) through gasification processes is a downdraft fixed bed gasifier coupled to an internal combustion engine [17], because the gas produced into reactor is forced to pass through a high temperature throat, which produces a low tar content gas. Despite the fact that an ideal downdraft gasifier produces very low tar content gases, in practice the tar and particulates levels are still higher than the recommended levels, < 50

$mg.Nm^{-3}$ and < 100 $mg.Nm^{-3}$, respectively [17]. consequently, it is necessary to use a gas cleaning system before feeding to an internal combustion engine.

the capacity utilization and the load factors of a rural village, where the demand for electricity is primarily for lighting, are commonly low and this lead to high electricity generation costs [21,24]. a low capacity utilization factor results in a underutilization of the biomass gasification power plant (BGPP) capacity. Furthermore, a low load factor has negative impacts on specific fuel consumption, and consequently in its conversion efficiency, and also in NOx and SOx emissions [19].

4. Economic feasibility

The economic feasibility of a BGPP is dependent on several factors, mainly the capital costs of the equipments (i.e. gasifier, engine-generator set, civil works and local distribution network), the specific fuel consumption, the capacity utilization factor (CUF) the useful lifetime of the equipments and fuel's prices. To assess the economic feasibility there are also several indicators, the most used are the levelized unit cost of electricity (LUCE) and the breakeven analysis values (e.g. the diesel price estimative or the distance of transmission lines under which the electricity generated by a BGPP becomes feasible), but also the Internal Rate of Return (IRR) and the Net Present Value (NPV) [17,20].

5. Methodology

Aiming to compare the financial results found in this study with other studies that considered different currencies, the values were converted to a common currency (Euro), considering the average of the quotations made in 2009 [23]. The conversion values are: 0.3608 (Brazilian Real), 0.7178 (American Dollar), 0.0148 (Indian Rupees) and 0.1046 (Chinese Yuan).

The non-monetary data that were needed to estimate the cost of electricity produced by the BGPP, as well as the methodology to calculate the LUCE were adopted based on the work of Nouni et al [21], this methodology is described below:

5.1. Levelized unit cost of electricity delivered output

The levelized unit cost of electricity (*LUCE*) delivered by BGPP, can be calculated as a function of the annualized cost of the BGPP and its amount of annual electricity delivered, as follows:

$$LUCE = \frac{AC}{E_O} \qquad (1)$$

Where AC is the annualized cost and E_O is the annual delivered electricity output of the BGPP with a rated power output (*P*) can be calculated by the following expression:

$$E_O = (P * LF) * (8760 * CUF) * (1-\alpha) * (1-l) \qquad (2)$$

Where *LF* represents the load factor of the BGPP, *CUF* is the capacity utilization factor, α is the fraction of generated power consumed by the auxiliaries of the BGPP and *l* is the losses in the local distribution network.

The annualized cost of the BGPP (*AC*) has been calculated as follows:

$$AC = FC + VC \qquad (3)$$

Where *FC* and *VC* represent the fixed and variable costs of the BGPP, respectively.
The *FC* are the costs that doesn't vary with the BGPP productivity, they can be estimated using Eq. (04):

$$FC = AC_g + AC_{eg} + AC_{cw} + AC_{ldn} \qquad (4)$$

Where *AC* represents the annualized capital cost of each item of the power plant, they are the gasifier (*g*), engine-generator set (*eg*), civil works (*cw*) and the local distribution network (*ldn*), they can be calculated according to their capital costs (C) and capital recovery factors (*R*), which is a function of the discount rate (*d*) established. The equation to obtain *R* is described below:

$$R = \frac{d(1+d)^T}{(1+d)^T - 1} \qquad (5)$$

Where *T* is the useful life time of each item of the power plant. The *AC's* were obtained according to Eq. (06), described below:

$$AC_x = C_x * R_x \qquad (6)$$

The *VC* represent the costs that vary according to BGPP productivity, as follows:

$$VC = AC_{O\&M} + AC_F \qquad (7)$$

Where $AC_{O\&M}$ are the annual operation and maintenance costs of each item of the BGPP, and AC_F are the annual costs with fuel, calculated as follows:

$$AC_{O\&M} = C_g * m_g + C_{eg} * m_{eg} + C_{cw} * m_{cw} + 8760 * CF * m_l * n \qquad (8)$$

Where m_g, m_{eg} and m_{cw} represent the fraction of the capital cost of each item of the BGPP that is necessary to its operation and maintenance, m_l is the Brazilian manpower wage rate and *n* is the manpower required.

$$AC_F = 8760 * CF * P * (c_d * sc_d + c_b * sc_b) \qquad (9)$$

Where c_d and c_b are respectively the local prices of diesel and biomass, sc_d and sc_b are the specific consumption of diesel and biomass in the power plant.

5.2. Simplifications and assumptions explanation

Table 1 shows all the values that were utilized to estimate the electricity generated cost of the BGPP:

5.2.1. Capital costs

The capital costs of equipments (i.e. the gasifier and the engine-generator set) were established with the intention of reflecting the reality of the Brazilian market. For this, it was made quotes from some of the industries that produce these equipments in a commercial scale, however, currently Brazil has only one company producing gasifiers in a commercial scale and the capital cost of the gasifier was obtained from this company. It refers to a 500 kW_{th} fixed bed downdraft gasifier including the additional costs with auxiliary systems (e.g. an automatic feeding system, two cyclones, a fabric filter and a gas cooling system) and transportation, resulting in a capital cost of € 70,350.00. The established capital cost for a 100 kW_e diesel engine-generator set adapted to operate on dual fuel mode represents an average cost of € 32,500.00. The civil works cost were estimated at € 7,200.00, the amount is related to a facility with 50 m² at a average specific cost of 144 $€.m^{-2}$. the capital cost of the local distribution network was estimated based on an average value obtained from a local energy company, called COPEL.

Table 1. Parameters values to LUCE calculation.

Parameter	Unity	Value
Power rated capacity of BGPP	kW_e	100
Capital cost of gasifier	€	70,350.00
Capital cost of engine-generator	€	32,500.00
Capital cost of civil works	€	7,200.00
Specific capital cost of local distribution network	$€.km^{-1}$	5,000.00
Size of local distribution network	km	3
Price of biomass	$€.kg^{-1}$	0.0180
Price of diesel	$€.L^{-1}$	0.7190
Specific consumption of biomass (referred to the electric output)	$kg.kWh^{-1}$	1.21
Specific consumption of diesel (referred to the electric output)	$L.kWh^{-1}$	0.10
Capacity utilization factor	%	25
Load factor (function of BGPP's rated capacity)	%	75
Generated power consumed by BGPP	%	10
Electrical losses in local distribution network	%	10
Discount rate	%	10
Useful lifetime of gasifier	h	10,000
Useful lifetime of engine-generator	h	20,000
Useful lifetime of civil works	y	20
Useful lifetime of local distribution network	y	20
Manpower required by BGPP	-	2
Brazilian's manpower wage	$€.man^{-1}.h^{-1}$	2.35
Maintenance cost of gasifier (function of its capital cost)	%	5
Maintenance cost of engine-generator (function of its capital cost)	%	10
Maintenance cost of civil works (function of its capital cost)	%	2
Northern Brazil's reference tariff	$€.MWh^{-1}$	105
Isolated systems reference tariff	$€.MWh^{-1}$	174

5.2.2. Brazilian's manpower wage

The forecast labor cost was calculated based on the Brazilian minimum wage, equal to about € 186 a month, with an additional of 104% related to the charges applied.

5.2.3. Specific fuel consumptions

Based on current market price, it was stipulated the value of 18 $€.t^{-1}$ for prepared wood. The value of 0.7190 $€.L^{-1}$ for diesel based on the average prices paid in 2008 by the Isolated Systems power plants [22].

6. Results

6.1. BGPP's capital cost

The BGPP's capital costs found in this study were 703.5 $€.kW_e^{-1}$ to gasifier, 325 $€.kW_e^{-1}$ to engine-generator set and 1100.50 $€.kW_e^{-1}$ to the power plant. These values don't differ much from the values presented by Nogueira and Lora [24] WHO stipulated 861.36 €.kW$_e^{-1}$ as a reference to power plants using gasifiers coupled to internal combustion engines. Liu et al [25] quoted a value around 1046 €.kW$_e^{-1}$ as the capital cost of a BGPP in China. Due to several factors involved in setting the capital cost of a BGPP (mainly the scale of the project and the technologies considered) can also be found values with greater discrepancy [26,27].

6.2. BGPP's annualized costs

Figure 1 shows the extent of the impact of the studied costs on the LUCE. The annualized capital cost proved to be the main factor impacting the BGPP annualized cost (approximately 47% of the total) out of which 33% are due to the gasifier capital cost. Expenditures with labor and diesel proved to be almost equivalent, around 17% and 19% respectively. Although several authors cite that the diesel can be responsible for less than 30% of the energy produced by an engine-generator set operating on dual fuel mode [15,19,27,28] the spending with this fuel has represented more than 3 times the spending with biomass, this occurs due to much higher diesel specific cost compared to the cost of biomass.

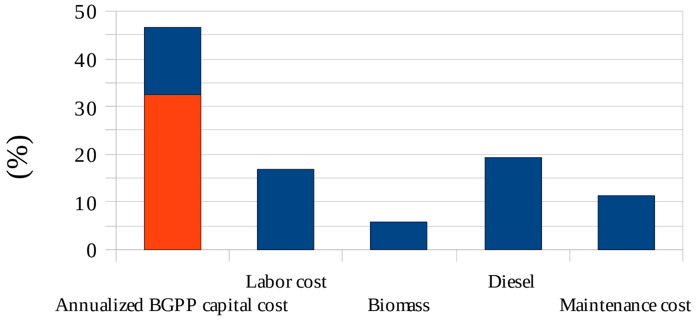

Fig. 1. Different costs responsibilities in BGPP annualized cost.

6.3. Delivered electricity cost

The estimated cost of electricity delivered by the BGPP under the established conditions was 459.83 €.MWh^{-1}, which represents approximately 4.38 times the price of the electricity paid by the customers in the Northern region of the country. Even when the comparison is based on the average price of electricity produced by diesel engine-generator sets in the Isolated Systems, the established luce showed no economic feasibility to an investment in a BGPP with these characteristics (264% of the isolated systems reference tariff).

6.4. Sensitivity analysis

As shown in Figure 2, the load factor is the parameter whose variation has greatest impact on the LUCE, if the BGPP operates at its rated capacity, the LUCE would be reduced to 380.41 €.MWh^{-1}, kept constant all the other factors. This reduction has even greater potential because the performance of both gasifier and engine-generator set tend to increase at higher load factors [19,21]. Also factor with important impact on LUCE were the electric conversion efficiency, the CUF and the gasifier useful lifetime, which with a 30% increase in their values could have respectively 7.5, 6 and 6% in LUCE reduction. Furthermore, a 30% reduction in gasifier capital cost could represent a 11.5% reduction in LUCE.

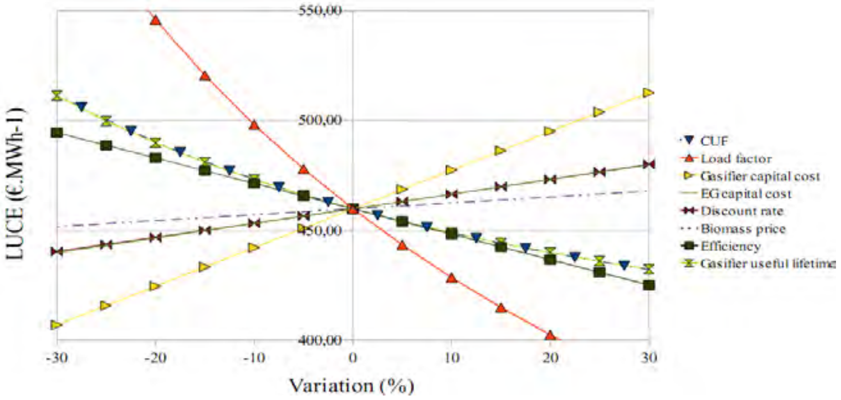

Fig. 2. Sensitivity analysis of BGPP.

7. Conclusions

It IS concluded that, under the studied conditions, the biomass gasification technology is still economically unfeasible to small-scale electricity generation in Brazil.

The main costs involved in BGPP electricity production, in descending order, were: the annualized capital costs (mainly the gasifier annualized capital cost), diesel, labor, maintenance and biomass costs.

In an attempt to reduce the LUCE of this BGPP, the load factor was the parameter that showed a higher sensitivity to reach this goal, followed by the gasifier capital cost, the electric conversion efficiency, the capacity utilization factor and the gasifier useful lifetime. however, with a variation of ±30% in the values previously established none of these factors would have a sufficient impact in LUCE to make this BGPP economically competitive in the Brazilian energy market. Even with a 30% variation of all factors at the same time (a 30% increase to the cuf, load factor, efficiency and gasifier useful lifetime and a 30% reduction of the gasifier and eg capital costs, discount rate and biomass price) the LUCE would be equal to 232.95 Euros. This value is still higher than the isolated systems reference tariff.

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Evaluation of biodiesel production from babassu oil and ethanol applying alkaline transesterification under ultrasonic technology

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Abstract: Babassu oil is a clear light yellow vegetable oil extracted from the seeds of the babassu palm (Attalea speciosa), which grows in most areas of South America. It is about 70% lipids, with 50% of lauric composition. Brazil is the world's second largest producer of ethanol and the world's largest exporter; the advantages of ethanol are concerned to its renewable origin and low toxicity. In this work ethyl esters of babassu oil were synthesized by alkaline catalysis in homogeneous medium. The experimental design was used as a tool for optimization of the transesterification reaction and also in identifying key factors influencing the conversion into ethyl esters. The transesterification reactions were performed using two methods - the traditional mechanical agitation and agitation promoted by ultrasound waves. The nuclear magnetic resonance spectroscopy was used to quantify the conversion of all reactions of transesterification. According to the model obtained by the experimental design for mechanical agitation, conversions above 99% are obtained when the stoichiometric ratio is set at 6:1, with 1.0% KOH, under stirring at 400 rpm, in 60 min. Alkaline transesterification assisted by ultrasound waves produced the best results with respect to time of reaction and phase separation of glycerin and ethyl esters. The experimental model showed that conversions above 99% can be obtained in 10 min after adjusting the other independent variables.

Keywords: *Biodiesel, Babassu oil, Transesterification, Ethanol, Ultrasound.*

1. Introduction

The vegetable oil transesterification yields biodiesel as the main product. However, the final mixture is composed of free glycerol, alcohol, catalyst and unreacted mono-, di- and triglycerides [1]. These contaminants can lead to environmental and operational problems. Achieving high conversions in mono-alkyl esters, to ensure the removal of free glycerin, catalyst, alcohol and fatty acids in biodiesel are critical issues to the quality control and is one of the main challenges to be overcome to make feasible the industrial production of these fuels. In another approach, the fatty acid composition of vegetable oils is a significant factor influencing the performance of biofuels, carbon chains with a high number of unsaturations are more susceptible to oxidation as well as they have better performance with low temperatures, in contrast, saturated chains are desirable [2,3], especially due to the higher oxidation resistance and improved cetane number, but its use in cold climates is conditioned to its cloud point.

Among all feasible vegetable oil to cultivation and to oil extraction , this study employed the babassu, a generic name given to palm oil belonging to the *Palmae* family and members of the genera *Orbignya* and *Attalea*. The babassu oil constitutes 66% of kernel weight, and its composition is mainly saturated (83% of the grease composition) which makes it an excellent alternative for biodiesel production. In fact, in Brazil there is a range of oilseed crops that can be used in biodiesel production; currently almost all manufacturing process uses soybean oil as the main raw material. However, some oilseeds, especially soybean oil, run directly into the food industry market, besides extensive area must be used to afford good production. In this sense, non edible crops, as the babassu oil which presents annual productivity and a good yield per hectare, became an excellent alternative [4].

This work proposed ethanolysis of babassu oil employing the alkaline hydroxides most commercially used, the sodium and potassium hydroxides, which were evaluated independently. The aim was to study the process performance aided by statistical methodology proposed by Genichi Taguchi [5] to obtain robust processes, i.e., processes with low variation due to uncontrolled variables. So, the homogeneous alkaline transesterification reaction was evaluated in the presence of side reactions – the saponification and hydrolysis, which are inherent to the use of these hydroxides to generate the effective catalysts [6].

2. Methodology

The Taguchi designs with orthogonal arrays were performed according to the factors and levels presented in Table 1 to the conventional agitation and in Table 2 to the ultrasound method .

Table 1. Levels and controllable factors used in babassu oil ethanolysis reaction with conventional agitation.

Factor	Units	Levels	
		1	2
Turbulence	rpm	200	400
Temperature	ºC	30	60
Molar ratio ethanol/oil	Mol	4:1	6:1
Hydroxide/oil ratio	% by weight	0.5	1.0
Reaction time	min	30	60
Hydroxide type		NaOH	KOH

Table 2. Levels and controllable factors used to babassu oil ethanolysis reaction with ultrasound agitation.

Factor	Units	Levels	
		1	2
Molar ratio ethanol/oil	Mol	3:1	6:1
Hydroxide/oil ratio	% by weight	0.5	1.0
Reaction time	min	10	20
Hydroxide type		NaOH	KOH

2.1. Materials

Refined babassu oil was kindly provided by the company COGNIS Brazil Ltda.; NaOH (99%), KOH (85%), Na_2SO_4, anhydrous ethanol (99.8%) and hexane were obtained in analytical grade and used as received. The properties of the babassu oil in terms of fat acid composition was not determined and it was used the values available in the literature [7].

2.2. Procedure to the conventional transesterification reaction

Catalyst and anhydrous ethanol were premixed at 40 °C under magnetic stirring for 20 min or until complete dissolution. Then, the solution of the corresponding ethoxide was added to 70 g of refined babassu oil, previously heated at the same temperature. The reactions were performed in a jacketed glass reactor of 300 mL with reflux condenser; the temperature control was performed by a thermostatic bath. Mechanical stirring was performed with a mechanical stirrer and glass double curved blades; rotation control was done by mixer brand IKA RW20-digital model. After the predetermined time for each reaction, the reaction mixture was transferred to a vessel to ensure phase separation between ethyl esters and glycerin.

2.3. Procedure to the transesterification reaction with ultrasound

In a 125 mL Erlenmeyer flask, it was added 22 g of refined babassu oil. In parallel, appropriate amounts of anhydrous ethyl alcohol and sodium or potassium hydroxides were mixed until complete dissolution in a glass flask equipped with reflux condenser, under moderate magnetic stirring for 20 min at 40 °C. In the sequence, the solution containing the corresponding ethoxide catalyst was added to the flask containing the oil preheated to 30 °C. The tub of ultrasonic bath was filled with 300 mL of distilled water and then the flask containing the reactants was placed inside. The temperature was maintained in 30 ºC and the flask was not sealed, considering that at this temperature the evaporation of ethanol is negligible. The position inside the tub and height of the flask were standardized with markers, in order to use always the same tridimensional position. The equipment was set to operate at 600 W and 20 kHz.

2.4. Purification process and conversion evaluation

After phase separation and removal of glycerin produced (lower phase), 200 mL of hexane were added to the upper phase containing the non reacted intermediates and ethyl esters. This promotes new glycerin phase separation. After collecting this new phase, a new step involving several washings with 0.1 mol.L^{-1} solution of HCl were done, in order to reach neutral pH. After rinsing, this phase was dried with approximately 0.5 g of anhydrous Na_2SO_4 to remove remaining water, followed by vacuum filtration and, finally, residual alcohol and hexane were evaporated by a rotary evaporator at 72 °C during 20 min under atmospheric pressure.

The conversion into ethyl esters was evaluated by NMR in a Mercury 300 MHz – Varian spectrometer, with 5 mm glass tubes, using $CDCl_3$ as solvent and 0.3% TMS as internal standard. The calculations involving the conversion of esters were determined using the formula proposed by Garcia [8]. This methodology basically consisted in the identification, by ^{1}H NMR, of molecules that present peaks in the region of 4.05 to 4.35 ppm during a transesterification reaction.

3. Results

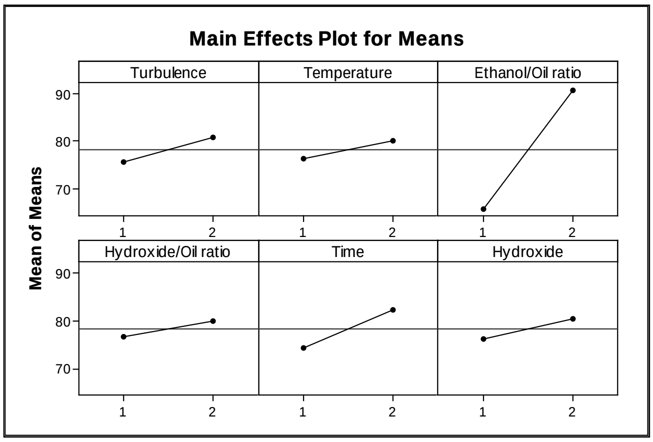
3.1. Evaluation of controllable variables as a function of the process noises

According to the methodology proposed by Taguchi [5], the signal to noise ratio (S/N) can, in this case, be interpreted as conversion into ethyl esters in the presence of noise (uncontrollable) factors. Figure 1 shows the effects of controllable factors in the signal to noise ratio, measured independently, i.e. without considering interactions between these factors, this figure was produced by the software Minitab®, that was used to perform the statistical analysis.

3.2. Molar ratio ethanol / babassu oil in the conventional procedure

The data showed that among all the factors, taken individually, the ethanol / oil ratio was the most important factor in conversions into ethyl esters. Due to the existence of a dynamic equilibrium between reactants and products, it is expected that excess alcohol increases the conversion to esters. In this sense, the results show that ethanolysis of babassu oil behaves similarly to the results already reported to other vegetable oils.

One of the advantages of applying statistical designs on the experiments is the evaluation of interactions between the factors; sometimes these interactions may be more important than the controlled variables. As stated, this factor presents a significant interaction with the reaction time, as it could be demonstrated by the interactions analysis, showing that regardless of the time adopted (30 or 60 min), the conversions are higher when used the molar ratio 6:1 of ethanol / oil.

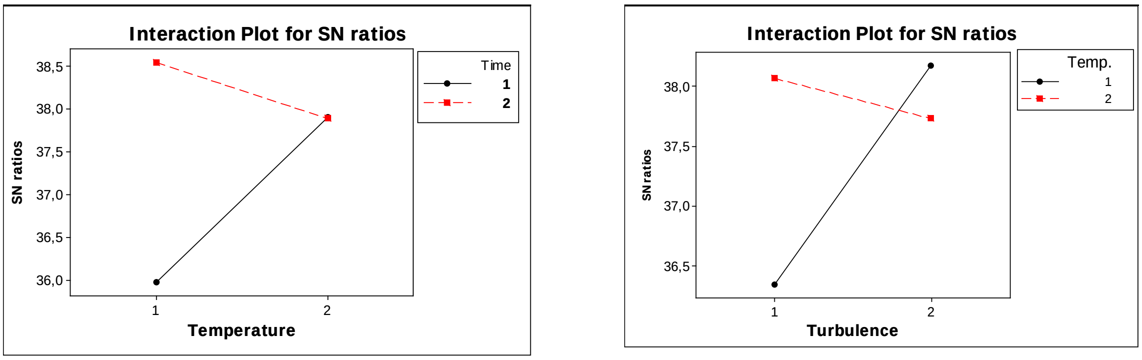


*1 and 2 correspond to low and high levels respectively

Fig. 1. Effects of controllable factors in the average conversion to ethyl esters as a function of noise in the conventional procedure

3.3. Effect of temperature

When temperature is evaluated individually its effect is modest, as it can be observed in Figure 1. However, considering the interactions, best conversions are obtained with temperatures set at low level, i.e., 30 °C (Figure 2a). Likewise, the turbulence generated by mechanical agitation at 400 rpm promotes best conversion into ethyl esters with temperature of 30 ºC (Figure 2b). This peculiar behavior can be explained by hydrolysis and saponification reactions, enhanced by higher temperatures, which promote the consumption of the catalyst reducing the yield of conversions [6].



(a) (b)

Fig. 2. Interaction of (a) temperature/time and (b) temperature/turbulence on the signal to noise ratio in the conventional procedure

3.4. Effect of amount and type of hydroxide

In most industrial processes the catalyst is expensive when compared to reagents and adds additional costs for its removal from the final product. The effective catalyst in a homogeneous transesterification reaction is the anion formed from the reaction between basic hydroxide and the alcohol. However, for practical and industrial purposes, the percentage ratio by weight of the hydroxide to vegetable oil is commonly used to describe the effect of the catalyst involved.

It was used 1 % (wt) of both hydroxides, what is equivalent to 0.0125 mol of KOH and 0.0175 mol of NaOH. So, regarding the type of hydroxide, the data show that the use of KOH is desirable, since lower molar quantities promoted better conversion into ethyl esters. Furthermore, the purification procedures were significantly facilitated when using potassium hydroxide, this experimental finding supports the conclusion that the generation of soap with KOH is lower.

Regarding the amount of hydroxide, this study showed that the use of 1 % by weight of it in relation to the mass of babassu oil leads to better results.

3.5. Effect of turbulence

The literature highlights the importance of agitation during the early stages of alkaline transesterification reactions, because during the initial stages, the mass transfer is limited [9,10]. The results suggested that the turbulence levels adopted in this study are sufficient for good conversions into ethyl esters, i.e., higher values of mechanical agitation than 400 rpm do not improve the yield of conversion.

Besides interaction with the temperature, this factor also had another significant interaction with the amount of hydroxide used, showing that the best conversions are obtained when these factors are set at higher level, i.e., mechanical agitation of 400 rpm and 1 % hydroxide (Figure 3). The behavior exhibited by this interaction can be explained by an improvement in the conditions of mass transfer with more turbulence and also due to increase on availability of catalysts for the reaction with the use of 1 % hydroxide in relation to initial mass of oil babassu.

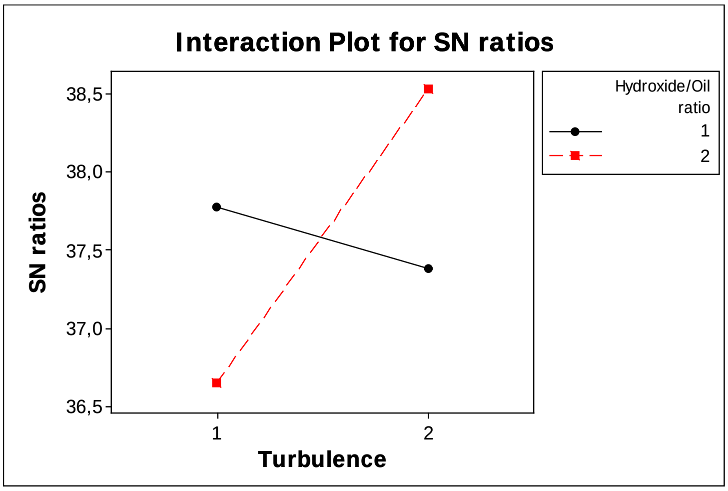


Fig. 3. Interaction plot between turbulence and % by weight ratio hydroxide / babassu oil in the conventional procedure

3.6. Effect of Time

The reaction time showed to be a dependent controllable factor, and with optimization of no other factors, the data showed that satisfactory conversions were reached within 60 min of reaction.

Thus the technological model obtained with this methodology was adjusted to the temperature at 30 °C, 400 rpm of mechanical agitation, using 1 % potassium hydroxide during 60 min of reaction. The conversion into ethyl esters obtained were above 99 %, determined by ^{1}H NMR, and the weight of esters recovered after the purification procedures was 94.59 % compared to the initial mass of this product.

3.7. Mathematical model

The evaluation of controllable factors to babassu oil ethanolysis reaction as a function of the noises was useful in determining the influence of the main variables in the conversion to ethyl esters, as can be seen in the Figure 1 and in the discussion about the effect of the temperature. After that, new experimental design was employed with the two main variables and the response surface methodology (RSM) was applied, with the development of new 2^2 complete factorial design with axial points, in order to identify the optimum conditions of babassu oil ethanolysis.

The mathematical model proposed to describe babassu oil ethanolysis is shown in Equation (1). The quadratic coefficients of correlation show that the model can explain 96.21 % of the variability in the response and further simulations with this equation are able to predict 80.47 % of the results.

$$\%CEE = 54.37 - 1.836\theta + 3.020r + 0.021\theta^2 - 0.025r^2 - 0.007(\theta \times r) \qquad (1)$$

Where %CEE is the ethyl esters conversion percentage, θ is the temperature and r the ethanol/Oil ratio

Figure 4 was generated with the software Minitab® from Eq. (1) and show the best fit to a babassu oil ethanolysis. As can be seen, with temperatures below 40 °C there is a narrow range in which the conversion into ethyl esters is higher, reaching the highest value in temperature around 30 °C and ethanol/oil ratio around 6:1 (60 in the figure).

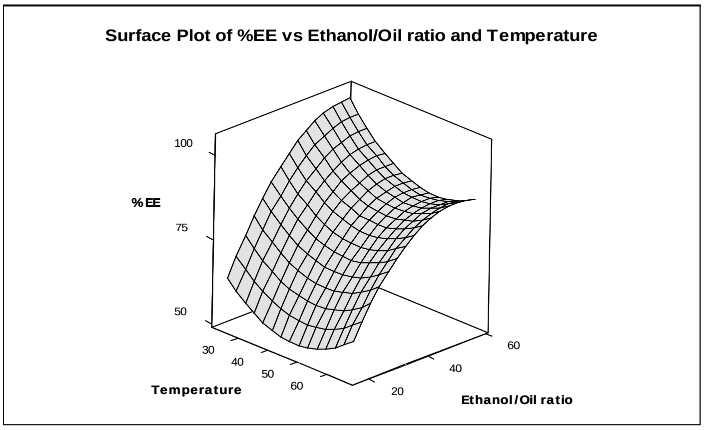


Fig. 4. Response surface to ethyl esters conversions as a function of the ethanol/oil ratio and temperature in the conventional procedure

3.8. The effect of the use of ultrasound

As it can be seen in de Figure 5, since there are no crossings between the effect lines of the variables, does not exist interactions of relevance to this system, thus the interpretation of controllable factors can be made directly.

In the Figure 6 it can be observed that the ratio ethanol/oil was also the most important factor involved in ethanolysis under ultrasound, showing that both processes, traditional agitation and sonication, are primarily dependent on this factor; no matter how intense are the physical conditions to which the medium is submitted. Similar results were reported in literature to the ethanolysis coconut oil [11].

Figure 6 also shows that the ratio hydroxide/oil was relevant to the sonolysis of babassu oil, the degree of conversion significantly responded to the variation of levels. The best conversions are obtained when employing the mass ratio of 1.0 % (wt) of catalyst of babassu oil. This result was expected because the greater availability of catalyst greater the generation of the active component of the reaction, in this case, the ethoxide catalyst and, due to the phenomena of sonoluminescence and cavitation noise, which are responsible for creating unique conditions for transfer mass, the greater amount of this active component had its effect enhanced [12].

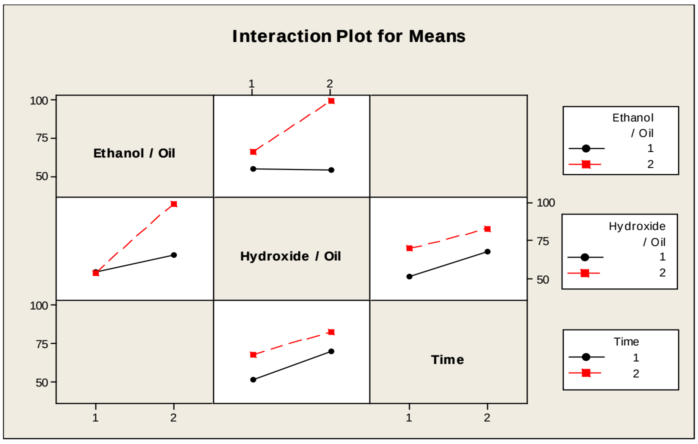


Fig. 5. Interaction plot on the signal to noise ratio for studied variables in the sonication procedure

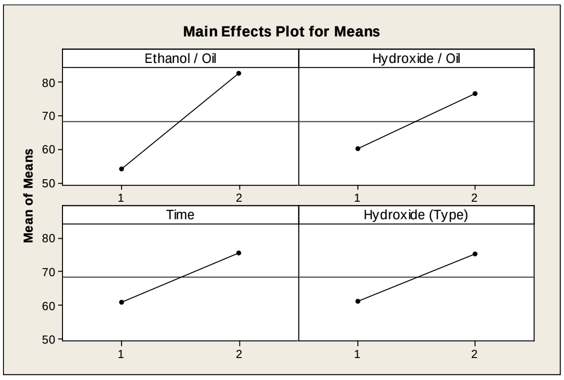


Fig. 6. Effects of controllable factors in the average conversion to ethyl esters as a function of noise in the sonication method

When compared to the traditional method, the time factor of sonication was considerably reduced and conversions above 99 % were obtained in 10 min, meaning that despite the significance showed for this variable in Figure 6, there is no practical reason to use the upper level of time. The important reduction in time compared to traditional methodology, can be explained by the intense mass transfer promoted by cavitation noise, implying a reduction of time intervals spent on the diffusion of reagents.

4. Conclusions

The refined babassu oil has shown excellent qualities as a raw material. Even in ethanolysis reaction this oil presented a similar behavior to reactions that used methanol showed in the literature [4,13]. The experiments showed that the correct tuning in the process variables is able to promote higher conversions into ethyl esters.

Among all the controllable factors evaluated, the ratio ethanol/oil decisively influenced the conversions into ethyl esters; highest conversions are achieved at the stoichiometric ratio of 6:1. The temperature showed a peculiar behavior, pointing out that the best conversions are obtained at 30 ºC. Other important conclusion is about the amount of hydroxide employed that suggests that a rate around 1.0 % is sufficient to obtain good conversions. KOH proved to be preferable if compared to NaOH, since better conversions were obtained and purification steps were easier.

The sonolysis of babassu oil showed considerable gain in time with respect to classical transesterification, principally during the stages of phase separation, which were substantially facilitated. Similar results were obtained for the preparation of biodiesel by the transesterification of coconut oil [11]. The remarkable results obtained with the reaction time can be explained by intense mass transfer afforded by the unique conditions generated by cavitation noise. In addition, possible reductions in the concentrations of mono- and di-glycerides during the reaction may explain the reduction in the time for phase separation. Thus, the method presents itself as a potential technological route of production of biodiesel, capable of meeting high demands in short periods of time. Adjustments related to the type of ultrasonic reactor (or transducer) and in the process of vegetable oils sonolysis can lead to an excellent alternative for biodiesel production, with energy costs that may be less than the expenses involved with the traditional method of mechanical agitation.

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A Comparative Study of Immobilized-Whole Cell and Commercial Lipase as a Biocatalyst for Biodiesel Production from Soybean Oil

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Abstract: Recently, there has been considerable attention in the direct use of intracellular lipase as a whole-cell biocatalyst (indirect immobilization of the enzyme) for biodiesel production since immobilization can be carried out spontaneously during the process of cell cultivation. In this research the ability of *Rhizopus oryzae* (ATCC 9374) whole-cell biocatalyst that was immobilized within biomass support particles (BSPs) was investigated and compared with Novozym 435 (most effective extracellular immobilized lipase) for methanolysis of soybean oil in solvent free system. The maximum methyl esters content in the reaction mixture reaches 84 wt% using *R.oryzae* whole-cell biocatalyst in optimum condition (6mm×6mm×3mm BSPs size, olive oil as carbon sources in basel medium, emulsification using ultrasonicated of reaction mixtures, 15 wt% water content and 7 wt% immobilized BSPs, addition of methanol at 0, 4 and 18 h) and at reaction time of 48 h which is remarkably comparable with yield of biodiesel at 90 wt% obtained with Novozym 435. Both the lipases can be used for repeated batches cycles. These findings indicate that, given the simplicity of the lipase production process and the long-term stability of lipase activity, the use of whole-cell biocatalysts immobilized within BSPs and treated with glutaraldehyde solution suggest a favorable means of biodiesel fuel production for industrial application.

Keywords: *Biodiesel, Whole-Cell Biocatalyst, Rhizopus oryzae, Novozym 435.*

1. Introduction

The consideration depletion of fossil resources and increasing social environmental awareness has led to a search for fuels that can be produced from renewable sources such as plant biomass [1]. A number of studies have examined the methods that are promising use of triglycerides (vegetable oils or animal fats) as an alternative fuel for diesel engines. However, the direct use of vegetable oils or oil blends is generally considered impractical because of high viscosity, acid composition and free fatty acid content. Facing these issues, transesterification; also called alcoholysis, were used to reduce viscosity and improve the physical properties of such fuels. Transesterification which has been recently developed to replace oils and fats as renewable energy resources is similar to hydrolysis reaction in which water is substituted with alcohol [2]. Biodiesel is explained as the non-petroleum-based diesel fuel be made up of short chain alkyl (methyl or ethyl) esters, typically made by transesterification of vegetable oils or animal fats, which can be used (alone, or blended with routine petrodiesel) in unchanged diesel-engine vehicles. It is biodegradable and nontoxic, has low discharge profile and so is environmentally advantageous [3]. Transesterification of triacylglycerides can be carried out by different catalytic processes. Alkali catalysis is widely applied for the commercial production of biodiesel fuel. However, enzymatic transesterification using lipase enzymes offers considerable advantages, including reducing process operations in biodiesel fuel production and an easy separation of the glycerol byproduct [4]. There are two major classification of enzymatic biocatalyst: (1) extracellular lipases (i.e. the enzyme has previously been recovered from the live-producing microorganism broth and then purified) which the major producer microorganisms are *Mucor miehei*, *Rhizopus oryzae*, *Candida Antarctica*, *Pseudomonas cepacia*; and (2) intracellular lipase which remains either inside or in the cell-producing walls which in both cases the enzyme is immobilized. The advantage of immobilization in this system is frequent utilization due to its easy recovery from the reaction mixture [5].

Several researchers have reported that the commercially available Candida antarctica lipase immobilized on acrylic resin (Novozym 435) was the most effective lipase between any of the extracellular lipases tested for transesterification reaction of vegetable oils where methanol is used as acyl acceptor [6-8]. Although immobilization of extracellular enzyme seemed to be a common method for enzymatic alcoholysis, it needs complicated methods for separation, purification and stabilization of lipases which in turn increase the process cost in industrial scale [9]. In recent years, there has been considerable interest in the direct use of intracellular lipase as a whole-cell biocatalyst (indirect immobilization of the enzyme) for biodiesel production. Utilizing whole cell overproducing intracellular lipase in which the purification and stabilization of the enzyme are not necessary instead of conventional immobilized lipase for biodiesel production is a potential way to reduce the biocatalyst cost, because immobilization can be carried out spontaneously during the process of cell cultivation [10]
In this research the ability of *Rhizopus oryzae* (ATCC 9374) whole-cell biocatalyst that was immobilized within biomass support particles (BSPs) made of reticulated polyurethane foam was investigated and compared with that of commercially available most effective lipase (Novozym 435) for methanolysis of soybean oil in solvent free system.

2. Materials and methods

2.1. Materials

Refined soybean oil was purchased from Behshahr Industrial Co. (Tehran, Iran). Commercial immobilized lipase from Candida antarctica, namely Novozym 435 was provided as a gift from Novo Nordisk (A.S., Denmark-Tehran Office).

Rhizopus oryzae ATCC 9374 purchased from PTCC (Persian Type Culture Collection, Tehran, Iran). Palmitic acid methyl ester, stearic acid methyl ester, oleic acid methyl ester, linoleic acid methyl ester, linolenic acid methyl ester were purchased from Sigma and were chromatographically pure. All other chemicals were obtained commercially and were of analytical grade.

2.2. R. oryzae whole cell biocatalyst preparation

Whole cell biocatalyst experiments were carried out using R. oryzae ATCC 9374, which has a 1,3-positional specify lipase. The culture medium contains in 1l tap water (its pH was initially adjusted to 5.6) were 70 g polypeptone (50 wt% pepton, 50 wt% trypton), 1 g NaNO3, 1 g KH2PO4, 0.5 g MgSO4.7H2O, and 30 g oil (refined olive, soybean and canola oil).

At first stage, R.oryzae grown on potato dextrose agar (PDA) slant. Erlen flask (500 ml) containing 100 ml of the basel medium were inoculated by aseptically transferring spores (about 106 spores) from slant, and incubated for 60–72 h at 35°C on a reciprocal shaker (150 oscillations/min) with 0.33 g BSPs subjected to prior sterilization. Reticulated Poly Urethane Foam (PUF) with a particle voidage of more than 97% and a pore size of 50 pores per linear inch used as BSPs. To examine the effect of BSPs size, these were cut into 6mm × 6mm × 3mm cuboids and 6mm cubes and added to basel medium. The R.oryzae cells became well immobilized within the BSPs as a natural result of their growth during shake-flask cultivation. After cultivation, the BSP-immobilized cells were separated from the culture broth by filtration, washed with tap water for few minutes, dried at 25°C temperature for 1 day, and for increase stability of lipase activity crosslinked with glutaraldehyde according to

Ban et al method [12]. In this way the dried cells were treated with a 0.1% (v/v) glutaraldehyde (GA) solution at 25°C for 1h then were shaken in phosphate buffer at 4°C for 5 min, washed with tap water for few minutes, and dried for 24 h at room temperature. Finally the GA-treated cells were used as a methanolysis catalyst.

2.3. Lipase-catalyzed transesterification

2.3.1. R.oryzae whole-cell biocatalyst

The methanolysis reactions have taken place at 35°C in a 50-ml erlen flask with incubation on a reciprocal shaker (150 oscillations/min). The reaction mixture contained: 9.65 g soybean oil, 0.1M phosphate buffer (pH 6.8) in range of 0–2.5 ml (0–25 wt.% water content by substrate weight), 0.1–1.0 g BSPs (1 – 10 wt%), 0.35 g methanol (One molar equivalent of methanol was 0.35 g against 9.65 g soybean oil) was added stepwise to the reaction mixtures three times at 0 and different hours after start of reaction. For full convert of oil to Fatty acid methyl esters, at least three molar equivalents of methanol are necessary.

2.3.2. Novozym 435 as a biocatalyst

The methanolysis reaction has taken place with the immobilized lipase from Candida antarctica (Novozym 435) in the solvent-free system in a 50-ml erlen flask at 35°C with incubation on a reciprocal shaker (150 oscillations/min). The reaction mixture contained 9.65 g soybean oil, 0.4 g immobilized lipase and 0.35 g methanol (without any distilled water) was added stepwise to the reaction mixtures three times at 0 and different hours after start of reaction.

2.4. Analytical procedure

The methyl esters contained in the reaction mixture was analyzed using a GC-3800CP gas chromatography (Varian Crop. Netherland) connected to a cpsil-5CB Capillary column (0.32mm×30 m, Varian, Netherland). Samples (200µl) were taken from the reaction mixture at specified time and centrifuged at 13,000 rpm for 5 min to obtain the upper layer. The methanolysis products were analyzed by capillary gas chromatography (cGC) as described below. The upper layer (80µl) and tricaprylin (20µl) which is served as the internal standard were precisely measured and mixed thoroughly in bottle with 2 ml hexane as solvent to which a small amount of anhydrous sodium sulfate as dehydrating agent were added. A 1.0 µl aliquot of the treated sample was injected into cGC. The column temperature was held at 150 °C for 1 min, raised to 200°C at rate of 20°C/min then raised to 207°C at rate of 1°C/min, finally raised to 300°C at rate of 30°C/min and maintained at this temperature for 24 min. The temperature for injector and flame ionization detector (FID) were set at 270 and 300°C, respectively.

3. Results and Discussion

3.1. Effect of BSPs size

To examine the effect of BSPs size on methanolysis of soybean oil, PUFs cut into 6mm×6mm×3mm cuboids and 6mm cubes and added to basel medium in different erlen flasks. After preparation as mention above, these cuboids and cubes use as BSPs and 50 BSPs added to reaction mixture in present of 15 wt% water. Table 1 presents data on the methanolytic activity of the different size of BSP-immobilized cells after adding methanol in start of reaction. Results indicated that in case of using 6mm×6mm×3mm immobilized BSPs methyl esters production is greater than 6mm cubes BSPs because of the specific surface area in 6mm×6mm×3mm BSPs is larger than other one. Therefore 6mm×6mm×3mm immobilized BSPs was used for this research study.

Table 1. Methyl esters production (Wt%) in different size of BSPs

Time(h)	6mm×6mm×3mm BSPs	6mm×6mm×6mm BSPs
4	29	21
8	30	27
12	32	31

3.2. Effect of carbon sources in basel medium

To elucidate the effect of carbon source on cell growth and methyl esters production, various refined oils were used as carbon sources in basel medium. Figure 1 shows the time course of methanolysis catalyzed by cells grown with different carbon sources. As shown in figure 1, we can see that during whole cell catalyzed methanolysis of soybean oil for biodiesel production, the cells cultured with refined olive oil have highest activity than cells cultivated with refined soybean and canola oils. So the experiments continued using olive oil as carbon source in basel medium.

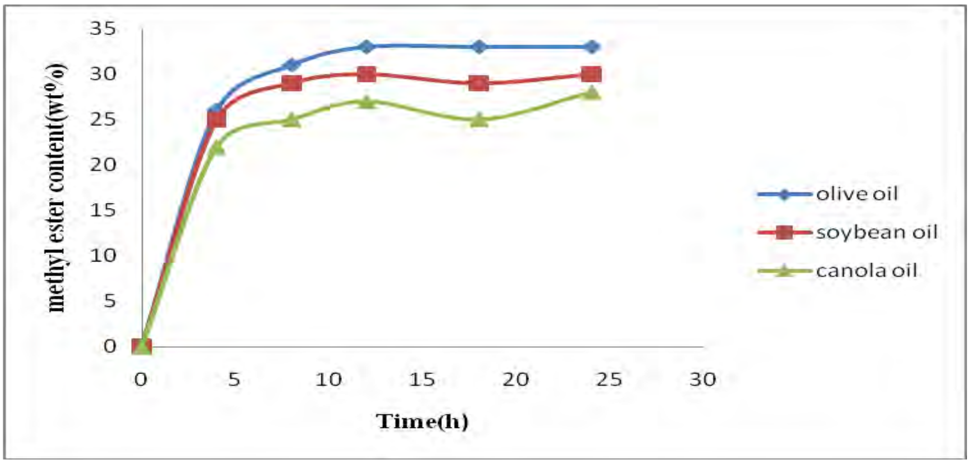

Fig. 1. Methyl ester content in methanolysis of soybean oil at different carbon source in cell cultivates (50 BSPs as a catalyst and reaction temperature at 35°C).

3.3. Effect of Emulsification of reaction mixture

To examine the effect of emulsifying of reaction mixture over producing methyl esters, ultrasonicated and non-ultrasonicated reaction mixtures were used for methanolysis of soybean oil. Figure 2 shows the time course of methyl esters content in reaction mixture with ultrasonicated and non-ultrasonicated feed. When the reaction mixture was emulsified before methanolysis, higher lipase activity was achieved. Because the lipase catalysis occurs in the interfacial layer between the hydrophobic and hydrophilic phases, the much larger surface area of the water/oil interface seems to result in increased accessibility of the substrates to the lipase [14]. This finding suggested that emulsification of the reaction mixture has an advantageous effect on biodiesel production using whole-cell biocatalyst. Further experiments were therefore made use of emulsified substrates.

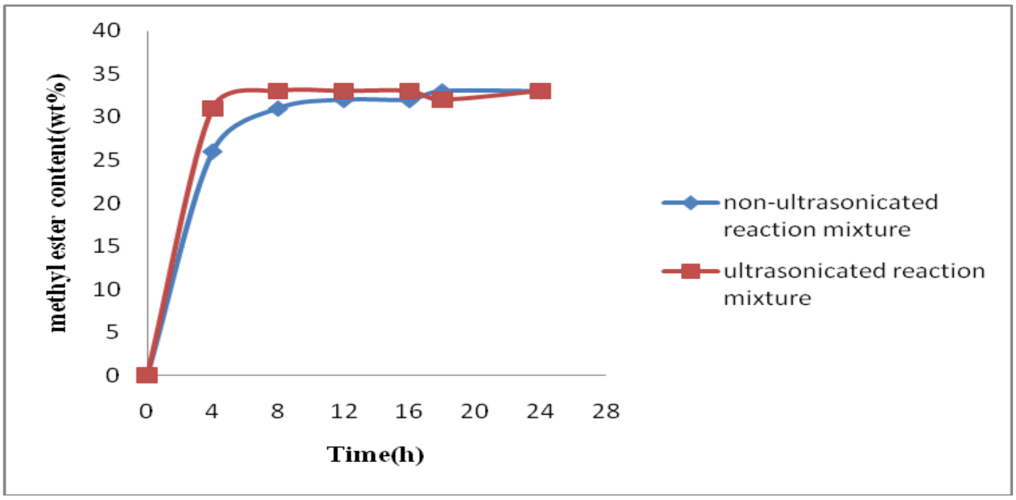

Fig. 2. Methyl ester content in methanolysis of soybean oil using ultrasonicated and non-ultrasonicated reaction mixtures (50 BSPs as a catalyst and reaction temperature at 35°C).

3.4. Effect of water content and weight of biocatalyst in reaction mixture

Figure 3 shows the activities of whole-cell biocatalyst at different water content and weight of biocatalyst. As shown in Figure 3 biodiesel achieved in the reaction mixture (after 96 h) increasing with increase in water content ratio up to 15 wt% and decreasing after that ratio. Therefore the optimum water content for Rhizopus oryzae whole cell was obtained as 15% that confirm results indicated by ban et al [12] whereas this parameter is limited the activity of Novozym 435 for methanolysis reaction since needs closely anhydrous reaction mixture [13]. Shimada et al [14] reported that water content (>500 ppm) in soybean oil decreased the rate of methyl ester production using Novozym 435 as biocatalyst. An insufficient amount of water in whole-cell biocatalyst methanolysis probably results in irreversible inactivation of lipase, which may be due to denaturation of the enzyme by methanol [15]. Moreover, figure 3 shows that by increasing weight of BSPs up to 7 wt%, methyl esters production increased and remained approximately constant up to BSPs amount of 10 wt%.

The highest methyl ester content (after 96 h); 84 wt%, was attained when the reaction mixture contained 1.5 ml buffer solution (15 wt% water by substrate to weight) and 0.7 g BSPs (7 wt.% BSPs by substrate to weight) which is remarkably comparable with methyl esters production using Novozym 435 as a biocatalyst. Since alkyl migration happens with intracellular lipase of immobilized cell and water can enhance cell permeability, the rate of methanolysis catalyzed by *R.oryzae* whole-cell biocatalyst increases in the presence of additional water. However, the excess water reduces methyl esters production due to its acts as a competitive inhibitor for lipase-catalyzed transesterification [16]. Subsequent experiments were therefore carried out using a 15 wt% water content and 7 wt% BSPs in reaction mixture.

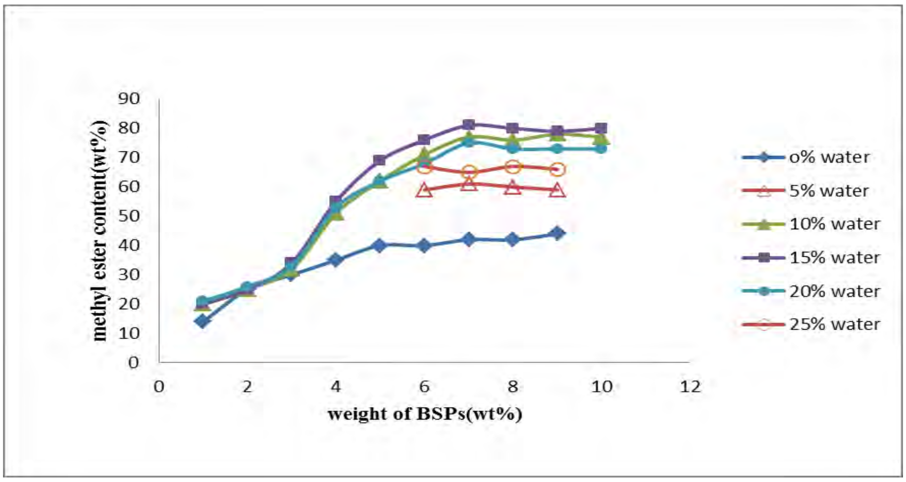

Fig. 3. Methyl ester content in methanolysis of soybean oil at different water content and weight of BSPs after 96 h (addition of methanol 0, 24, 48 h and reaction temperature at 35°C).

3.5. Time course methanolysis of soybean oil and optimization of methanol addition strategy

In this part the authors investigated the time course methanolysis of soybean oil with stepwise additions of methanol in 0, 24 and 48 h. Figure 4 shows the time courses of methyl esters production in different time after reaction started. As shown in figure 4, reaction continues up to 96 hours that is relatively long time while at the time such as 4 to 24 h and 36 to 48 h the methyl esters production had not much progress. The highest methyl ester content, 84 wt.%, was attained after 96 h. In order to reduce time of reaction progress, we tried to optimize the addition strategy of methanol. So the methanol was added in different strategy as stepwise additions of methanol in 0, 4 and 18 h after reaction. Figure 5 shows the time courses of methyl esters production using this new strategy of methanol addition. As shown in figure 5, 84 wt.% methyl esters production was attained after 48 h reaction.

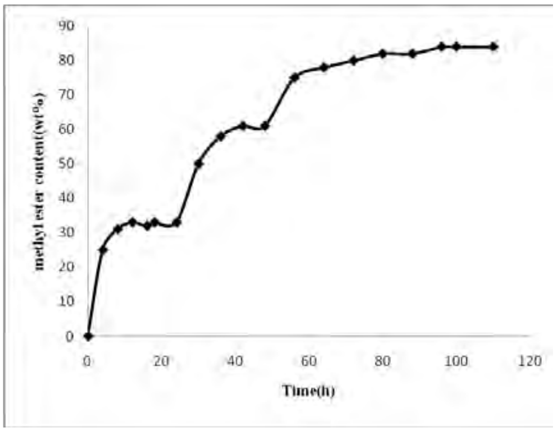

Fig. 4. Methyl ester content in methanolysis of soybean oil (addition of methanol at 0, 24 and 48 h).

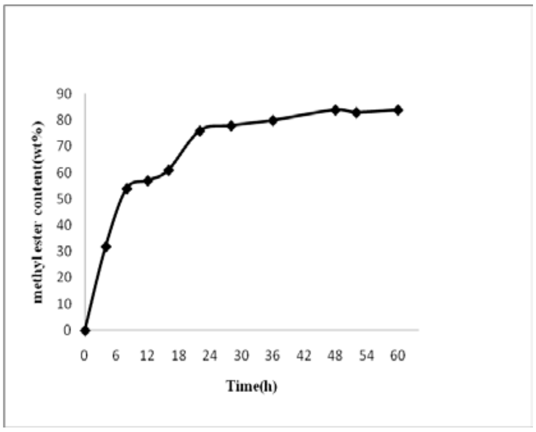

Fig. 5. Methyl ester content in methanolysis of soybean oil with new strategy (addition of methanol at 0, 4 and 18 h).

3.5. Enzymatic methanolysis reaction using Novozym 435 as a biocatalyst

For the methanolysis reaction using immobilized lipase from *Candida antarctica* (Novozym 435) in the solvent-free system, 0.35 g methanol was added stepwise to the reaction mixtures at the start of the reaction (0), 4 and 18 h. The reaction has been carried out for 48 h. The methyl ester content in the reaction mixture reached 90 wt% after 48 h that was slightly more than *R.oryzae* whole-cell biocatalyst.

3.6. Stability study of BSP-immobilized cells with GA treatment and Novozym 435 for methanolysis of soybean oil

In order to test the stability of Novozym 435 (stepwise addition of 1 molar equivalent methanol at 0, 4, and 18 h respectively) and GA treated *R.oryzae* whole-cell as biocatalyst with new methanol addition strategy (stepwise addition of 1 molar equivalent at 0, 4, and 18 h respectively), both the biocatalysts were separated from the reaction mixture by filtration and directly used for the next cycle. The time of methanolysis using *R.oryzae* whole-cell and Novozym 435 are kept constant at 48 h for each reaction cycle (as shown in figure 6). It was found that there was almost no significant decrease in methyl esters production even after 5 batches cycle in both lipases and both can be used for repeated batches cycles.

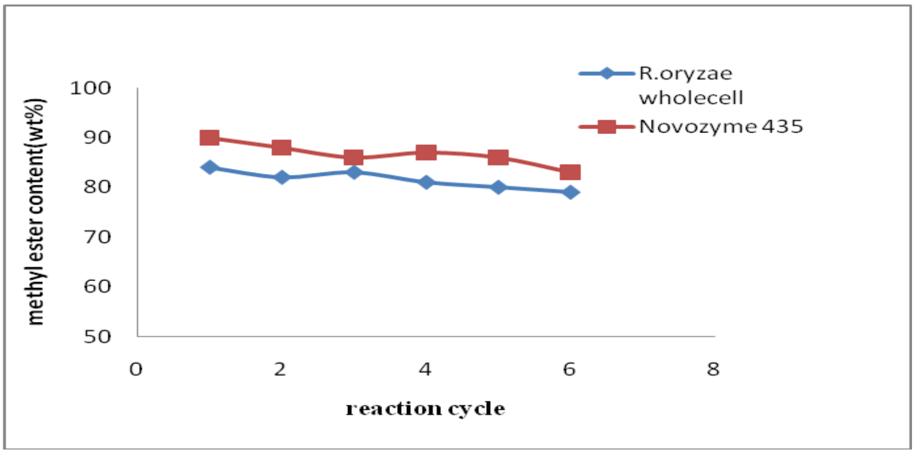

Fig. 6. Methyl ester content in methanolysis of soybean oil using GA treated R.oryzae whole-cell and Novozym 435 as biocatalyst for repeated reaction cycles (addition of methanol in 0, 4 and 18 h).

4. Conclusions

This work deals with the enzymatic transesterification of refined soybean oil using *Rhizopus Oryzae* (ATCC 9374) whole-cell biocatalyst and Novozym 435 (Commercial immobilized lipase from *Candida antarctica*) as biocatalyst. In the case of using whole-cell biocatalyst effect of BSPs size, carbon sources in basel medium, emulsification of reaction mixture, water content and weight of biocatalyst in reaction mixture on yield of biodiesel production were investigated. The maximum methyl esters content in the reaction mixture reaches 84 wt% using *Rhizopus oryzae* whole-cell biocatalyst in optimum condition of reaction after 48 h which is remarkably comparable with biodiesel yield 90 wt% of Novozym 435. The optimum water content for *Rhizopus oryzae* was obtained as 15% whereas this parameter is limited the activity of Novozym 435 for methanolysis. Both the lipases can be used for repeated batches cycles. These findings indicate that, given the simplicity of the lipase production process and the long-term stability of lipase activity, the use of whole-cell biocatalysts immobilized within BSPs and treated with GA solution suggest a favorable means of biodiesel fuel production for industrial application.

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Methyl ester production from chicken fat with high FFA

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Abstract: In biodiesel production, to use low cost feedstock such as rendered animal fats may reduce the biodiesel cost. One of the low cost feedstock is the chicken fat for biodiesel production. However, chicken fats often contain significant amounts of free fatty acid (FFA) which cannot be converted to biodiesel using an alkaline catalyst due to the formation of soap. Therefore, the FFA level should be reduced to desired level (below 1%) by using an acid catalyst before transesterification. For this aim, sulfuric, hydrochloric and sulfamic (amidosulphonic) acids were used for pretreatment reactions and the variables affecting the FFA level were investigated by using the chicken fat with 13.45% FFA. After reducing the free fatty acid level of the chicken fat to less than 1%, the transesterification reaction was completed with an alkaline catalyst. Potassium hydroxide, sodium hydroxide, potassium methoxide and sodium methoxide were used as catalyst and methanol was used as alcohol for transesterification reactions. The effects of catalyst type, reaction temperature and reaction time on the fuel properties of methyl esters were investigated. In terms of high ester yield, the measured fuel properties of the chicken fat methyl ester met EN 14214 and ASTM D6751 biodiesel specifications.

Keywords: *Biodiesel, Low cost feedstock, Chicken fat, Transesterification*

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1. Introduction

Biodiesel which can be produced from vegetable oils and animal fats is an alternative fuel for diesel engines. Biodiesel is nontoxic, biodegradable and environmentally friendly fuel. Biodiesel contains almost no sulfur and does not contribute to greenhouse gases due to its closed carbon cycle [1]. The major component of oils and fats is triglycerides which compose about 90-98% of total mass [2]. Transesterification is a chemical process of reacting triglycerides with alcohol in the presence of a catalyst. If the reaction is not completed, then there will be mono-, di- and triglycerides left in the reaction mixture [3-5]. Alcohols such as methanol, ethanol or butanol can be used in the transesterification [5, 6]. The most preferred alcohol used in biodiesel production. The most commonly preferred catalysts are sulfuric, sulphonic, and hydrochloric acids as acid catalysts, and sodium hydroxide (NaOH), sodium methoxide (NaOMe), potassium hydroxide (KOH) and potassium methoxide (KOMe) as alkaline catalyst [7]. Water is formed when KOH and NaOH are used to produce the methoxide. Water limits the completion of transesterification reaction. Therefore, industrial biodiesel processes run on alkoxides such as NaOMe and KOMe which can be bought as liquid form. They do not contain water and are usually commercially available as ready-to-use methanol solution [8]. NaOMe is offered as a 30% or 25% methanol solution and KOMe as a 32% methanol solution whereas NaOH and KOH are offered as solids and not premixed in methanol [9].

The most common feedstock of biodiesel is rapeseed oil in Europe and soybean oil in the United States of America [10]. The major handicap is the high cost of biodiesel for its commercialization. Chicken fat is a low cost feedstock for biodiesel production compared to high-grade vegetable oils. It is extracted from feather meal which is prepared from chicken wastes such as chicken feathers, blood, offal and trims after rendering process. Feather meal contains significant amount of chicken fat. The fat content of the feather meal varies from 2 to

12% depends on the kind of used feathers [11, 12]. However, they often contain significant amounts of free fatty acid (FFA). The fats with high FFA cannot be converted to biodiesel using alkaline catalysts. FFAs react with an alkaline catalyst and thus soaps are produced by this reaction. Soaps prevent the separation of the ester, glycerin, and wash water [13]. Acid catalysts are too slow to be suitable for converting triglycerides to biodiesel. However, they appear to be quite effective at converting FFAs to esters [14]. For these reasons, an acid catalyst can be used to esterify the FFAs to esters. The acid-catalyzed process is called as pretreatment. FFAs are converted to monoesters through the pretreatment of the feedstock with high FFA and thereby the FFA level reduces. The major handicap for the acid-catalyzed esterification of FFAs is the water formation. The water formation is the primary mechanism limiting the completion of the acid catalyzed esterification reaction with FFAs [13]. After pretreatment, the pretreated feedstock can be transesterified with an alkali catalyst to convert the triglycerides to esters [15-17]. Some researchers [18, 19] stated that the feedstock should not contain more than 1% FFA for alkaline catalyzed transesterification reactions, whereas some researches [1] stated that an alkaline catalyst can be used in the transesterification up to the FFA level of 5%, but it reduces the biodiesel yield.

Many researchers have investigated the availability of animal fats and waste oils for biodiesel production. However, few researchers have studied on the chicken fat especially with high FFA. Mattingly [20] produced biodiesel from chicken fat with 2.3% FFA. He concluded that it was needed to perform a pretreatment reaction to get high biodiesel yield. Bhatti et al. [21] obtained high ester yields up-to 99% from chicken fat after 24 h in the presence of sulfuric acid. Kondamudi et al. [11] chosed the chicken fat for biodiesel production. They used potassium hydroxide to remove FFA in the form of soap. After separating the soap, the optimization of transesterification parameters was researched. They obtained good results and managed to produce biodiesel whose fuel properties were suitable for American Society of Testing and Materials (ASTM) biodiesel standards. Schulte [22] investigated optimum reaction parameters for biodiesel production from chicken fat. He obtained high biodiesel yields up-to 91% by using supercritical methanol. The purpose of the present study was to produce biodiesel from chicken fat with high FFA. Therefore, the optimization of pretreatment reaction was investigated with different acid catalysts to reduce FFA level (below 1%) of chicken fat. The effects of catalyst type, catalyst amount, alcohol molar ratio and reaction time on the FFA level were also analyzed. After the optimum pretreatment parameters were determined, the transesterification reaction was carried out with an alkaline catalyst to produce biodiesel. The optimization of biodiesel production from the chicken fat was investigated with different alkaline catalysts, reaction temperatures and reaction times. The obtained esters were characterized by determining its fuel properties according to the standard test methods. The obtained products were named as chicken fat methyl ester (CFME) because all fuel properties in the standards were not measured.

2. Materials and method

In this study, chicken fat was obtained from Şenpiliç Chicken Slaughterhouse in Sakarya, TURKEY. The chicken fat was subjected to a heating at 110°C for one hour to remove water and then filtered to remove the insoluble materials. The FFA level of the rendering plant feedstock is generally between 5% and 25% [14]. The researchers have suggested that the FFA level of the feedstock should be reduced to less than 1% before using an alkaline catalyst [18, 19]. This was the initial target for the pretreatment. The chicken fat used in this study had an acid value of 26.89 mg KOH/g which corresponds to FFA level of about 13.45%. Because the acid value of the chicken fat was greater than 2 mg KOH/g, it was needed to perform a pretreatment to the feedstock. Some properties and fatty acid composition of the chicken fat are shown in Tables 1 and 2, respectively.

Table 1. Some properties of chicken fat

Properties	Unit	Chicken Fat
Density (at 15°C)	$kg.m^{-3}$	932
Viscosity (at 40°C)	$mm^2.s^{-1}$	59.2
Acid Number	$mg\ KOH.g^{-1}$	26.89
Heat of Combustion	$kJ.kg^{-1}$	39407
Water Content	% mass	0.3

Table 2. Fatty acid composition of chicken fat

Fat	Fatty acid composition (%)						
	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:4
Chicken	19.82	3.06	6.09	37.62	31.59	1.45	0.37

2.1. Pretreatment Process

Sulfuric acid (Merck), hydrochloric acid (Merck) and sulfamic acid (Merck) were used as catalyst and methanol was used as alcohol for the pretreatment of chicken fat. The esterification process of FFAs was repeated for different alcohol molar ratios, amounts of acid catalysts based on the weight of FFAs and reaction times at 60°C. In the calculations, the molecular weight of FFA was obtained from the reference [22]. The experiments were performed in a laboratory scale apparatus. The chicken fat was added into the reaction flask equipped with reflux condenser, magnetic stirrer and thermometer, and then it was heated. When the temperature reached to 60°C, the alcohol/catalyst mixture was added into the fat. The final mixture was stirred for the desired reaction time at 60°C. The mixture was settled overnight and two phases were formed after the pretreatment. The upper phase consists of a mixture of methanol, sulfuric acid and water whereas the lower phase mainly consists of chicken fat and esterified FFAs. The upper phase was removed. After this step, the lower phase was subjected to a heating at 110°C for one hour to remove any remaining alcohol and water. And then, the acid value of the fat-ester mixture was measured and recorded.

2.2. Transesterification Process

In this study, potassium methoxide solution (32% in methanol) and sodium methoxide solution (30% in methanol) were supplied from Evonik Industries in Germany. These alkoxides, potassium hydroxide (Carlo Erba) and sodium hydroxide (Merck) were used as the catalysts for transesterification reactions to investigate the effect of catalyst type on the fuel properties of biodiesel. Molar ratio between alcohol and fat-ester mixture was 6:1 for the transesterification reaction. The catalyst amount was selected as 1% of the weight of the initial amount of fat in the chicken fat and the neutralization amount which was calculated from the reference [3] for KOH and NaOH catalyst whereas the catalyst amounts were (FFA% x 0.64) + 1.7% and (FFA% x 0.78) + 2.0% for NaOMe and KOMe catalysts, respectively. The catalyst amounts for NaOMe and KOMe were calculated according to the manufacturer recommendation. In the calculations for transesterification, the molecular weight of chicken fat was obtained from the reference [22]. The transesterification process and laboratory apparatus were the same as those of pretreatment experiments except for catalyst. The reaction temperature was selected as 25°C and 60°C, and reaction time was selected as one, two and four hours. After the transesterification reaction, the glycerin layer was separated in a separating funnel and the ester layer was washed with warm water. After washing, the methyl ester was subjected to a heating at 110°C to remove excess alcohol and water, and then filtered. The obtained methyl esters were characterized in the Fuel Laboratory of the Department of Automotive Engineering Technologies and Alternative Fuels R&D Center in Kocaeli University.

3. Results and discussion

Some researchers [14, 16] tried to reduce high FFA level of the feedstock by two step pretreatment process. After the first treatment, the reaction mixture is allowed to settle. Since the water formation when the FFAs are converted to esters inhibits the reaction, the methanol-water mixture is separated from the oil phase. Then, additional methanol and acid catalyst can be added and the reaction continued for the second step. Increasing the number of pretreatment steps reduces the ester yield due to the solubility of the fat and ester in methanol [15]. Therefore, in this study, it was tried to reduce the FFA level by one step pretreatment to get high ester yield and save time for producing biodiesel.

3.1. Pretreatment of the Chicken Fat with Sulfuric Acid

Sulfuric acid was selected as reference catalyst. The esterification process was repeated for different alcohol molar ratios (10:1, 15:1, 20:1, 25:1, 30:1) and amounts of sulfuric acid (3%, 6%, 15%, 20%, 35%) based on the FFA level of the chicken fat for one hour reaction at 60°C. The initial experiments were performed with 3% and 6% catalyst at different methanol molar ratios. Good results were not obtained when using 3% and 6% sulfuric acid, and methanol molar ratios from 10:1 to 30:1 for one hour reaction at 60°C. The FFA level was only reduced to 11.25% when using 6% sulfuric acid and methanol molar ratio of 30:1. Therefore, greater amount of sulfuric acid and methanol molar ratio were used. The reaction conditions of the next pretreatments were two different methanol molar ratios of 20:1 and 30:1, and three different sulfuric acid amounts of 15%, 20% and 35% for one hour reaction at 60°C. The FFA level of the chicken fat decreased with rising of sulfuric acid amount and methanol ratio in the pretreatment reaction. The FFA level was reduced to 6.26%, 2.27% and 1.20% for 15%, 20% and 35% sulfuric acid with methanol molar ratio of 20:1, respectively. The aim of the pretreatment reaction was to decrease the FFA level from 13.45% to less than 1%. Therefore, the methanol ratio was raised to 30:1. In this case, the FFA level decreased to 4.92%, 1.40% and 1.04% for 15%, 20% and 35% sulfuric acid, respectively.

3.2. Pretreatment of the Chicken Fat with Hydrochloric Acid

The pretreatments were repeated with 6%, 15% and 20% hydrochloric acid and methanol molar ratio of 20:1 and 30:1 for one hour reaction at 60°C. Six percent of hydrochloric acid was not effective in decreasing the FFA level of the chicken fat with methanol molar ratios 20:1 and 30:1 for one hour reaction at 60°C such as in sulfuric acid experiments. The FFA level was only reduced to 12.99% and 12.46% with using 6% hydrochloric acid for methanol molar ratio of 20:1 and 30:1, respectively. Consequently, the catalyst amount was raised to 15% and 20%. The FFA level of the chicken fat was reduced to 5.26% and 2.83% for 15% and 20% hydrochloric acid at methanol molar ratio of 20:1, respectively. The FFA level of the chicken fat was strongly affected by the molar ratio of methanol. With using methanol molar ratio of 30:1, the FFA level was reduced to 3.89% and 1.67% for 15% and 20% hydrochloric acid, respectively. The FFA level of the chicken fat was decreased to about 1% when using 20% hydrochloric acid and methanol molar ratio of 30:1. The pretreatment results with sulfuric and hydrochloric acids were very close to each other. The differences of FFA level were only 0.56% and 0.27% for 20% acid catalyst with methanol molar ratio of 20:1 and 30:1, respectively.

3.3. Pretreatment of the Chicken Fat with Sulfamic Acid

The third acid catalyst which was used for esterification of FFAs was sulfamic acid in this study. Sulfamic acid is slightly soluble in methanol. For this reason, it needs to be heated to prepare a mixture of alcohol-acid catalyst. The esterification process was repeated for 6% sulfamic acid and alcohol molar ratios of 20:1 and 30:1. Six percent of sulfamic acid did not affect the FFA level of the chicken fat significantly with methanol molar ratios of 20:1 and 30:1 for one hour reaction at 60°C. The FFA level was only reduced to 12.78% and 12.32% when using 6% sulfamic acid for methanol molar ratio of 20:1 and 30:1, respectively. Therefore, the catalyst amount was raised to 15% with methanol molar ratio of 30:1 for one hour reaction at 60°C. But, satisfactory results were not reached with 15% sulfamic acid. The FFA level was only reduced to 11.97%. For this reason, the pretreatment was not continued with sulfamic acid.

3.4. Effect of Reaction Time on the FFA Level of Chicken Fat with Sulfuric Acid

According to the results, sulfuric acid gave the best results among the three acid catalysts used in this study. The initial target was to reduce the FFA level of the chicken fat less than 1%. Thirty-five percent of sulfuric acid was better than 20% for converting FFAs to monoesters. However, the loss of feedstock after the pretreatment was the highest for 35% sulfuric acid. Lower feedstock amount means lower biodiesel yield after transesterification. For this reason, 20% sulfuric acid was selected as acid catalyst amount. Beside, methanol molar ratio was raised to 40:1 to decrease the FFA level below 1%. The effect of reaction time on the FFA level of the chicken fat was investigated. Reaction time was chosen as 60, 70 and 80 minutes at 60°C in these pretreatments. The FFA levels of the chicken fat were 0.93%, 0.80% and 0.67% for 60, 70 and 80 minutes with 20% sulfuric acid and methanol molar ratio of 40:1, respectively. The FFA level decreased below 1% for these three experiments. The pretreatment with 20% sulfuric acid and methanol molar ratio of 40:1 for 80 minutes at 60°C was thought to be sufficient for reducing FFA level less than 1% to get high ester yield after transesterification. Thus, these reaction parameters were selected for pretreatment.

3.5. Characterization of Fuel Properties after Transesterification

After pretreatment reaction, the FFA level of the chicken fat was 0.67% which is sufficient to complete the reaction with alkaline catalysts. The effects of variables such as catalyst type, reaction temperature and reaction time on the fuel properties of the CFMEs were investigated. The gathered ester yield results are shown in Table 3. The ester yield increased with the increasing reaction temperature from 25°C to 60°C for all esters. But the ester yield did not change significantly with the increasing reaction time. In this study, the minimum and maximum ester yields were 71.3% (at four-hour, 25°C and NaOH catalyzed reaction) and 88.5% (at one-hour, 60°C and KOMe catalyzed reaction), respectively. The total-free glycerin, mono-, di- and triglyceride results are illustrated in Table 3. Standard total glycerin results were obtained only when using KOH and NaOH in the transesterification. Better total glycerin results were determined for NaOH catalyzed reactions compared to KOH. However, the ester yield was significantly lower for NaOH catalyzed reactions. Free glycerin results show that it is not directly affected by reaction parameters. Mono-, di and triglyceride values generally reduced with increasing reaction time at 25°C. But, these values show different changes at 60°C because of reversible reaction.

*Table 3. Fuel properties of produced CFMEs **

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
a	25	1	886	1	170	0.04	4	40.1	0.49	0.03	0.71	0.82	1.50	0.30	5.4	80.2
a	25	2	885	1	171	0.11	3	40.3	0.35	0.03	0.56	0.54	0.90	0.29	5.2	82.1
a	25	4	884	1	172	0.13	3	40.3	0.16	0.03	0.40	0.03	0.20	0.25	5.1	84.8
a	60	1	885	1	171	0.01	2	40.2	0.20	0.03	0.55	0.03	0.27	0.25	5.1	88.1
a	60	2	884	1	171	0.01	2	40.2	0.19	0.04	0.45	0.11	0.14	0.24	5.0	87.6
a	60	4	883	1	172	0.01	2	40.2	0.19	0.02	0.56	0.09	0.12	0.22	4.9	87.4
b	25	1	885	1	170	0.12	3	40.1	0.05	0.02	0.01	0.13	0.06	0.30	5.4	72.8
b	25	2	885	1	172	0.06	2	40.1	0.08	0.03	0.16	0.01	0.04	0.29	5.3	71.7
b	25	4	884	1	172	0.03	2	40.2	0.07	0.02	0.16	0.01	0.03	0.24	5.2	71.3
b	60	1	885	1	171	0.20	2	40.1	0.10	0.02	0.31	0.01	0.02	0.28	5.2	79.1
b	60	2	884	1	172	0.08	2	40.2	0.12	0.01	0.41	0.01	0.01	0.24	5.1	78.4
b	60	4	883	1	172	0.09	2	40.3	0.15	0.01	0.55	0.01	0.02	0.23	4.9	77.3
c	25	1	891	1	170	0.02	4	40.0	NT	NT	NT	NT	NT	0.30	6.7	84.6
c	25	2	890	1	172	0.01	3	40.1	1.10	0.02	1.99	2.81	1.57	0.27	6.3	82.7
c	25	4	888	1	172	0.01	3	40.1	0.68	0.01	1.30	1.08	1.74	0.25	5.8	81.9
c	60	1	887	1	171	0.01	3	40.1	0.55	0.01	0.90	0.84	1.81	0.29	5.6	88.5
c	60	2	886	1	172	0.01	3	40.1	0.49	0.01	0.99	0.15	2.04	0.26	5.6	85.2
c	60	4	886	1	172	0.01	3	40.1	0.72	0.01	1.02	1.25	2.56	0.24	5.6	86.2
d	25	1	891	1	171	0.03	4	39.9	NT	NT	NT	NT	NT	0.30	6.8	75.8
d	25	2	890	1	171	0.12	3	40.1	1.07	0.02	1.50	2.23	3.31	0.28	6.2	79.1
d	25	4	888	1	172	0.05	3	40.1	0.71	0.04	1.23	1.58	1.18	0.25	5.9	80.3
d	60	1	886	1	171	0.20	2	40.2	0.50	0.02	0.96	0.70	1.32	0.26	5.4	85.9
d	60	2	886	1	173	0.12	2	40.2	0.58	0.01	0.94	0.91	1.94	0.25	5.5	85.3
d	60	4	885	1	173	0.15	2	40.1	0.44	0.01	1.52	0.04	0.34	0.22	5.5	88.3

*1: catalyst (a: KOH, b: NaOH, c: KOMe, d:NaOMe), 2: reaction temperature (°C), 3: reaction time (hour), 4: density (15°C, $kg.m^{-3}$), 5: copper strip corrosion (degree of corrosion), 6: flash point (°C), 7: methanol content (%), 8: pour point (°C), 9: heat of combustion ($MJ.kg^{-1}$), 10: total glycerin (%), 11: free glycerin (%) 12: monoglyceride (%), 13: diglyceride (%); 14: triglyceride (%), 15: acid number (mg $KOH.g^{-1}$), 16: viscosity (40°C, $mm^2.s^{-1}$), 17: ester yield (%)., NT: not tested.

Generally, the density of CFME decreases with increasing of reaction time and reaction temperature. There is no significant difference among the densities for transesterification reactions catalyzed with KOMe and NaOMe compared to KOH and NaOH. In general, the viscosity of CFME decreases with the increasing reaction time and reaction temperature. However, there is a significant difference among the viscosities when using KOMe and NaOMe catalysts compared to KOH and NaOH. The viscosities of CFMEs are higher for transesterification reactions catalyzed with KOMe and NaOMe. This situation can be explained with incomplete transesterification reaction. The methanol contents of CFMEs vary from 0.01% to 0.20% as seen in Table 3. It clearly shows that the methanol content values of biodiesel do not directly depend on transesterification reaction parameters. The flash points of CFMEs do not change mostly and range from 170°C to 173°C. The CFMEs produced in this study have high pour point. The minimum and maximum pour point is 2°C and 4°C, respectively. The acid value of pretreated chicken fat was 1.34 mg $KOH.g^{-1}$ and this value was reduced to 0.22 mg $KOH.g^{-1}$ after transesterification reaction. The maximum acid value was measured to be 0.30 mg $KOH.g^{-1}$ which is much below the required biodiesel standards.

The heat of combustion results are around 40 MJ.kg^{-1} and they are slightly lower than those of petroleum diesel fuels. According to the results, there is no significant difference among the heat of combustion results depending on transesterification reaction parameters. The copper strip corrosion results gathered with each of CFME are the lowest level of corrosiveness (No 1a). This means that corrosion would not be a problem for CFMEs.

4. Conclusion

The objective of this study was to produce biodiesel from low-cost chicken fat with high FFA. The FFA level of the feedstock should be reduced to less than 1% before using the alkaline catalysis. For this aim, three acid catalysts were used in the pretreatment reactions and the variables affecting the acid value including alcohol molar ratio, acid catalyst amount and reaction time were investigated. After determining the optimum pretreatment conditions to reduce the FFA level of the chicken fat below 1%, the process was completed by using the alkaline catalysts. The effects of the variables on the fuel properties such as catalyst type, reaction temperature and reaction time were investigated. According to the results, the following conclusions can be drawn:

- The acid catalyst type and amount have effect to reduce the FFA level of the chicken fat in the pretreatment reaction. Sulfuric acid is the best catalyst for reducing FFA level among the acid catalysts used in this study. Low amount of acid catalyst (3% and 6%) is not effective for reducing FFA level of the feedstock for all acid catalysts.
- The FFA level of the chicken fat is strongly affected by the molar ratio of methanol, acid catalyst amount and reaction time. Sulfuric and hydrochloric acids give similar pretreatment results.
- Sulfamic acid does not have significant effect on the reduction of acid value of the chicken fat. The FFA level of the chicken fat with about 15% FFA may be reduced to below 1% when using 20% sulfuric acid and methanol molar ratio of 40:1 for 60, 70 and 80 minutes at 60°C. The ester yield increased with increasing reaction temperature.
- The viscosity and glyceride values of CFME decreased with increasing reaction temperature. The catalyst type especially affects viscosity and glyceride values.
- The fuel properties such as density, flash point, methanol content, pour point, heat of combustion, acid value and copper strip corrosion values did not change significantly with the reaction parameters.
- The required viscosity for EN 14214 standards was only obtained using KOH and NaOH at 60°C. KOH and NaOH are superior to KOMe and NaOMe with the catalyst amounts used in this study. But, the effect of catalyst amounts for KOMe and NaOMe on the fuel properties should be investigated for further studies.
- The measured fuel properties of the CFME met both the ASTM D6751 and EN 14214 biodiesel standards when using KOH and NaOH at 60°C for a four-hour reaction.

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Optimization on the use of crude glycerol from the biodiesel production to obtain poly-3-hydroxybutyrate

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Abstract: The biotechnological production of poly-3-hydroxybutyrate (PHB) from crude glycerol obtained during the biodiesel production was techno-economically assessed. For the fermentation process, two different strains, *Cupreavidus necator* and *Bacillus megaterium* were considered. Moreover, three downstream processes for PHB separation and purification were analyzed. Thus, in total six biotechnological schemes to transform the crude glycerol obtained in the biodiesel industry were compared. Each biotechnological scheme considered five main process stages namely: (*i*) glycerol purification, (*ii*) glycerol fermentation to PHB, (*iii*) mass cell pretreatment, (*iv*) PHB isolation, and (*v*) PHB purification. Aspen Plus and Aspen Icarus were used for the processes simulation and for the economic assessment, respectively. During the processes simulation the crude glycerol stream was purified from 60 to 98 wt %, and the fermentation process was considered in two continuous stages where mass cell growth and PHB accumulation occurred, respectively. Also, the three downstream processes were based on: (*i*) heat pretreatment and chemical-enzymatic digestion, (*ii*) high pressure homogenizer and solvent extraction, and (*iii*) alkaline pretreatment and chemical-enzymatic digestion. Economic results showed that the best technological scheme uses *C. necator* for the fermentation stage, with a heat pretreatment and enzymatic-alkaline digestion for the downstream process.

Keywords: *Glycerol fermentation, PHB production, Process simulation, Process assessment.*

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1. Introduction

Glycerol as a by-product on biodiesel production is obtained at high concentration in a weight ratio of 1/10 (glycerol/biodiesel) [1]. Moreover, the growing market of biodiesel has generated a glycerol oversupply, where its production increased 400% in a two-year period and consequently the commercial price of glycerol fell down about 10 times. As a result of the low prices of glycerol, traditional producers such as Dow Chemical and Procter and Gamble Chemicals, stopped the glycerol production [2].

Since glycerol sales have represented an important profitability for the biodiesel industry, it is reasonable to think that low prices of glycerol could affect negatively the economy of biodiesel producers. For this reason, the correct exploitation of glycerol as raw material should be focused on its transformation to added-value products [3]. Thus, the use of glycerol is a high-priority topic for managers and researchers related to the production of biodiesel. In this sense, the establishment of glycerol's biorefineries capable to co-generate added-value products is an excellent opportunity not only to increase the biodiesel profitability, but also to produce high-demanded chemicals from a biobased raw material [4].

Glycerol as the structural component of many lipids is abundant in nature. It is produced by yeasts during osmoregulation to decrease extracellular water activity due to its compatible solubility [5]. Wide glycerol occurrence in nature allows different kinds of microorganisms to metabolize it as a sole carbon and energy source. Thus, in some industrial fermentation processes, glycerol can substitute traditional carbohydrates, such as sucrose, glucose, and starch [5]. In this way, one of many promising applications to take advantage of the glycerol surplus is its bioconversion to high value compounds through microbial fermentation. An interesting application is to transform glycerol to poly-3-hydoroxybutyrate (PHB), which has similar properties to conventional plastics such as polypropylene or polyethylene. Also, PHB can be extruded, molded, spun into fibers, made into films, and used to make heteropolymers with other synthetic polymers [6].

Here, the biotechnological production of PHB from crude glycerol obtained during the biodiesel production was techno-economically assessed. For the fermentation process, two different strains, *Cupreavidus necator* and *Bacillus megaterium* were considered. Moreover, three downstream processes for PHB separation and purification were analyzed. Thus, six biotechnological schemes to transform the crude glycerol obtained in the biodiesel industry were compared.

2. Methodology

The approach used for the processes design was a knowledge-based strategy that considers both heuristic rules and researcher's experience. Process simulation and economic assessment were carried out utilizing the Aspen Plus software and the Aspen Icarus package, respectively. Material and energy balances were obtained as simulation results for each technological scheme. As a result, requirements of raw materials, services, and energy were obtained. Also, estimation of energy consumption and related costs were calculated based on the simulation results for thermal units such as heat exchangers, reboilers, and evaporators. This methodology has been previously presented by Cardona et al. [5-10].

2.1. *Process description*

The PHB production process from crude glycerol requires five main stages [11], namely: glycerol purification, glycerol fermentation (cell growth and PHB accumulation), mass cell pretreatment, PHB isolation, and PHB purification. *Cupreavidus necator* and *Bacillus megaterium* were considered as the bacterial strains in order to compare the fermentation process. Glycerol purified at 98 wt % was considered as substrate in all cases and the three different downstream processes were analyzed with each strain, as shown in Fig. 1.

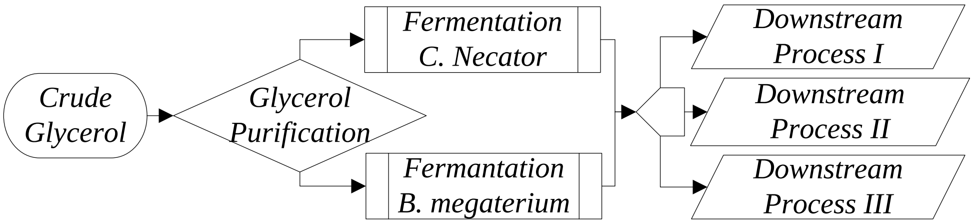

Fig. 1. Schematic representation of the PHB production from crude glycerol by C. necator and B. megaterium.

2.1.1. *Glycerol purification*

A typical composition for a crude glycerol stream obtained from the biodiesel production process is as follows: 32.59 wt % methanol, 60.05 wt % glycerol, 2.62 wt % $NaOCH_3$, 1.94 wt % fats, and 2.8 wt % ash [3].

Fig. 2 shows the flowsheet for crude glycerol purification up to 98 wt % [4]. The crude glycerol is initially evaporated and 90 % of the methanol is recovered at 99 wt %. Also, this obtained stream meets the necessary conditions to be reused in the transesterification process. The resulting bottom stream from the evaporation stage is neutralized using an acid solution where both the salts produced during the neutralization and the remaining ashes are removed by centrifugation. The fluid stream is washed with water using a weight ratio of 2.4 (water/glycerol stream), and thus an aqueous glycerol free of salts and solids, with a low concentration of methanol and triglycerides is obtained. More than 90 % of water and the remaining methanol are then removed by evaporation. At this point the purity of the obtained glycerol is 80 wt %, and the glycerol stream is finally purified through a distillation column up to 98 wt %.

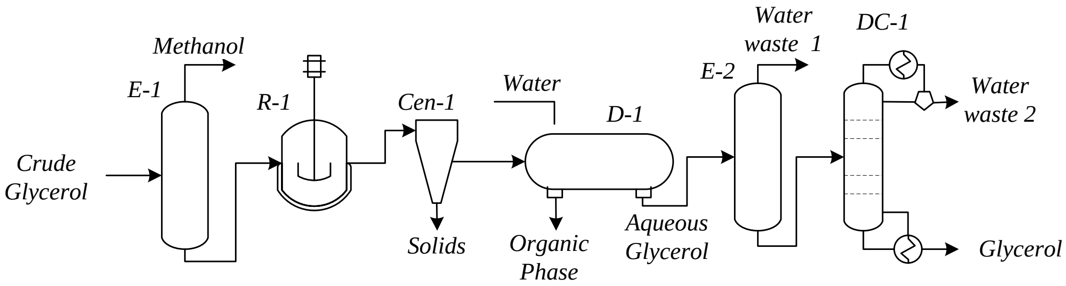

Fig. 2. Simplified flowsheet of the glycerol purification process up to 98 wt%.E-1: Evaporator I, R-1, Neutralizing Reactor I, Cen-1: Centrifuge I, D-1: Decanter I, E-2: Evaporator II, DC-1: Distillation Column I.

2.1.2. Fermentation process

Biotechnological production of PHB from glycerol requires a limitation of an essential nutrient such as: N, P, Mg, K, O or S, and an excess of a carbon source. Some of the bacterial strains capable of doing this transformation are *Bacillus megaterium*, *Cupriavidus necator, Alcaligenes eutrophus, Pseudomonas extorquens, and Pseudomonas oleovoran,* among others. Also, during the fermentation process the PHB accumulation could reach values between 40 to 70 wt %, with productivities up to 1.5 g/(L h) [6].

For the fermentation process two strains were compared, *C. necator* and *B. megaterium*, using a two stages fermentation process. In the first stage the cell growth occurs, while in the second stage the PHB accumulation takes place. Since the dissolved oxygen in the cell growth media must be between 15 and 20 %, air and oxygen should be fed in the first fermentation stage. Prior to the fermentation process, the diluted glycerol should be sterilized at 25 atm and 139 °C, as shown in Fig. 3.

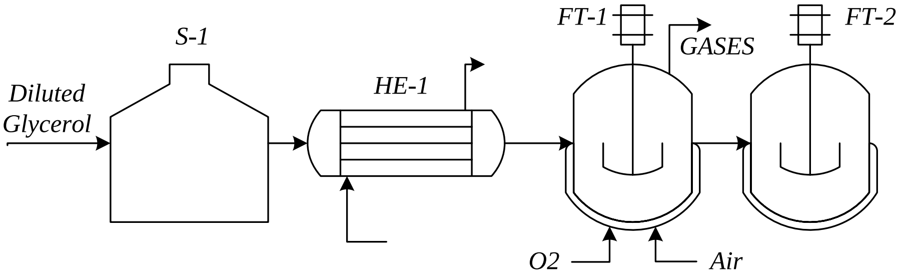

Fig. 3. Simplified flowsheet for the glycerol fermentation to PHB. S-1: Sterilizator I, HE-1: Heat Exchanger I, FT-1: Fermentation Tank I, FT-2: Fermentation Tank II

When the fermentation is carried out by *C. necator* the glycerol stream is diluted at 249 g/L [12], and the residence time for both fermentation stages are 21 and 22.5 h. In the case of *B. megaterium*, the glycerol stream is diluted at 50 g/L [13] with the respective residence times of 75 and 21 h.

2.1.3. Downstream processes

The downstream process for PHB purification from a fermentation broth can be divided in three parts: pretreatment, extraction, and purification. In the pretreatment step, cell disruption can be carried out by the action of heat, alkaline media, salty media, or freezing. In the case of extraction, some alternatives such as: solvent extraction, chemical digestion, enzymatic digestion, mechanical cell disruption, supercritical fluid extraction, cell fragility, and spontaneous liberation can be used. Finally, the purification methods involve a hydrogen peroxide treatment combined with the action of enzymes or chelating agents. [11].

The first considered downstream process starts with a heat pretreatment stage at 85 °C, followed by a simultaneous chemical-enzymatic digestion with both NaOCl (30 wt %) and the enzyme *Burkholdeira sp. PTU9* (2 wt %), at 50 °C and pH 9. Then the disrupted mass cell is discarded by a centrifugation process. The suspended PHB stream is washed with a H_2O_2 diluted stream (1.2 v/v %). Finally, the PHB is purified up to 99.9 wt % by evaporation and spray drying, as shown in Fig. 4.

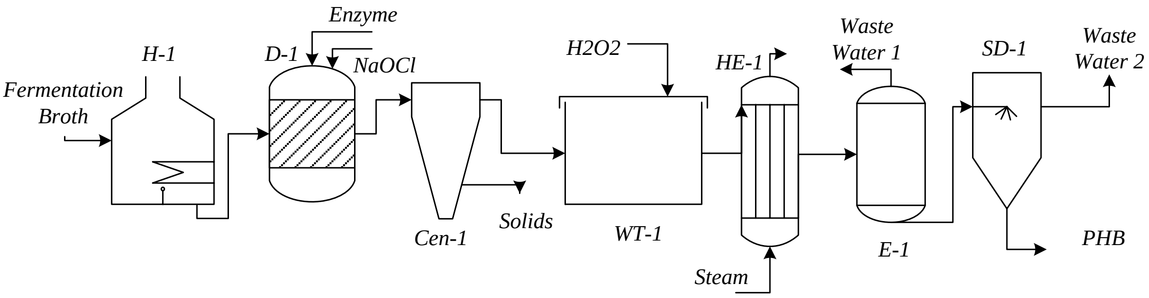

Fig. 4. Simplified flowsheet for the first downstream process. H-1: Heater I, D-1: Digestor I, Cen-1: Centrifuge I, WT-1: Washer Tank I, HE-1: Heat Exchanger I, E-1: Evaporator I, SD-1: Spray Drier I.

The second downstream process starts with a high pressure homogenizer at 70 MPa and 110 °C, where the cell mass is disrupted. Then, the centrifugation is carried out prior to the solvent extraction. In this extraction diethyl-succinate (DES) at 110 °C in a mass ratio of 1/20 (PHB/solvent) is used. A second centrifugation stage is employed in order to withdraw the residual cell mass. Thus, a mixture of PHB-water is gelled by cooling and the DES is recovered. Finally, the PHB at 99.9 wt % is obtained by spray drying, as shown in Fig. 5.

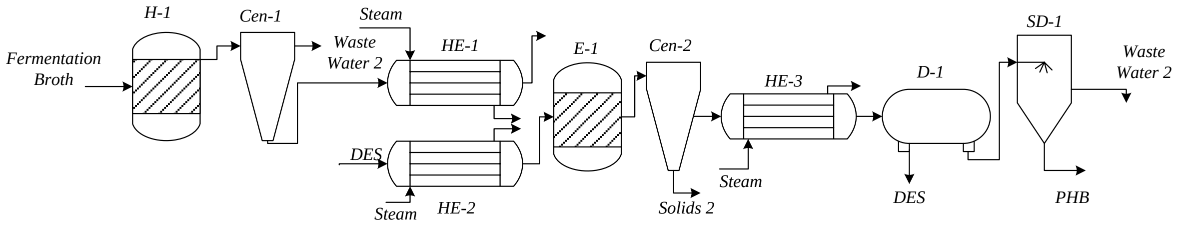

Fig. 5. Simplified flowsheet for the second downstream process. H-1: Homogenizer I, Cen-1: Centrifuge I, HE-1: Heat Exchanger I, HE-2: Heat Exchanger II, E-1: Extractor I, Cen-2: Centrifuge II, HE-3: Heat Exchanger III, D-1: Decanter I, SD-1: Spray Drier I.

In the third downstream process, the fermentation broth is pretreated with an alkaline solution of NaOH at 70 MPa and 110 °C. Then, a digestion process is carried out using NaOCl and sodium dodecylsulfate (SDS) at 55 °C. The disrupted cells are centrifuged and the PHB is washed with H_2O_2 (1.2 v/v %). The obtained mixture is subjected to an evaporation process and most of the water content is discarded. Finally, PHB at 99.9 wt % is obtained by spray drying, as shown in Fig. 6.

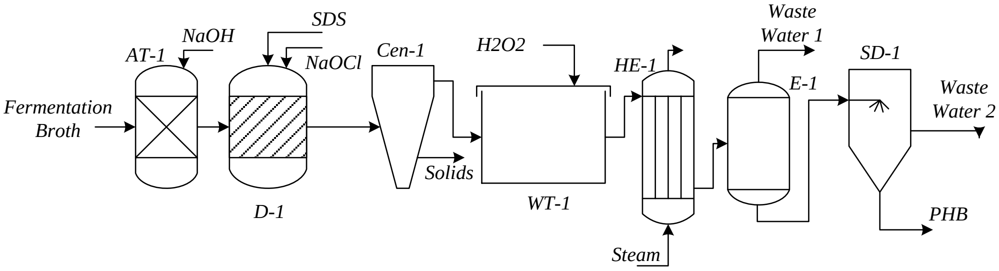

Fig. 6. Simplified flowsheet for the third downstream process. AT-1: Alkaline Tank I, D-1: Digester I, Cen-1: Centrifuge I; WT-1: Washer Tank I, HE-I: Heat Exchanger I, E-1: Evaporator I, SD-1: Spray Drier I.

2.2. Simulation procedure

The PHB production processes were simulated using Aspen Plus (Aspen Technologies Inc., USA). Thus, the design of the distillation columns in all cases required the definition of the preliminary specifications using the DSTWU shortcut method included in Aspen Plus. This method uses the Winn–Underwood–Gilliland procedure providing an initial estimate of the minimum number of theoretical stages, the minimum reflux ratio, the localization of the feed stage, and the products split. To perform the rigorous calculation of the distillation columns, the Rad-Frac module (based on the MESH equations) was used. Also, in order to study the effect of the main operation variables (e.g., reflux ratio, feed temperature, number of stages, etc.) on the glycerol composition, a sequential design procedure including a sensitivity analysis was performed.

On the other hand, *C. necator* and *B. megaterium* were simulated as solid compounds while the enzymes were simulated as non-conventional compounds. For the thermodynamic analysis, the UNIFAC model was used. The fermentation process was simulated based on a yielding approach where glycerol is completely consumed in two continuous fermentation stages. The first fermentation stage is governed by mass cell growth and the second fermentation stage is governed by PHB accumulation. The enzymatic digestion was simulated based on a stoichiometric approach. Calculation of energy consumption was based on the thermal energy required by heat exchangers, reboilers, flash drier units and the power supply required by the pumps.

The economic analysis was performed using the Aspen Icarus (Aspen Technology, Inc., USA) package. This software estimates the capital costs of process units as well as the operating costs, among other valuable data, utilizing the design information provided by Aspen Plus and the data introduced by the user for specific conditions such as project location among others. This analysis was estimated in US dollars for a 10-year period at an annual interest rate of 16 %, considering the straight-line depreciation method and a 33 % income tax. The cost of crude glycerol was USD$ 0.0554/L [3]. The labor cost used for operatives and supervisors was USD$ 2.14/h and USD$ 4.29/h, respectively. Also, the prices used for electricity, water and low pressure vapor were USD$ 0.03044/kWh, USD$ 1.252/m^3 and USD$ 8.18/ton, respectively [5]. All of these values are based on Colombian conditions.

3. Results and Discussions

The PHB production processes from crude glycerol require the glycerol purification up to 98 wt %. During this purification process, methanol at 99 wt % is recovered and thus for the economic assessment, two scenarios can be analyzed. In the first scenario, the obtained methanol is considered as a process waste. In the second scenario the methanol is considered as a co-product which could be recycled to the transesterification process and an economic value is given to this stream. The lowest cost for glycerol purification was obtained under the second scenario conditions (0.149 USD$/kg). This value was used as the raw material cost in all cases, thus only the purification cost was considered since the purification process was assumed to be adjacent to the biodiesel production process.

Glycerol fermentation was analyzed using two different strains and two glycerol concentrations in the fermentation media were considered (249g/L and 50 g/L). The cell mass values were 81.6 and 15.8 g/L and the PHB concentrations were and 57.1 and 8.8 g/L when *C. necator* and *B. megaterium* were used respectively. Thus, the reached yields to biomass and PHB were 5.16 and 6.49 fold higher when *C. necator* was used. These differences may be due to the fact that the first strain is a well adapted bacterium meanwhile the second one is still under adaptation to the fermenting conditions used in this work.

The fermentation broth is mainly a mixture of incorporated PHB in the cell mass and water. In order to recover the PHB from this broth, three different downstream processes were compared. The total production costs of PHB at 99.9 wt % from crude glycerol using *C. necator* and *B. megaterium* are shown in Table 1, where the costs were discriminated by raw material, services, operatives, maintenance, administration, and depreciation.

Table 1. Total PHB production cost from crude glycerol using C. necator and B. megaterium.

Item	***Cost (US$/kg) and Share (%)***	***Downstream Process I***		***Downstream Process II***		***Downstream Process III***	
		B. megat.	*C. necator*	*B. megat.*	*C. necator*	*B. megat*	*C. necator*
Raw material	***Cost***	*0.149*	*0.149*	*0.149*	*0.149*	*0.149*	*0.149*
	Share	*3.80*	*7.71*	*3.15*	*6.27*	*3.60*	*7.07*
Utilities	***Cost***	*1.358*	*0.658*	*1.908*	*0.953*	*1.691*	*0.841*
	Share	*34.64*	*33.96*	*40.36*	*39.97*	*40.88*	*39.77*
Operating labor	***Cost***	*0.151*	*0.066*	*0.156*	*0.068*	*0.146*	*0.064*
	Share	*3.85*	*3.41*	*3.30*	*2.85*	*3.53*	*3.03*
Maintenance and opera. charges	***Cost***	*0.479*	*0.210*	*0.492*	*0.236*	*0.485*	*0.223*
	Share	*12.22*	*10.84*	*10.41*	*9.90*	*11.73*	*10.55*
Plant overhead and admin. costs	***Cost***	*0.407*	*0.186*	*0.427*	*0.218*	*0.414*	*0.191*
	Share	*10.38*	*9.6*	*9.03*	*9.14*	*10.01*	*9.03*
Depreciation of capital	***Cost***	*1.376*	*0.668*	*1.595*	*0.76*	*1.251*	*0.646*
	Share	*35.10*	*34.48*	*33.74*	*31.87*	*30.25*	*30.55*
Total	***Cost***	***3.920***	***1.937***	***4.727***	***2.384***	***4.136***	***2.114***
	Share	***100***	***100***	***100***	***100***	***100***	***100***

The glycerol purification process represents only between 3.1 and 3.8 % of the total PHB production cost when *B. megaterium* is used. These values are higher, between 6.3 and 7.7%, when *C. necator* is used. In all cases, the raw material cost is lower than the obtained value for traditional chemical processes considering that for most industrial processes the cost of raw material represents near 50% of the total production cost. In this way, the use of crude glycerol represents a significant decrease in the cost for raw material.

In general terms, due to the higher PHB yield, substrate tolerance, and lower energy requirements in the downstream processes, the lower production costs are obtained when *C. necator* is used for the fermentation process. Also, for both strains, the higher value for the total production cost was obtained in the second downstream process, which uses a solvent extraction stage. This extraction requires heating the expensive solvent DES up to 110 °C which increases the utility costs.

The total PHB production costs were between 3.92 and 4.73 US$/kg when *B. megaterium* was considered in the fermentation process, and between 1.94 and 2.38 US$/kg when *C. necator* was considered. These production costs were close to the sale prices of PHB reported in the literature for other substrates (i.e., 2.75-6.27 USD/Kg) [6].

Economically wise, the first downstream process was the most appropriate since the total production costs were the lowest obtained for both strains. This process was based on the BIOPOL flowsheet [14]. Moreover, the total production cost was almost twice as higher when *B. megaterium* was used for the fermentation stage compared to *C. necator*.

Generally, it has been suggested that the higher share of the total PHB production cost from other raw materials is the substrate cost [6]. Meanwhile, if crude glycerol is used as feedstock this share is lower than 8 %. These results indicate that using crude glycerol as feedstock to produce PHB could be a profitable alternative to develop biorefineries in the biodiesel industry.

4. Conclusions

Three downstream processes and two strains, *C. necator* and *B. megaterium,* were techno-economically compared to produce PHB from crude glycerol. Although in all the simultaed cases it was possible to obtain PHB at 99.9 wt %, the total production costs were twice as higher when *B. megaterium* was used compared to *C. necator*. This result is explained by the fact that *C. necator* is capable to consume glycerol at a higher concentration and yield than *B. megaterium*. The comparison showed here is important for the industrial production of PHB using crude glycerol since not only a profitable alternative was designed but also the fermentation conditions that take to a profitable process were clarified.

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Theoretical Bioenergy Potential in Cambodia and Laos

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Abstract: This paper investigates theoretically potential energy of residues of some biomass sources in Cambodia and Laos by considering agricultural residues and forestry residues for the year 2006 since both country have limited access to grid-quality electricity. The theoretical potential biomass energy of rice husk, straw, corn cob, cassava stalk, bagasse and sugarcane trash and logging residues, sawnwood and plywood residues are calculated by using their lower heating values (LHV). The potential biomass energy obtained from these residues in Cambodia can contribute approximately 1.4 Mtoe to the total final energy consumption of Cambodia. On the other hand, 0.6 Mtoe biomass energy can be obtained potentially from the biomass residues in Laos, 2006. Furthermore, the paper presents the theoretical bioethanol production from some biomass residues such as rice straw, corn stover, bagasse, and cassava pulp in Cambodia and Laos. The potential bioethanol production in Cambodia is about 0,648 Gl for the year 2006 whereas 0,355 Gl of bioethanol can be produced in Laos from 2006 biomass residues. The potential results are investigated in whole country level and they do not consider the collecting and transportation cost of the biomass residues, their possible other usage purposes, exports and imports.

Keywords: *Biomass, Energy Potential, Crop Residue, Cambodia, Laos.*

1. Introduction

Due to the increase in energy demand and environmental concerns over fossil fuel consumption, biomass has been of interest in recent years in terms of renewable energy source [1]. Biomass energy can be converted into useful energy for both traditional and modern uses. Firing for cooking and heating is a simple example of traditional uses. In modern uses allow to conversion of biomass in the form of electricity, steam and liquid biofuels next to the heating use [2].

Ethanol, as a modern form of biomass energy, can be converted from any kind of starchy biomass source which is rich in sugar content. Agricultural crops, forestry products and their residues are potential sources for ethanol production. Ethanol has a great energy potential in terms of transportation fuel. It can be blended with gasoline and used in the commercial forms of E5, E10 and E85 [2, 3].

This study estimated the biomass energy potential of Cambodia and Laos in terms of agricultural and forestry biomass residues as solid fuel and their ethanol production capacity considering production quantities in 2006. In order not to cause any conflict between food and energy production and considering the high poverty rates of Cambodia and Laos, this study only focused on the biomass energy obtained from agricultural residues and forestry wastes. Mainly, the potential of biomass energy of rice husk, rice straw, corn cob, cassava stalk, bagasse, and trash of sugarcane were estimated. Furthermore, the residues of coconut-husk, shell, and frond- and groundnut-shell- were considered as potential biomass energy sources for Cambodia. Moreover, the study found that some residues such as rice straw, corn stover, bagasse and cassava pulp have a potential to contribute a considerable amount of bioethanol in both countries. Finally, the amount of potential energy obtained from biomass residue resources examined for Cambodia and Laos was compared to the total final energy consumptions of the countries in the same year.

2. Methodology

The production data of each biomass resource was obtained from FAO statistics (FAOSTAT) [4]. The production quantities in 2006 for related biomass sources were used in order to compare the available energy consumption in 2006 for Cambodia and Laos. The production data statistics of Laos taken from FAO were also compared with the statistics presented in National Statistics Centre of Lao PDR [5]. Both production data statistics were found to be consistent. However, Cambodian production data statistics presented in FAOSTAT was used without any modifications as only data source in this study. Also, in order to estimate the amount of agricultural biomass residues RPR (residue-product ratio) values were used. The RPR values of rice husk are specific for Cambodia and Laos. However, the RPR value of rice straw, which is specific for Laos, was also used for Cambodia. These values were taken from previous studies carried out in these countries [6, 7]. However, other biomass residues were calculated in this study by taking the RPR values which have been used in similar studies conducted for Thailand [8]. On the other hand, recovery rates (RR) of forestry biomass residues were used in this study to estimate the available amount of logging residues, mill residues and plywood residues. The recovery rates of mill residues and plywood residues were taken from FAO [9]. On the other hand, recovery rate of logging residues were based on the study of A. Koopmans and J. Koppejan for Cambodia and Laos [10].
Lower Heating Values (LHV) of agricultural residues were taken from the study conducted for Thailand biomass energy estimations [8]. LHV of forestry wastes, however, were based on values studied by Suzuki and Yoshida (2009) [11].

Bioethanol production calculations in Cambodia and Laos for the year 2006 were carried out in the light of the ethanol yield according to a study by Kim and Dale (2003) [2]. That study was conducted by first calculating theoretical ethanol yields of each biomass residue and converting this theoretical yield to possible yield by assuming that ethanol production efficiency from other crop residues is equal to approximately 67%, which is the ethanol production efficiency of corn stover [2]. The same procedure was followed to estimate the potential bioethanol production in Cambodia and Laos.

This study did not consider the imports and exports of any biomass sources. All the potential residues of biomass sources in Cambodia and Laos were calculated in the study without considering their other possible usage purposes and the losses due to the transportation.

3. Results

3.1. Agricultural Residues

3.1.1. Rice

Rice is the main agricultural crop and staple food in both Cambodia and Laos. 84.4% of cultivated area in Cambodia is used for rice cultivation and it constituted 25% of Cambodian agricultural GDP in 2006 [12]. In Laos 80% of area under cultivation has been devoted to rice. Rice accounted for 38% of agricultural GDP, which is higher than Cambodia (1999) [13, 14]. High amount of rice production in both countries contributes to high availability of rice residues such as rice husk and rice straw. These residues could be an option for any biomass energy systems. Rice husk is the outer cover of rice which comes from rice milling process as by-product. The unutilized rice husk mainly causes waste disposal problems and breathing problems because of its low density. The usage of rice husk as solid fuel can be a promising way to avoid these problems and provide considerable amount of useful energy [15]. Rice straw, on the other hand, is another by-product of rice and great bio-resource since it is one of the richest material in terms of its lignocelluloses [16]. However, it has to be taken into account that rice straw is an import fodder for animals in Cambodia. RPR and LHV of rice husk and rice straw are shown in the Table 1 with their calculated potential energy values.

Table 1. 2006,rice residues biomass energy

	Rice (Mt)	Rice Residue	RPR	Residue (Mt)	LHV (MJ/kg)	Potential Energy (10^6GJ)
Cambodia	6.26 [4]	Husk	0.27 [8]	1.69	12.85 [8]	21.73
		Straw	0.33 [7]	2.07	14 [17]	28.92
Laos	2.66 [4]	Husk	0.25[7]	0.67	12.85 [8]	8.56
		Straw	0.25 [7]	0.88	14 [17]	12.31

3.1.2. Maize

Since maize is the second most produced crop after rice for both Cambodia and Laos, it can supply a considerable amount of corn cob as biomass energy source. Moreover, the chemical and physical properties of corn cob enable it to be suitable feedstock for several energy generation methods [14]. Table 2 below shows potential energy obtained from corn cob.

Table 2. 2006, corn cob biomass energy

	Maize (Mt)	RPR	Corn cob (Mt)	LHV (MJ/kg)	Potential Energy (10^6GJ)
Cambodia	0.38 [4]	0.25 [8]	0.09	16.63 [8]	1.57
Laos	0.45 [4]	0.25 [8]	0.11	16.63 [8]	1.87

3.1.3. Cassava

Cassava is another important agricultural crop in Cambodia and Laos as staple food and animal feed in similar way as in many subtropical regions [18]. Cassava stalk, the residue of cassava, is an agricultural biomass feedstock which can be used for biomass energy purposes. Its primary energy was tabulated in Table 3 for Cambodia and Laos.

Table 3. 2006, cassava stalk biomass energy

	Cassava (Mt)	RPR	Cassava stalk (Mt)	LHV (MJ/kg)	Potential Energy (10^6GJ)
Cambodia	2.18 [4]	0.088[8]	0.192	16.99 [8]	3.26
Laos	0.17 [4]	0.088[8]	0.015	16.99 [8]	0.26

3.1.4. Sugarcane

Bagasse and top and trash of sugarcane are the main residues of sugarcane. While bagasse is dry, fibrous residue remaining after sugarcane stalk after extraction of juice, trash of sugarcane is the remaining of the plant in the field after the harvest [19]. The primary biomass energy of bagasse and trash of sugarcane was tabulated by assuming their RPR and LHV as same in Table 4.

Table 4. 2006, sugarcane residues biomass energy

	Sugarcane (Mt)	Sugarcane Residue	RPR	Residue (Mt)	LHV (MJ/kg)	Potential Energy (10^6GJ)
Cambodia	0.14 [4]	Bagasse	0.250 [8]	0.035	6.43[8]	0.228
		Trash	0.302 [8]	0.043	6.82[8]	0.292
Laos	0.217[4]	Bagasse	0.250 [8]	0.054	6.43[8]	0.349
		Trash	0.302 [8]	0.066	6.82[8]	0.447

3.1.5. Groundnut Shell and Coconut

Groundnut shell and coconut husk - rough exterior shells of the coconut -, shell, and empty bunches and frond can be counted as considerable biomass energy sources in Cambodia. Table 5 was prepared to show the potential biomass energy value of these residues.

Table 5. Cambodia, 2006, groundnut shell and coconut residues biomass energy

	Production (Mt)	Residue	RPR	Residue (Mt)	LHV (MJ/kg)	Potential Energy (10^6GJ)
Groundnut	0.024 [4]	Shell	0.323[8]	0.0077	11.23 [8]	0.086
Coconut	0.07 [4]	Husk	0.362 [8]	0.025	14.71 [8]	0.373
		Shell	0.160[8]	0.011	16.43 [8]	0.184
		Frond	0.225[8]	0.016	14.55 [8]	0.229

3.2. Forestry Residues

3.2.1. Logging Residues

Logging residues constitute woody residues that remain after cutting in the forest area, such as tops and branches. Logging residue calculations require the amount of industrial round wood production and an average recovery rate (RR) which is generally estimated since logging can be done in many innumerable and unsystematic ways [9]. Logging recovery rate can be estimated with the idea that “6 cubic meters of logs extracted from the forest leave 4 cubic meters of waste remaining in the forests” [10]. Cambodia’s and Laos’ forestry biomass energy estimations were carried out and tabulated in the Table 6.

Table 6. 2006, logging residue biomass energy

	Industrial round wood (10^6CUM)	RR	Logging Residue (10^6CUM)	LHV (GJ/m^3)	Potential Energy (10^6GJ)
Cambodia	0.113 [4]	0.60 [10]	0.075	7.4 [11]	0.557
Laos	0.194 [4]	0.60 [10]	0.129	7.4 [11]	0.955

3.2.2. Mill Residues from Sawnwood Production Residues

The residues from wood-processing factories are called mill residues [11]. Therefore, the calculations are based on the amount of sawnwood production volume. Table 7 shows the primary biomass energy content of mill residues.

Table 7. 2006, mill residue biomass energy

	Sawnwood (10^6CUM)	RR	Mill Residue (10^6CUM)	LHV (GJ/m^3)	Potential Energy (10^6GJ)
Cambodia	0.002 [4]	0.43 [9]	0.0029	8.4 [11]	0.024
Laos	0.13 [4]	0.60 [9]	0.087	8.4 [11]	0.728

3.2.3. Plywood Residues

Plywood residues comprise of the which are log ends and trims, bark, log cores, green veneer waste, dry veneer waste, trimmings and rejected plywood [9]. Calculations of primary energy of plywood residues in this study are shown in the Table 8 for both countries.

Table 8. 2006, plywood residue biomass energy

	Plywood (10^6CUM)	RR	Plywood Residue (10^6CUM)	LHV (GJ/m^3)	Potential Energy (10^6GJ)
Cambodia	0.0045 [4]	0.47 [9]	0.0051	8.4 [11]	0.043
Laos	0.027 [4]	0.47 [9]	0.031	8.4 [11]	0.256

3.3. Bioethanol Production

This part of the study estimated how much bioethanol can potentially be produced from rice straw, corn stover, bagasse, cassava pulp. Bioethanol calculations were carried out on dry-based biomass residues and are shown in Table 9 in Cambodia and Laos.

Table 9.Cambodia and Laos, 2006,bioethanol production from agricultural residues

	RPR	Residue,Mt Cambodia	Residue,Mt Laos	Ethanol yield(l/t)	Ethanol,10^6l Cambodia	Ethanol,10^6l Laos
Rice Straw	0.33[7]	807	0.77	280 [2]	506	214.9
Corn Stover	1 [2]	0.38	0.45	290 [2]	109.3	130.5
Bagasse	0.25 [8]	0.018	0.03	280 [2]	4.96	7.6
Cassava pulp	0.15[21]	0.327	0.03	83.3 [21]	27.28	2.18

3.4. Final Energy Potential of Biomass

In this study the total potential biomass energy from biomass residues in Cambodia and Laos was found to be about 1.4 Mtoe ($57*10^6$ GJ) and 0.6 Mtoe ($26*10^6$ GJ) respectively. The total final energy consumption (TFEC) in Cambodia was about 4.5 Mtoe in 2005 [22]. This means that the biomass residue energy potential is about one third of the total energy consumption in Cambodia. The total final energy consumption (TFEC) in 2006 in Laos was about 2.0 Mtoe [22]. This indicates that the biomass residue energy potential estimated for Laos could contribute about 30% of the total energy consumption.

Figure 1.a, 1.b and 2.a, 2.b show the total final energy consumption and theoretically calculated potential biomass energy from residues and the contributions of different sources to energy potentials in ktoe in Cambodia and Laos, 2006.

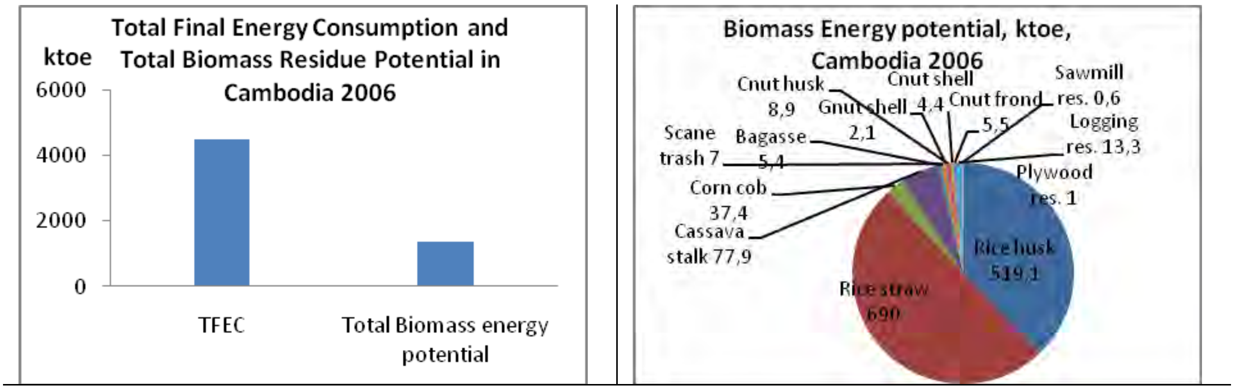

Figure 1.a. Total final energy consumption and calculated potential biomass residue energy content 1.b. Different sources of biomass residue energy potentials in Cambodia, 2006

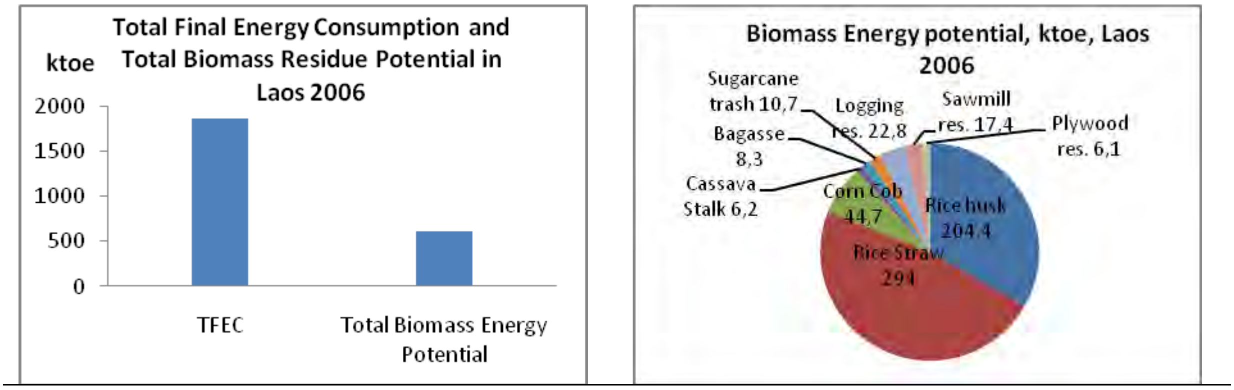

Figure 2.a. Total final energy consumption and calculated potential biomass residue energy content 2.b. Different sources of biomass residue energy potentials in Laos, 2006

3.5. Bioethanol Potential

The study found that some agricultural residues in Cambodia such as rice straw, corn stover, bagasse and cassava pulp have a potential to produce approximately $648*10^6$ l ethanol production for the country. However, the potential of ethanol production from same residues in Laos was estimated about $355*10^6$ l. The amounts of potential bioethanol for both countries were found to be enough to correspond to the amount gasoline consumed in road transport in Cambodia and Laos. Figure 3.a, 3.d and Figure 4.a and 4.b s ummarize the gasoline consumption in 2006 and the potential gasoline production from biomass residues and the contributions of different biomass residues for gasoline productions in Cambodia and Laos, 2006 [21, 22].

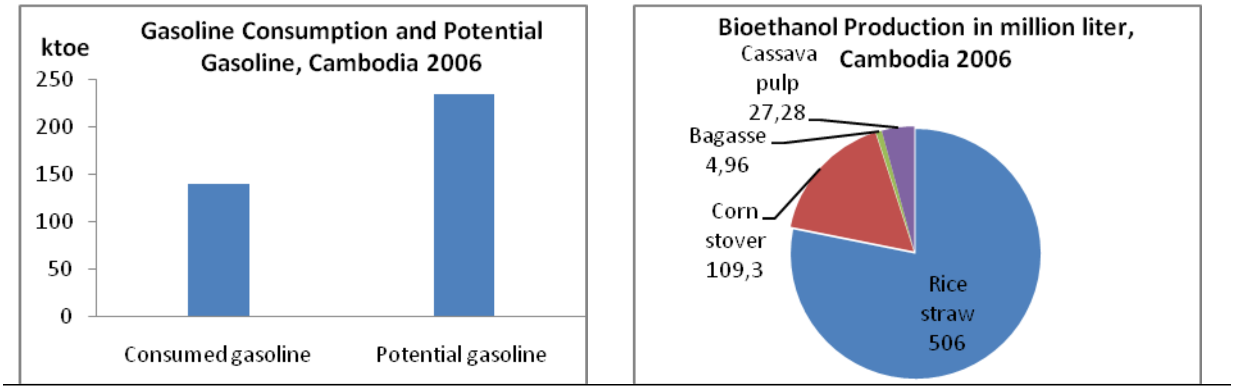

Figure 3.a. Gasoline consumption and potential biomass residue based gasoline production 3.b. Different sources of biomass residue potential for ethanol production in Cambodia, 2006

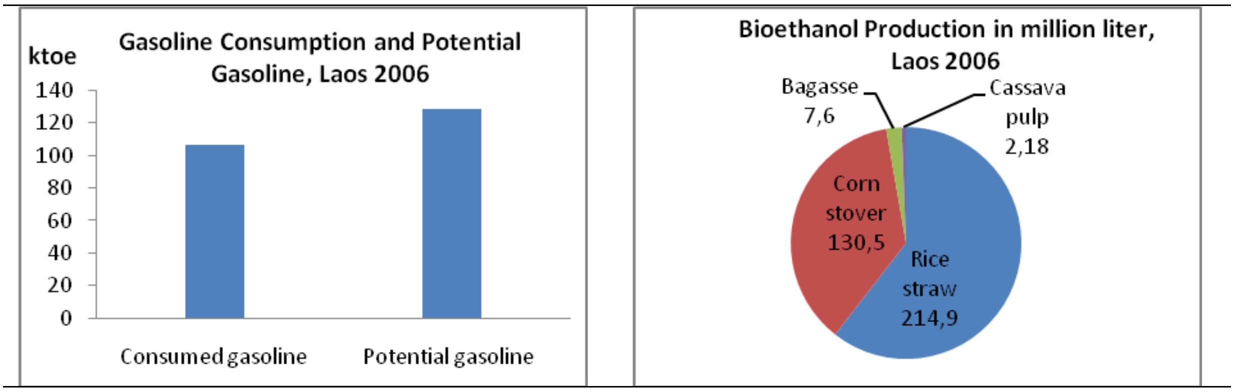

Figure 4.a. Gasoline consumption and potential biomass residue based gasoline production 4.b. Different sources of biomass residue potential for ethanol production in Laos, 2006

4. Conclusions

The results indicate that the biomass residue potential could contribute such energy production that can reach up to 30% of energy consumed in 2006 for both Cambodia and Laos. There are, however, some practical limitations and restrictions in the use of the residues such as collection and transportation of them, marketing systems and other usage possibilities. Furthermore, the results show that rice straw and rice husk in Cambodia and Laos seem to be potentially the most favorable biomass sources in terms of the quantity of biomass production availability and comparably higher contribution to biomass energy production. Totally, all biomass residues including both agricultural residues and forestry residues have a potential to provide 1.4 Mtoe and 0.6 Mtoe energy productions in Cambodia and Laos respectively.

Moreover, the study covers the bioethanol production from some residues such as rice straw, corn stover, bagasse and cassava pulp in Cambodia and Laos. Theoretically, potential bioethanol production in Cambodia has and Laos could provide approximately the same amount of energy as the present gasoline consumption is in both countries.

The results clearly show that biomass residues provide a promising potential for distributed renewable energy production in Cambodia and Laos.

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Growing Biomass Fuel Industry, Declining Local Forage Demands, and Changing Greenhouse Gas Emissions from US Agriculture: A Case Study

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Abstract: This paper investigates the effect of a biomass crop introduction in a local market where field crops, cattle forage and biomass crops compete for the agricultural resources and determine land use. A simulation study for a State in the US (Minnesota) with extensive and diverse agricultural resources that could also support a biomass industry is reported. Local market impact on prices and land use is summarized. A local biofuel industry with 1.0 billion gallon capacity can transform declining local land values to stable or moderately increasing land values, partly because secular declines in cattle forage can be replaced with biofuel demands. The effects of greenhouse gas emissions and sinks are also estimated. The local agriculture sectors' net greenhouse gas changes are converted from a net emission to a net sink position with a biofuels industry-we calculate an annual net improvement of 55 bil. Lbs CO_2 –equivalent, due, in part, declining cattle emissions and favorable land use effects from expanding hay production.

Keywords: *Land rent, Land Use, livestock emissions, Switchgrass, Greenhouse gas(GHG).*

In the US, Biomass fuel technology broadens the potential agricultural resource base to include marginal land that is not suitable for corn production. There are some concerns about increasing greenhouse gas emissions when a land conversion process accompanies a biomass processing expansion [1]. However, existing analyses do not account for the market environment and dynamic adjustments already occurring in local agricultural resource markets. This paper accounts for the local competition between biomass feedstock and cattle forage, the land conversion that would accompany an unrestricted biomass fuel expansion, and the cattle industry decline that is already occurring in potential biomass supply areas of the United States. Since the relevant markets are local, we report a case study of a *representative* State (Minnesota) in the United States that has extensive and diverse agricultural resources that could adapt to biomass crops.

The first section reports an econometric estimation of the profit and dynamic factors influencing cattle population. The second section summarizes a model of the local forage market that presently defines the use of low grade agricultural land. The third section reviews CO_2 accounting procedures, specifically explaining how market changes influence emissions from crops, livestock, and pasture land. Estimates of changes in equilibrium soil carbon levels are also provided. The fourth section presents some 10 year projections of economic variables and global warming indicators. A well-known baseline for US agriculture is the reference for the global commodity markets that define resource market outcomes, and global warming indicators. Then local market outcomes and global warming indicators are given for the case where an expanding biomass fuel industry uses some of the local resources in the given market environment.

1. Market Environment

This section is an overview of the simulation model. There are three main elements in the market model. First, a land use model defines the amount of land used for crops, pasture, and left idle. Second, new estimates of the factors determining local cattle populations are presented. Third a model that incorporates the competition among supply of the three main forage types(hay, pasture and stover) is discussed. *Additional documentation, such as the* *land use model, Worksheets for greenhouse gas emissions and sinks, and the local forage baseline are available at www2.econ.iastate.edu/faculty/gallagher*

1.1. Land Use.

Land demand is determined in local agricultural land rental markets. We use an updated version of a recent land use model [2]. Revised estimates land use data from the 2007 census of agriculture, and include land demands for each major crop (corn, soybeans, wheat, cotton, and hay).

1.2. Cattle Population Adjustment

Minnesota's cattle population adjustment is typical of the states in the eastern half of the US. That is, there has been a steady decline mixed with episodes of cyclical adjustment. The decline is likely due to contracting US beef consumption and squeezing marginal producers. Cyclical adjustments likely occur in response to changing market conditions. Beef and Dairy cattle response estimations for Minnesota suggests population slowly adjusts to past profits, populations and also exhibits a secular decline. Our results were estimated using data from the 1969 to 2009 period:

$$\begin{array}{l} Nb_t = 0.741 + 0.118\pi b_t + 0.952 Nb_{t-1} - 0.191 Nb_{t-2} + 0.118\ln(T) \\ \qquad (2.3) \quad (1.8) \qquad (6.0) \qquad (1.1) \qquad (1.8) \\ \qquad adj - R^2 = 0.96 \qquad DW = 1.9 \qquad s = 0.103 \end{array} \tag{1}$$

$$\begin{array}{l} Nm_t = 0.105 + 0.710\pi b_t + 0.710 Nb_{t-1} 0.021\ln(T) \\ \qquad (1.5) \quad (2.2) \qquad (2.2) \qquad (2.2) \\ \qquad adj - R^2 = 0.97 \qquad DW = 2.5 \qquad s = 0.037 \end{array} \tag{2}$$

where k=b for beef, d for dairy
Nk_t is the cattle population in year t, in million head;
πk_t is the profit margin, in \$/lb output
T=1 before 1976, 2 in 1976,3 in 1977,…,

1.3. Forage Substitution Model

We assumed that forage demand is a fixed proportion of the cattle population. Then substitution among the three main forage inputs (hay, pasture, and corn stover) is described with a constant elasticity of substitution demand function. The demand equation satisfies baseline market shares of hay, pasture, and stover. It also has an elasticity of substitution of 3.0.

A 2009 baseline for forage consumption and market shares of hay, pasture, and stover was deduced available information. Total forage demands were developed from recommended rations and averages were constructed across a typical age and sex distribution. Pasture consumption of forage was approximated from baseline cattle populations, grazing season length and daily forage requirements. Hay consumption is approximated by hay production. Finally, stover demand is the difference between total forage demand versus hay and pasture demand.

2. Measuring Global Warming Sinks and Emissions

Existing procedures for measuring CO_2 equivalent emissions were restated as functions of appropriate economic variable instead of numbers calculated on baseline levels, in order to account for the effect of changes in economic variables. Generally, emissions functions depend on production, area, and livestock populations. All relationships are proportional. All measurements are expressed in a common CO_2-equivalent basis.

The GREET model of agricultural emissions is used for corn and soybeans. But revisions for recent fertilizer and energy use data were included [3]. Similarly, GREET fertilizer and fuel emissions coefficients were combined with appropriate fertilizer and fuel data for wheat, hay and switch grass.

IPCC Tier I procedures for beef and dairy cattle were used to estimate livestock based emissions [4]. Enteric and Manure emission of dairy and beef cattle in North America are included. Also, the N2O equivalent emissions from spreading livestock manure on land are included with livestock instead of land, because this activity is economically linked to the livestock population.

Estimates of the equilibrium soil carbon stock are also provided. Here we use the IPCC teir I procedure, which identifies a reference level for soil carbon in undisturbed soil, and a set of multipliers for several different categories of land use [5]. The reference carbon level and multipliers for the land use categories in our model are shown below:.

Table 1.multipliers for soil carbon, by land type

IPCC Classification (Table #)	Native-C multiplier (0/1)	Model's land use variable (symbol)
Native (5-11)	1.00	Other farmland (Lg-Gs)
Unimproved Grassland (5-10)	0.77	Pasture Supply (Gs)
Idle cropland (5-12)	0.70	Cropland in pasture (Cdg)
Set Aside<20 yr (5-12)	0.80	CRP land (Cdz)
Cropland in Crops (5-12)	0.70	Corn, Soybeans, Wheat (Cdc,Cds,Cdw)
Improved pasture, Hay (5-10)	1.10	Hay (Cdh)
Improved pasture, Hay (5-10)	1.0	Switchgrass (Cdsg), conservative

Native C-stock: 80 mt / ha (130.87 ton CO_2 / acre)

It is important that minimal carbon release is possible when converting land from pasture to hay or biomass crops. Indeed, switch grass is already used as forage in managed pasture [6]. Further, no-till planting methods for switch grass on pasture appear to have a minimal environmental effect [7].

Three main aspects of Carbon are summarized in simulations. First, the CO_2 sink associated with the switch grass crop is an initial approximation for the fossil fuel replacing benefit of biofuel. Second, the change in livestock emissions, a decline, represents a potential offset for adverse lanc-conversion emissions associated with starting a bio fuel industry. Third, the change in soil carbon stocks (expressed as CO_2-equivalent) is calculated as the difference between annual estimates of equilibrium soil carbon stocks. Also, the net sink of other crops (corn, soybeans, wheat, and hay) is also calculated, even though much of this sink likely belongs to an out-of-state carbon budget for corn-ethanol, consumption in other states, or use in a foreign country. It is helpful to see how field crop CO_2 sinks change with changes in switchgrass sinks, livestock emissions, or soil carbon capture/release.

3. Baseline

The most recent USDA 10 year baseline defines reference levels for the main commodity prices that drive (are exogenous to) the local biomass supply/forage demand model [8]. However, the reference prices for corn, soybeans, wheat, beef, and milk are adjusted to reflect a distortion-free policy environment that would put a new biomass industry on equal footing with other established industries.

First, the corn-ethanol industry has over-expanded as a result of a mandate for minimum ethanol use, called the Renewable Fuel Standard (RFS). About 4.0 billion gallons per year (BGY) of the RFS extends beyond supply increases that can be gathered from corn yield growth on land that is presently used. The price-effects of one-half of the overexpansion, or 2.0 BGY, is subtracted from the baseline corn and soybean prices using multipliers developed elsewhere [9]. Hence some overexpansion effects, which result in artificially high prices for substitute commodities and land rent, are removed from the baseline.

Second, a 30% import duty on US Beef imports [10] artificially holds US beef prices above market levels, encourages overproduction, and inflates local forage demands and prices for marginal land. For a first approximation, USDA baseline prices for beef are reduced by 30%. Milk prices are also reduced by 30%, because domestic milk prices are supported by an elaborate quota system.

Other exogenous assumptions for the projection period also fit today's apparent circumstances. For instance, cropland declines at 0.7 million acres (3.1%) per decade, as defined by the most recent census of agriculture. But other(non-cropland)farmland remains constant at about 5.0 million acres. Hay yields remain constant at at the average of recent values- the experience of the last two decades. Corn yields increase 20% over the first few years of the projections, and then remain level. Finally, a zero inflation rate for the CPI reflects today's depressed macro-economy.

The hypothetical baseline defines a scenario of declining commodity prices, cattle populations (figure 1), and local land prices (figure 2). Consequently, the demands for local resources are also declining. The prices of grains that are internationally traded would also gradually decline. Thus, the demand for local land resources and land rental rates are also declining.

Figure 1. The catle pouplation will continue declining in the future and decline somwhat faster with switchgrass

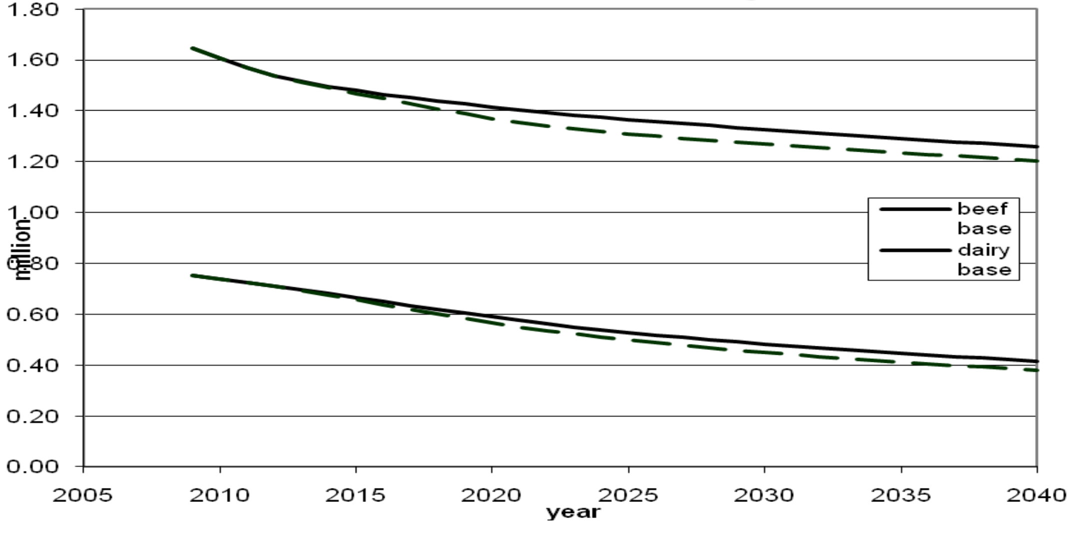
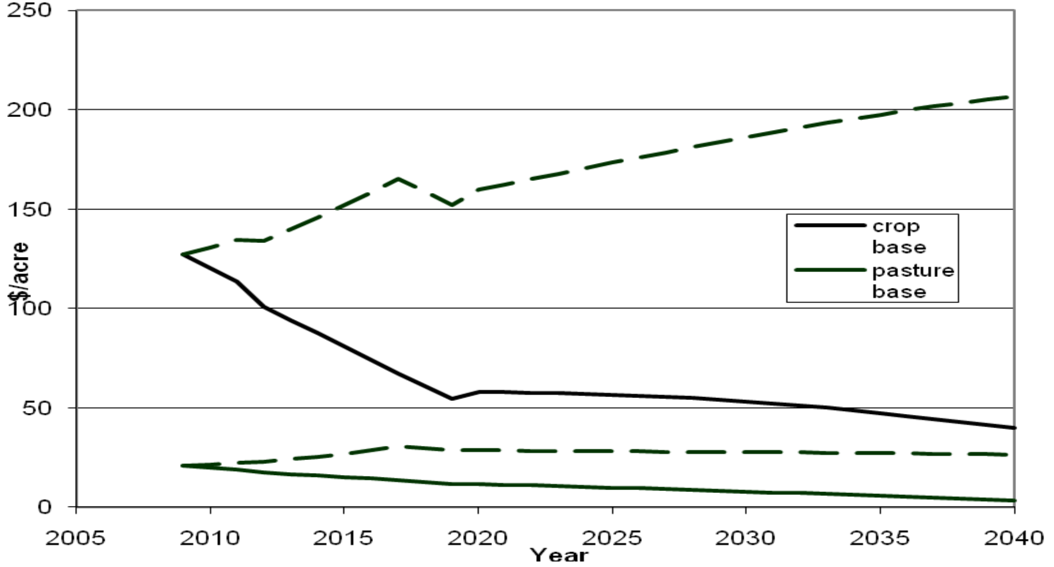
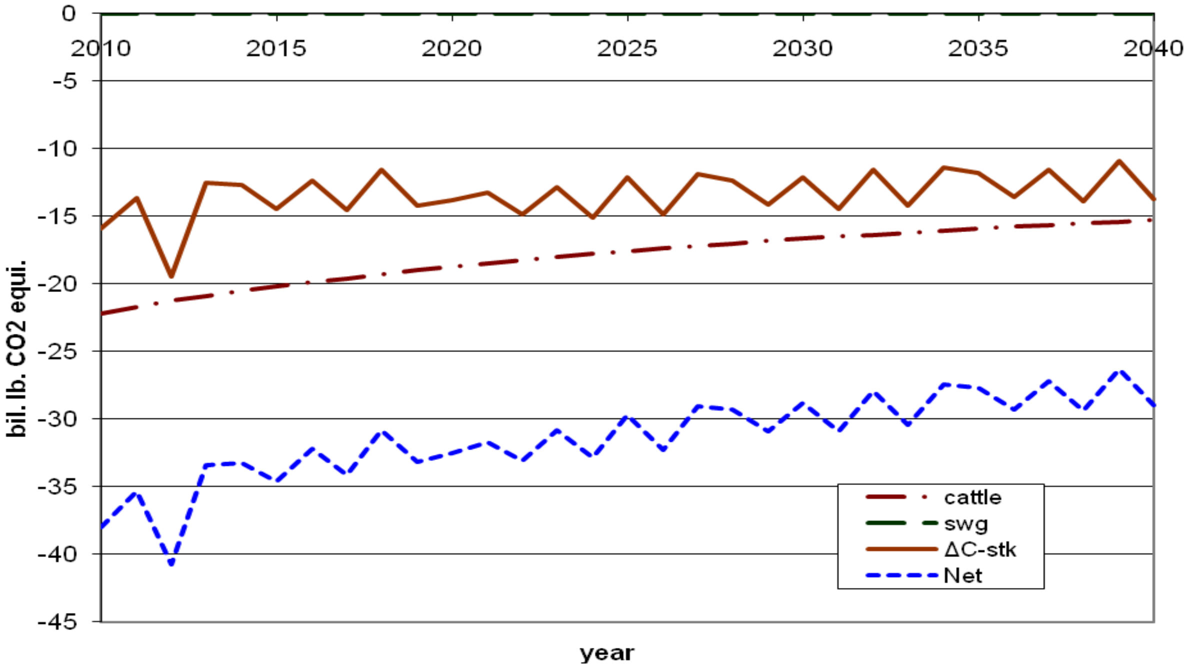


Figure 2. Land rental values decline until the switchgrass expansion stablizes pastureland values and induces risingcropland values



Emissions for two of our three main activities are reinforcing, and produce net CO_2 emissions under baseline conditions. Cattle emissions are substantial, but declining. In 2009, emissions are 22.6 bil. lbs CO_2-equivalent, but decline to 15.2 bil. lbs at the end of the simulation period. Equilibrium Carbon stocks decrease steadily at a rate of about 12.0 bil. lbs CO_2, annually, throughout the 30 year simulation period (figure 3b).

Figure 3b. local land change and cattle emissions contribute to global warming without switchgrass although emissions improve with cattle



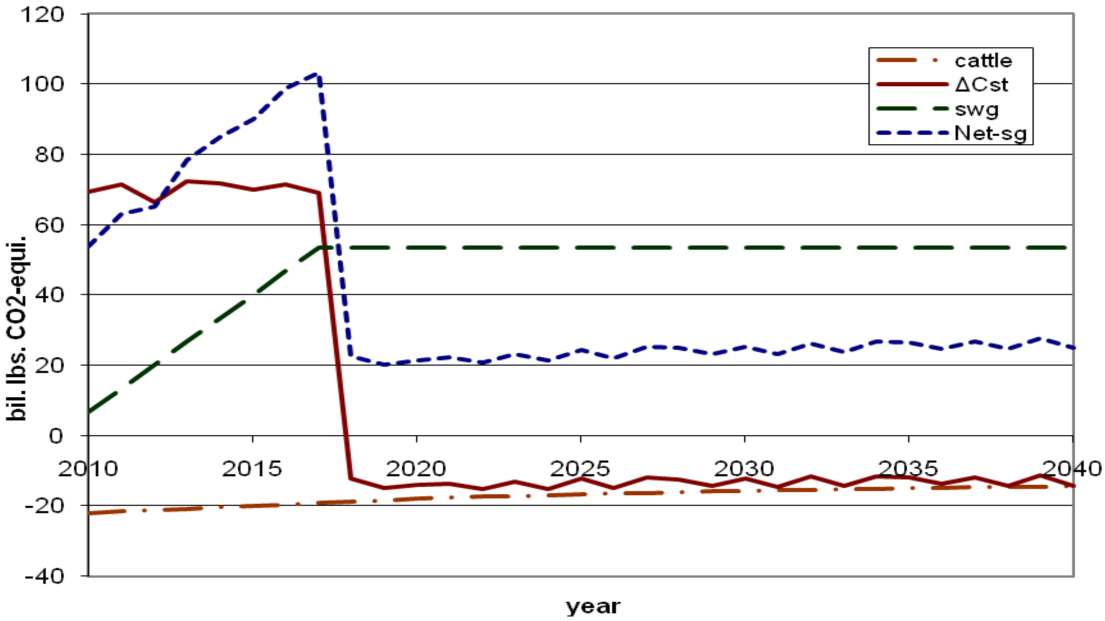
4. Biomass Fuel expansion

Here, an exogenous land demand expansion for a biomass crop (switchgrass) gradually increases the total area used for biomass to 4.0 million acres over a 5 year period that begins in 2010 (the first year of the simulation). The 4.0 million acre area is split equally between cropland and pastureland. Switchgrass is only one of several potential biomass crops, but still has a representative crop yield and carbon sink/emission profile.

The gradually expanding land demands restore increasing land prices (figure 2). But the increases are moderate; cropland rentals take three decades to double; pasture rental rates increase by about 20% over the first ten years, and remain stable thereafter.

The Greenhouse gas profile would also improve (figure 3s). First, increasing switchgrass production implies a substantial net carbon sink, most of which replace fossil fuels. Second, livestock emissions continue to improve through cattle reductions, accounting for about 20% of switchgrass emissions. Third, the equilibrium carbon stock would increase substantially during the biomass crop expansion phase, mainly because of the carbon storage profile of switchgrass. But the annual increment to the equilibrium carbon stockreverts to an emission thereafter. Nonetheless, three main activities combine for a net carbon sink (figure 3s).

Figure 3s. GHG sink from growing biomass fuel adds to a beneficial land use sink and offsets cattle emissions.



5. Conclusions

This study looks at the introduction of biomass fuel in local agricultural markets where land use and forage demand are defined. The hypothetical biomass expansion was split between cropland and pastureland, even though land costs per unit of biomass appear lower using marginal land.

The reference point is a distortion-free baseline created by removing recent over-expansion in corn ethanol and protection for livestock products. The baseline is characterized by declining land use values for cropland and pasture land.

The substantial biomass expansion is enough to support a 1.0 billion gallon ethanol industry. And the expansion merely restores stable or moderately increasing land values. Hence, The local agricultural resource is large enough to accommodate biomass ethanol production at a large scale.

The expansion on marginal land has mainly a local market impact. About 40% of the marginal land comes from the secular decline in cattle population and overall forage needs.

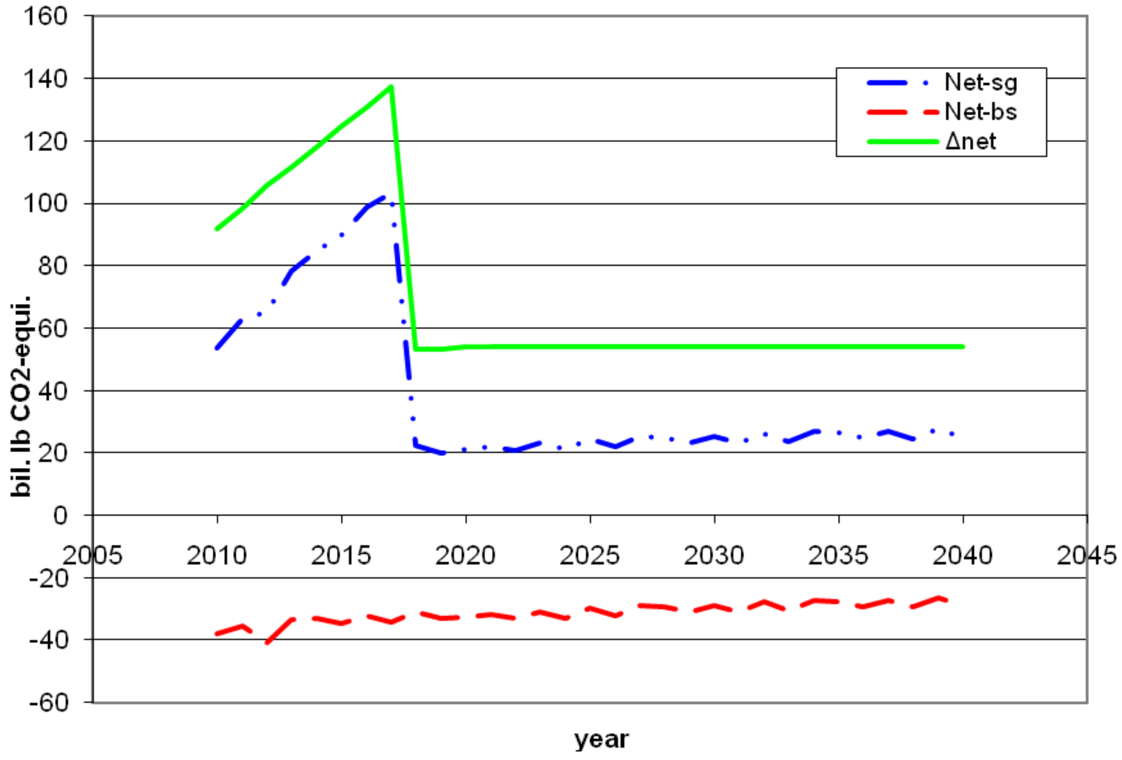
Otherwise, cattle rations shift away from pasture and towards hay and corn stover. In fact, hay demand grows despite declining cattle populations in the biofuel scenario. Compared to the baseline, the switch grass expansion restores stability to pasture rental rates.

The CO2 accounting focuses on changes in local agriculture as well. First, the direct benefit for switchgrass used as biofuel is included. Second, declining cattle emissions are also included. Third, the land use change effects on equilibrium soil carbon storage are included. Results suggest an increase in soil carbon storage, especially during the switchgrass expansion phase. Increasing hay production likely contributed to improving carbon storage as well. The change in net greenhouse gas sinks from the three local sources is 60 bill lbs CO2 equivalent, annually, after switchgrass production is established. The change in net sinks exceeds 100 bill. Lbs during the switchgrass expansion phase.

Two tasks remain for a comprehensive CO2 accounting. First, several other states with similar agricultural resources that are potential biomass supply areas should be incorporated into the analysis. Second, the totality of local changes must be considered in national and international markets. It seems plausible that the cattle decline would be absorbed into a declining demand for beef. However, the corn land expansion induced by the cropland expansion for switchgrass already appears large relative to the corn ethanol shift used to produce a distortion-free baseline. Accordingly, further simulations might usefully focus exclusively on expansions on marginal land.

The moderate price impact, beneficial lifecycle analysis, and potentially local impact for the marginal land expansion merits further attention. EPA regulations that restrict changes in use of permanent pasture may also deserve further scrutiny.

Figure 4. moderate net GHG sink with biomass replaces a net GHG emission without biomass for a large improvement.



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Enhanced Renewable Energy Adoption for Sustainable Development in India: Interpretive Structural Modeling Approach

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Abstract: Poverty alleviation and social upliftment of rural India is closely linked with the availability and use of energy for development. At the same time, sustainable supply of clean and affordable renewable energy sources is required if development is to be sustainable, so that it does not cause any environmental problems. The purpose of this paper is to determine the key variables of renewable energy implementation for sustainable development, on which the top management should focus. In this paper, an interpretive structural modeling (ISM) - based approach has been employed to model the implementation variables of renewable energy for sustainable development. These variables have been categorized under 'enablers' that help to increase the implementation of renewable energy for sustainable development. A major finding of this research is that public awareness regarding renewable energy for sustainable development is a very significant enabler. In this paper, an interpretation of variables of renewable energy for sustainable development in terms of their driving and dependence powers has been examined. For better results, top management should focus on improving the high-driving power enablers such as leadership, strategic planning, public awareness, top management support, availability of finance, government support, and support from interest groups.

Keywords: *Sustainable development, Renewable energy, Performance measures, Interpretive structural model, India*

1. General structure of the paper

The world energy forum has pointed out that coal and gas reserves will become depleted in less than the next 10 decades. Ashwani Kumar et al, [1] observed that fossil fuels account for around 79% of the energy consumption in the world, and 57.7% is consumed by the transport sector and is being depleted very speedily. Apart from this, various environmental problems are also related with the increasing use of fossil based oils, coal and gas. So there is an urgent need to develop the alternative energy resources in order to overcome the future energy shortage. Also, the depletion of natural resources and increasing demand of energy nowadays has forced policymakers to consider alternative energy sources for sustainable development. 'Sustainable development' means development which is capable of being sustained for the future stability. Where, renewable energy sources are regenerative and do not get exhausted. Renewable energy helps the world in reducing their carbon emission and cleans up the air and helps in achieving sustainable development. The most important feature of renewable energy sources is their environmental suitability but sustainable development does not only revolve around the environmental stability but it also deals with social and economical stability. Hence, nowadays investigation of energy strategies for renewable energy has become crucial, particularly for the stability of future energy.

India's population has been increasing very rapidly and it is also the fastest growing economy in world (with GDP of $ 1 trillion measured in 2008) after china, which further leads to a hike in energy demand and its impact on the environment in India. Mohit Goyal et al, [2] pointed out that India's power sector has shown tremendous increase from 30,000 MW in 1981 to 143,000 MW by March 2008. As the fossil fuels are depleting fast, India will face the energy shortages in future which need to be addressed by developing alternative energy resources the country can rely on. India is left with no option but to concentrate towards the maximum use of renewable energy. Fortunately India has plenty of renewable resources such as wind energy, biomass energy, small hydro power and solar energy to exploit for sustainable development. India is set to reach the aim of producing 10% of total power supplied through renewable energy by 2012 [1]. The government of India has promoted the use of renewable energy for sustainable development through several policy and provision interventions. Since 2007 power generation from renewable wind energy has increased by 3,857 MW; small hydro has increased by 619.53; biomass has increased by 322 MW; solar energy has increased by 8.10 MW and industrial and urban waste to energy has increased by 20.10 MW. Investment of around 3.9 billion Indian rupees ($86 million) has been made for different renewable energy projects and programs. Meanwhile, the World Bank has also allotted $4 billion in loans for India's renewable energy projects.

The purpose of this paper is to search the variables affecting the progress of the renewable energy for the sustainable development in India. Policy makers would face many difficulties in implementing renewable energy for sustainable development due to various variables affecting its performance. These variables not only affect the performance of renewable energy development but also act upon each other. Hence, the methodology of Interpretive Structural Modeling (ISM) has been applied in this paper to establish the conceptual relationship amongst various variables which are hindering the path of renewable energy for the sustainable development.

2. Literature review

A lot of research has been done before to find out the variables which affect the implementation of the renewable energy for the sustainable development. Fred Beck et al, [3] have observed the main barriers to renewable energy development in 2004. McCormic et al, [4] observed the major barriers that affect the implementation of energy for the sustainable development on the basis of research conducted by Bioenergy network of excellence. Himri et al, [5] has worked on formulating barriers which are hindering the full potential and advantages of the renewable. Lidula et al, [6] has formulated the barriers for clean and sustainable energy in the ASEAN member countries. Mayfield et al, [7] has developed a new methodology to deal with the barriers affecting the performance of Biomass operations. Sharma et al, [8] has studied the parameters of waste management in India. New York State Energy Research and Development Authority and Oak Ridge National Laboratory (ORNL) have identified some of the barriers to energy through research [9].

An important barrier for renewable energy development is lack of leadership qualities in managers. A good strategic plan identifies the renewable energy goals and then formulates policies to achieve these goals. Sustainable energy development strategies should deal with energy saving, improvement in the efficiency of energy production and replacement of the fossils based oils, coal and gas reserves [10]. There are two major factors which have affected the energy pattern most; the technological changes and the availability of energy resources [11]. Renewable sources are present in abundance but still cannot be harnessed for sustainable development due to lack of technology and public awareness. Continuing innovation in technology is necessary to harness each form of renewable energy [12]. The major challenge for the renewable energy industry is the timely availability of resources [10]. Himri et al, [5] has pointed out that lack of information dissemination would lead to lack of support from different stake holders. So, the availability of data and information acts as an enabler for the renewable energy for the sustainable development. The shortage of skilled professionals which includes designers, installers, service and sales representatives, policy analysts, scientists, engineers, teachers and researchers can also affect the quality of the system [13].

Government has put lots of effort towards enhancing the use of renewable energy for the sustainable development through subsidies, fiscal incentives and has encouraged investors to invest in renewable energy through various relevant supportive policies. Moreover, huge amount of investment is needed in developing the advanced technology required to fully exploit some renewable resources. Due to longer investment periods the risk of return on investment is high [14]. Hence it is necessary to incorporate the relevant policies in order to attract the interest groups to invest in it. The market for renewable energy has increased significantly and manufacturers are investing huge amount of money in R&D (research and development) of RET (renewable energy technology) which will further lead to economically sustainable growth. Table 1 below shows the 14 variables chosen based on the previous research.

Table 1. Variables affecting the performance of renewable energy for sustainable development

S. No.	Variables
1.	Leadership
2.	Strategic planning
3.	Availability of technology
4.	Public awareness
5.	Top management support
6.	Sustainable growth
7.	Return on investment
8.	Availability of finance
9.	Skilled man power
10.	Government support
11.	Availability of data and information
12.	Availability of energy resources
13.	Support from interested groups (stake holders)
14.	Efficiency of process and execution

3. Methodology

Interpretive structural modeling is a tool which here is applied for the analysis of the interaction amongst variables of the renewable energy for sustainable development. This approach has been used in many fields by scholars to investigate the inter-relationship amongst many variables. Warfield, [15] is the one who has introduced interpretive structural modeling (ISM) and Malone, [16] is the second one who conducted brief review of the ISM. It provides us means by which order can be imposed on the complexity of such elements [17, 18]. This method is known as 'interpretive structural modeling' because all the variables and their interrelationships are decided by group judgment. The ISM methodology is an interactive learning process in which a set of different and directly or indirectly related elements affecting the system under consideration is structured into a comprehensive systemic model [9]. Finally the graphical representation of the relationships among the variables is demonstrated. This methodology (ISM) has attracted a great deal of interest recently due to its high flexibility. Following are the steps involved in the formulation of ISM:

1.The variables affecting the performance of the system are listed with the help of literature review and expert opinion.

2.A conceptual relationship amongst the variables is made by the help of opinion of the experts.

3.Then a structural self-interaction matrix (SSIM) is formulated which entails the pair wise relation of the variables.

4.Now, the reach ability matrix is derived from the structural self interaction matrix (SSIM) by putting '1' and '0' which shows pair wise relationship accordingly.
5.Then the transitivity is removed from the reach ability matrix and transitivity rule says that if variable 'A' leads to variable 'B' and 'B' leads to variable 'C' then 'A' will also lead to variable 'C'.
6. The reachability matrix is divided into different partition levels.
7.The directed graph is drawn on the basis of the relationship between the variables discussed in the above reachability matrix and all the transitive links are removed.
8. The digraph is converted into ISM by converting variables nodes in to statements.
9. Finally a review of the ISM model is done and any necessary modifications are carried out.

After the final ISM structure MICMAC analysis of the variables is done on the basis of their driving and dependence power. MICMAC was first proposed by Duperrin and Godet in 1973 [19]. MICMAC analysis can be used to categorize variables in a complicated system [20]. The prime function of MICMAC analysis is to examine the driving and dependence power of the variables [17, 18]. Here the barriers are divided into four classifications according to their driving and dependence power known as autonomous, linkage, dependent and independent barriers [18]. The first cluster is known as 'autonomous barriers' which have very weak driving power and simultaneously have weak dependence power. These variables mostly have no connection with the system or with other variables; they only share few links which can be strong. The second cluster is known as 'dependent barriers' which consist of variables having weak driving power and strong dependence power. These variables mostly depend on other variables so; any action on other variables will affect the dependent variables. The third cluster consists of the 'linkage variables' which have strong driving and strong dependence power. These variables are highly unstable so, any action on these variables will affect other variables and also have a feedback effect on the linkage variable. Lastly the fourth cluster is basically the 'independent barriers', consists of variables which have strong driving power and weak dependence power.

4. Results

The ranking of all variables is known through level partitions so they have been put at their respective levels in the ISM hierarchy. Interpretive structural model is finally formulated with the help of final reach ability matrix and level partitions, which is shown in Fig. 1. It is observed from the ISM based model that public awareness about renewable energy is a very important variable as it has highest driving power and zero dependence power. This means this variable is very significant and drives all other variables. So, the policy maker has to keep more focus on public awareness in order to implement renewable energy for the sustainable development successfully. Awareness about renewable energy among the public will lead to top management support (variable 5). Conversely leadership qualities of a manager (variable 1) can act as a tool only if there is a top management support. Good strategic planning (variable 2) needs manager leadership quality and incentive support from top management. Support from interested groups (variable 13) cannot exist if there are no top management support withinpolicy makers. Availability of finance (variable 8) is ensured by support from the interested groups (stakeholders). Skilled man power (variable 9) and availability of information is very necessary for the successful implementation of renewable energy projects for sustainable development. Availability of finance actually helps in achieving the skilled man power as skilled man power is highly costly. Information management (variable 11) ensures the effective utilization of the resources.

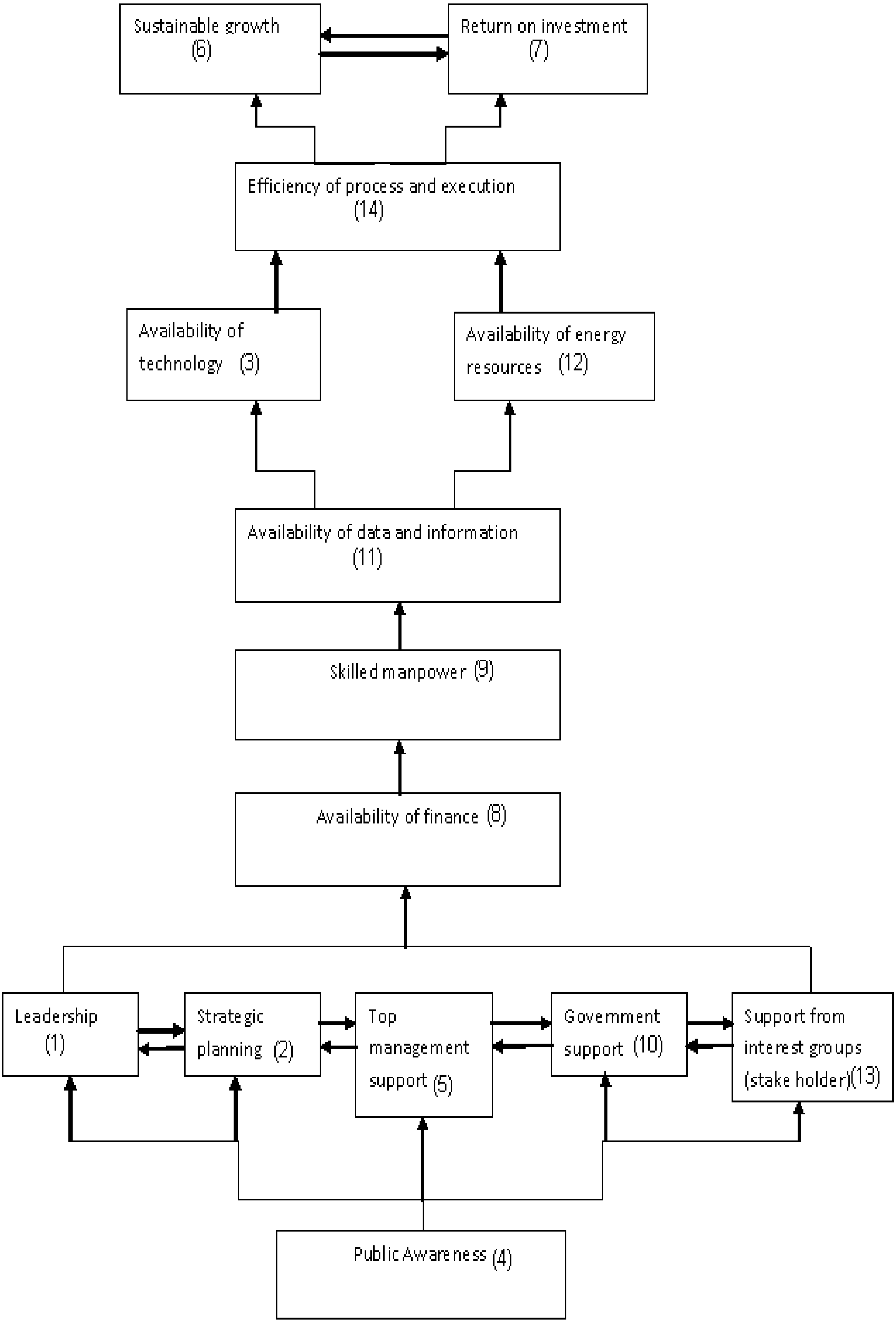

Fig. 1. ISM Based Model

Lack of appropriate data and information will lead to lack of interest from public and management, which further leads to lack of energy resources (variable 12) and lack of renewable energy technology (variable 3). Outdated technology has a direct impact on the efficiency of the process and its execution (variable 14). So, more and more money should be invested in the development of new technologies for the successful implementation of the renewable energy projects. High efficiency of the process will lead to sustainable growth (variable 6), which further leads to return on investment (variable 7) or vice versa. Good return on investment is a symbol of an economically sustainable system. This study shows that all the above discussed variables are enablers which enable the successful implementation of the project. According to ISM hierarchy there is a great need to work upon these variables for the sustainable development through renewable energy sources.

The MICMAC analysis has been drawn as shown in Fig. 2 below, the driving and dependence power has been shown in final reachability matrix. In the MICMAC diagram below the column and rows represent the driving and dependence power respectively. All the variables have been placed in the diagram according to their driving and dependence power. As an example variable 4 (public awareness) has driving power of 14 and dependence power of 1 and therefore has been placed accordingly in the MICMAC diagram at the extreme top left of the diagram.

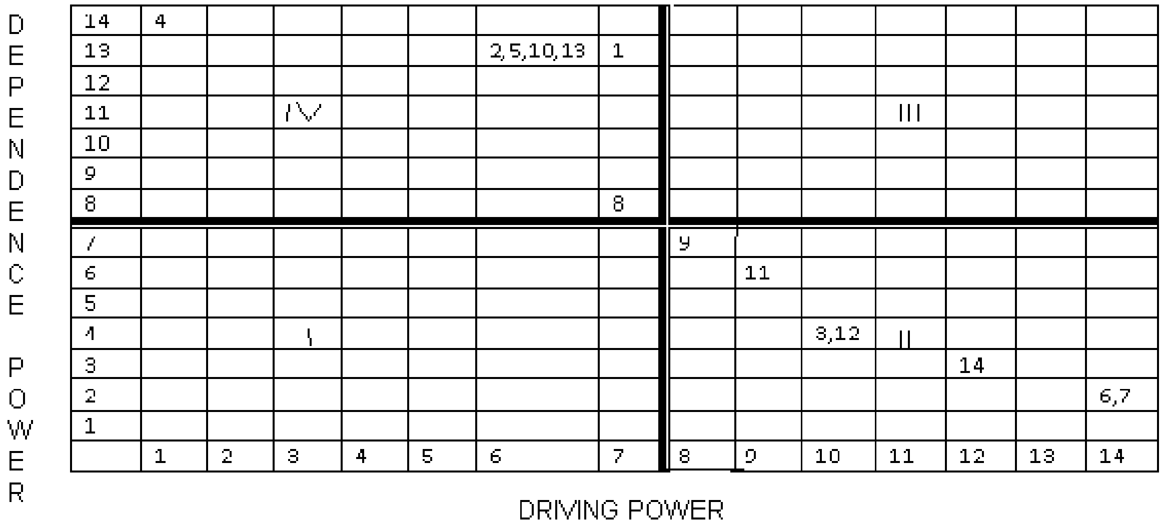

Fig. 2. MICMAC Diagram

5. Discussion and Conclusion

India is growing very fast approximately at a rate of 9% and the situation of energy shortage gets darker with the increase in the economic growth of the country. India has to exploit all sources of renewable energy in order to tackle the energy shortage problem [2]. The only solution remaining to the policy makers is using renewable energy as fossil based oils, coal and gas reserves are at the verge of depletion. But there are lots of variables which affect the implementation of renewable energy for sustainable development. Policy makers therefore face lots of challenges in identifying these variables and then working upon them to improve the performance of the system. Some variables termed as 'enablers' have been identified in this paper and interrelationships among these variables have been formulated using ISM methodology. This provides the hierarchy of action which has to be performed by the policy makers in order to improve the efficiency of the system.

From ISM based model (drawn above) it can be concluded that variable 4 (public awareness) is of top most priority as it has highest driving power of 14 and lowest dependence power of 1. This also states that policy makers have to create public awareness about the use of renewable energy for the sustainable development. In MICMAC analysis this has been concluded that there are no autonomous variables which prove that all variables stated above influence the implementation of the renewable energy for the sustainable development. Similarly from the MICMAC analysis it has also been concluded that there are no variables in the third cluster which is linkage barriers. This shows that all the variables stated above are stable. From the diagram it has been observed that variables such as leadership, strategic planning, public awareness, top management support, availability of finance, government support, and support from interest groups (stakeholders) fall under the fourth cluster which is 'independent barriers'. All these variables have high driving power and policy makers should focus more on these variables as they affect or influence other enabling variables. Availability of technology, availability of data and information, sustainable growth, return on investment, skilled manpower, availability of energy resources and efficiency of processes are those variables which fall under second cluster (dependent barrier) and have high dependence power.

Basically ISM based model in Fig.1, represents an overall picture of the problems in implementing renewable energy for the sustainable development in front of the policy makers. This research has most importantly identified the variable affecting the performance of the process and interrelationship among them. This model works for the better managerial decisions in order to have more efficient and effective renewable energy project for sustainable development. Also this work identifies leadership, strategic planning, public awareness, top management support, availability of finance, government support, and support from interest groups (stake holders) as very important factors, which needs immediate and high attention from the policy makers.

In this research work, interrelationship among the variables of implementation of renewable energy for sustainable development has been formulated, but it has to be mentioned that this model is not statistically validated. SEM (Structural equation modeling) sometimes also referred as linear structural relationship approach acts as a tool in order to test the validity of such hypothetical models [18]. The scope for future work following this research is to test the validity of this hypothetical model i.e. ISM using SEM.

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Promoting Biofuels Adoption in Nigeria: A Review of Socio-economic Drivers and Incentives

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Abstract: The adoption of biofuels holds a diversity of opportunities and potentials for the Nigerian economy. Some of these opportunities are key socio-economic drivers and incentives promoting the increasing adoption of biofuels. From the upstream to the downstream sub-sectors, there is an increasing entry of players and participants (private and public investors). This paper explores the underlining socio-economic drivers and incentives promoting and encouraging more investments in the biofuels subsectors of the Nigerian economy. The research sourced data from basically secondary sources and through desk-reviews. The papers identifies essential socio-economic indices which include the default dependence of biomass fuels, poverty and unemployment, declining agricultural productivity, underutilization of arable lands, potential demand for biofuels and government policy and incentives. As the global trend shows increasing adoption of biofuels, this paper reveals and discusses the socio-economic drivers peculiar to Nigeria. These key factors identified are issues to put into consideration for sustainably managing biofuels investments in Nigeria. Some of these factors present prospects and problems requiring medium and long term policy interventions from government to ensure an efficient transition into a bioenergy driven economy. The socio-economic factors identified also presents key variables for further socio-economic and bio-economic modelling studies focusing on Nigeria.

Keywords: *Biofuels, Drivers, Incentives, Policy, Bioenergy, Economy.*

1. Introduction

This paper explores the underlining socio-economic drivers and incentives promoting and encouraging the investments and participations in biofuels adoption, development and utilization in Nigeria. Nigeria joined other nations in the quest for adopting biofuels as the continuous reliance on the fossil fuels continues to receive criticism and fire from scientists, activists, and a wide range of peoples and interests promoting and implementing a shift in energy sources to more clean and environmentally friendly options. The global cries for renewable alternatives energy sources combine with default potentials for large scale production of biofuels created the platform for Nigeria's gradual incursion into the biofuel era. Though Nigeria is a major petroleum exporting country (1, 2), the drivers and incentives for promoting biofuels adoption are deeply connected with the roots of the many problems impeding the growth and development of the nation's economy. There is a preponderance of rural communities and populations with a default energy reliance sourced mainly from renewable sources and primary biofuels such as fuelwood, charcoal, palm kernel shells, palm-oil wastes (shaft and slurry), sawmill waste, cow dung among others. Though there is also a rapid growth of urban centers across Nigeria, majority of the population in urban areas also still depend on these renewable sources such as charcoal because of the very low rate of access to electricity, natural gas or other improved energy sources.

This paper identifies and explores the underlining socio-economic drivers, relative incentives as well as exogenous and endogenous inducements for promoting and encouraging more investments in the biofuels subsectors of the Nigerian economy. From the analysis, the paper presents a multilevel, multifactor and multi-actors framework that constitute the drivers for biofuels adoption in Nigeria.

2. Methodology

This research is a review of the socio-economic and related factors that explain the default renewable energy dependence and stimulating the trend in the investments in the broader biofuels subsector ranging from feedstock production to biofuels refining and biofuels distributions networks across Nigeria. The research sourced data from basically secondary sources and through desk-reviews. This review work is limited by the inability to conduct primary survey and the attendant gaps in information. Secondary data are sourced from the Nigeria Bureau of Statistics reports and other available secondary sources including previous publications and report from the International Energy Agency. Data sourced were analysed using descriptive statistics. The paper also presents a preliminary framework for driver of biofuels.

3. Biofuel Development in Nigeria

3.1 Biofuels in Nigeria

Though the traditional energy sources in Nigeria are predominantly combustible renewable fuels (3), there is an increasing shift and adoption of the first and second generation biofuels. The first generation biofuels which include biodiesel, bioethanol and biogas (4) are sourced mainly from edibles sources or current food material such as maize, soyabean, sugarcane, cassava for ethanol or oil production which can also be used as energy sources after further processing. The second generation biofuels which are fuels sourced from mainly non-edible sources such as jatropha, algae (4). A range of first generation biofuels are already being produce at small scales in Nigeria. Ethanol production is part of the traditional livelihood systems in the Niger Delta area and extending to some part of the south western States. Various individual and public investment projects in first generation biofuels are taking up in various part of Nigeria. These investment projects are at various stages of implementation ranging from feasibility studies to refinery plant installation. Progress have been reported in the designing of biogas plants at the Usman Danfodiyo University where a biogas digester with 425 litres capacity adequate for household cooking energy need has been developed (5). Other experimental efforts are also ongoing at the University of Nigeria, Nsukka and at the Global Network for Environment and Economic Development Research (GNEEDER) in Ibadan. Nigeria import about 4.5 tonnes of motor gasoline in 2008 (6) from refineries in countries which are already blending the fuels according to their blending regimes. There is no information on the blending rate of fuel used in Nigeria sourced from imports or refined locally.

3.2 Nigerian Biofuel Policy and Incentives

In promoting biofuels, the government in 2005 gave the Automotive Biomass Program for Nigeria directive to the Nigerian National Petroleum Corporation (NNPC) to facilitate the adoption on biofuels and promote investment in the sector. This led to the birth of the Nigerian biofuel policy and incentives (7), a government whitepaper for promoting biofuels in Nigeria. The white papers provide a broad policy platform for promoting the adoption of biofuels and for fast tracking the investment in biofuels value chain from feedstock production to biofuel refining and distribution. It set a target of 10 years for attaining full E-10 blending of gasoline and by implication B-10 for diesel. Though the whitepaper identified very few source of biofuels feedstock in Nigeria particularly for producing first generation biofuels, Nigeria has the potential for producing feedstocks for second generation biofuels including jatropha, algae and Shea nut. The underlining objectives for government interest in a national biofuel promotion are among other revenue diversification, job creation, improving agricultural productivity, meeting energy needs as well as deriving environmental benefits.

4. Drivers of Biofuels Adoption

4.1 Default dependence on renewable biomass fuels

International Energy Agency (3) estimates put the total energy consumption for Nigeria at 4 Quadrillion Btu or 107,000 kilotons of oil equivalent. This IEA estimate shows that combustible renewable fuels providing 80.2 percent of the total energy need. According to the IEA report, the highest contribution for renewable biomass fuels serves the energy requirements for heating, and cooking needs particularly in the rural areas where access to the national grid is currently not available or still a dream in the pipeline. A previous national survey of the National Bureau of Statistics - NBS in 2005 which profiled the poverty level in Nigeria provided national estimate of the sources fuel for cooking as shown in Figure 1. Firewood contributed nearly 70 percent based on this estimate (8). In 2007, an economic survey by the NBS shows there has a gradually climb in the proportion of the population of Nigeria who depend on fuelwood for cooking. NBS estimates put the proportion at 74.1 percent. Previous study (5) had also reported a 1991 energy source survey in which fuelwood contributes about 66 percent. The electricity supply and sources survey for the same year 2007 also indicated that only about 47 percent of the population access electricity from the main national grid while considerable proportion (41 percent) do not have access to any form electricity supply. IEA data for 2008 indicated that electrification rate for Nigeria was 47 percent for the entire country. In urban areas, 69 percent of the population had access to electricity compared to rural areas where electrification rates were 26 percent. Approximately 81 million people do not have access to electricity in Nigeria.

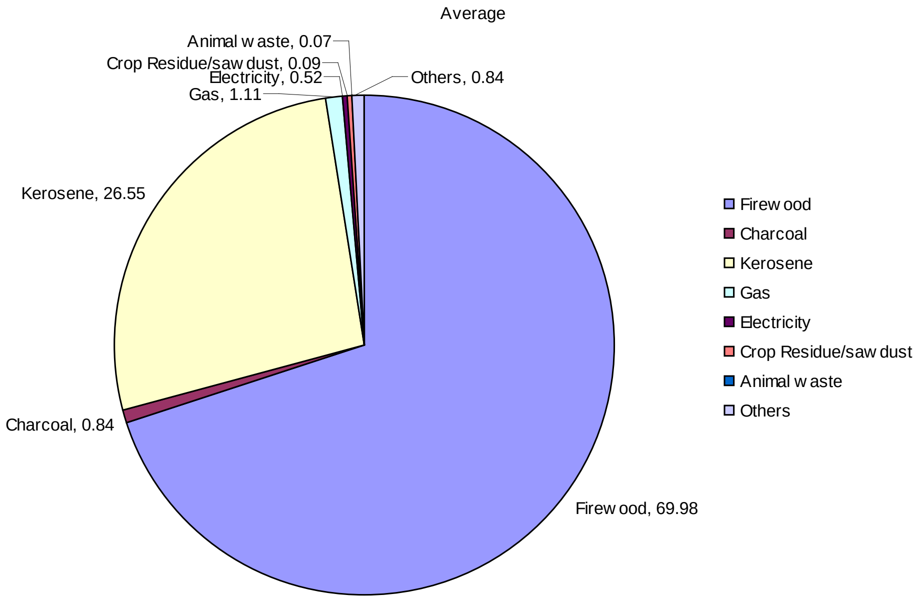

Fig. 1. Energy consumption by source in Nigeria (Source: NBS, 2007)

4.2 Poverty and Unemployment

The poverty level and unemployment rate in Nigeria and the declining capacity for electricity generation has deeply entrenched the dependence on renewable biomass fuels. The current level of poverty and the default reliance of energy from renewable source provide opportunity for a transition to improved technologies and techniques of using the traditional biofuels. The use of improved wood stoves and small family biogas initiatives, briquetting of sawdust and other agricultural waste in yet another option in promoting biofuels. Though the use of traditionally produced fuels of kernel oil or other oil as lighting reduced over the years, there is an opportunity to stimulate the local production of biodiesel for off-grid electricity for powering homes and appliances that are far from the national electricity grid infrastructure. Table 1 below shows the increasing poverty rate and incidence in Nigeria between 1980 and 2004. The increasing poverty level is an indicator of the lack of access to improved energy sources, an existing need and potential demand for alternatives such as biofuels.

Table 1. Trends in Poverty Levels between 1980 and 2004

Year	Population Estimate (million)	Poverty Incidence (%)	Rate of Poverty Increase	Rate of Population Growth
1980	65	28.1	0	0
1985	75	46.3	64.8	15.4
1992	91.5	42.7	-7.8	22.0
1996	102.3	65.6	53.6	11.8
2004	126.3	54.4	-17.1	23.5

4.3 Potential Demand for biofuels

The Nigerian Biofuel Policy and Incentive gave an estimate of fuel ethanol requirement at 10-percent blending rate to be about 1.3 billion litres per annum with projected increase to 2 billion litres by 2020. This estimate gives the worth of the bio-ethanol market at a 30 percent less the price of gasoline to be $391 million annually. Table 2 below shows the various substitution capacity for biofuels based on the 2008 average consumption of the petrol, household kerosene and diesel. A combined capacity for the major fuels consumption at the blending rate 10-percent proposed by the Nigerian biofuels policy gives a demand of 2.8mt of biofuels.

Table 2. Nigeria’s Biofuel substitution capacity on 5, 10, 20, 30 percent fuels blending rates (‘000 mt)

Fuel Types	Yearly Average Consumption (‘000 mt)	Biofuels substitution capacity for blending rates			
		5	**10**	**20**	**30**
PMS	20,822.45	1041.12	2082.25	4164.49	6246.74
HHK	3,766.13	188.31	376.61	753.23	1129.84
AGO	5,524.94	276.25	552.49	1104.99	1657.48

PMS – Premium Motor Spirit (Petrol), HHK – Household Kerosene, AGO – Automotive Gas Oil (Diesel)

4.4 Feedstocks production and productivity improvement

Nigeria falls with the region of the world rated to have high potential for biofuel production based on the three-criterion of the level water availability, level of available arable land and the state of food insecurity (10). This high potential is further buttressed by the current production capacity for the basic feedstocks for first generation biofuels. The argument for improving the level of productivity of crops with very high potentials and currently command a high demand for biofuel production was made in previous study (2). Table 3 shows the key crops for which Nigeria ranked between first and twentieth position in terms of nominal production globally. The ranking of productivity per hectare cultivated for this crops shows Nigeria has much room for improving on productivity of these crops. The data shows even for cassava for which Nigeria leads in the production globally, the country ranks 13th globally in terms of productivity per hectare cultivated. This underpins one of the underlining objectives for promoting crops based biofuels investment in Nigeria. The Nigerian biofuels policy classified investments with the biofuels value chain as an agro-allied sector to benefit from various incentives such as government guaranteed insurance, long term loans, value added tax waiver and custom duties waiver in attempt to stimulate biofuels production for achieving multi-objectives.

Table 3. Nigeria's production, productivity and cultivated area ranking for edible feedstocks

Crop	2008 Average Yield (MT)	Nigeria's Nominal Production Rank (Global)	Nigeria's Yield (land productivity) Rank (Global)	*Nigeria's Cultivated Area (Ha) Rank*
Sesame	110000	7th	13th	*6th*
Palm fruits	8500000	4th	20th	*3rd*
Ground Nut	3900000	3rd	6th	*3rd*
Soybean	591000	13th	20th	*10th*
Coconut	234000	19th	10th	*17th*
Cotton Seed	492000	12th	18th	*9th*
Cassava	44582000	1st	13th	*1st*
Maize	7525000	14th	17th	*7th*
Maize Green	*5709000*	*3rd*	*17th*	*2nd*

Source: Adapted from Food and Agriculture (FAO) Statistics 2008

5. Framework for Biofuels Adoption in Nigeria

The review of available literatures, the adopted National policy on biofuels and incentives brought to the fore key drivers promoting biofuels adoption in Nigeria. Figure 2 shows a multilevel, multifactor and multi-actors framework that constitute the drivers for biofuels adoption in Nigeria. On the government side are exogenous and endogenous inducements which brought about the development of biofuel policies and laws, incentives and investment funds for driving the national Automotive Biomass Programme for Nigeria. The government whitepaper target the private sectors and other players including State governments, cooperative groups and associations for the economic, environmental, socio-cultural and technical and infrastructural benefits which the increase in the biofuels investments will bring to the country.

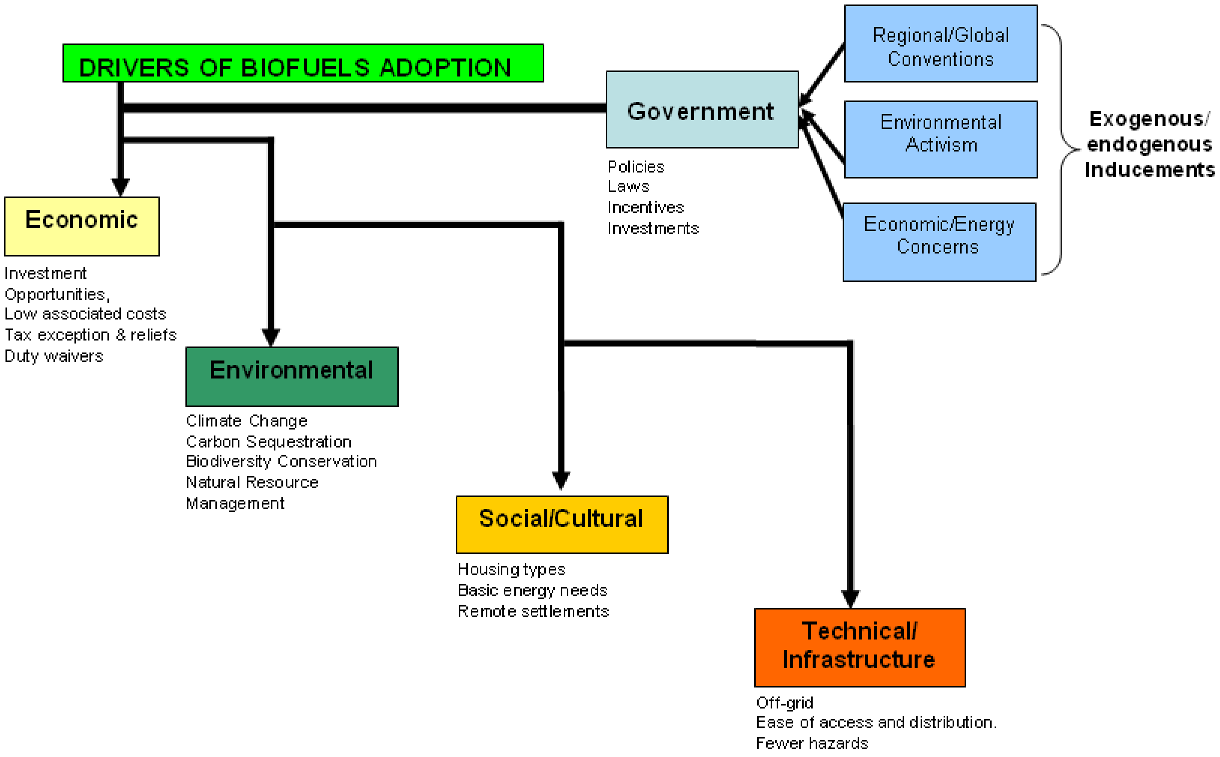

Fig. 2: Framework of biofuels adoption in Nigeria

6. Conclusion

This paper attempted to highlight some of the key drivers of biofuels adoption in Nigeria. The current dependence on renewable biomass fuels, poverty level, unemployment and the existing lack of access to improve energy sources are evidences of the existing gap in energy supply. This gap provides a strong incentives for attracting investment in biofuel production value chain considering the enabling environment and incentives created by the government. The multilevel framework on biofuels adoption identified the key drivers and the underlining motivations. The drivers which are peculiar to the Nigerian socio-economic condition hold the key to the nation's capability to be a major player in the increasing global biofuels market. These key factors identified are issues to put into consideration for sustainably managing biofuels investments in Nigeria. Some of these factors present prospects and problems requiring medium and long term policy interventions from government to ensure an efficient transition into a bioenergy driven economy. The socio-economic factors identified also presents key variables for further socio-economic and bio-economic modelling studies focusing on Nigeria. The framework provides a pillar for further analysis of the relationship between actors, the drivers and motivations for biofuels adoption in Nigeria.

Acknowledgement

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The bioenergy potential for the centre Region of Portugal: the use of biomass as a fuel source

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Abstract: Renewable energy is one of the most effective ways to achieve the sustainability essential for our future. The consumption of fossil fuels is rapidly depleting resources deemed essential for Man's survival.

This work's main focus is to increase bioenergy use in the centre region of Portugal by allying R&D to facilitate bioenergy availability and distribution throughout the study area.

Accordingly, the available bioenergy potential was important to determine once this knowledge is very limited in the Centre Region of Portugal. Biomass residues for forest stands, burned areas, shrublands and agriculture land uses, municipal solid waste, animal husbandry waste, used vegetable oils, agricultural and food industry and energy crops were the considered material, once they represent great part of the regional available biomass. Additionally, the ideal location for the implementation of the Bioenergy Competency Centre (BCC) was determined, using a GIS approach that considered four scenarios.

Results show the most favorable for the yield of each of the bioenergy sources for bioenergy and that there are minor variations for the BCC best location for the 4 considered scenarios.

Keywords: *Geographical Information Systems, Bioenergy potential, Land use, Bioenergy resources, Kyoto protocol.*

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1. Introduction

Fossil fuels are extremely attractive as energy sources, once they are relatively easy to distribute, especially oil and gas which are fluids [1]. It is still unknown when cheap fossil fuels will end, but it is estimated that it may happen in just one generation, or even sooner. We currently live what may be considered an oil crisis. Just recently, the price of the barrel of crude oil was above of 135 dollars, whereas in 2004, the price was located at around 35 dollars per barrel [2]. The substantial fluctuation of the oil price may cause serious worldwide economic disruption and lead to protests, as seen recently all around the world [1].

Oil exhaustion is a recurrent subject, with specialists indicating the year that production will reach its peak and when the major oil reserves will finally be depleted [3]. Knowing that fossil fuels will become a rare commodity in the near future, and knowing that humanity is utterly dependant on energy, a new path needs to be traced as to support our energy consuming way of life. Otherwise, serious consequences will outcome from this fact. Sustainability is a key point in today's society, once it involves environmental, social and operational management strategies, an equilibrium that is not easy to control due to their interdependency. According to Boyle [3], a sustainable energy source is ideally one that is not substantially depleted by continued use, does not entail significant pollutant emissions or other environmental problems, and also does not involve the perpetuation of substantial health hazards and/or social injustices. But only a few energy sources come close to this ideal: they are essentially inexhaustible and their use usually entails much lower emissions of GHG or other pollutants, and fewer health hazards [3]. With the use of natural and renewable resources as an alternative to fossil fuels for the production of energy, a higher level of sustainability may be achieved by modern society [4]. The renewables are based on energy flows that are replenished by natural processes, not becoming depleted with use. The environmental impacts of renewable energy sources vary, but they are generally much lower than those of conventional fuels [1].

Countries with low or inexistent access to fossil fuels such as Portugal have an elevated price to pay for oil importation: in 2007 the consumption of primary energy from oil represented approximately 54% of the total [5]. However, Portugal has a final energy consumption per inhabitant that is still low when compared with other EU countries – 1,7 toe/inhabitant against an EU-25 mean of 2,5 toe/inhabitant [6]. Nevertheless, the price raise of fossil fuels represents an exit of a substantial amount of currency to foreign countries, consequently weakening the economy. All together, oil, natural gas and coal represent over 80% of the Portuguese national energetic balance [5].

Bioenergy is the general term for energy derived from biomass material, such as trees, plants, manure, and sometimes wastes. Such materials can be processed through transformation processes, where the biomass is transformed into biofuels, bioheat or bioelectricity and used for energetic purposes [5, 7]. The renewable energy directive [8] defines biomass as being "the biodegradable fraction of products, wastes and residues from biological origin from agriculture (including vegetable and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste" [7].

1.1. Aim

Therefore, the first and utmost goal is to analyze the potential of bioenergy for the Centre Region of Portugal for several bioenergy sources, namely from forest stands, burned areas, shrublands and agriculture land uses, municipal solid waste, animal husbandry waste, used vegetable oils, agricultural and food industry and energy crops. To achieve this goal, spatial and non-spatial data is collected, transformed into a comparable energy unit (tonne of oil equivalent - toe) and analyzed in order to evaluate the availability of biomass for energy production throughout the study area.

Having the previously stated information, an analysis of the optimal location for the Bioenergy Competency Centre (BCC) is made. This is an entity that includes a large range of services before and after bioenergy production, such as technical assistance during the production process, research, personnel training and product certification. The adequate implementation of this infra-structure in the terrain is essential for a flourishing development of the use of bioenergy in the study area.

The two overall outcomes of the developed work will be a map of the bioenergy potential for the Centre region of Portugal and a map with recommendations for the optimum location of the implementation of the BCC.

1.2. Characterization of the study area: the Centre Region of Portugal

Portugal is geographically located on the European west coast, in the Iberian Peninsula. Is has Spain as boundaries to the North and West and to its West and South, it encounters the Atlantic Ocean. The Centre Region of Portugal is divided into 12 NUTS III areas: Baixo Vouga; Baixo Mondego; Pinhal Litoral; Pinhal Interior Norte; Dão-Lafões; Pinhal Interior Sul; Serra da Estrela; Beira Interior Norte; Beira Interior Sul; Cova da Beira; Oeste and Médio Tejo (Fig. 1). It occupies a total area of 28.200 km^2, 30,6% of the country. All these areas comprise a total of 100 municipalities (25,2% of the countries' total) [9]. According to the

2001 Census, this region has a population of 2.371.700 inhabitants, 22,6% of the Portuguese total, with a population density of 83,5 inhab/km^2 [9].

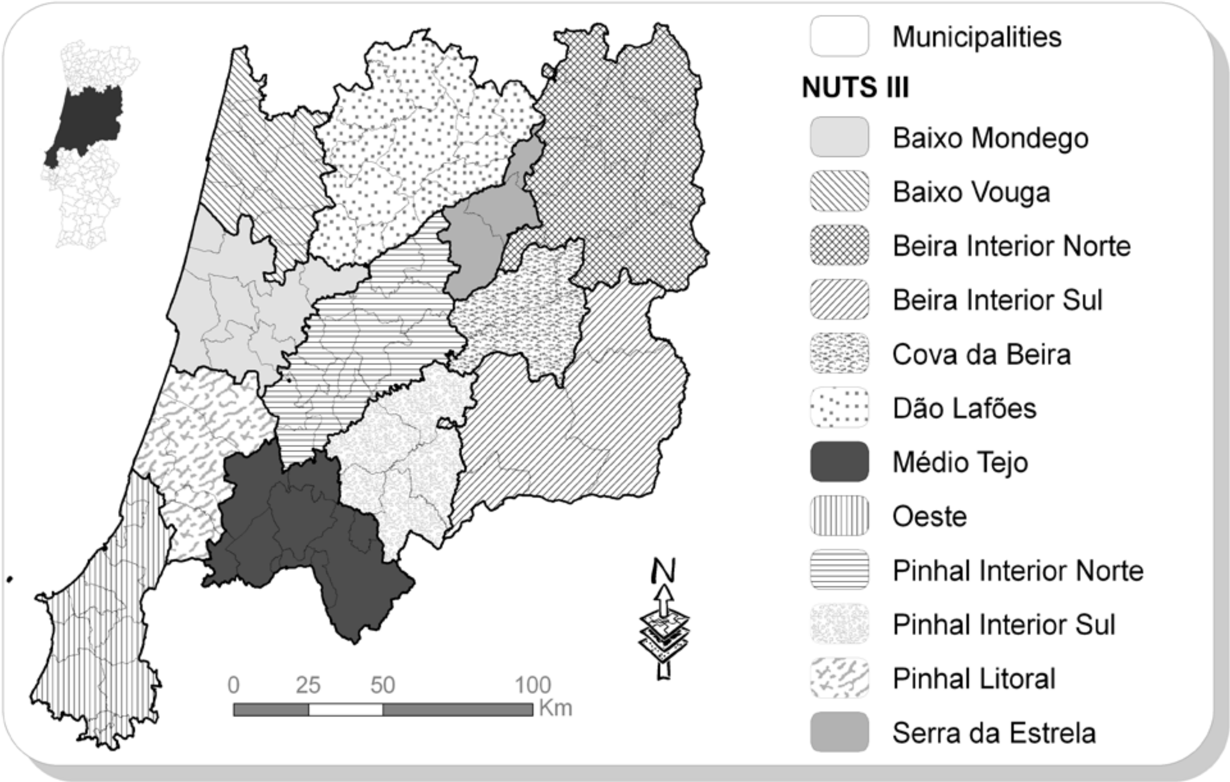

Fig. 1. Study area, the Centre Region of Portugal.

2. Methodology

2.1. The Bioenergy Potential Map for the Centre Region of Portugal

A primordial step was to join all pertinent information to calculate the amount of the various residues that are passable to be transformed into bioenergy. This extensive research work consisted in using freely available information from several Portuguese organizations that aim to produce both numerical and statistical data for the general public. In what respects to the date of the available information, the most recent data was preferable in opposed to more dated records; nevertheless, some of the gathered information is rather old (e.g., 1999 agricultural census). Regarding to the geographical data, only the Official Administrative Map of Portugal (CAOP) was used [10]. This information uses the European Terrestrial Reference System 89 (ETRS89) coordinate system with a Transverse Mercator projection.

Multiple information was collected and treated for a variety of sources, namely: Forest residue biomass; Agricultural residues biomass; Energetic cultures; Animal husbandry residues; Municipal solid waste; Used vegetable oils; Agricultural and food industries. The collected information was treated as to obtain bioenergy production values in toe. Note that each bioenergy transformation process has a determinate yield for each of the presented residues. However, in this stage of the study, 100% of the transformation yield was considered.

Afterwards, GIS software was used in order to process all the collected and treated information. For that effect, a model was created which allowed uniting all the information, presenting an output as a final result for the determination of the bioenergy potential of the Centre Region of Portugal.

2.2. Location of the Bioenergy Competency Centre

The BCC will not produce energy itself. Rather, it will have several critical functions for the further development of the bioenergy production area. This Centre will encompass a logical integrated network with the main stakeholders in the Centre Region of Portugal, as to maximize the profitability of the various laboratorial, management and economical infrastructures and available knowledge. Information flow will be crucial in this organism's work processes. Acknowledging the significance of its activities, it should be in a location that is of easy access to all the stakeholders.

For its implementation, several suppositions have to be taken into consideration, some of common sense and others of environmental and legal restraints. As before, all the used information is freely available to the general public. Both alphanumerical and geographical information is used as to achieve the best possible results. This information is collected from several national and international institutes [10, 11, 12, 13, 14]. GIS software was once again used as a valued resource to build this tool.

All the input information is classified into five different classes, being 1 the least preferable condition and 5 the most preferable condition. Four different scenarios are considered in order to verify the applicability of the tool and compare results, where each one varies an input parameter weighting in order to understand its influence on the final result.

3. Results and Discussion

3.1. The Bioenergy Potential Map for the Centre Region of Portugal

Intermediate results for each of the biomass types have different expressions throughout the territory. Where in some cases, biomass was more prominent in the inland area (e.g., forest biomass), in other cases bioenergy production was more expressive in the littoral area (e.g., animal biomass).

The final result's most influencing component is forest waste biomass. The amount of bioenergy that this source is capable to produce actually overshadows the remaining sources, mainly due to the contribution that forest shrublands make. As an overall result, we verify that the most promising area in terms of bioenergy production is the northern inland area, Beira Interior Norte. This may be due to the combination of climatic factors (e.g., high water availability) with the high amount of rural agricultural and forest areas, leading to a higher biomass yield. The littoral part of the Centre Region of Portugal has significantly lower potential for the production of bioenergy, whereas the middle and Oeste regions of the study area is not at all optimal for production of biomass for bioenergy (Fig. 2).

Shrubland residues aren't correctly handled in most areas, remaining unmanaged in the terrain, hampering greatly the amount of biomass passable to be used. In order to use this material, proper management has to be made in order to guarantee that the full potential can be used for bioenergy, without damaging forest ecosystem equilibrium. Other than yielding bioenergy, another very important consequence would take place, which is the prevention of wildfires, helping to drastically reduce the risk. These ravage the country on a yearly basis leading to important environmental, social and economical losses.

Another consideration may be the analysis of the actual production of bioenergy from some sources. In some cases, using an energy source may be more expensive than not using it (in an energetic perspective). In this particular study, it is thought that energy crops are a source of this type, once the amount of produced bioenergy by the different crops is very low, being that their use would be simply impermissible.

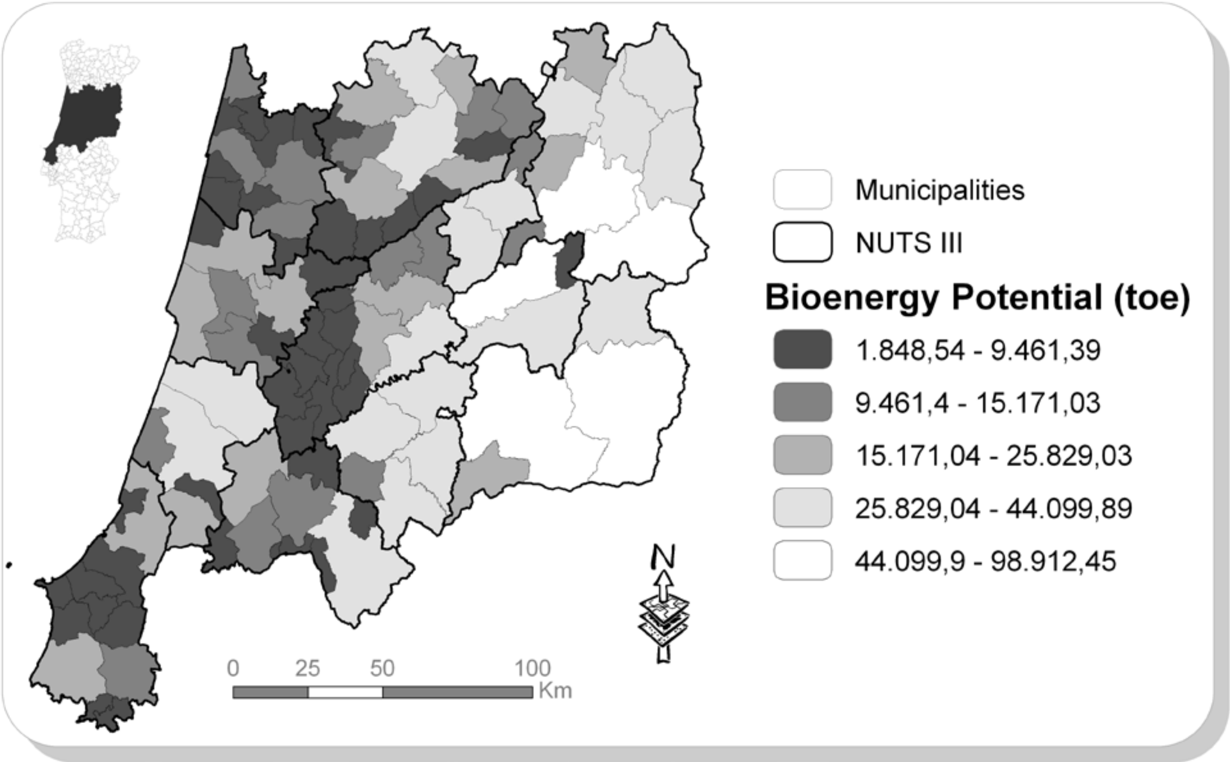

Fig. 2. Bioenergy potential for the Centre Region of Portugal.

3.2. Location of the Bioenergy Competency Centre

Properly locating the BCC is of great importance, once it will allow easier access to all stakeholders to the services to be provided by this institution. All inputs are considered key to the location of this institution, once they take into account different aspects that represent reality constraints and allowances. For this study, these are: road types, road distance, travel time, bioenergy potential and slope.

Four different scenarios are traced as to evaluate how different weightings can affect the location of the BCC. For the final map, only values of 4 and 5 are selected. It is also considered that the inputs slope and restrictions have the same weight in each scenario. A delicate balance is used to consider the inputs, and overall, it is thought that the achieved weighting is quite satisfying to construct viable outputs (Fig. 3).

When analyzing the results, at first glance we can verify that they are very similar between them. Most of the locations suggested in the different scenarios are coincident, although with visible changes in the area for every scenario. Another clearly visible result is that there are more areas to implement the BCC with a classification of 4 than with a classification of 5.

By making a global analysis of all scenarios, we can say that Scenario 2 is the most limitative one, once a lower area with classification 5 is usable. Scenario 3 is the broadest of them, where a higher area is available, although the one with classification 5 is higher in Scenario 1.

If it were preferable to use only locations with classification 5, the solution would be almost the same in all scenarios. In general, preferable locations would be situated in the main inland urban municipalities. For the majority of the remaining cases, values vary from scenario to scenario. In most cases, Scenario 3 has the most amount of area for almost all municipalities.

It should be noted that after a final selection of the location for the BCC, it should be confronted with the Municipal Master Plans of the respective municipality. This is a matter of extreme importance, once this legal document will determine the ability or inability to locate the BCC at a given location.

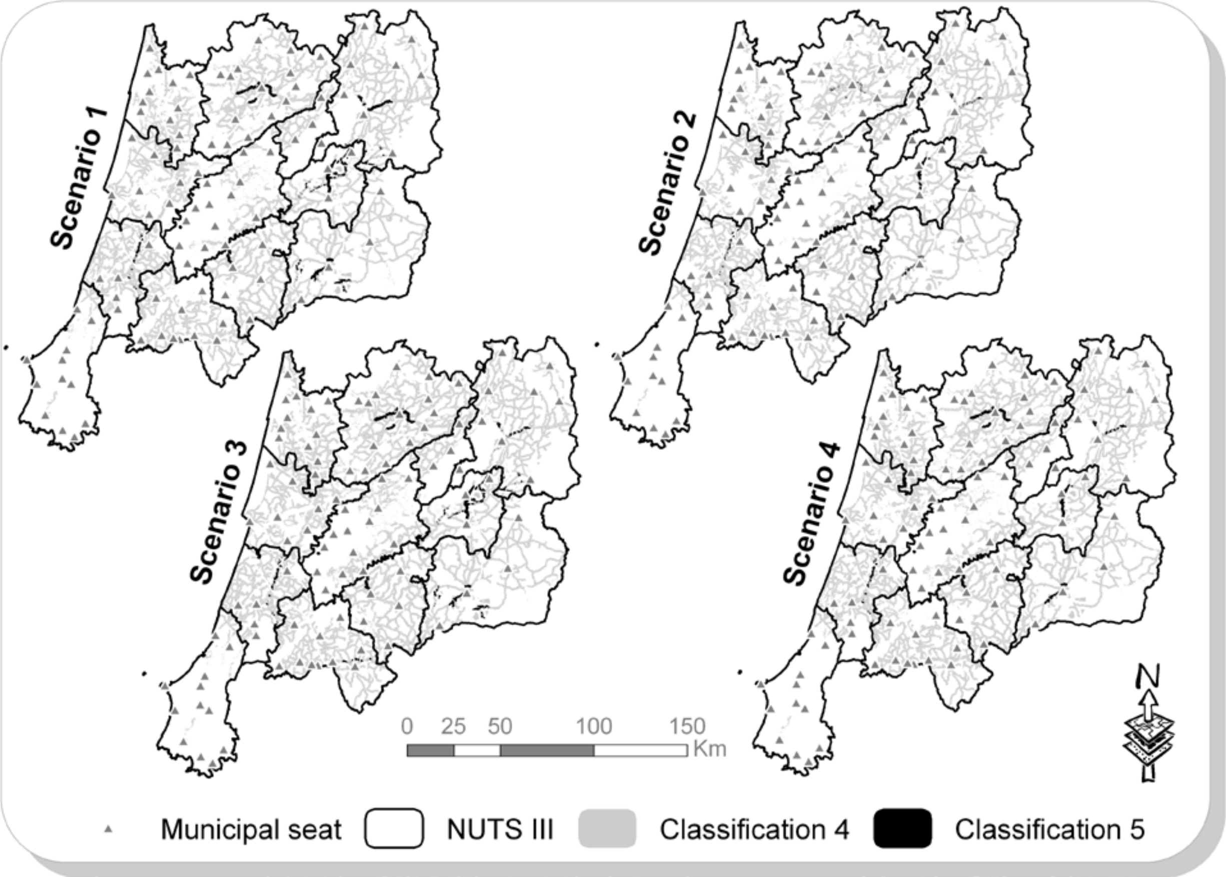

Fig. 3. Scenario results for the location of the Bioenergy Competency Centre.

Picking a specific location for the BCC depends widely on what the directors and main stakeholders are looking for. Do they want more options? Do they want a lesser amount of optimum locations to pick from? Do they only want locations with classification 5? Is there no difference in using classification 4 or 5? Are they interested in a certain municipality? As like other technologies, GIS and its results are socially constructed via negotiations between various social groups such as developers, practitioners, planners, decision-makers, special interest groups, citizens, and others who may have interest in the planning and policy making process [15]. All these questions have to be weighted by these key actors, mainly by the directors of the future BCC.

An interesting option for the location of the BCC could be the inland area of the country, giving dynamism to this area, once that this population is increasingly fleeing to the littoral, looking for better life conditions. This leads to the abandonment of the land, turning rich soils into inaccessible and unusable terrains for agriculture, forestry, or whichever activity over time. This location could very well mean local creation of more jobs, as well as the possibility of awakening the surrounding population to the possibility of this new business and delay (or even mitigate) the abandonment of land.

4. Conclusions

The world will soon face an energy problem with the potential to destroy civilizations. It is urgent to seek new energy sources and new management strategies in order to prevail, ones that are optimized and sustainable. So why not use available disposable material and make it work for mankind?

Resources with great promise exist in the Centre Region of Portugal, but one stands out. Forest wastes are a main contributor for the augmentation of the amount of bioenergy that the study area can produce. Another advantage of the use of this material is that it is homogeneously distributed throughout the whole study area, in high amount. The use of this type of material in particular has a double function: the production of bioenergy and the aid in the prevention of forest fires, a yearly affliction for Portugal. As for the other biomass sources presented in this work, they also assume an interesting role in bioenergy production, although not as an important one as forest biomass.

The Centre Region of Portugal has, in general, great potential for the use of biomass for the production of bioenergy. As can be seen in the final results, the interior region of the study area is the one with higher bioenergy potential yield. This fact may bring several consequences to these areas, in which local richness may be enhanced. Reactivating these rural areas and giving them a sustainable way to earn money would greatly help the overall conditions of this population and local environment.

The location of the BCC is the second result from the present study, where the main results point to more adequate areas in the inland area, a highly desirable result. Varying the weights of the input information has little influence regarding the location of the BCC. Favorable results were generally very similar for all the four scenarios. What varied greatly between these scenarios was the amount of available area in each classification.

By having a rather large study area, several particularities of each and every municipality had to be overlooked. This study only presents an initial evaluation of the bioenergy potential, and not an in depth analysis for a given municipality. Regrettably, these small particularities may come to influence the final result of the potential for the municipality. That is why further analyses have to be done as to verify in detail the actual potential for a given municipality.

A strong point of this study is the adaptability of the resulting models. In a fairly easy way, one can open the created tool and alter whatever needed parameters as to meet emerging requirements. This is an extremely important aspect of these tools, once flexible tools accompany the necessary changes in reality throughout time

As to enhance the present study results, some alterations/improvements are necessary in the future, such as introduction of recent information in the modeled tools; consideration of transformation yields of the several bioenergy sources; introduction of other sources of bioenergy present in the study area (e.g., biogas from wastewater treatment plants and industrial sources); and results validation through, e.g., SWOT analysis.

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Improvement of sweet sorghum bagasse hydrolysis by alkali and acidic pretreatments

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Abstract: The present work deals with enzymatic hydrolysis of sweet sorghum bagasse to fermentable sugars. The bagasse was treated with phosphoric acid and sodium hydroxide prior to enzymatic hydrolysis by commercial cellulase and β-glucosidase. The phosphoric acid pretreatment was performed at 50°C for 30 min, while 12% NaOH was used for the alkali treatment at 0°C for 3 h. The phosphoric acid pretreatment resulted in improving the subsequent enzymatic hydrolysis up to 79% of the theoretical yield. However, the best results of enzymatic hydrolysis were obtained in the hydrolysis of pretreated bagasse by NaOH solution, where more than 92% of the theoretical sugar yield was obtained.

Keywords: *Lignocellulosic material, Sweet sorghum, Enzymatic hydrolysis, Pretreatment*

1. Introduction

Fossil fuel limitations and constraints on carbon dioxide emissions have a high impact in the market of bioethanol, which is the most commonly used biofuel for petrol substitution in the world [1]. Fermentative ethanol can be produced from a variety of feed stocks such as saccharine materials, starchy materials and many types of lignocellulosic waste and harvestings, whichever has the best well-to-wheel assessment [2]. Lignocellulosic biomass is considered a future alternative for the agricultural products that are currently used as raw material for bioethanol production, because it is more abundant and less expensive than food crops, especially when waste streams are used. Furthermore, the use of lignocellulosic biomass is more attractive in terms of energy balances and emissions [3]. Sweet sorghum is an interesting annual plant that can be cultivated in widespread areas from tropical to temperate climates with the potential to produce more ethanol per acre than corn [4]. In addition, it has a high yield of green biomass and different part of this plant, such as bagasse, can be hydrolyzed to fermentable sugar before further bioconversion to ethanol. Similar to all lignocellulosic biomass, the main components of SSB are cellulose, hemicellulose and lignin [4, 5]. Hydrolysis of cellulose part can be carried out by dilute acid, concentrated acid or enzymatically, whereas the latter can be performed under mild condition with higher yield of glucose [6, 7]. However, the main purpose of this article was to enzymatic hydrolysis of the sweet sorghum bagasse (SSB) to fermentable sugars. In any case, access of cellulase to cellulose and lignin strongly limits the efficiency of enzymatic hydrolysis because Lignin, which is a complex polymer, provides structural integrity in plants. Therefore, the pretreatment is an important process before hydrolysis in order to remove or alter lignin and increase the accessibility of enzyme to cellulose [3]. Among all methods available for the pretreatment of lignocelluloses, acidic and alkaline treatments have been proven to have practical advantages. Concentrated phosphoric acid can dissolve cellulose in the presence of water without inhibitory effect, while it is non-corrosive, safe to be used and inexpensive chemical [8]. Similarly, sodium hydroxide can remove the lignin barrier and reduce cellulose crystallinity and therefore, increase the accessibility of enzyme cellulose part [9]. In addition, both processes utilize lower temperatures and pressures compared to other pretreatment technologies and even may be carried out at ambient conditions.

The current study deals with the effect of sodium hydroxide (12%) and phosphoric acid (85%) pretreatments on improvement of sugar yield in enzymatic hydrolysis of sweet sorghum bagasse.

2. Materials and Methods

2.1. Raw materials

The sweet sorghum bagasse (Sofra, Italy) used in all experiments was kindly provided by Dr. A. Almodares (Department of Biology, University of Isfahan, Iran). The bagasse was initially dried at room temperature and then was hammer milled and screened to achieve a particle size in the range of 20-80 mesh.

2.2. Sodium hydroxide pretreatment

The sweet sorghum bagasse was treated with 12% (W/V) NaOH solution. A 5% bagasse suspension (based on the dry weight) was thoroughly mixed for 10 min at 0°C, then placed in a laboratory ice-water bath for 3 h and mixed every 15 min. The pretreated materials were then washed with distilled water until pH 7 was detected. The solids were then dried at 40±1°C until constant weight and kept in a refrigerator until use.

2.3. Phosphoric acid pretreatment

The bagasse was thoroughly mixed with phosphoric acid (85%) in a 50 mL plastic centrifuge tube at 12.5% solid loading. The mixture shacked at 90 rpm and the temperature was controlled at 50±1°C for 30 min. The treated slurry was then washed with 20 mL cold acetone and centrifuged at 4000 rpm for 20 min. The washing process was repeated three times with 40 mL acetone, followed by three times with 40 mL distilled water. The residual acetone from washing stages was removed from supernatant after simple evaporation in a fume hood. The treated bagasse was finally washed by hot distilled water to neutralize the pH to 7.

2.4. Enzymatic hydrolysis

Commercial cellulase (Celluclast 1.5L, Novozyme, Denmark) and β-glucosidase (Novozyme 188, Novozyme, Denmark) were used for all enzymatic hydrolysis. Celluclast 1.5-L showed 87 FPU/ml activity, measured according to the procedure presented by Adney and Baker [10], while β-glucosidase activity was 240 IU/ml according to Ximenes et al. method [11]. The hydrolysis process was performed at 45±0.5°C in 50 mL sodium citrate buffer (0.05 M) using 115 mL glass bottles. The initial pH was adjusted to 4.8±0.1, and substrate concentration was 20 g/L dry weight for untreated and pretreated materials. The suspension was then autoclaved at 121°C and pre-incubated for 20 min prior to addition of enzymes. The enzymes loadings for hydrolysis were 20 FPU cellulase and 50 IU β-glucosidase per grams of dry substrates. The reaction mixture hydrolysis performed at 120 rpm for 72 h and the samples were periodically taken for sugar analysis. The yield of enzymatic hydrolysis was calculated as a ratio of theoretical glucose production yield using the following equation:

$$\text{Yield of enzymatic hydrolysis}\left(\%\right)=\frac{\text{Produced glucose }\left(g/L\right)\times 100}{1.111\times \text{Substrate concentration}\left(g/L\right)\times F} \quad (1)$$

where F in denominator is the biomass glucan fraction, which is presented in Table 1 for untreated and different pretreated bagasse. The conversion factor of 1.111 was applied to consider the conversion of glucan to glucose.

2.5. Analytical methods

The untreated and pretreated sweet sorghum bagasse were analyzed for carbohydrate and lignin (acid-soluble and insoluble) according to the method presented by Sluiter et al. [12]. The method was based on degradation of carbohydrates to monomeric sugars by two-stage acid hydrolysis and quantification of the sugars by HPLC. Furthermore, the acid-soluble was determined by UV/vis spectroscopy at 320 nm, and acid-insoluble lignin contents was determined by drying of the acid treated samples at 575°C.

The structural properties of the bagasse, before and after pretreatment by sodium hydroxide were analyzed by Fourier transform infrared (FTIR) spectrometer (Impact 410, Nicolet Instrument Corp., Madison, WI). The spectra were obtained using 60 scans of the samples with resolution of 4 cm-1 in the range of 600 to 4,000 cm-1. Nicolet OMNIC 4.1 analyzing software was used for correcting baseline and smoothing of the spectra.

Scanning electron microscopy (SEM) was used for study of the effect of pretreatments on physical property changes in the biomass. The freeze-dried samples were placed on carbon taps and subjected to the high performance scanning electron microscope (Quanta 200 ESEM FEG, FEI, ORA) and the micrographs were taken using an Everhart Thornley Scanning Electron Detector (ETD) at 20 Kv and a high vacuum mode.
The detection of sugars including glucose, xylose, mannose, galactose, and arabinose in the hydrolyzates and carbohydrate analyses were performed by High performance liquid chromatography using an anion-exchange column (Aminex HPX-87P, Bio-Rad) at 85ºC with 0.6 ml/min eluent of ultra-pure water.

All the experiments were performed in duplicates and all data reported in this paper are the average of the two replications.

3. Results

3.1. Pretreatment and materials characterization

The sweet sorghum bagasse used in this study mainly contained glucan (41.3%), xylan (17.9%), and lignin (18.2%) (Table 1). The native bagasse was pretreated with NaOH solution at 0°C for 3 h and concentrated phosphoric acid for 30 min at 50°C. The composition of the bagasse after the pretreatments was analyzed and results are presented in Table 1.

Table 1. Composition of the bagasse before and after pretreatments.

Pretreatment method	Glucan (%)	Xylan (%)	Mannan (%)	Galactan (%)	Arabinan (%)	Acid soluble lignin (%)	Acid insoluble lignin (%)
Untreated	41.33	17.96	0.85	1.26	1.94	1.78	16.47
Sodium hydroxide	58.66	12.72	0.69	0.66	1.10	1.01	11.50
Phosphoric acid	52.25	11.88	0.34	0.39	0.46	1.15	23.02

Glucan was the dominant component in all materials in the range of 41.3% to 58.6% and xylan was in the second place in the range of 11.8-17.9%. Other carbohydrates were mannan, galactan, and arabinan with 0.34-0.85%, 0.39-1.26%, and 0.46-1.94% depending on the pretreatment method. There was a remarkable increase in glucan fraction after the pretreatments. The glucan fraction increased by 41.9% and 26.4% after the pretreatment by sodium hydroxide and phosphoric acid, respectively. On the contrary, to glucan, other sugars decreased after the pretreatments. In addition, all pretreatments reduced the acid-soluble lignin and the minimum change, from 1.78% to 1.15%, was observed in phosphoric acid pretreatment. The highest loss in acid soluble and insoluble lignin was observed in sodium hydroxide pretreatment where the total lignin content decreased from 18.2% to 12.5%. However, an increase in acid-insoluble lignin content in phosphoric acid pretreated bagasse was detected.

The structural change in the bagasse was followed by FTIR analysis. As an example, the spectra of untreated and sodium hydroxide pretreated bagasse are presented in Fig. 1. Comparing the FTIR spectra of untreated and pretreated bagasse shows that the absorbance at 898 cm-1, which is assigned to cellulose I, increased after pretreatment by sodium hydroxide. The total crystallinity indexes (TCI) that was defined as the absorbance ratio of A_{1430} to A_{898} were 0.83 and 0.73 for untreated and NaOH treated, respectively. In addition, the absorbance at about 3,350 cm-1, which is related to O-H stretching band of hydroxyl group, was increased after pretreatment by sodium hydroxide. Moreover, sodium hydroxide resulted in broadening at this wave number. This indicated the weaker intra- and intermolecular hydrogen bonding and lower crystallinity. Lignin characteristic can be followed by the peaks at 1218 cm-1 (C-O of guaiacyl ring). The band intensity at this wavelength for pretreated materials was significantly lower than that of the untreated bagasse, indicating the delignification effect of the corresponding pretreatment.

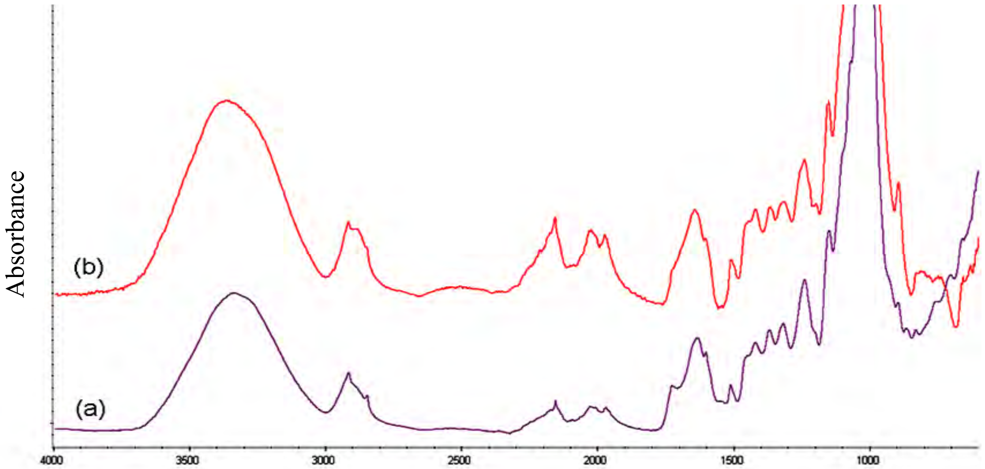

Fig. 1. FTIR spectra of (a) untreated bagasse and (b) NaOH pretreated bagasse.

SEM was used to study the morphological features and surface characteristics of materials after the pretreatment compared with the untreated bagasse. The pretreatment resulted in significant physical changes (Fig. 2). Both sodium hydroxide and concentrated phosphoric acid disrupt the structure of the fibers. Furthermore, the structure of the lignocellulosic biomass was opened up and more sponge-like structures were observed after the pretreatment that can provide higher surface area for subsequent enzymatic reactions.

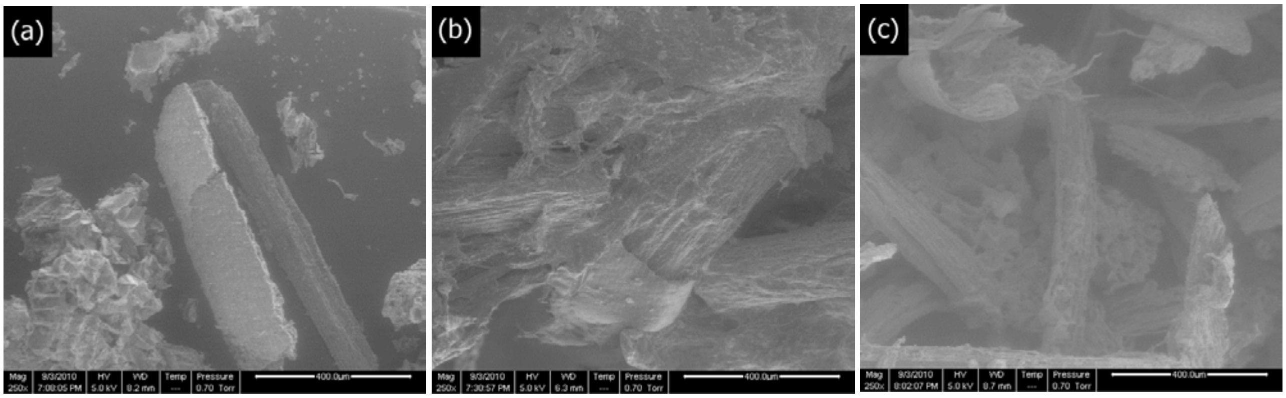

Fig. 2. SEM images of (a) untreated, (b) NaOH pretreated and (c) phosphoric acid pretreated bagasse.

3.2. Enzymatic hydrolysis

Different preparations of sweet sorghum bagasse were subjected to 72 h enzymatic hydrolysis by addition of cellulase and β-glucosidase. Pure cellulose was used as a reference in the hydrolysis experiments. The most important hydrolysis results are presented as percentages of theoretical sugar yield in Table 2. The yield of hydrolysis of native bagasse was effectively improved after sodium hydroxide and concentrated phosphoric acid pretreatments. The sugar content in the hydrolyzates increased sharply in the first 12 h and gradually continued until 72 h. Hydrolysis of the untreated bagasse resulted in 42% and 65% conversion after 12 h and 72 h, respectively. The hydrolysis yield increased from 65% to 79% after 30 m in pretreatment by concentrated phosphoric acid. The best results of enzymatic hydrolysis were obtained in the hydrolysis of pretreated bagasse by NaOH solution, where more than 92% of the theoretical glucose yield was obtained.

Table 2. Yield of enzymatic hydrolysis for the bagasse before and after the pretreatments.

	Yield of enzymatic hydrolysis (% theoretical sugar yield)		
Pretreatment method\Hydrolysis time	12h	24h	72h
Untreated	42%	43%	65%
Avicell	46%	60%	70%
NaOH	79%	80%	92%
Phosphoric acid	70%	79%	79%

3.3. Discussion

Sweet sorghum considered as a potential energy crop in nearly all temperate, subtropical, and tropical climates. It produces sugars juice, grains with high starch content, and bagasse. The bagasse is usually used for energy production by incineration. The native sweet sorghum bagasse which was used in the current work contains over 63% carbohydrate mainly in the form of glucan and xylan, respectively, and about 18% lignin, which is comparable with the typical composition of other agricultural residues. The present work dealt with the pretreatment of sweet sorghum bagasse by sodium hydroxide and phosphoric acid followed by enzymatic hydrolysis to fermentable sugars.

As expected, a pretreatment was necessary in order to efficiently convert the cellulose in the bagasse to fermentable sugars by hydrolytic enzymes. Besides, the pretreatment could increase the glucan fractions. The bagasse was partially delignified by sodium hydroxide pretreatment.
The FTIR technique can be applied to examine the structural changes in the biomass during pretreatments [13]. The analysis showed increasing the band intensity at 898 cm^{-1} and decreasing the band at 1,427 cm^{-1} which indicated the lower crystallinity and increasing the amorphous form of cellulose as a result of alkali pretreatment.

Also, the SEM images showed the rigid structure of untreated bagasse. The fibers of pretreated materials appear to be distorted and separated from the initial connected structure, thus increasing the external surface area and the porosity. Such improved morphological properties generated by pretreatments appeared to be the primary reason for the enhancement of enzymatic hydrolysis yield.

3.4. Conclusion

It can be concluded that the sweet sorghum bagasse is a remarkable feedstock for ethanol production regarding to its easy cultivation and favor properties as well as high glucan fraction. The comparison between the hydrolysis results of pretreated and untreated bagasse proved that enzymatic hydrolysis of sweet sorghum bagasse could be significantly improved after pretreatment by sodium hydroxide and phosphoric acid. However, it seems that the sodium hydroxide is a more efficient pretreatment method before production of fermentable sugars from sweet sorghum bagasse for further processing to, e.g. ethanol.

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Intensification of Bioethanol Production by Simultaneous Saccharification and Fermentation (SSF) in an Oscillatory Baffled Reactor (OBR)

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Abstract: Bioethanol is an alternative transport fuel produced mainly by the biochemical conversion of biomasses. This can be carried out efficiently and economically by simultaneous saccharification and fermentation (SSF): a process which integrates the enzymatic saccharification of the cellulose to glucose with the fermentative synthesis of ethanol. However, the SSF unit operation still contributes nearly 50% to the cost of ethanol production. For cellulosic ethanol to be cost competitive, there is the need to intensify the production process in smaller, more efficient and more economical bioreactors. In this work, SSF was performed in an intensified form of plug flow reactor, called the Oscillatory Baffled Reactor (OBR). The OBR is a continuous tubular reactor fitted with equally-spaced orifice plate baffles. An oscillatory component, provided by moving bellows in this design, is superimposed on the net flow through the reactor, generating short-lived vortices due to the interaction of the oscillating fluid with the baffles. This results in uniform mixing in each of the inter-baffle regions, with each behaving as a stirred tank reactor (STR), producing a plug flow residence time distribution (RTD) for the reactor as a whole, in which the mixing effects are largely decoupled from the mean flow (unlike conventional PFRs). The process was evaluated using 2.5% SigmaCell cellulose, 40 FPU cellulase loading/g of cellulose and 10% cellobiase. *Saccharomyces cerevisiae* was employed as the fermenting organism at 38 ^{o}C and pH 4.8. In the first part of this work the use of the OBR resulted in a 7% increase in glucose yield compared to a shake flask, after 48 h of saccharification and 8.0 g/L ethanol in the OBR. This represented 89.8 % of the theoretical yield, as compared to 7.7 g/L in the shake flask representing 81.29%, a difference of 9 percentage point. This increased glucose yield is attributable to better mixing in the OBR.

Keywords: *Cellulose, Cellulase, Saccharification, Fermentation, OBR.*

1. Introduction

The need to meet the ever-increasing demand for energy is probably one of the greatest challenges that society has to grapple with in this new millennium. Virtually every aspect of life on planet earth (heating, transportation, etc.,) requires energy input in one form or another. Hitherto, this energy need has been met principally by the use of fossil fuel resources [1]. However, it has been recognised that global crude oil reserves are finite, and their depletion is occurring much faster than previously predicted [2, 3]. In 2008, just at the onset of the global economic meltdown, crude oil price rose steeply up to a record USD 145. Also, the combustion of fossil fuels inevitably contributes significantly to elevated levels of greenhouse gases (GHG) and the attendant global warming [4]. Therefore, the need for more environmentally sustainable energy sources and the increased concern for the security of oil supply has put pressure on society to find renewable fuel alternatives [5].

Currently bioethanol is the dominant global renewable transport fuel and offers GHG savings of up to 80% over conventional fossil fuels [6]. It is produced primarily by the fermentative action of microorganisms (principally yeasts) on simple sugars [7]. Simultaneous saccharification and fermentation (SSF) can be used to convert the cellulosic part of biomass efficiently and commercially [8]. SSF combines the enzymatic saccharification of polymeric cellulose to simple monomeric forms such as glucose and its eventual fermentation by yeast to ethanol in the same vessel [9, 10]. The enzymatic hydrolysis of cellulose is a complex reaction that depends on the synergistic action of several cellulases, which include endoglucanases that attack β-1,4 bonds randomly within the cellulase chains, β-1,4 cellobiohydrolases that remove successive cellobiose units from free chain ends, and β-glucosidase that break cellobiose up into glucose units[11, 12].

Most bioethanol companies that employ SSF technology use traditional stirred tank reactors in batch or continuous modes. Technology drawbacks associated with these conventional bioreactors are well-documented. These include inadequate mixing resulting in inconsistent product qualities. Ni et al.[13] have demonstrated that consistent product quality results from and is inherently associated with consistent fluid mechanics in OBRs. Also, Mackley and Ni [14] have shown that product uniformity is determined by efficient fluid mixing which also is dependent on efficient heat and mass transfer. Other drawbacks include huge inventories[15], the prohibitive costs of large reactors, and associated downtimes which impact negatively on profitability. In spite of the advantages the SSF brings to bioethanol fermentation, its unit operation still contributes nearly 50% to the cost of ethanol production [16]. For cellulosic ethanol to be cost competitive, there is the need to intensify the production process in smaller, more efficient and more economical bioreactor. The oscillatory baffled reactor (OBR) is one such bioreactor.

1.1 The Oscillatory Baffled Reactor

The OBR is a continuous tubular reactor fitted with equally-spaced orifice plate baffles[15]. An oscillatory component, provided by moving bellows in this design, is superimposed on the net flow through the reactor, generating short-lived vortices due to the interaction of the oscillating fluid with the baffles. This results in uniform mixing in each of the inter-baffle regions, with each behaving as a stirred tank reactor (STR)[13], producing a plug flow residence time distribution (RTD), in which the mixing effects are largely decoupled from the mean flow (unlike conventional PFRs)[17]. It has been demonstrated by Mackley and Ni[18], Ni et al.[19], and Ni et al.[20] that excellent mixing conditions in a tubular reactor can be achieved when vigorous eddies are generated between periodically-spaced baffles as a result of the introduction of oscillations. A typical OBR configuration is revealed in Figures 1 while Figure 2 shows a typical flow pattern in a cell.

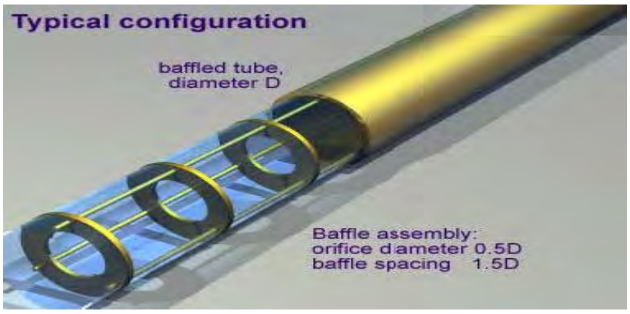

Figure 1. Layout of the OBR[21]

The intensity of the mixing under oscillatory flow is characterised by the oscillatory Reynolds number, Re_0 defined as:

Oscillatory Reynolds number: $\mathrm{Re}_o = \dfrac{\rho 2\pi f x_o d}{\mu}$

where d is the internal tube diameter (m), f is the fluid oscillation frequency (s^{-1}), x_o is the fluid oscillation amplitude (m) measured from centre-to-peak, and μ and ρ are the fluid viscosity (kg m^{-1} s^{-1}) and density (kg m^{-3}), respectively.

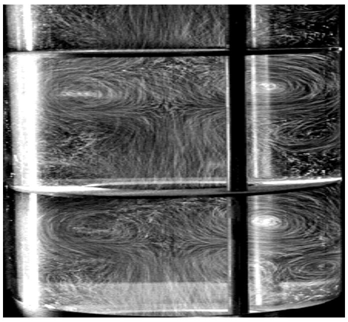

Figure 2 Flow patterns showing vortices and mixing in individual OBR cells[13].

The OBR has already been touted [22] to have the potential to lower costs by 50% and process times by 90% in the manufacture of commodities including chemicals, drugs and biofuels. Reis et al.[23] have demonstrated the potential of the OBR for bioreactions by achieving a 50% decrease in process time of the production of γ-decalactone compared to the stirred tank bioreactor and shake flasks. Gaidhani et al.[24] demonstrated the adaptability of the OBR in the cultivation of microorganisms for the synthesis of pullulan when then they also achieved a 50% reduction in process time in comparison with a parallel STR. They argued that the process time reduction is as a result of a more uniform mixing environment for cell growth and excellent mass transfer characteristics.

In this study the OBR is used in the simultaneous saccharification and fermentation of cellulose to produce ethanol.

2 Methodology

2.1 Enzymatic saccharification

The enzymatic saccharification was carried out using SigmaCell cellulose, Type 50 from Sigma-Aldrich following the NREL LAP, “Enzymatic saccharification of lignocellulosic biomass”[25]. This method measures the rate of conversion of cellulose by the synergistic action of cellulases. 250 mL conical flasks were used in the shake flask experiments and a total saccharification volume of 50 mL containing 2.5% w/v cellulose loadings. Cellulolytic enzymes, cellulose and β-glucosidase (both kind gifts from Novozymes, Denmark) with activity of 100 Filter Paper Unit (FPU)/g and 250 Cellobiose Units (CBU)/g respectively were employed. 10, 20, 40 70 and 100 FPU/g cellulose loadings each containing 10% β-glucosidase were evaluated. The shake flasks were incubated at 50 ^{o}C, the optimum temperature of the enzymes, and a pH of 4.8 and 200 RPM agitation. The saccharification was also carried out at 38 ^{o}C the optimum fermentation temperature of the yeast ascertain the glucose available to the yeast during the fermentation. However, the saccharification medium contained 1% yeast extract and 2% peptone on this occasion. The experiments were run for 168 h and replicate samples collected periodically over time.

In the OBR saccharification 2.5, 5 and 10% w/v cellulose loadings were also evaluated but with 40 FPU/g and 10% β-glucosidase at the same temperatures and pH as the shake flasks. The oscillation frequency was 3 Hz, centre-to-peak amplitude 0.03m and a Reynolds number Re_o of 1760. The OBR experimental set up is as shown in Figure 3 below.

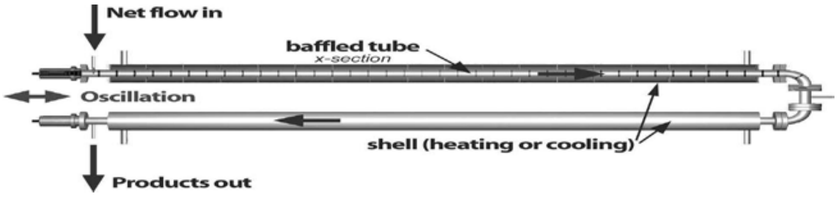

Figure 3 Typical OBR experimental set up[26].

2.2 Simultaneous Saccharification and Fermentation (SSF)

The SSF experiments were performed using 2.5% w/v cellulose and 40 FPU/g in both the shake flasks and OBR. YP medium (10 g/L yeast extract and 20 g/L peptone) was used. The pHs was 4.8 and temperature 38 ^oC in both systems and were also all equipped with carbon dioxide traps to simulate anaerobic conditions. The same agitation conditions were maintained in both systems as in the saccharification experiments. The inocula were prepared from a pure culture of baker's yeast *Saccharomyces cerevisiae* and cultivated on YPD medium (10 g/L yeast extract, 20 g/L peptone and 50 g/L glucose-filter-sterilised). The NREL LAP "SSF Experimental Protocols- Lignocellulosic Biomass Hydrolysis and Fermentation"[27] was followed completely in the SSF experiments in both cases. A 10% inoculum was used to initiate the SSF and replicate samples collected periodically.

2.3 Analyses

In both the saccharification and fermentation experiments, samples were collected periodically, spun in a microcentrifuge (Sanyo) at 13000 RPM. The supernatants were analysed for glucose using the dinitrosalicylic acid (DNS) method [28] and absorbance measured with a Jenway 6105 UV/VIS spectrophotometer. Ethanol was analysed using gas chromatograph (Hewlett-Packard 5890 Series II) with column packed with porapak 50/80 mesh as instructed in the NREL LAP[29].

3 Results

Enzymatic saccharification experiments in both the shake flasks and OBR were carried out under identical conditions and the degree of cellulose conversion- representing the concentration of glucose produced were monitored (Figure 4). 78.3% saccharification of cellulose was observed in the shake flasks at 100 FPU/g cellulose and 71% at 40 FPU/g cellulose after 144 h of hydrolysis at 50 ^oC. Hence 40 FPU/g cellulose was used in the OBR experiment which represented a trade-off between cellulase efficiency and enzyme cost. 78% saccharification was recorded in the OBR at the end of 144 h of hydrolysis at 50 ^oC.

The 5 and 10% cellulose loadings exhibited various degrees of reduced saccharification (data not shown). Figure 5 represents the results of the saccharification experiment at 38 ^oC, the fermentation temperature of the yeast. The OBR also showed at least 10 percentage point more conversion than the shake flask at 40 FPU/g of cellulose.

Samples were taken periodically during the SSF and analysed for glucose and ethanol as described above. Figure 6 shows the time-course of the ethanol production and glucose production/utilisation during the SSF of 2.5% cellulose at 40 FPU/g cellulose in both shake flasks and OBR. Whereas ethanol fermentation peaked at 45 h in the OBR it was at 70 h in the shake flasks. Glucose production peaked at 20 h and then began to drop steeply until it was almost completely used up by the yeast by the end of the fermentation. Ethanol yield

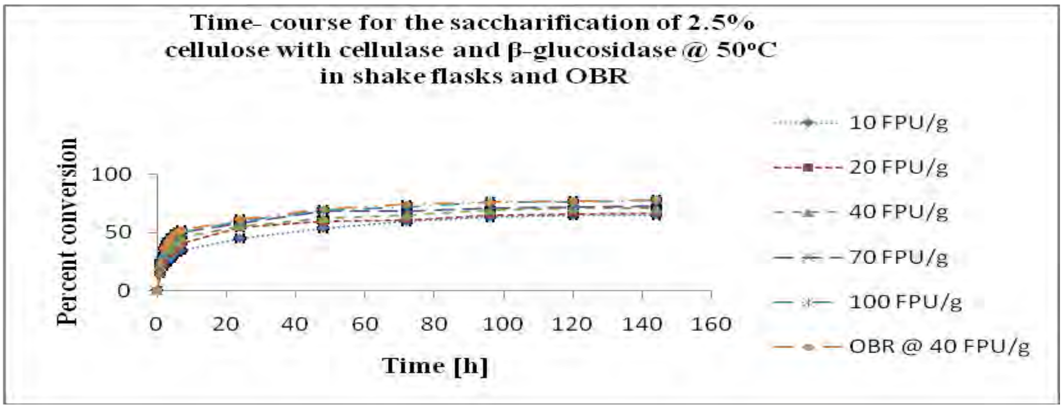

Figure 4. Time-course for the saccharification of 2.5% cellulose with cellulase and β-glucosidase @ 50 °C in shake flasks and OBR.

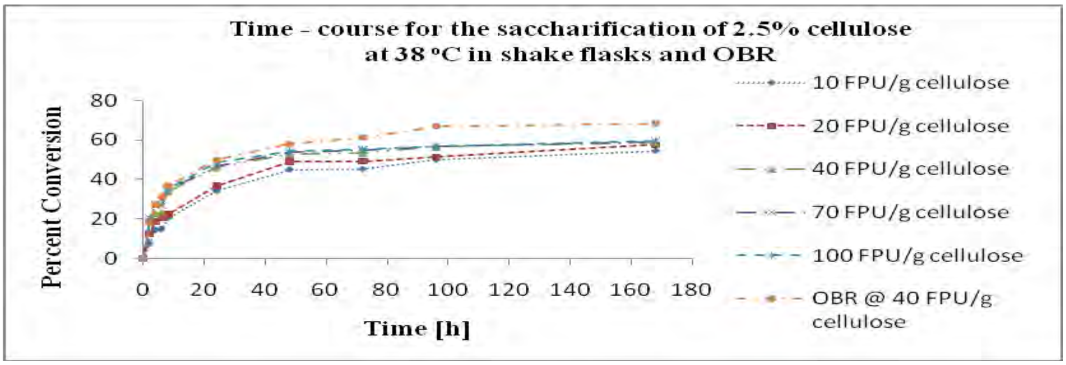

Figure 5. Time-course for the saccharification of 2.5% cellulose at 38 °C in shake flasks and OBR.

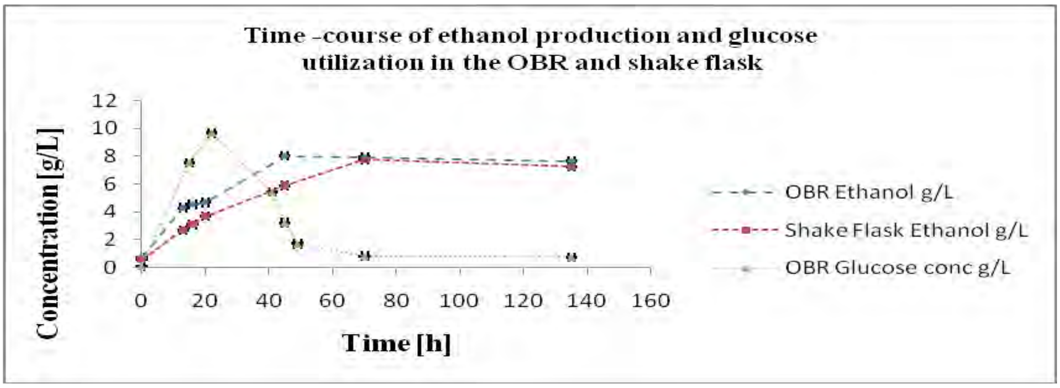

Figure 6. Time-course of ethanol production and glucose utilization in the OBR and shake flask.

increased steadily in both systems but in the OBR it peaked at 8 g/L (89.8% of theoretical yield) after 45 h fermentation and then began to decline. However, in the shake flasks it peaked at 7.7 g/L (81.29% theoretical yield) after 70 h fermentation and began to decline.

4 Discussion and conclusion

The saccharification experiments exhibited classical cellulosic hydrolysis characteristics: an initial rapid saccharification phase within the first 24 h and a much slower later phase (Figure 4 and 5) [30, 31]. The initial rapid phase may be as a result of the easily digestible amorphous part of the cellulose which is more readily available to the cellulases [32]. The later slower phase may be as a result of the crystalline, more recalcitrant part of the cellulose which limits accessibility to the enzymes [9]. The OBR and shake flask experiments exhibited a similar

SSF pattern. 2.5% cellulose loading was chosen for the SSF as it registered the highest percent saccharification as compared to the 5 and 10% (data not shown). The probable reason may be mixing problems and substrate inhibition as the substrate concentration increases [30, 31]. However using the OBR resulted in 7% more saccharification over the shake flask at the end of 168 h of saccharification is possibly as a result of a better mixed hydrolysis environment.

During the first phase of the SSF glucose accumulated within the first 22 h of the process (Figure 6) indicating the yeast cells could not cope with the rate of glucose generation by the enzymes[9]. But as cell mass continued to increase there was also a corresponding uptake of glucose which resulted in a steady rise in ethanol concentration up to the 45 h in the OBR and 70 h in the shake flasks. However, as the generated glucose was used up, the cells began to use ethanol as a carbon source corresponding to the gradual decline in the concentration of ethanol. This probably happened during sampling as air entered the systems to enable a switch of carbon source to ethanol by the cells. A similar phenomenon was also observed by Philippidis and Smith[9].

Although the concentration of ethanol from the two systems were similar (8 g/L OBR vs. 7.7 g/L shake flask), the OBR attained this concentration 25 h earlier than the shake flask. This would lead to a ~30% higher productivity for the same size of reactor. Furthermore it should be noted that OBRs are scaleable: what can be achieved at this scale, can probably also be achieved at industrial scale [33]. The same cannot be said of conventional stirred vessels, in which reaction times increase with scale, as good mixing becomes increasingly difficult to achieve. This also is possibly due to a better mixed SSF environment in the OBR which promoted better mass transfer characteristics. It agrees with the findings of Gaidhani et al.[34] who showed that it took 52 h for the cells to reach the stationary phase in the OBR compared to128 h in the STR.

These results provide a platform for further investigation into the applicability of the OBR in continuous SSF.

Acknowledgement

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Chemical and Microbial Hydrolysis of Sweet Sorghum Bagasse for Ethanol Production

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Abstract: Sweet sorghum (*Sorghum bicolor L.* Moench) is the potential raw material of ethanol production. As a lignocellulosic material, hydrolysis is needed to transform it to sugar. Usually, this sugar was used as substrate for ethanol production by fermentation. In this study, the composition of sweet sorghum bagasse was analyzed. The compositions of the sweet sorghum bagasse before hydrolysis are 58.23% cellulose, 25.42% hemicellulose and 14.95% lignin. It was then cut, dried and pretreated at 121 °C, 25 min by sodium hydroxide. Then the experimental design is performed to design the experimental runs. Box-Behnken was used to design the experiment of chemical hydrolysis. The factors of sulfuric acid concentration (15-55 %w/w), solid to liquid ratio (1:10-1:30 w:w) and reaction time (40-120 minutes) affecting reducing sugar production were optimized for the chemical hydrolysis. At the optimum condition, the maximum reducing sugar was equal to 33.49% (g/g dry substrate). On the other hand, microbial hydrolysis with *Trichoderma harzianum* gave the maximum reducing sugar of 10.34 % (g/g dry substrate) at optimum condition. Then type of reducing sugar was analyzed using High Performance Liquid Chromatography (HPLC). It is obvious that glucose is the dominated reducing sugar. Finally, the reducing sugar (glucose, xylose and arabinose) from chemical and microbial hydrolysis is usually fermented with *Saccharomyces cerevisiae* to produce ethanol.

Keywords: *Hydrolysis, Sweet Sorghum Bagasse, Ethanol, Trichoderma harzianum*

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1. Introduction

Sweet sorghum (*Sorghum bicolor L.* Moench) is a renewable, cheap, widely available resource. It is used as an alternative material for ethanol production since it is high biomass and sugar yielding crop. It contains soluble (glucose and sucrose) and insoluble carbohydrates (cellulose and hemicellulose) [1]. The juice extracting from the fresh stem is easily converted to ethanol. The remaining solid residue (bagasse) is a byproduct representing about 30% of the whole plant fresh weight. Bagasse, an important residue from sweet sorghum processing, could become an important biomass source for saccharification and fermentation for bioethanol production in the near future.

Sweet sorghum bagasse which is lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. Cellulose is a linear polymer that is composed of glucose subunits linked by β-1, 4 glycosidic bonds. These long chains linked together by hydrogen bonds and van der Waals forces. Cellulose is usually present as a crystalline form while a small amount of nonorganized cellulose chains forms amorphous cellulose. Hemicellulose is a polysaccharide with a lower molecular weight than cellulose. Hemicellulose contains xylose, mannose, galactose, glucose, arabinose and glucuronic acids, and are linked together by β-1,4- and sometimes by β-1,3-glycosidic bonds. Lignin is physical seal of hemicellulose and cellulose, which is an impenetrable barrier in the plant cell wall [2]. In order to obtain sugar, it is necessary to degrade the polymers to monomer, which can be done by physical, chemical or biological methods.

Generally, the chemical used in the hydrolysis is sulfuric acid. Acids can breakdown the heterocyclic bonds between sugar monomers in polymeric chain, which are formed by hemicellulose and cellulose [3].

For microbial hydrolysis, numerous bacterial and filamentous fungi can produce cellulolytic enzyme such as cellulase and hemicellulase. One of the most extensively studied of cellulolytic microorganism is *Trichoderma spp.,* which is also industrially used for enzyme production.

The aim of this work was to determine the optimum conditions for reducing sugar production from sweet sorghum bagasse by acid hydrolysis comparing with *Trichoderma harzianum* hydrolysis. In this experiment, three factors were optimized namely acid concentration, solid to liquid ratio and reaction time. Response Surface Methodology (RSM) using Box-Behnken Design (BBD) was applied for optimizing these independent variables.

2. Methodology

2.1. Microorganisms

The fungal strain *Trichoderma harzianum*, was obtained from Uniseeds Co., LTD. The inoculum of *T. harzianum* was in powder form and contained 10^8 spores per gram.

2.2. Substrate preparation and compositional analysis

Sweet sorghum bagasse was obtained from Suwan Farm, Kasetsart University. This material was thoroughly washed and dried at 65 ^{o}C until constant weight was obtained. The air-dried bagasse was then milled and subsequently sieved to a size of 2-4 mm. The composition of material was then analyzed by the methods of Goering and Van in 1970 [4] to analyse cellulose, hemicellulose, lignin and ash content in the material.

2.3. Alkali pretreatment

The sweet sorghum bagasse was soaked with 1, 5, 10 and 15% (w/w) NaOH solution at a solid to liquid weight ratio of 1:10 and consequently autoclaved at 121 ^{o}C for 25 min. The mixture was filtered to separate the solid residues and the filtrate fraction. At the end of the reaction, the solid residues were thoroughly washed with water to remove the residual alkaline until neutral pH was obtained, then dried at 65 ^{o}C, and analyzed the compositions of the solid residues.

2.4. Optimization of reducing sugar production by acid hydrolysis

One gram of pretreated material was soaked with 10-30 gram of 5-55% (w/w) sulfuric acid solution in the 250 ml Erlenmeyer flask and then autoclaved at 121^{o}C for 40-120 minutes. After hydrolysis, the suspended material was separated using filter paper. The total reducing sugars in the filtrate were determined by the 3,5-dinitrosalicylic acid (DNS) method described by Miller in 1959 [5].

RSM was applied for the optimization of the reducing sugars production. Three parameters namely concentration of sulfuric acid (X_1), solid to liquid ratio (X_2) and reaction time (X_3) with the ranges of minimum (-1) , maximum (+1) and central point (0) were assigned to investigated experimental conditions of reducing sugar production. The levels of parameters for the experimental design are shown in Table 1.

Table 1. Experimental range and coded levels of factors for reducing sugars production

Factors	Symbol	Range and levels		
		-1	0	1
concentration (%v/v)	X_1	15	35	55
solid:liquid ratio (w:w)	X_2	1:10	1:20	1:30
reaction time (min)	X_3	40	80	120

The total of 15 experimental runs with three variables was designed according to a BBD using the statistical software MINITAB release 14. The detailed experimental designs with coded of three parameters are shown in Table 3. The behavior of the system was explained by the following quadratic model equation which includes the effects of linear, quadratic and interaction was used to determine the predicted response as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

Where Y is the predicted response, β_0 is the intercept; β_1, β_2 and β_3 linear coefficient; β_{11}, β_{22} and β_{33} square coefficient; and β_{12}, β_{13} and β_{23} interaction coefficients with X_1, X_2 and X_3 corresponding to the principal factors of sulfuric acid concentration, solid to liquid ratio and reaction time, respectively

2.5. *Reducing sugar production by microbial hydrolysis*

Reducing sugar production under Solid-State Fermentation (SSF) was conducted in the 250 ml flask covered with cotton at optimum conditions previously optimized for maximum reducing sugar from pretreated sweet sorghum bagasse by *T. harzianum* [6]. Each flask containing 5 g dried pretreated sweet sorghum bagasse, which was used as the carbon source. Standard Mandel medium in 50 mM sodium citrate buffer (pH 4.8) that contained of 0.3 g/l urea, 1.4 g/l $(NH_4)_2SO_4$, 2.0 g/l KH_2PO_4, 0.4 g/l $CaCl_2 \cdot 2H_2O$, 0.3 g/l $MgSO_4 \cdot 4H_2O$, 0.75 g/l peptone, 0.25 g/l yeast extract, 5 mg/l $FeSO_4 \cdot 7H_2O$, 1.6 mg/l $MnSO_4 \cdot 4H_2O$, 1.4 mg/l $ZnSO_4 \cdot 7H_2O$ and 20 mg/l $CoCl_2 \cdot 6H_2O$, was added into the substrate for adjusting initial moisture content (77.5% w/w) before autoclaving at 121 ^oC for 20 min. Each flask was inoculated with 10% (w/w) fungal spore of *T. harzianum* and incubated at 25^oC for 88 hours. After suitable periods of time, reducing sugar was extracted from the fermented medium by adding 100 ml distilled water to each flask. The flasks were then shaken at 200 rpm for 2 hr at 60 ^oC. Suspended solid were separated and the reducing sugars (filtrate) were determined by the DNS method [5]. The composition of reducing sugars (glucose, xylose and arabinose) in hydrolysates was determined by HPLC.

3. Results and discussion

3.1. *Chemical composition of substrates*

The main compositions as cellulose, hemicelluloses, lignin and ashes content of sweet sorghum bagasse before and after pretreatment with 1, 5, 10 and 15% (w/v) of sodium hydroxide are shown in Table 2.

The alkali pretreatment was conducted by pretreating sweet sorghum bagasse at high temperature. When the concentration of sodium hydroxide increased, lignin content was decreased. As a result, the cellulose fraction increased more than 90% (w/w) when 10 and 15% (w/v) of sodium hydroxide were used. This is typical of alkaline pretreatment, which generally has a stronger effect on lignin than cellulose [7]. It was observed that pretreated biomass was swollen, which leaded to the decrease in the degree of polymerization and crystallinity, disruption of the lignin structure, and separation of structural linkages between lignin and carbohydrates [8]. However, the compositions of sweet sorghum bagasse when using 10 and 15% (w/v) of sodium hydroxide were not different, so that 10% (w/v) of sodium hydroxide was chosen for the pretreatment as the suitable concentration.

Table 2. Main compositions of sweet sorghum bagasse in untreated bagasse and after alkaline pretreatments

Composition (%dry weight)	NaOH concentration (%w/v)				
	Untreated bagasse	1	5	10	15
Cellulose	58.23	68.66	86.18	90.37	91.10
Hemicellulose	25.42	19.28	9.70	5.97	5.82
Lignin	14.95	12.02	3.97	3.56	2.97
Ash	1.40	0.04	0.15	0.10	0.11

3.2. Optimization of reducing sugar production by acid hydrolysis

In the present study, BBD was used to investigate the optimal conditions of the reducing sugar production from pretreated bagasse. There were three factors namely concentration of sulfuric acid, solid to liquid ratio and reaction time and three levels of each parameter were varied as shown in Table 3.

Table 3. Reducing sugar from pretreated bagasse in experiments obtained by Box-Behnken design

Run number	Level of experimental factors			Reducing sugar (%g/g dry weight)
	Concentration (X_1)	Solid to liquid ratio (X_2)	Reaction time (X_3)	
1	-1	-1	0	28.46
2	1	-1	0	16.90
3	-1	1	0	24.99
4	1	1	0	6.53
5	-1	0	-1	23.06
6	1	0	-1	13.01
7	-1	0	1	27.35
8	1	0	1	7.75
9	0	-1	-1	25.81
10	0	1	-1	18.09
11	0	-1	1	20.36
12	0	1	1	12.24
13	0	0	0	31.11
14	0	0	0	29.81
15	0	0	0	29.92

The fifteen experiments were designed as shown in Table 3 and the maximum reducing sugar is 31.11% (g/g dry substrate), which was observed at the experimental run number 13. The statistical software MINITAB release 14 was used to design of experiments, to determine the coefficients of linear, quadratic and interaction terms, and to build the quadratic model and response surface plots.

The BBD was used to investigate the effects of the assigned parameters on the reducing sugar production. The experimental results were analyzed by regression analysis consisting of the effect of linear, quadratic and interaction which gave the following regression equation with reducing sugar production as a function of concentration of sulfuric acid (X_1), solid to liquid ratio (X_2) and reaction time (X_3). Reducing sugar (Y) at specific combination of three variables can be predicted by substituting the corresponding values of each variable in Eq. (2).

$$Y = -24.5581+1.1226X_1+1.1375X_2+0.7000X_3-0.0155X_1^2-0.0175X_2^2 -0.0039X_3^2-0.0030X_1X_3 \quad (2)$$

The probability value (p-value) is a tool for evaluating the significance and contribution of each parameter and the statistical polynomial model equation. The smaller p-value is an indication of high significance of corresponding coefficient [9]. The regression coefficient in the response surface model for the linear, quadratic and interaction effects of the variables are shown along with p-value in Table 4. The p-value suggested that the coefficient for the linear effect of sulfuric acid concentration ($p < 0.01$), solid to liquid ratio ($p < 0.01$) and reaction time ($p < 0.01$) were statistically significant for reducing sugar production.

Table 4. Estimated regression coefficient and corresponding p-value for reducing sugar production

Term	Coefficient	p-value
Constant	-24.5581	0.027*
X_1	1.1226	0.003**
X_2	1.1375	0.007**
X_3	0.7000	0.001**
X_1^2	-0.0155	0.001**
X_2^2	-0.0175	0.003**
X_3^2	-0.0039	0.001**
X_1X_2	-0.0052	0.102
X_1X_3	-0.0030	0.039*
X_2X_3	-0.0001	0.913

* $p < 0.05$, ** $p < 0.01$

Analysis of variance (ANOVA) for proposed model is shown in Table 5. The p-value of the regression model ($p<0.001$) implies that the model is significant. In addition, the coefficient of variation ($R^2 = 0.986$) indicates a high correlation between the observed and predicted values from model Eq. (2). Therefore, this equation can be used for predicting the amount of reducing sugar production under parameter ranges of assigned three variables.

Table 5. Analysis of variance (ANOVA) for reducing sugar production

Source	Degree of Freedom (DF)	Sum of square (SS)	Mean square (MS)	F	*p*-value
Regression model	9	2024.63	224.959	38.49	0.000
Residual Error	5	29.22	5.844		
Total	14	2053.85			

R^2= 98.6% R^2 (adj) = 96.0%

The two-dimensional (2D) contour plots and three-dimensional (3D) response surface of the interactions are presented in Figure 1, 2 and 3. These observations also identified the optimal conditions with the maximum response for the levels of the factors in the design of experiments. The maximum response is referred to the surface confined in smallest ellipse in the contour plot. The perfect interaction between the independent variables can be shown when elliptical contours are obtained [9].

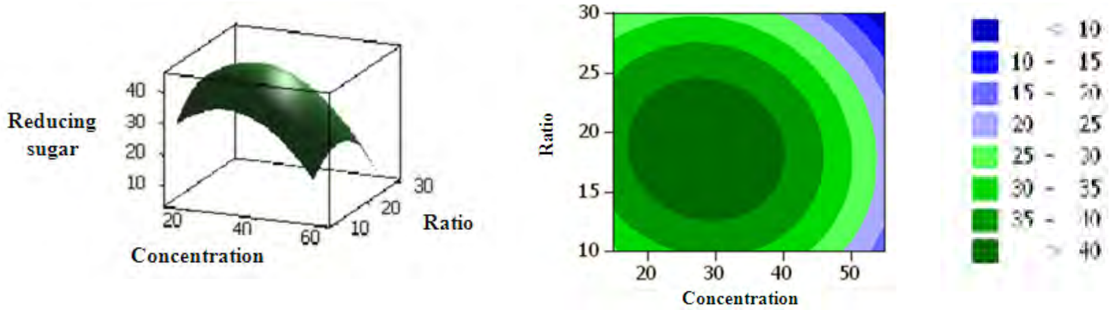

Fig. 1. Contour plot and response surface for the effects of acid concentration and solid to liquid ratio at a constant reaction time (80 minutes).

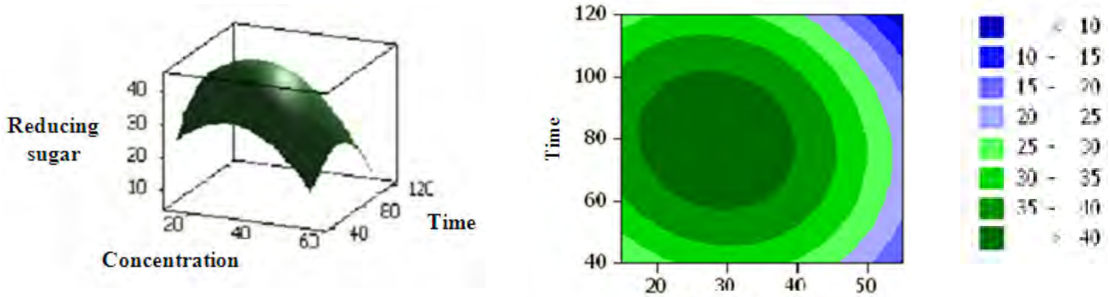

Fig. 2. Contour plot and response surface for the effects of acid concentration and reaction time at a constant solid to liquid ratio (1:20).

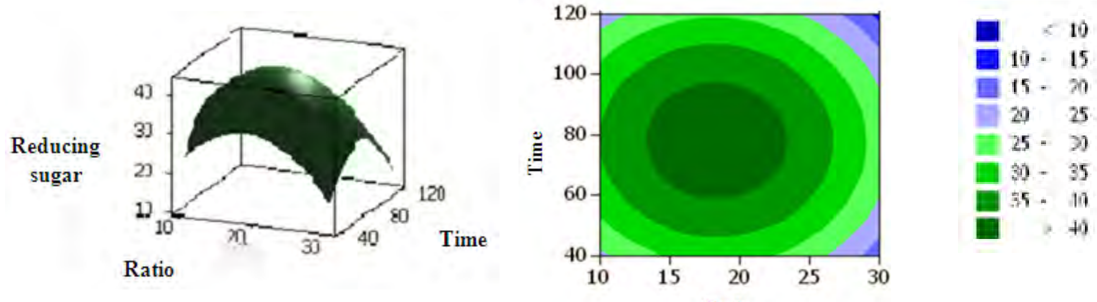

Fig. 3. Contour plot and response surface for the effects of solid to liquid ratio and reaction time at a constant acid concentration (35% v/v).

Application of RSM with BBD predicted that the maximum reducing sugar production must occur at decoded values of condition parameters at sulfuric acid of 21.44% (v/v), solid to liquid ratio of 1:12.5 and reaction time of 73.24 minutes. At this maximum condition, the reducing sugar should reach 34.97% (g/g dry substrate). A repeat acid hydrolysis for reducing sugar production under optimal conditions is carried out to confirm the prediction. After performing the hydrolysis under optimal condition, the obtained reducing sugar is 33.49% (g/g dry substrate). Since the difference between predicted and actual confirmed result was only about 4.23%, it should be regarded as acceptable.

3.3. Reducing sugar production by microbial hydrolysis

In this respect, preatreated sweet sorghum bagasse was conducted for the production of reducing sugar by *T. harzianum* under SSF. An inoculum (10%w/w) was added to a medium of 77.5% (w/w) moisture content and incubated at 25°C for 84 hours. Reducing sugar was expressed based on weight of dry substrate and carried out in triplicates and standard deviation was less than 6%. As shown in Figure 4, the highest reducing sugar, 10.34 % (w/w), was obtained at 56 hours of fermentation time. The conditions used in the experiment were the optimum conditions previously studied [6].

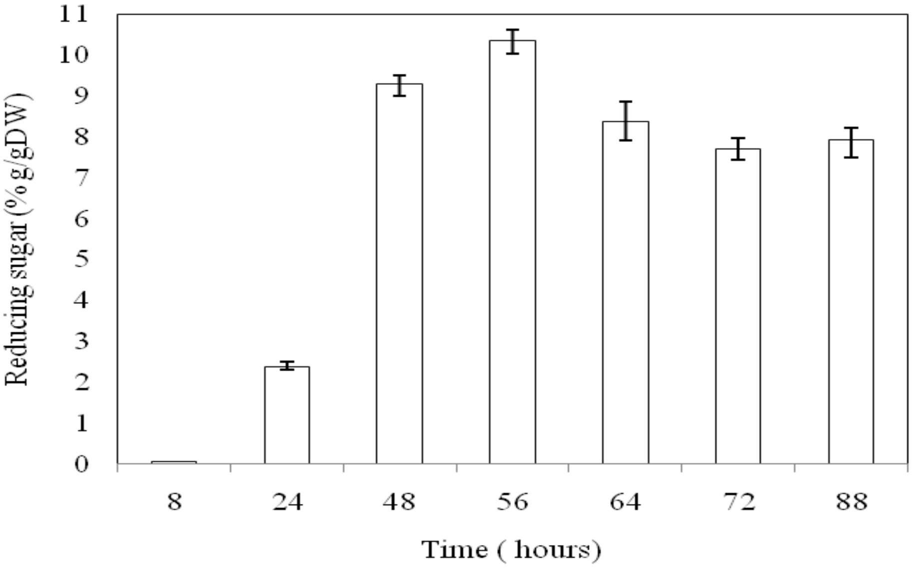

Fig. 4. Reducing sugar production by T. harzianum under SSF using pretreated sweet sorghum bagasse as the substrate (inoculum of 10% w/w and moisture content of 77.5% w/w)

The reducing sugar obtained from acid hydrolysis (33.49%) was higher than from microbial hydrolysis (10.34%) because the conditions of chemical hydrolysis are stronger than microbial hydrolysis. However, acid hydrolysis has several disadvantages over microbial hydrolysis due to formation of toxic compounds, such as furfural, hydroxylmethylfurfural, acetic acid, formic acid, levulinic acid etc. These toxic compounds can inhibit the yeast fermentation in next step of ethanol production. Removal of these compounds increases the additional costs for ethanol production [10].

The advantages of microbial hydrolysis include low energy requirement, mild conditions and the ready sugar for further fermentation. However, the rate of hydrolysis in most microbial hydrolysis processes is very low.

4. Conclusions

The optimal conditions obtained through a statistical Box-Behnken Design are successfully determined to maximize the reducing sugar production from acid hydrolysis. The result from the second order polynomial model developed indicated that the optimal conditions for reducing sugar production from pretreated sweet sorghum bagasse by sulfuric acid hydrolysis are 21.44 %(v/v) of sulfuric acid, solid to liquid ratio of 1:12.5 and reaction time of 73.24 minutes which give the maximum reducing sugar of 33.49% (g/g dry substrate) higher than the maximum reducing sugar of microbial hydrolysis (10.34% g/g dry substrate).

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Ethanolysis of Soybean Oil Using Mesoporous Molecular Sieves

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Abstract: This study evaluates the use of nanostructured materials as catalyst in biodiesel production from soybean oil using ethanol as transesterificant agent. Ethanol can be environmentally advantageous over methanol (more frequently used as reagent in biodiesel production) because it can be obtained from renewable sources whilst methanol is usually derived from mineral sources. The catalyst (La_{50}SBA-15) has lanthanum oxide as active phase which was inserted by isomorphous substitution into the SBA-15 network. The LaSBA-15 mesoporous molecular sieves were synthesized using pluronic (P123) dissolved in aqueous HCl solution with tetraethyl orthosilicate and a given amount of hydrated lanthanum chloride (Si:La = 50) at 333K. The reaction was performed using the molar ratio soybean oil:ethanol of 1:20 at inert atmosphere (N_2) at 343K with 1wt% of catalyst mass relative to total oil mass added to the reaction mixture. The reaction was evaluated for ethyl ester conversion after 3h and 6h. The ethyl esters content was measured using low frequency ^{1}HNMR spectroscopy (200MHz). A conversion of soybean oil in ethyl esters (biodiesel) of 80% after reaction time of 6h was obtained. The La_{50}SBA-15 heterogeneous catalyst showed good performance in the ethanolysis of soybean oil, comparing well with previous reports for methanolysis of soybean oil.

Keywords: *Biodiesel, ethanolysis, heterogeneous catalysis, La_{50}SBA-15.*

1. Introduction

Biodiesel can be defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. The most common process for biodiesel production consists in a transesterification reaction in which a triglycerides source (vegetable oil or animal fat) reacts to a short chain alcohol (usually methanol) in catalyst presence [1-3]. Since ethanol is largely obtained in Brazil from renewable sources (mostly sugarcane) it might be advantageous to replace methanol in the transesterification reaction for biodiesel production [4].

The transesterification reaction may be catalyzed by acids, bases or enzymes [5]. Industrially, basic homogeneous catalysts such as potassium hydroxide and sodium hydroxide are often used in biodiesel production, because they display high reactivity, low cost and mild reaction conditions. However, as usually observed in homogeneous catalyst systems, they require downstream separation of the catalyst and byproducts, thus increasing the process complexity and cost [6-9]. Therefore process development for biodiesel production from heterogeneous catalysts has been largely studied in recent years [5,6,10-12]. Albuquerque et al. [11] studied calcium oxide catalytic proprieties supported on several mesoporous SBA-15 silica in transesterification of castor and sunflower oil with methanol. Yan et al. [6] studied the use of calcium oxide modified with lanthanum in the transesterification reaction with methanol. The mixture CaO-La_2O_3 showed higher catalytic activity than when using pure calcium oxide or pure lanthanum oxide. Yan et al. [7] also studied the use of ZnO-La_2O_3 as heterogeneous catalyst in the transesterification of unrefined or waste oil with methanol with noticeable strong interaction between zinc and lanthanum species. The catalyst sample with a 3:1 zinc lanthanum molar ratio displayed higher activity compared to pure metal oxides. Sun et al. [13] studied the properties of ZrO_2 impregnated with La_2O_3 as a catalyst in sunflower oil transesterification with methanol . The best methyl ester conversion was found when using a catalyst concentration of 21wt.% La_2O_3 on ZrO_2.

This study intends to investigate the use of La_{50}SBA-15 in soybean oil transesterification using ethanol. The La_{50}SBA-15 has lanthanum oxide as active phase inserted into SBA-15 framework by isomorphous substitution.

2. Materials and Methods

2.1. Catalyst Preparation and Characterization

The SBA-15 modified with lanthanum was synthesized by hydrothermal method using 4.0 g of Pluronic P123 (BASF Co.) as template, dissolved in 10.3 mL of aqueous HCl solution (VETEC, Brazil). Thereafter 10.3 mL of tetraethyl orthosilicate (Sigma-Aldrich) and a given amount of previously dissolved hydrated lanthanum chloride (VETEC, Brazil) were added (Si/La = 50), and the mixture stirred for 22 h at a temperature of 333 K. The resulting gel was placed into a Teflon container and submitted to hydrothermal treatment at a temperature of 373 K for 48 h. The solid was then filtered at room temperature, washed with a solution of HCl in ethanol 2 wt%, dried at 333 K for 1 h, and finally the solid was calcined at 823 K (heating rate=1 K/min). The samples, designated as La_{50}SBA-15 (where 50 refers to the Si/La molar ratio) were characterized through X-ray diffraction (DRX), N_2 adsorption and desorption isotherms at 77 K, and scanning electron microscopy (SEM). Further details may be found in Quintella [14].

2.2. Reaction

The reaction experimental set-up consisted of a 100 mL round-bottomed flask with four outlets. A thermometer was attached to the first outlet for temperature control. The reflux condenser was inserted into the second one to minimize the ethanol loss through evaporation and the third received nitrogen flow providing inert atmosphere. The fourth outlet was used to introduce the catalyst and remove aliquots in order to monitor the reaction.

Initially the catalyst was activated at 1073 K, under inert atmosphere, during 1 hour in order to convert carbonates eventually formed by atmosphere contact into oxides since carbonates do not show catalytic activity [10]. In the transesterification reactor, 30.3 g of commercial soybean oil (Liza, Sao Paulo, Brazil) were added to 99.6% ethanol (J.T.Baker, Mexico). The molar ratio of soybean oil and ethanol used was 1:20. The reaction was carried out at inert atmosphere using 1000 rpm agitation. When the oil and alcohol mixture reached the desired temperature, 343 K, the catalyst was inserted to the reaction mixture using a catalyst/oil mass ratio of 0.01. Samples of 5 mL were taken after 3h and 6h, filtered under vacuum to extract the catalyst from the reaction mixture. To improve the phase separation in the reaction mixture, 99.5% dichloromethane (Cromolina, Diadema, Brazil) was added, and subsequently vaporized from the ester phase at 373 K.

The ethyl ester conversion was evaluated through hydrogen nuclear magnetic resonance spectroscopy (^{1}H NMR) with 60 MHz frequency using Varian EM-360 equipment and $CDCl_3$ as solvent [15,16]. The ^{1}H NMR technique for ethyl esters determination is based on the analysis of three sets of signals: (A_1) the hydrogen from the ester ethoxy carbons; (A_2) the four methylene hydrogens from glycerol; (A_3) the α-methylene carbonyl hydrogen present in all mono, di and triglycerides from both oil and fatty acid ethyl esters [17]. The conversion of soybean oil (EE) into biodiesel (ethyl esteres) was obtained from the ^{1}H NMR technique using Eq. (1).

$$EE(\%) = \frac{(A_1 - A_3)}{A_2} \times 100 \qquad (1)$$

3. Results and Discussions

3.1. Catalyst Characterization

The diffractograms of SBA-15 and La_{50}SBA-15 are shown in Fig. 1. Three major peaks, referring to Miller index crystalline plans (100), (110) e (200), are characteristic of hexagonal symmetry p6mm (punctual planar group two-dimensional 6mm), common in mesoporous materials similar to SBA-15 [18-20]. It may be observed that the incorporation of lanthanum did not affect the hexagonal structure typical of SBA-15.

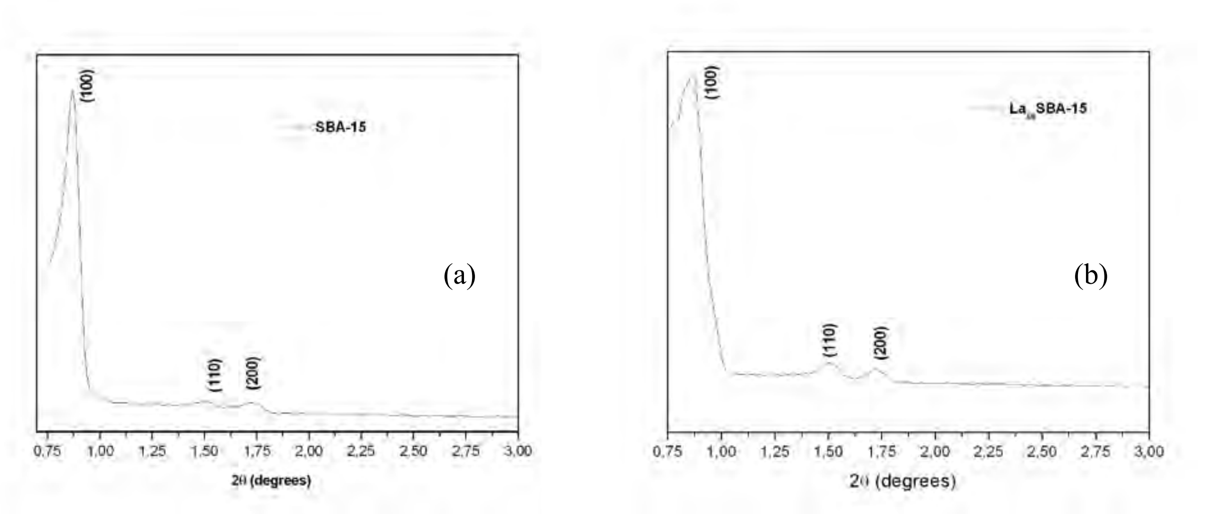


Fig. 1. X-Ray Diffractograms (a) SBA-15 ; (b) La_{50}SBA-15.

The nitrogen adsorption and desorption isotherms for samples show a type IV shape (Brunauer classification) as characteristic for nanoporous materials (see Fig. 2). Table 1 summarizes the textural properties of both samples (SBA-15 and La_{50}SBA-15).

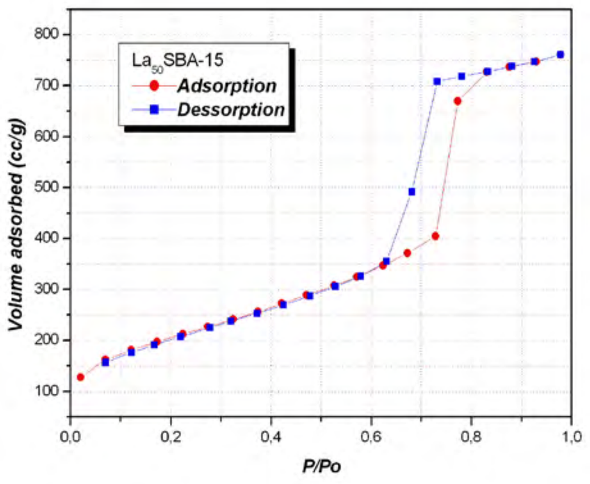
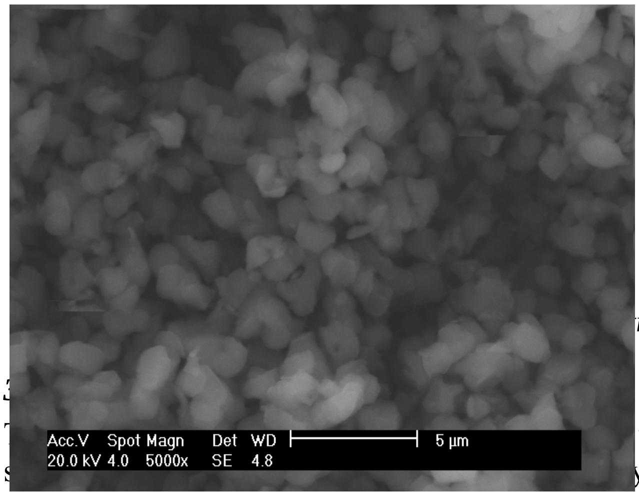


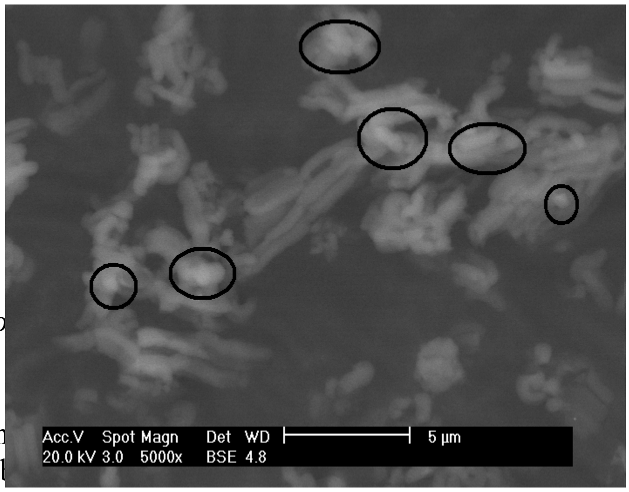
Fig. 2. N_2 adsorptior

Table 1. Textural characteristics synthesized materials samples

Sample	a_0(nm)	D_p(nm)	V_p(cm^3g^{-1})	S_{BET}(m^2g^{-1})
SBA-15	11.88	4.33	0.95	931.3
La_{50}SBA-15	11.88	7.29	1.09	735.2

The SEM micrographs for both samples are shown in Fig. 3. It may be observed that SBA-15 displays a non uniform morphology showing irregular spheres (Fig. 3a). For La_{50}SBA-15 (Fig. 3b), it may be noted some regions with clearer areas than others, indicating the presence of another material, probably lanthanum, which had not been observed in Fig. 3a. The lanthanum addition to the support framework caused morphological changes indicated by the noticeable stick shapes.





glycerol methylenic hydrogen; four glycerol hydrogens; dimethylenic hydrogens; three CH_2 α-carboxílic groups; CH_2 carbon groups neighboring the unsaturated carbons; CH_2 carbons neighboring the saturated carbons; CH_2 carbons bonded to 2 saturated carbons atoms; and three terminal methyl groups.

The ^1H RMN spectrum of the ethyl ester product is shown in Fig. 5. The quartet signal relative to the OCH_2- group hydrogen, which appears exclusively at the spectrum of the ethyl esters molecule, may be observed in the region of 3.8-4.2 ppm. Also, the triplet signal relative to α-CH2- groups, which may be found in both oil and ethyl esters, is seen in the region of 2.2-2.5 ppm.

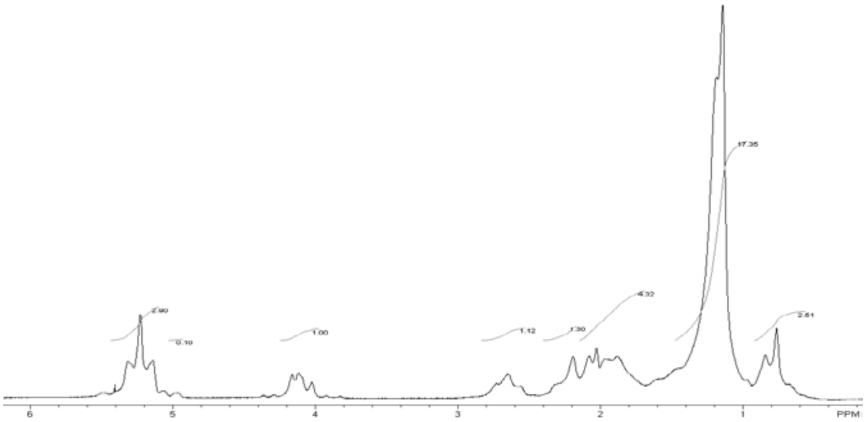


Fig. 4. ^1H NMR spectrum of pure soybean oil.

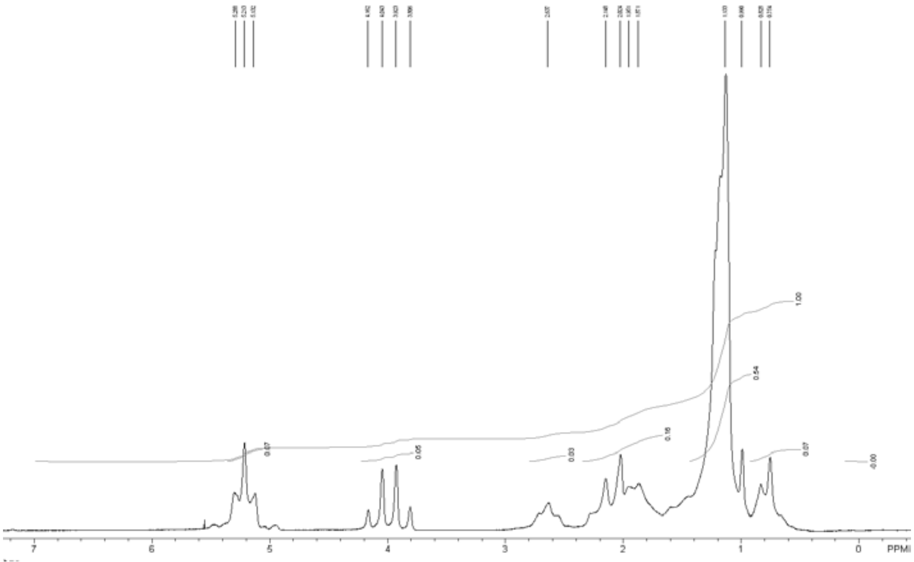


Fig. 5. ^{1}H NMR spectrum of the ethyl ester after 6 hours of reaction.

The ^{1}H RMN spectrum of the product after reaction time of 3 hs showed no conversion to ethyl ester. After 6 hs (Fig. 5), the calculated value of the conversion of soybean oil with ethanol using as catalyst in the transesterification reaction was 80% v/v, which is comparable to previously reported values (see Table 2). The classical homogenous process catalyzed by KOH is reported using ethanol as transesterificant agent with conversions as high as 96%v/v, however the downstream separation of the products (ester/glycerin phases) is rather difficult if compared to heterogeneous systems.

Other studies using heterogeneous catalysts with methanol, instead of ethanol, have been reported (also seen in Table 2). Those studies present somewhat higher values for conversion (as high as 98%v/v of methyl ester), however at more extreme operation conditions (temperature and time) and higher ratios of alcohol/oil and catalyst/oil.

Table 2. Comparison of conversion to biodiesel with previously reported values.

Oil/Alcohol	Alcohol/Oil molar ratio	Catalyst	Catalyst/oil mass ratio	Temp. (K)	Time (h)	Conv. (%vv)	Ref.
Soybean/EtOH	20	LaSBA15	0.01	343	6	80.0	This study
Soybean/EtOH	18.8	homogeneous (KOH)	0.01	n.a.	4	96.0	22
Soybean/MeOH	21	Ca_3La_1	0.05	331	3	94.3	6
Waste/MeOH	36	$ZnO-La_2O_3$	0.023	473	2	95.0	7
Sunflower/MeOH	30	La_2O_3/ZrO_2	0.05	473	5	98.1	13

4. Conclusions

The results of the transesterification reaction of soybean oil using La_{50}SBA-15 as heterogeneous catalyst confirm the possibility of its use in the ethanolysis of soybean oil at milder operation conditions than previously reported studies with methanol. A conversion of 80.0%v/v could be obtained using oil/ethanol molar ratio of 1:20; catalyst/oil mass ratio of 0.01; temperature 343 K; inert atmosphere; and 6 hours of reaction.

Acknowledgments

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Parametric study of portable floating type biogas plant

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Abstract: In this paper, an attempt has been made to design and test the performance of a portable floating type biogas plant of volume capacity 0.018 m3 for outdoor climatic condition of New Delhi, India. The field study has been carried under the monsoonal season of New Delhi, India. In this experiment, we have taken an aluminium made digester of 30 Kg slurry capacity for batch system. In the batch system, the slurry has been added once to the digester for whole duration of the process. The rate of biogas production with slurry temperature has been observed.

It has been observed that (i) the biogas production depends strongly on slurry temperature and (ii) the retention period is nearly 85 days. The range of slurry and ambient temperature of atmosphere recorded during the observed period have been found as 26 to 42 ºC and 30 to 40 ºC respectively. Physical and chemical analysis of biogas and slurry have also been carried out. Further, the CO2 mitigation and carbon credit has also been evaluated for the present system.

Keywords: *Biogas, Batch system, Carbon credit, Digester.*

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1. Introduction

Biogas technology provides an alternate source of energy in rural India, and is an appropriate technology that meets the basic need for cooking fuel in rural areas by using local resources, viz. cattle waste and other organic wastes. Realization of this potential and fact that India supports the largest cattle wealth led to the promotion of National Biogas Programme in major way in the late 1970s as an answer to the growing fuel crisis. In India alone, there are an estimated over 250 million cattle and if one third of the dung produced annually from these is available for production of biogas, more than 12 million biogas plants can be installed which have the estimated biogas potential capacity of 17,000 MW.

Biogas is produced from organic wastes by concerned action of various group of anaerobic bacteria through anaerobic decomposition. Anaerobic decomposition is a two-stage process as specific bacteria feed on certain organic materials. In the first stage, acidic bacteria dismantle the complex organic molecules into peptides, glycerol, alcohol and the simpler sugars. When these compounds have been produced in sufficient quantities, a second type of bacteria starts to convert these simpler compounds into methane. These methane producing bacteria are particularly influenced by the ambient conditions, which can slow or halt the process completely. Globally, the reduction of green house gas emissions particularly of CO_2 has become more important. Currently much of the carbon dioxide emitted to the atmosphere is a result of anthropogenic activities from the use of the fossil fuel in the transportation and energy sectors. Significant emission reductions may be achieved in the energy sector by improving efficiency through the use of alternative fuels. Through the use of biogas plant we can save the CO_2 emission in the atmosphere which has been measured in the term of carbon credit.

Carbon credit is a key component of national and international attempts to mitigate the growth in concentrations of green house gases (GHGs). One Carbon Credit is equal to one ton of carbon, which is the chief element of carbon dioxide. Carbon trading is an application of an emission trading approach through carbon credit. Greenhouse gas emissions are capped and then markets are used to allocate the emissions among the group of regulated sources. The idea is to allow market mechanisms to drive industrial and commercial processes in the direction of low emissions than are used when there is no cost to emitting carbon dioxide and other GHGs into the atmosphere. Since GHG mitigation projects generate credits, this approach can be used to finance carbon reduction schemes between trading partners and around the world.

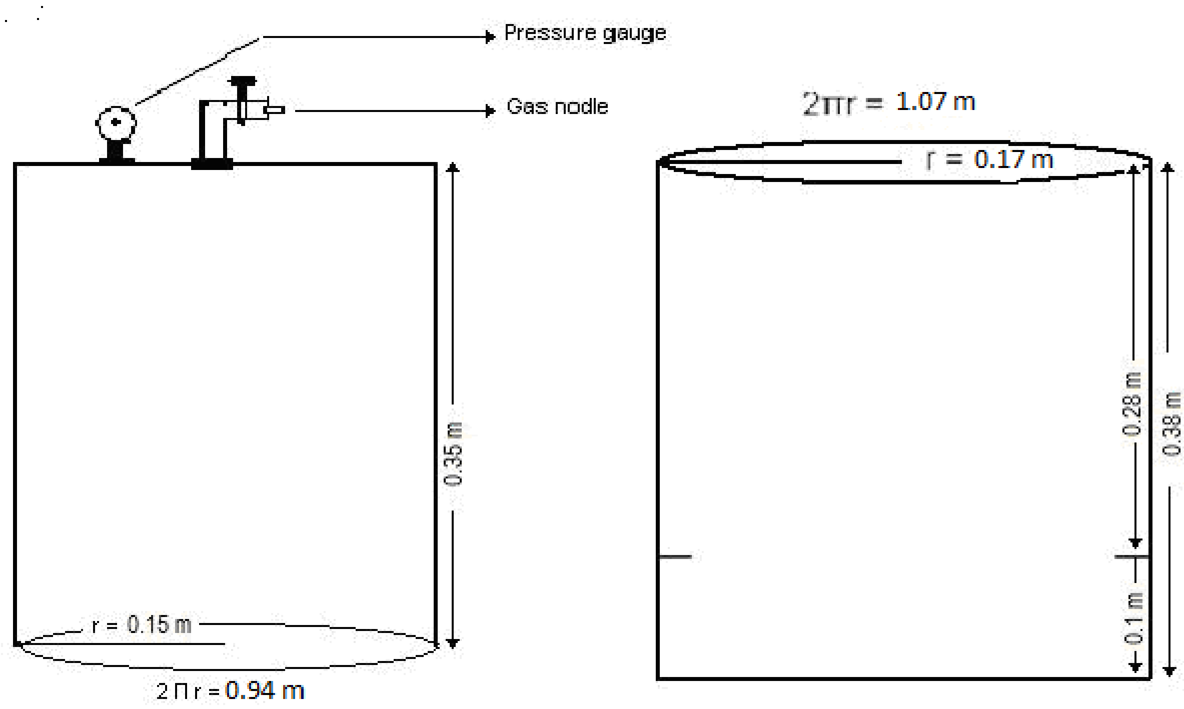
Usmani et al (1996) have analysed the performance of a greenhouse integrated biogas plant. In this paper their basic aim was to reduce thermal loss to ambient in harsh cold climates. According to Lau et al. (1987) due to the lower temperature, biogas production decreases drastically and may stop. Thus, for enhancing biogas production, a higher digester temperature than ambient temperature is required. The green house concept should be integrated for larger capacity biogas plant. Tiwari et al. (1988) and Tiwari and Chandra (1986) have suggested that the rate of biogas production and the period to achieve the optimum temperature are function of the temperature of the slurry. Also, for a required production rate of biogas, the period to achieve the optimum temperature should be reduced. Tiwari et al. (1992) have suggested heating of the slurry by a heat exanger connected to a flat plate collector. Gupta et al. (1998), Sodha et al. (1987, 1989), Tiwari et al. (1997) have suggested installation of PVC greenhouse type structure over a biogas plant. This allowed solar heating of the substrate from 18 °C to about 37 °C. Kumar et al. (2008) have done experiments with solar greenhouse assisted biogas plant in hilly region and have come to conclusion that biogas- green house hybrid system may be successful in hilly regions where average temperature remains below 37 °C throughout the year. Prabhakant et al. (2009) evaluate the carbon credits earned by energy security in India and also analyses the return on capital for biogas plants with and without embodied energy.

The 70% of livestock in India is owned by 67% of small and marginal farmers and by the land less farmers. The 60% of livestock farming labor is provided by women and more than 90% of work related to care of animals is rendered by womenfolk of the family. India ranks fifth after Australia, China, Iran, and New Zealand. The fabrication of biogas plant is tried with different materials based on which the cost of installation is highly dependent. The few data of biogas production and its composition (CH_4 fraction) with the operating temperature of slurry is available in the literature. In this paper an attempt has been made to study the biogas production with its composition with the temperature throughout retention period w.e.f. July 12, 2010 to September 29, 2010.

2. Experimental setup and instrumentation

An aluminium made biogas chamber of 30 kg slurry capacity has been used under the outdoor simulation above the ground, so that the digester and dome both can direct receive the solar radiation. The diameter and height of digester have been taken as 0.34 and 0.38 m respectively. Similarly the diameter, depth and weight of dome have been taken as 0.30 m, 0.35 m and 0.18 kg, respectively.

Aluminium metal is more efficient to increase the sufficient temperature inside the digester which increases the production rate of biogas. Four calibrated thermocouples have been used to measure ambient, slurry, gas and dome temperature by using digital temperature indicator of resolution 0.1 °C. A thermocouple is a junction between two different metals that produces a voltage related to temperature difference. Thermocouples are a widely used type of temperature sensor for measurement and control and can also be used to convert heat into electric power. They are inexpensive and interchangeable, are supplied fitted with standard connectors, and can measure a wide range of temperatures. The main limitation is accuracy system errors of less than one degree Celsius can be difficult to achieve. These thermocouples are calibrated by constant temperature controlled calibration baths. A calibration bath is a uniform temperature enclosure with a constant temperature setting that can be adjusted manually or with automation. This field study has been done at the Solar Energy Park, IIT Delhi, New Delhi, under the monsoonal season, which is highly under the fluctuating environmental condition.



(a) (b)

Figure 1. Schematic view (a) Dome (b) Digester

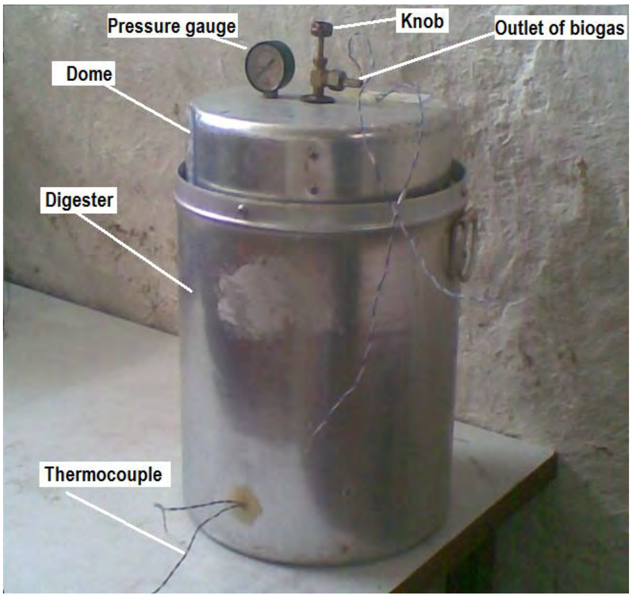


Figure 2. : Photograph of experimental setup

These observation has been taken during day time due to presence of sunlight at 9:00 am, 1:00 pm and 5:00 pm during the month of July to September 2010 (monsoon season) in Delhi, India. Ambient temperature, relative humidity, average precipitation and solar intensity have been measured during this experiment. Gas production have been recorded on daily basis by the observation of upliftment of dome and volume production. This biogas sample have been taken out by the help of toddler bags, which is safe to carry biogas without any leakage and entry of atmospheric air, which has been tested through gas chromatography.

3. Methodology and experimental observations

Different parameters like solar intensity, ambient temperature, slurry temperature, average humidity and average precipitation are measured on daily basis. These data have been taken at the interval of 4:00 hours between 9:00 am to 5:00 pm due to presence of solar radiation. Three readings have been taken in every day at 9:00 am, 1:00 pm and 5:00 pm. Under the analysis we have calculated the average of solar intensity and relative humidity at these three different times in a day upto every two weeks, until the biogas production inside the biogas chamber stop. In this manner we have also calculated the average ambient temperature and average slurry temperature to find the different result and observation, which shown in figure 3 and figure 4. We have also tried to measure the pressure inside the dome through the help of pressure gauge in kg/cm^2 but it did not provide any data due to generation of very less pressure inside the dome. The production rate and methane fraction has also been observed under the influence of various temperature range during the monsoonal season in New Delhi, India.

4. Results and discussions

In this study, it has been observed that the production of biogas is dependent upon the temperature and the solar intensity of the atmosphere. The methane fraction has found to increase up to first six weeks and then it become constant. The synthesis of biogas have been started from the third day of the slurry feeding inside the biogas chamber. There has no role of humidity and precipitation under biogas production. Initially solar intensity increased upto two weeks but after this it decreases due to cloudy weather condition, because the monsoonal season is very fluctuating. Where as the slurry temperature was always more than ambient temperature during the whole experimentation period. These all parameters are shown in figure 3. In this continuation, initially in first two week, the rate of biogas production was very fast but after it gradually decreases. During experimentation, the minimum and maximum fraction range of methane and the rate of biogas production has also been observed in every week which shown in figure 4.

The total biogas volume produced during the experimentation has been recorded 0.378 m^3 under three month of observation. So the total volume of biogas produced in a year (4 × 0.378 m^3) 1.512 m^3 . Therefore the total carbon credits which has been earned in a year 0.019 units/year or € 0.285 / year. Carbon dioxide mitigation and carbon credit are calculated below:

Carbon credit earned by biogas plant

Total volume of biogas produced during experiment (July to September) = 0.378 m^3

Total volume of biogas produced in a year = 4 × 0.378 m^3 = 1.512 m^3

(Taking calorific value of biogas = 6 kWh/ m^3)
So total energy produced in a year = 6 × 1.512 = 9.072 kWh

(Taking 1kWh = 2 kg CO_2 under mitigation)
Total CO_2 mitigated = 9.072 × 2 = 18.144 kg/ year

It is known that in one meter cube of biogas there is an average 62.5% natural gas by volume and the weight of natural gas is 0.68 kg/ m^3

The weight of natural gas present in the given volume of biogas = 0.68 × 1.512 = 1.028 kg/ year

Methane is 18.25 times more potent than carbon dioxide. Taking this ratio the equivalent carbon dioxide can be computed as = 18.25 × 1.028 = 18.761 kg/ year = 0.019 ton/year
(1 ton CO_2 = 1 credit)

Therefore total carbon credits earned in a year = 0.019 units/year = € 0.285 / year.
(Assuming 1 carbon credit = € 15/ unit)

Table 1. Different parameters (solar intensity, relative humidity, ambient temperature, slurry temperature and average precipitation) and their effect with biogas production and methane fraction.

	Observation	**2 week**	**4 week**	**6 week**	**8 week**	**10 week**	**12 week**
Avg. solar intensity (W/m2)	9:00 am	230	248	226.5	215	218	209.5
	1:00 pm	491.5	504	613	511	474.5	557.5
	5:00 pm	121.5	124.5	145	134.5	131.5	166.5
(AVG.) (W/m2)	(9:00 am to 5:00 pm)	**281**	**292.2**	**328.2**	**286.8**	**274.7**	**311.2**
Avg. humidity (%)	9:00 am	67.1	73	76.5	80.2	64.2	64.9
	1:00 pm	52.6	63	69.9	67.3	56.9	60.3
	5:00 pm	61.6	70	79.3	80.3	58.9	67.7
(AVG.) (%)	(9:00 am to 5:00 pm)	60.4	68.7	75.2	75.9	60.0	64.3
Avg. Ambient temperature (°C)	Whole day (24 hours)	31	30.5	30.3	30.0	29.5	29
Avg. Slurry temperature (°C)	(9:00 am to 5:00 pm)	**32.4**	**32.5**	**35.1**	**36.5**	**35.7**	**35.1**
Volume of biogas (m3)	Whole day (24 hours)	**0.033**	**0.133**	**0.102**	**0.040**	**0.054**	**0.016**
Methane fraction(min.) (%)	Whole day (24 hours)	**5**	**35**	**40**	**40**	**40**	**30**
Methane fraction(max.) (%)	Whole day (24 hours)	**40**	**55**	**55**	**55**	**55**	**40**

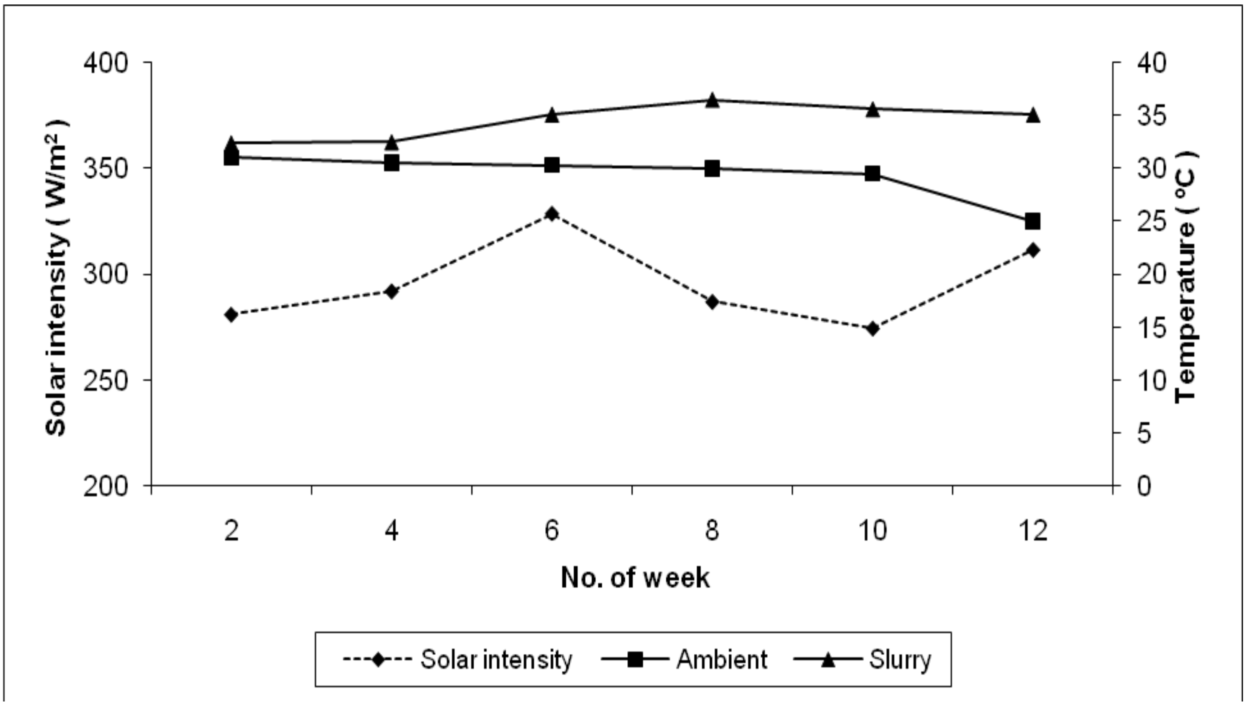


Figure 3. The weekly variation of solar intensity, ambient temperature and slurry temperature

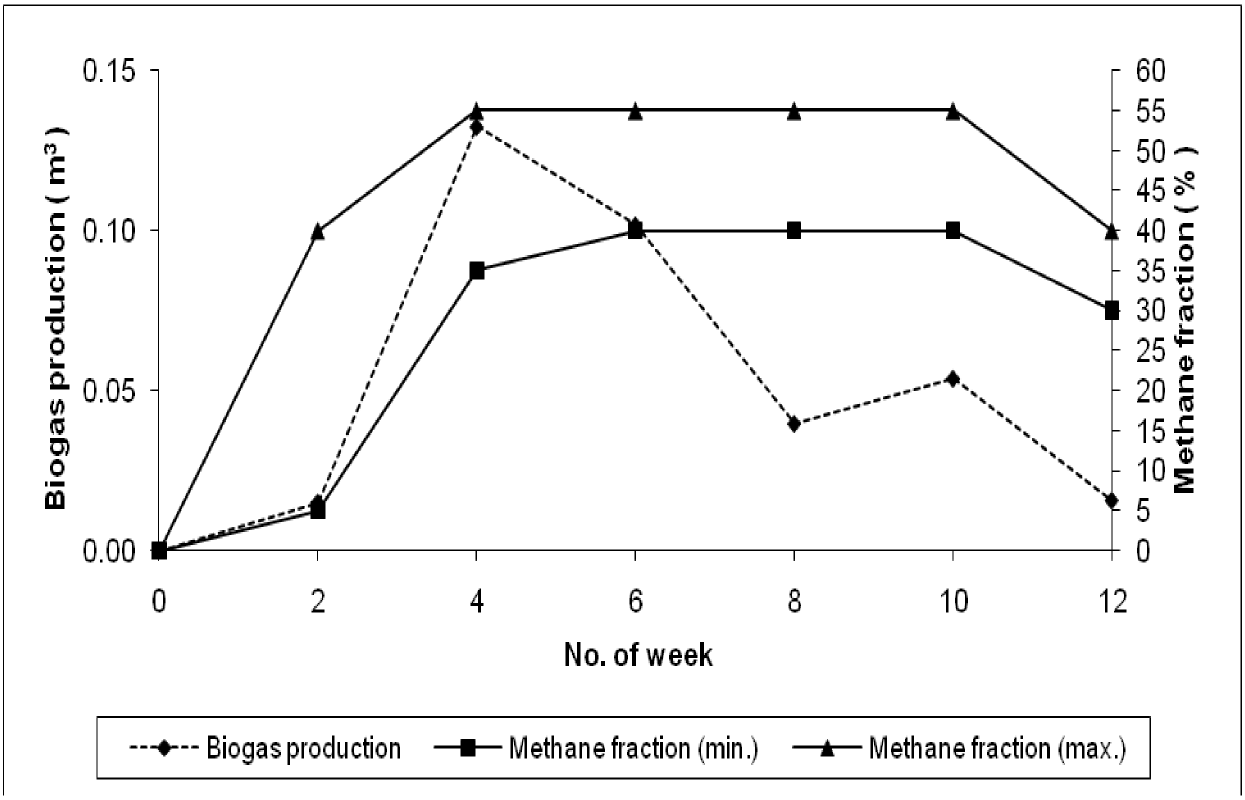


Figure 4. Rate of biogas production and methane fraction shown on weekly basis

5. Conclusions and recommendations

In this experiment it has been observed that the biogas plant is successful during the monsoon season because here the temperature varies between 26 to 39°C. Aluminium made biogas plant is other alternative which we can use for biogas production because it is more durable, less prone to corrosion, light in weight and more heat absorbing capacity comparative to iron made biogas plant, so it maintains sufficient temperature inside the digester which increases the rate of production of biogas. These are also economically feasible for developing country specially for India. We can also increase the slurry temperature inside the digester if we coat a black paint on the surface of aluminium made biogas chamber. Because it will increase the absorbtion capacity of sunlight on its surface. In next experiment we will also analyse the rate of production of biogas and its methane fraction under greenhouse chamber.

Acknowledgement

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Effect of organic loading rates (OLR) on production of methane from anaerobic digestion of vegetables waste

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Abstract: In this study, experiments were conducted to investigate the production of biogas from vegetable wastes by using anaerobic digestion process. The complete-mix, pilot-scale digester with working volume of 70 l was used. The experimental protocol was defined to examine the effect of the change in the organic loading rate on the efficiency of the production of biogas and to report on its steady-state performance. The digester was operated at different organic feeding rates of 1.4, 2 and 2.75 kg VS/ (m^3.d). The biogas produced had methane composition of 49.7- 64% and biogas production rates of 0.12-0.4 m^3 biogas/(kg VS input). The reactor showed stable performance with highest methane and yield (0.25 m^3CH4/kg VS) with VS reduction of around 88% during loading rate of 1.4 kg VS/(m^3.d). As the organic loading rate was increased, the VS degradation and biogas yield decreased. Based on data from this study, OLR of 1.4 kg VS/(m^3.d) is suggested as design criteria with methane production rate of 0.25 m^3CH_4/kg VS input and successful implementation of anaerobic digestion as the method of waste treatment leads to the regional utilization of renewable energy resources, energy requirements and costs.

Keywords: *Anaerobic Digestion, Biogas, Methane, Vegetable Wastes*

1. Introduction

Municipal solid waste (MSW), when landfilled, causes several environmental problems such as the biogas production, volatile organic compounds emission, leachate, public health hazard and plants toxicity [1]. In light of rapidly rising costs associated with energy supply and waste disposal and increasing public concerns with environmental quality degradation, conversion of food wastes to energy is becoming a more economically viable practice. Anaerobic digestion has become an established and proven technology as a means of managing solid organic waste [2]. Besides generating biogas for energy use, the process also destroys pathogens and produces stabilized material to be used as fertilizer in land applications. Anaerobic digestion may lead to environmental benefits with regard to waste treatment, pollution reduction, energy production and improvements in agricultural practices [3]. The amount of MSW generated in Iran is around 60000 ton/day and contains more than 70% of organic wastes. The easy biodegradable organic matter content of vegetables waste with high moisture facilitates their biological treatment and shows the trend of these wastes for anaerobic digestion [4]. Many factors affect the performance of anaerobic digestion processes. Some of them are related to feedstock characteristics, reactor design and operational conditions [5]. The organic loading rate (OLR) is an important parameter because it indicates the amount of volatile solids to be fed into the digester each day [6]. Volatile solids represent that portion of the organic-material solids that can be digested, while the remainder of the solids is fixed. The ‘fixed’ solids and a portion of the volatile solids are non-biodegradable. The actual loading rate depends on the types of wastes fed into the digester [6], because the types of waste determine the level of biochemical activity that will occur in the digester. The aims of this study were to investigate the influence of OLR on performance and treatment efficiency (based on volatile solids removal) of vegetable wastes digestion.

2. Materials and methods

2.1. Experimental setup

The digester experiments were carried out in a semi-continuously pilot-scale with a total volume of 70 L. Fig.1 illustrates the experimental set-up. The reactor was fitted with a top plate, which supported the mixer, mixer motor, gas sampler. Sampling valves were located at positions corresponding to the top, middle and bottom layer of digester contents. The reactor had one outlet at the bottom for effluent removal. The contents of the reactor were mixed as controlled by a timer, which was activated for 15min every 45 minutes. Reactor temperature was maintained at 34 ºC.

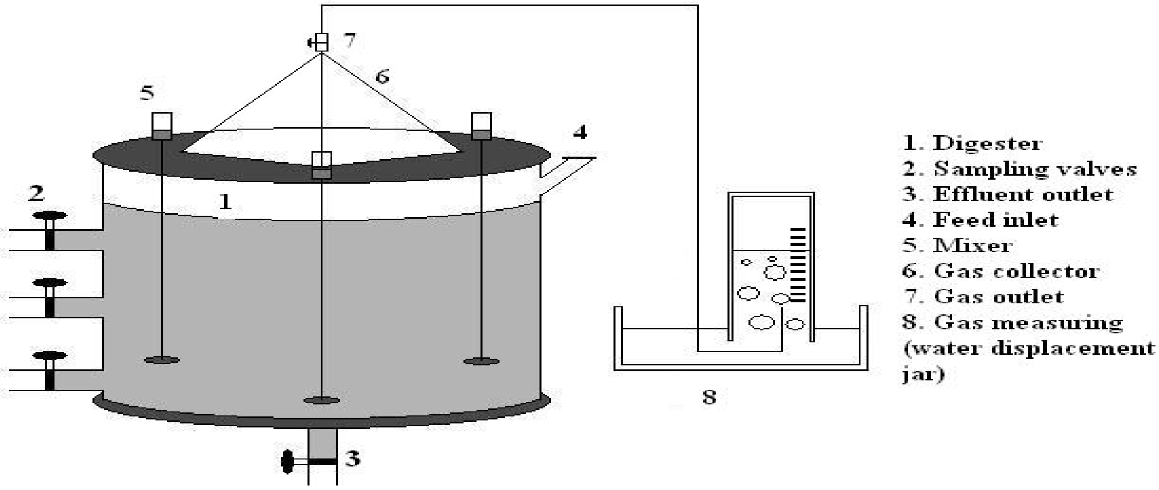

Fig. 1. The experimental set-up

2.2. Wastes sources and characteristics

The vegetable wastes used in this study were collected from the group market of Iran. The vegetable wastes consisted of potatoes, lettuce, tomatoes, eggplant, cucumber, and carrot to give 8-9% TS with VS content of 95-97%. The COD/N ratio of vegetables waste is balanced, being around 30 and therefore, no nitrogen was added to the reactor. In fact the optimum C:N ratio for microbial activity involved in bioconversion of vegetable biomasses to methane is 25-30 [7]. The anaerobically sludge from Ekbatan wastewater treatment plant was added as seed.

2.3. Anaerobic digester operation

Experiments were operated in semi-continuous mode with daily feeding. Dry semi-continuous anaerobic digestion of vegetable waste was investigated in mesophilic condition with three different organic loading rates (OLR) of 1.4, 2 and 2.75 kg VS/(m^3.d) for constant retention time of 25 days. Retention time of 25 days was maintained by feeding 2.4 l of substrate and removing 2.4 l of effluent daily. Table 1 shows the characteristics of each feeding rate.

Table 1: Characteristics of each feeding rate

	Organic loading rate (kg VS/m^3.d)	%TS	%VS	Wet waste (kg/d)	Inlet COD (mg/l)
Loading rate 1	1.4	8.9	95	1	2150
Loading rate 2	2	8.7	95	1.5	3300
Loading rate 3	2.75	8.6	96	2	4100

2.4. Analytical methods

The biogas produced was measured daily by water displacement method and its composition was measured by gas chromatograph. Total solids (TS), volatile solids (VS), pH, alkalinity were determined according to the APHA Standard Methods [8]. Total nitrogen (TN) was estimated by the Kjeldahl method [9].

3. Results and discussion

3.1. Biogas and methane production

One of the main objectives of this research was to determine the performance of the anaerobic digestion process when operated at different loading rates. For this reason, it was highly important to evaluate process performance in term of biogas composition and production to various loading rates. Production of biogas during anaerobic process at different organic loading rates is shown in Fig. 2. The daily biogas production obtained during run 2 and 3 were approximately 27.6 l/d and 21.3 l/d respectively whereas the daily biogas production in run 1 was found approximately 33.3 l/d. Further increase of the organic loading rate as 1.4kgVS/(m^3.d) results in decreased biogas production rates.

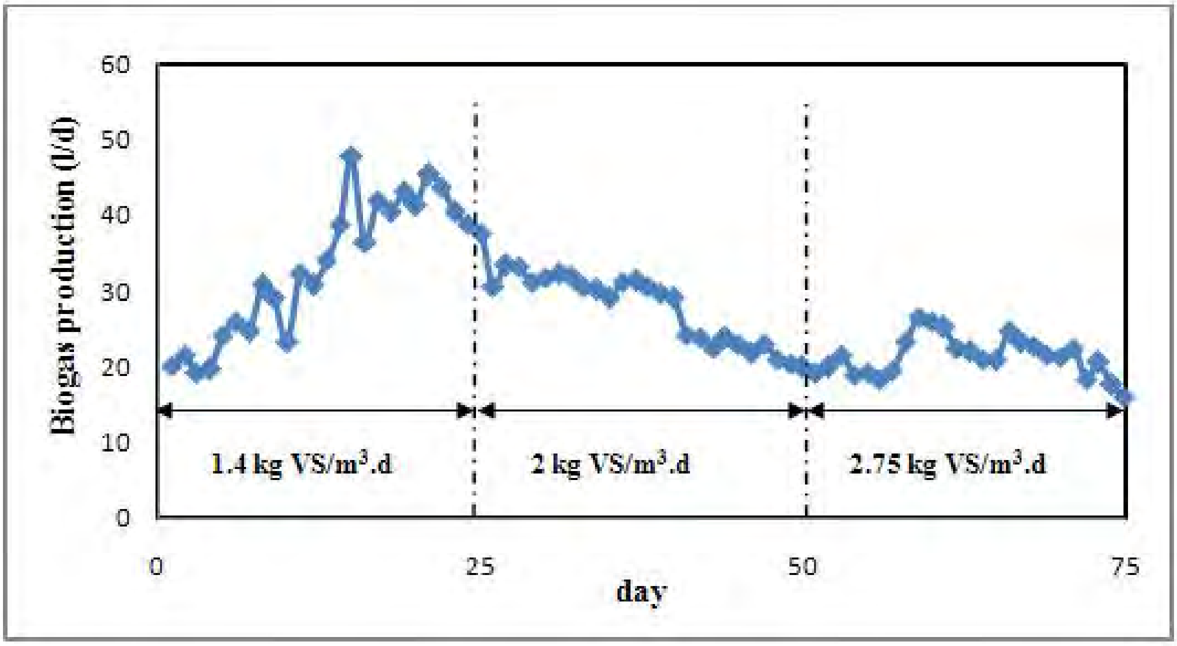

Fig. 2. The amount of biogas production for various loading rates

The reactor showed stable performance with highest methane (64%) during loading rate of 1.4kgVS/(m^3.d). Fig.3 illustrates the biogas composition. Methane concentration in biogas was observed around 60% in run 2 whereas it was found less than 49.7% in run 3. The measurement of the quantity and composition of the biogas produced in terms of methane and carbon dioxide content is of fundamental importance to evaluate the performance of the process. The increase of carbon dioxide in biogas means that the acidifying microorganisms are prevailing on the methanogens which may lead to volatile fatty acids accumulation.

3.2. Leachate characteristics

The stability of the reactor performance was investigated through leachate characteristics analysis besides biogas production and composition. In the anaerobic digestion process, methanogenic bacteria are more sensitive to environmental conditions than hydrolytic and acidogenic bacteria.

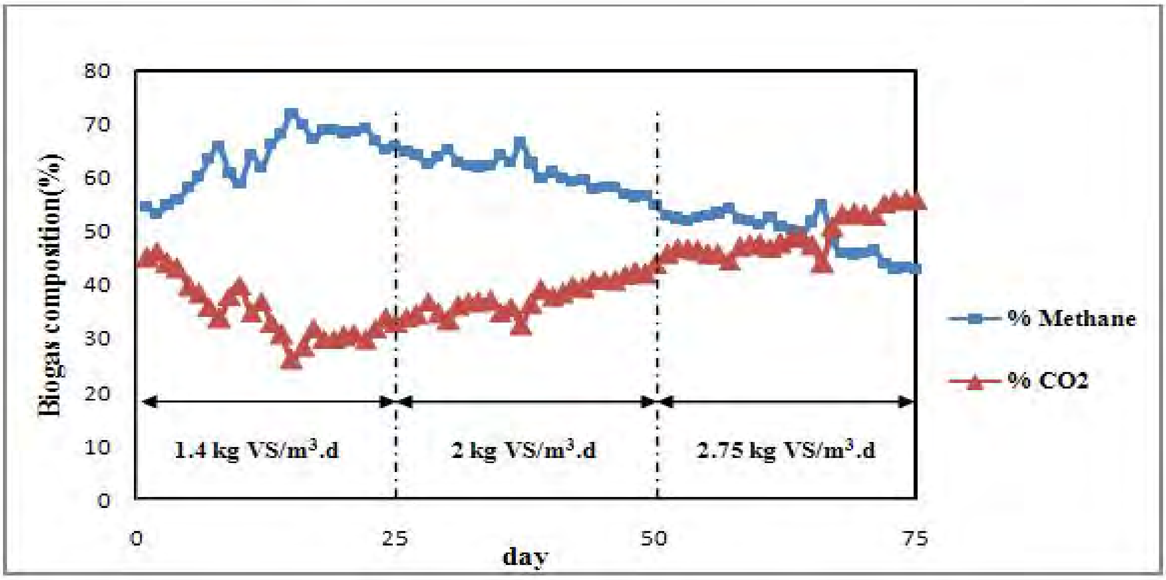

Fig. 3. Biogas composition for various loading rates

Among the environmental conditions, the pH is the most sensitive parameters. For example, the pH of digester liquid effluent indicates the stability of the system and its variation also depends on the buffering capacity of the system [10]. The pH of effluent leachate from the continuous digester remained steady state to the range of 7.75 - 8.0 during the loading rate of 1.4 kg VS/m^3.d. This shows that the system was well buffered. When the loading rate was increased to 2 kg VS/(m^3.d), the pH value dropped from 7.75 and reached to lower value of 7.3 but it was still above 7 which were in the methanogenic range. The methane content in the biogas also dropped and the system showed signs of overloading. As the pH was in the methanogenic range, the methane content in the biogas was above 60%. Fig.4 illustrates that the pH in loading rate of 2.75 kg VS/m^3.d was dropped from 7.3 to 6.8. Since the pH is controlled by the volatile organic acids concentration, the alkalinity showed similar trends. This was resolved by immediately stopping the feeding and adding alkaline solution. But the condition could not be recovered during run 3.

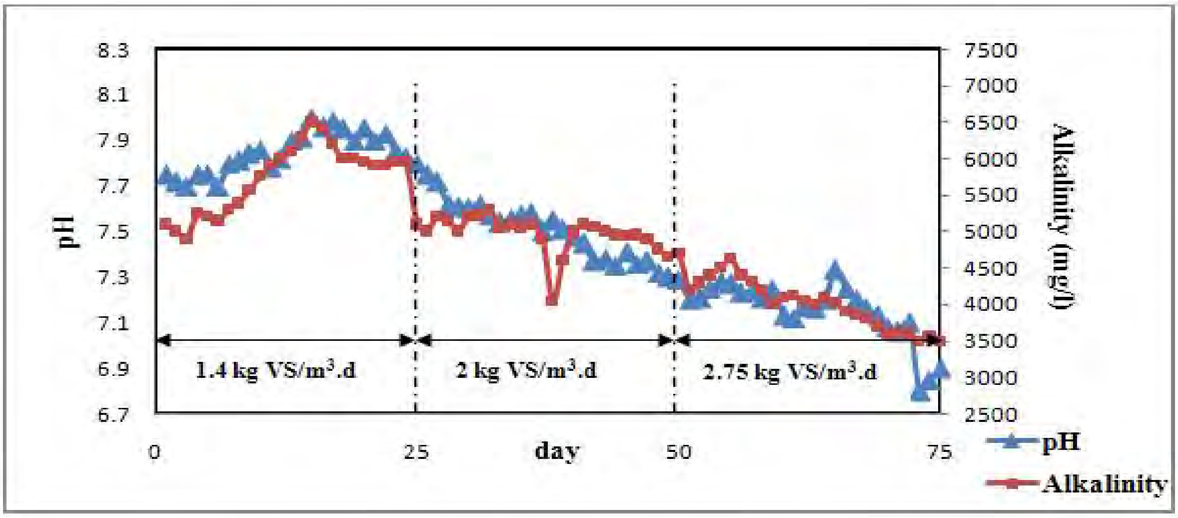

Fig. 4. Values of pH and alkalinity for various loading rates

In loading rate of 1.4 kg VS/(m^3.d), the COD concentration was decreased significantly after the completion of the retention time. While in run 2 and 3 higher concentrations of COD were observed. This can be explained that there was higher hydrolysis but less methanogenesis activities. In general hydrolytic bacteria are more robust to environmental condition.

3.3. Process efficiency

For the purpose of evaluating the effect of loading rate on the process efficiency, VS reduction and biogas yield were both taken into account as the indicators to assess the reactor performance and efficiency of each loading rate. VS degradation value of 88 % was achieved while operating loading rate 1.4 kg VS/(m^3.d). This VS reduction is higher compared with the result of 77.1% reported by Castillo [11]. By increasing the loading rate in run 2 and 3, VS removals were decreased to 80 % and 76 % respectively as illustrated in Fig. 5. The COD degradation was also decreased while organic loadings were increased. In run 1, the reactor stabilized and the COD was reduced to 65%, which corresponds to high efficiency of COD removal.

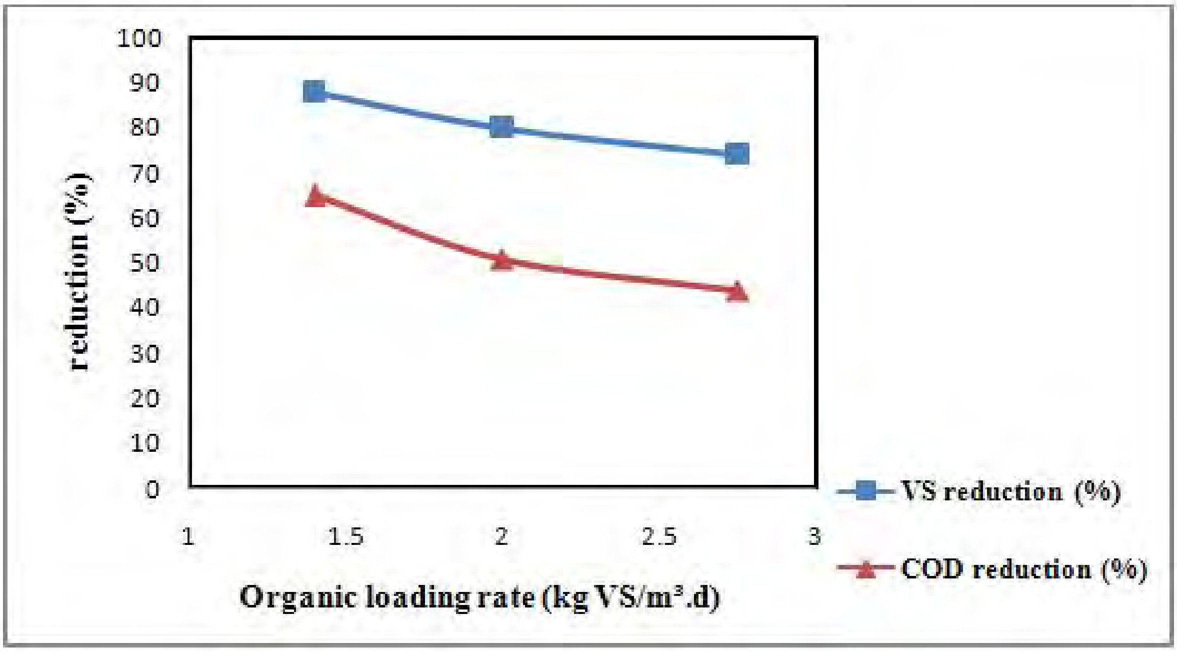

Fig. 5. VS and COD degradation for various organic loading rates

For further illustration, biogas and methane yield for various loading rates are presented in Fig.6. The highest biogas and methane yield observed was 0.4 m^3biogas/kg VS and 0.25$m^3$$CH_4$/kg VS in run 1 (1.4 kg VS/m^3.d). As the loading rate was increased, a gradual decrease in the biogas production (0.22 and 0.12 m^3biogas/kg VS in run 2 and 3 respectively) were observed. The overloading was marked by the fall in pH and gas yield and increase of carbon dioxide content in the biogas. In this study, the best results were obtained with an organic loading rate of 1.4 kg VS/(m^3.d). The biogas and methane yield of 0.4m^3biogas/kg VS obtained in this optimum loading rate was found to be satisfactorily successful when compared to literature data which were obtained using fruit and vegetable wastes (Table 2). It should be cautioned here that the optimum loading rate of 1.4 kg VS/(m^3 .d) observed here is not universal as the optimal rate depends upon the reactor configuration and other operating conditions.

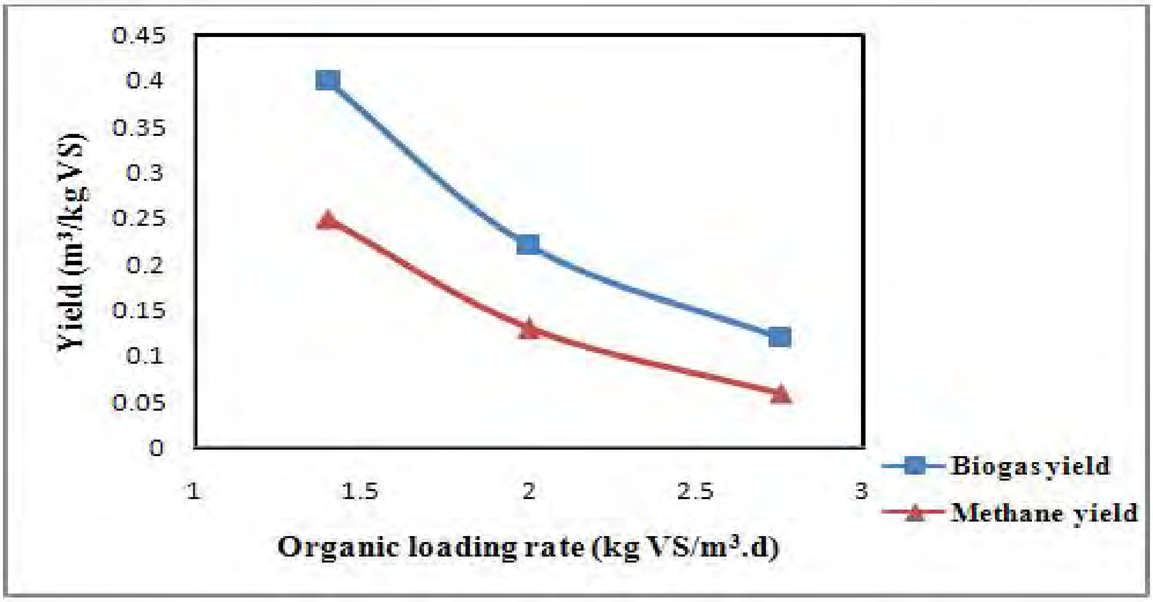

Fig. 6. Biogas and methane yield for various organic loading rates

Table 2. Performance data of different anaerobic process

Substrate	**Organic loading rates (kg VS/m^3.d)**	**Biogas yield (m^3/kg VS)**	**Methane (%)**	**Degradation (% of VS)**	**References**
Vegetable wastes	1.4	0.4	64	88	Current study
Organic fraction of municipal solid wastes	0.8	0.26	60	61	[12]
Municipal solid wastes	2.5	0.38	61	70	[13]
Fruit and vegetable wastes	0.3-1.3	0.3	54-56	67	[14]
Fruit and vegetable wastes	1.6	0.47	65	88	[15]

4. Conclusion

Anaerobic digestion is promising process for reducing the amounts of biodegradable waste in MSW stream and is also an energy producer from renewable resources. Considering the characteristics of the high-moisture solid waste, anaerobic digestion represents a feasible and effective method to convert the waste to biogas fuel. The reactor showed stable performance with highest methane (64%) with VS reduction of around 88% during loading rate of 1.4 kg VS/(m^3.d). Based on data from this study, OLR of 1.4 kg VS/(m^3.d) is suggested as design criteria with methane production rate of 0.25 m^{3}CH$_4$/kg VS input. Successful implementation of anaerobic digestion as the method of waste treatment leads to the regional utilization of renewable energy resources, as well as the disposal of high moistening content of MSW.

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Potential for the production of biogas in alcohol and sugar cane plants for use in urban buses in the Brazil

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Abstract: Brazil is one of the major alcohol and sugar producers in the world. The plants of alcohol and sugar cane have as waste the vinasse, which is used as organic fertilizer in the cane plantations and it cause contamination of the soil and water. The anaerobic digestion treatment can be used to reduce the pollution with vinasse, and at the same time increase the production of biogas. In this study, is proposed to find the potential of biogas production from anaerobic digestion of vinasse in Brazil and the availability of its use in urban buses as gas fuel. Biogas can be important to reduce the dependence of diesel, a non renewable fuel, in Brazil. Theoretical data of vinasse and biogas production, 14,6 m^3 of biogas per 1 m^3 of vinasse, were used to estimate the biogas potential. Using an estimated consumption of biogas in buses, 295,5 m^3 per bus with 400 km of autonomy per day, the total of buses supplied with biogas was estimated. The potential of biogas production estimated in Brazil by vinasse (2008/2009) is 4016892452 $m^3.crop^{-1}$ or approximately 20 million per day, which could replace 64,7% of the urban buses fleet in Brazil. A big plant of alcohol production has autonomy to supply 1018 buses per day. It has been assumed in this study the plant will produce biogas only during 200 days per year, in the others 165 days the buses could running with compressed natural gas (CNG) or the digesters can be fed on of bagasse's sugar cane as wet feedstock.

Keywords: *Bioenergy, fuel, vinasse, waste*

1. Introduction

Biomass is an important renewable source of energy in the world and its increasing has been useful to replace the fossil fuels. There are some kinds of agricultural feedstocks those can be converted in biofuels, as alcohol, biodiesel and others. The wastes of the process in food industries could be utilized for anaerobic digestion for biogas and biofertilizer production. The biofuels are expected to be one of the most important in the near future, because they will contribute to the decreasing of the global warming in the world.

The commercial sugar cane produced in Brazil is destined for alcohol and sugar production. The alcohol is utilized for domestic supply and exportation; it is available in Brazil since year 1973 as fuel in vehicles, mixed in the gasoline and in the bi-fuels vehicles. The alcohol is one renewable fuel and its combustion produces less pollution than fossil fuel. The wastes produced in the processing of alcohol and sugar is the bagasse and the vinasse.

The sugar cane industrialized in Brazil, increased 47% in five years, reaching 569063 million of tonnes in 2008/09 crop, where the central south of Brazil is responsible for 89% of the production. [1]. An increasing of the exportation of sugar and the high consumption of alcohol in Brazil have been the mainly factors of expansion the sugar cane production and its processing.

Sugar cane after the harvest gets to the mill and the juice is extracted and leavened, then the results are the alcohol and a raw material called vinasse, which is produced at high temperature and has a high chemical oxygen demand (COD), organic matter and high polluting power. In Brazil the plants of alcohol use the vinasse as a fertilizer directly applied in the soil, because it is rich in potassium. On the other hand, there is a limit of application by the environmental agencies [2,3]. The major problem of the vinasse application is the possibility of its flowage to rivers and lakes, specially during rainy days. Moreover there is the risk of contamination the superficial water, which is response to the supply of water in some cities and rural community. In some regions of Brazil the locals environmental agencies has not powerful and the owners of sugar and alcohol plants does not respect the law.

Vinasse before disposed in the soil, should be treated in anaerobic reactors as a thermophilic UASB [2]. This kind of treatment will produce the biofertilizer and biogas. The table 1 shows the physical chemical parameters of the São Martinho Industry of Sugar and Alcohol before and after the biodigestion [4,5].

Table 1. Physical and chemical parameters – São Martinho Industry of Sugar and Alcohol.

Parameter	Vinasse before the digestion	Vinasse after the digestion
pH	4,0	4,9
Chemical oxygen demand, COD ($mg.L^{-1}$)	29.000	9.000
Nitrogen total, N ($mg.L^{-1}$)	550	600
Phosphor, P2O5 ($mg.L^{-1}$)	17	32
Sulfate, SO2 ($mg.L^{-1}$)	450	32
Potassium, K2O ($mg.L^{-1}$)	1.400	1.400

According to table 1, the anaerobic digestion of the vinasse will reduce the organic charge, but the power as fertilizer will remain the same. On the other hand the plant of sugar and alcohol will produce biogas.

According to [3] biogas is composed of methane (40-75%), dioxide of carbon (25-40%) and other compounds. The biogas can be used as biofuel in engines of internal combustion. In this study is proposed estimate the supply of urban buses with biogas produced in the big plants of sugar and alcohol in Brazil.

2. Methodology

The production of biogas of vinasse and the bus supply capacity were estimated using data from literature. The most of plants of cane processing are placed in central south region of Brazil, where the cities of São Paulo, Rio de Janeiro, Belo Horizonte, Brasília, Goiania, Curitiba and Porto Alegre are situated. The biggest plant of sugar and alcohol in Brazil is São Martinho, which process about 40.000 $ton.day^{-1}$ of sugar cane, during approximately 200 days per year [1] and is close to São Paulo.

According to [4,6], the production of 1 liter of alcohol discharges 10 liters of vinasse and with the digestion of 1 m^3 of vinasse approximately 14,6 m^3 of biogas are produced. These values were used to estimate the production of biogas and vinasse in the plants of sugar cane studied and the total estimation of biogas production in Brazil.By using data of alcohol production in Brazil and in the plants of production obtained of UNICA [1], was possible estimate the production of vinasse and biogas.

According to literature [7,8,9] the biogas (55% methane) has an energy value of 20,8 $MJ.m^{-3}$ and the diesel has 36,4 $MJ.L^{-1}$. In the composition of biogas, there are approximately 55% of methane (CH_4), which has a specific mass of 0,714 $kg.m^{-3}$, then 1 m^3 of biogas is equivalent 0,393 kg of methane [8]. The currently specific consumption of diesel in one bus is 0,40

L.km^{-1} [10,11]. Once upon time the bus autonomy assumed is 400 km per day, the diesel daily consumption of one bus is 160 liters, which has an equivalent energy of 5824 MJ.

Volvo's bus has an autonomy of 400 km running with compressed natural gas cylinders (200 bar) of 1055 m^3 and weigh 136,20 kg [10]. If compressed natural gas has an energy value of 47,5 MJ.kg^{-1} [9], then a volvo's bus consumes a daily energy equivalent of 6469,5 MJ. Analysing the data above, was estimated a daily medium biogas consumption of approximately 6147 MJ per bus or 295,5 m^3 of biogas per bus. These data were utilized in the estimation of the number of bus supplied with biogas.

The data of the bus fleet in Brazil were obtained from CNT and ANTT [12,13], and the estimation of carbon emission by bus was made using the index 74.100 kg CO_2.TJ^{-1} of diesel found in the guidelines of IPCC [14], this index is 2,61 kg CO_2.L^{-1} or 0,71 kg C.L^{-1} of diesel, and was useful to estimate the decreasing of carbon emission with the replacement of diesel for biogas.

3. Results

Table 2 below shows the production of alcohol in Brazil and the estimated production of vinasse. The alcohol production were obtained from UNICA [1]. The amount of vinasse disposal in the environment in 2008/09 crop was 275 million of m^3, certainly it caused a high environmental impact in Brazil polluting the water and soil. The production of vinasse increases a rate of 12,7% per year since 2000/01 to 2008/09 crop. Brazil has between 12 and 20% of the potable water in the world and the increasing of the sugar cane industries could be a threat because of the directly disposal of the vinasse on the soil. If the vinasse would have been treated in anaerobic reactor the impact would be less.

Table 2. Production of alcohol and estimated vinasse production in Brazil .

Crop	Alcohol production in Central South (m^3)	Alcohol production in North Northeast (m^3)	Total alcohol production in Brazil (m^3)	Total Vinasse estimated in Brazil (m^3)
00/01	9064364	1528671	10593035	105930350
01/02	10176290	1359744	11536034	115360340
02/03	11152084	1471141	12623225	126232250
03/04	13068637	1740068	14808705	148087050
04/05	13591355	1825313	15416668	154166680
05/06	14352542	1594452	15946994	159469940
06/07	16006345	1712864	17719209	177192090
07/08	20333466	2193358	22526824	225268242
08/09	25101963	2410999	27512962	275129620

With the vinasse disposed in 2008/09 crop could produce 4016892452 m^3 or 20 million m^3 per day of biogas, enough to supply 67968 buses, or better, 64,7% of the Brazilian fleet of urban bus, which have been estimated on 105000 buses in 2008 [12].

The biogas that could be produced in Brazil, only with vinasse (4 billion m^3, 2008/09), correspond to 40% of the biogas produced in Europe, 10 billion m^3, in 2005, which is derived essencialy from landfills (64%), degradation of urbans and industrial waste (18,8%), and agriculture and energy crops (17,2%) [15]. According a study aimed in Brazil [3], the potential of biogas from vinasse estimated was 2,74 billion m^3 (2003/04). Both studies show that Brazil has an enormous potential of biogas production by vinasse.

Table 3 presents some plants of sugar and alcohol localized in the central south region and the respective capacity of biogas and biomethane production.

Table 3. Production of alcohol and estimated vinasse in central south region of Brazil(2008/2009) .

Industry of alcohol	Alcohol m^3/crop 08/09	Vinasse m^3/crop 08/09	Biogas m^3/day	Buses (400 km of autonomy per day)
São Martinho	411991	4119910	300753	1018
Equivap	347298	3472980	253528	858
Da Barra	315804	3158040	230537	780
Santa Elisa	246591	2465910	180011	609
Colombo	200093	2000930	146068	494
Santa Candida	142436	1424360	103978	352
Santo Antônio	111615	1116150	81479	276

Figure 1 and table 3 presents the number of buses that could be supplied for the industries of alcohol above. The biggest industry (São Martinho) could supply 1018 buses per day, which represents 2,7 % of replacement the diesel fleet running in the city of São Paulo.

A big plant milling of 40.000 ton.day^{-1} could supply 1018 buses and a smaller plant milling 12.500 ton.day^{-1} 276 buses. In São Paulo state there are 145 plants with milling between 40.000 and 4.000 ton.day^{-1}, those would supply all buses of São Paulo city with biogas. The advantage is that they are not placed far from São Paulo city.

According to literature [10], in 1996 the bus fleet that could be fuelled with biogas from landfills of São Paulo city were estimated in 3005 buses which could supply 8% of the São Paulo's fleet currently. In comparison, three big plants of sugar and alcohol (milling 40.000 ton.day-1) could produce the same amount of biogas.

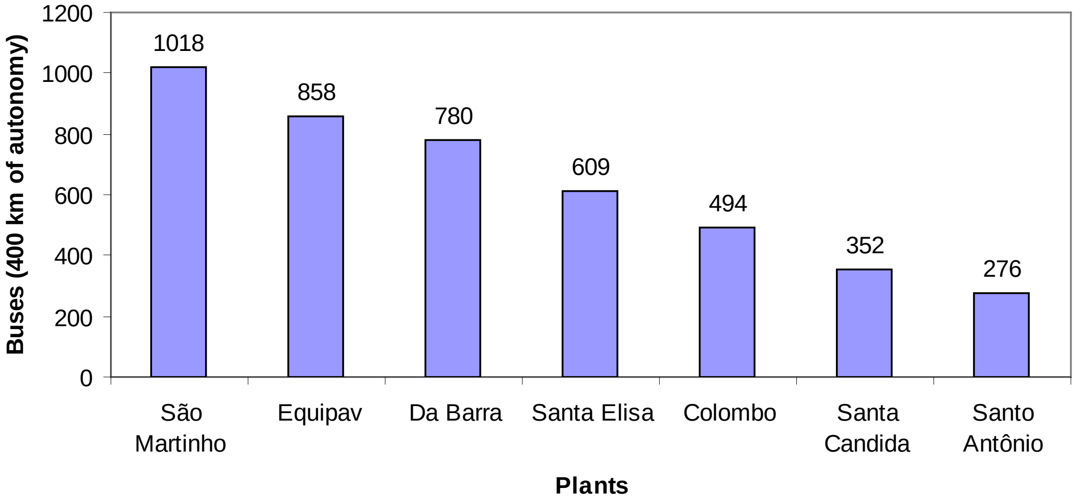

Fig. 1. Number of buses possibly supplied by industry of alcohol.

The total replacement of the bus fleet of São Paulo city for biogas could avoid the emission of 4,3 ton.day^{-1} of carbon from fossil fuel (diesel) into atmosphere.

One limitation in this study is that the plant will produce biogas only during 200 days per year, in the others 165 days the buses could running with compressed natural gas (CNG) or the digesters can be use the bagasse's sugar cane as wet feedstock.

Figure 2 presents the bus fleet running in the big cities in Brazil in the year 2007 [13].

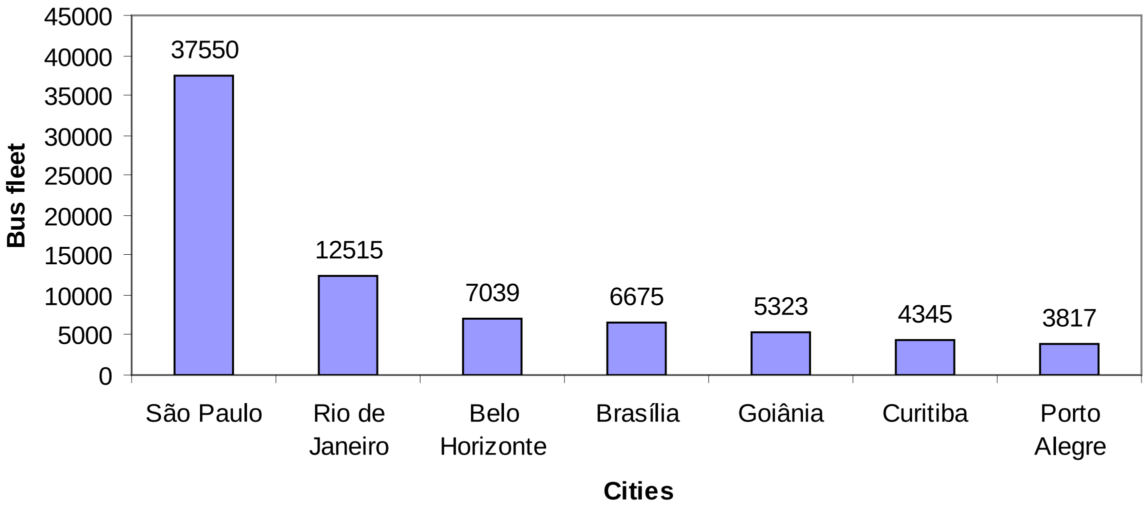

Fig. 2. Bus fleet in the mainly cities of central south region from Brazil (2007).

The possibility of replacement the buses to run with biogas could became the big cities in Brazil more sustainable, by other hand there are technical and market limitations. The gaseous form of biogas at normal temperature and pressure require its compression in cilynders to be used and, the cost will increase.

There is a lack in technology innovation to convert the vinasse to biogas in Brazil. Surely , the use of diesel is aconomically better than biogas to the owner's buses and the utilization of biogas feasibility depends of financial and policy incentives by the government.

In Brazil there is other forms of feedstocks to biogas production which could be explored togheter with vinasse and, the biogas in set with liquid biofuels (alcohol and biodiesel) could help the big cities of the country became more sustainable. By other hand the urban transport system need to be organized before this. The major of the big cities in Brazil need create BRT's as Curitiba city, an international reference.

The economy of Brazil is growing quickly and there is yet a lack of development in technological innovation in diverse sectors of economy, specilly in the development of the new forms of renewable energy, wich could help it increase with an economy sustainable.

4. Conclusions

With the increase rate (12,7% per year) of the vinasse disposal in Brazil, the better option is to promote the anaerobic digestion of the vinasse and produce biofertilizer and biogas. Brazil has a great number of buses, running mainly in the central south region cities, that could use the biogas as fuel replacing the diesel.

The biogas that could be produced with digestion of vinasse in Brazil had been estimated in 20 million m^3 per day, enough to supply 67968 buses, or better, 64,7% the Brazilian fleet. The use of the biogas to supply this fleet could reduce the emission of carbon from fossil fuel diesel in 21 $ton.day^{-1}$.

Acknowledgments

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Brazil's potential for generating electricity from biogas from stillage

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Abstract: The aim of this study was to evaluate potential of vinasse as an alternative source of electricity generation through the burning of biogas produced by anaerobic digestion process. The stillage residue is a process of producing ethanol, used as fertilizer on farming’s, but with environmental problems of its application. This study was conducted on the basis of theoretical data to calculate the potential for methane generate and energy. Our purpose is to use an up flow anaerobic-UASB to accomplish the digestion of stillage and engines to burn the gas and electric power generation. The paper presents a case study of a distillery with a production of 580 m^3 day^{-1} ethanol. In Brazil in the harvest 2009/10 would have produced the stillage potential to produce 1.81 billion m^3 of methane and 4.070 GWh of energy. Whereas the case study of sugarcane in the interior of Parana, are produced 5,800 m^3 day^{-1} stillage, with the potential to generate 2.75 MWh of electricity $month^{-1}$, which results in a income of US$ 218,586,32 a month. The use of vinasse as a source of energy has great potential energy for Brazil.

Keywords: *Cane Sugar, Anaerobic Digestion, UASB, Renewable Energy.*

1. Introduction

Sugar cane is as one of the most promising crops of the country to generate energy through biomass. To produce 1 m^3 of alcohol are needed 13 tons of cane sugar, which should generate 10 m^3 of slop, this figure varies from 10 to 15 m^3. Due to nutrient content, stillage is used of fertigation, as far as not even there an alternative more practical and economical use of this waste, and in this case, there is an effective cost reduction with fertilization [1].

Despite the significant amount of fertilizer, this residue has a huge potential for generating energy by converting organic matter into methane, while minimizing any risk of accidents during handling of this waste, facilitating its application in agriculture due to increased pH neutralization of the effluent [1], [2].

The use of vinasse as fertilizer causes concern because of their high degree of impact when distributed in the environment, while there are technological mastery of the chain of sugar cane, today there is real need for studies to would define the best rate application in the extrinsic characteristics of soil and vinasse [2].

Due to the chemical oxygen demand (COD) is the a wastewater stillage with high pollution potential. The reason for this striking power is due to the high content of colloidal organic matter, which leads to oxidation of virtually all the available oxygen in the water. The use of stillage for biogas production is an alternative that may become viable economically and environmentally by three points: treatment of the waste, producing biogas for electricity generation and still has treated fertilizer of application in farming’s [2].

With the increase of ethanol production in recent years, there was increased production of vinasse, increasing the environmental risks of its application in nature. Seeking an alternative for the treatment of stillage and also produce renewable energy, the objective this study was to evaluate the potential use of vinasse as an alternative biomass in the Brazilian energy as a source of generating electricity by burning biogas generated by anaerobic digestion process.

2. Methodology

This paper is an exploratory literature research and a case study, based on published data in literature. The sources consulted for the preparation of this work were government agencies and the productive sector of sugar cane from Brazil, using historical data from the past 20 years, compared to growth of the ethanol market in Brazil during this period.

Data regarding the production of sugar cane and ethanol were obtained from the Union of Industries of Cane Sugar (UNICA) [3], the representative organization of the sugar and ethanol from Brazil. The paper presents the process of biogas production in an up flow anaerobic reactor (UASB reactor), demonstrating feasibility aspects of the project.

The feasibility of anaerobic treatment of vinasse in Brazil was confirmed with the use of UASB reactors (reactors and up flow anaerobic sludge blanket) under conditions mesophilic and thermophilic and reactor fluidized, both with suspended biomass [2]. The UASB reactor enables the movement of stillage through a region with high concentration of microorganisms. This reactor allows the separation of solid phases, liquid and gas, with the gas being driven to the top and solids and liquids directed.

Following suggestion from Rego and Hernandez [1], the biogas collected should be sent to a pressurized gas tank in which pressure is maintained at 1.15 bar for a diaphragm. For safety and to prevent leaks, any possible unused of gas will be automatically sent to burn. The treated effluent will be sent through channels to ponds or storage tanks for later be used as liquid biofertilizer.

Table 3 shows the parameters used in the work to convert the theoretical potential for electric energy production of vinasse into electrical energy by burning biogas produced by its anaerobic digestion in UASB.

Table 1. Parameters used for the elaboration of the potential for energy production

Parameter	Indicator	Unit	Reference
Vinasse production	10	m^3 m^{-3} of ethanol	[3]
Ethanol production	90	L t^{-1} cane	[3]
COD typical of vinasse	20	kg m^{-3}	[4]
Concentration methane in biogas	60	% Methane	[5]
Typical production of methane	0.35	Nm^3 kg^{-1}CODremoved	[6]
Net calorific value of methane	35.558	kJ Nm^{-3}	[7]
Overall efficiency of motor-generator	26	% to IBW	[8]
Energy	9.88	kWh m^{-3} methane	Calculated from the PCI methane
Amount received from sale of energy	79.41	US$ MWh^{-1}	[9]
Dollar exchange rate (US$ 1.00)	1.70	R$	Commodities- BMF

Nm^3=normal m^3

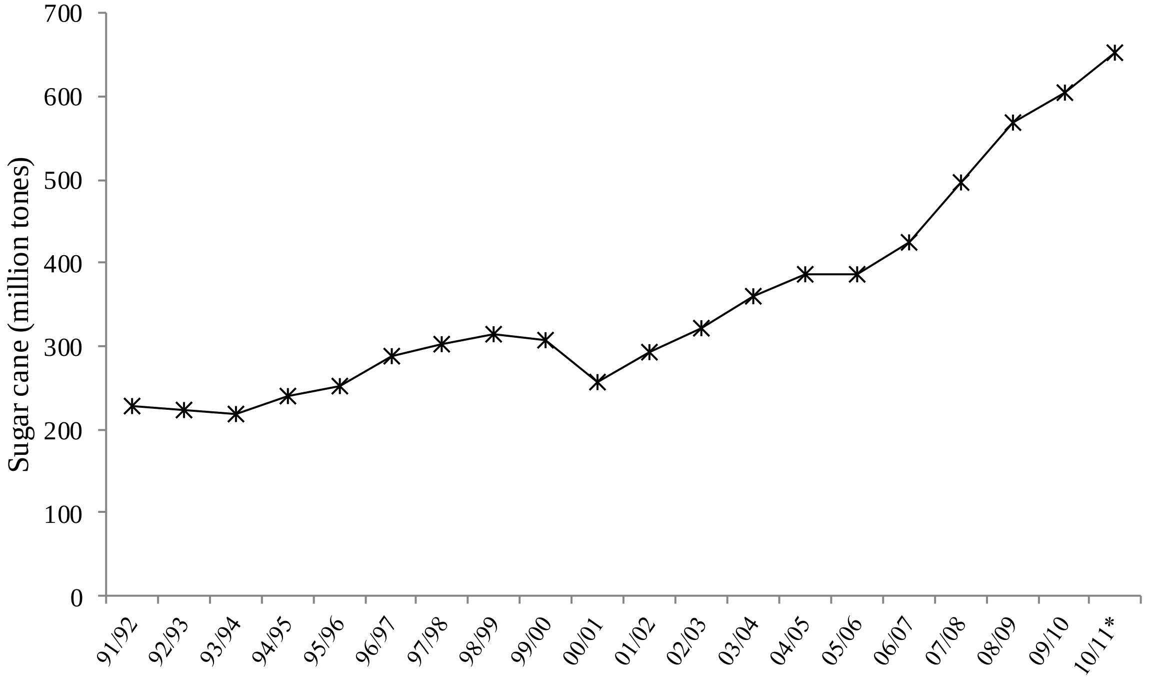
For the calculations were accounted directly the amount of methane produced, discounting the other gases present in the biogas, using the theoretical stoichiometric value of 0.35 m^3 CH4 kgDQO^{-1}removed [6].

Contributing to the analysis, presents a case study from a plant producing 580 m^3 day^{-1} of ethanol, located within the State of Parana. With data from ethanol production proceeded to the calculations of potential generation vinasse quantity and biogas produced, and how much electricity could be generated using internal combustion engines to gas burning. The production of vinasse this plant is 5,800 m^3 day^{-1}, since for each m^3 of ethanol is produced approximately 10 m^3 of vinasse.

The selling price of electricity was calculated based on power purchase auctions conducted by ANEEL (National Electric Energy Agency), federal government agency that regulates power sector. The available data were processed in a spreadsheet, for construction generation of graphs and figures of the potential production described [9].

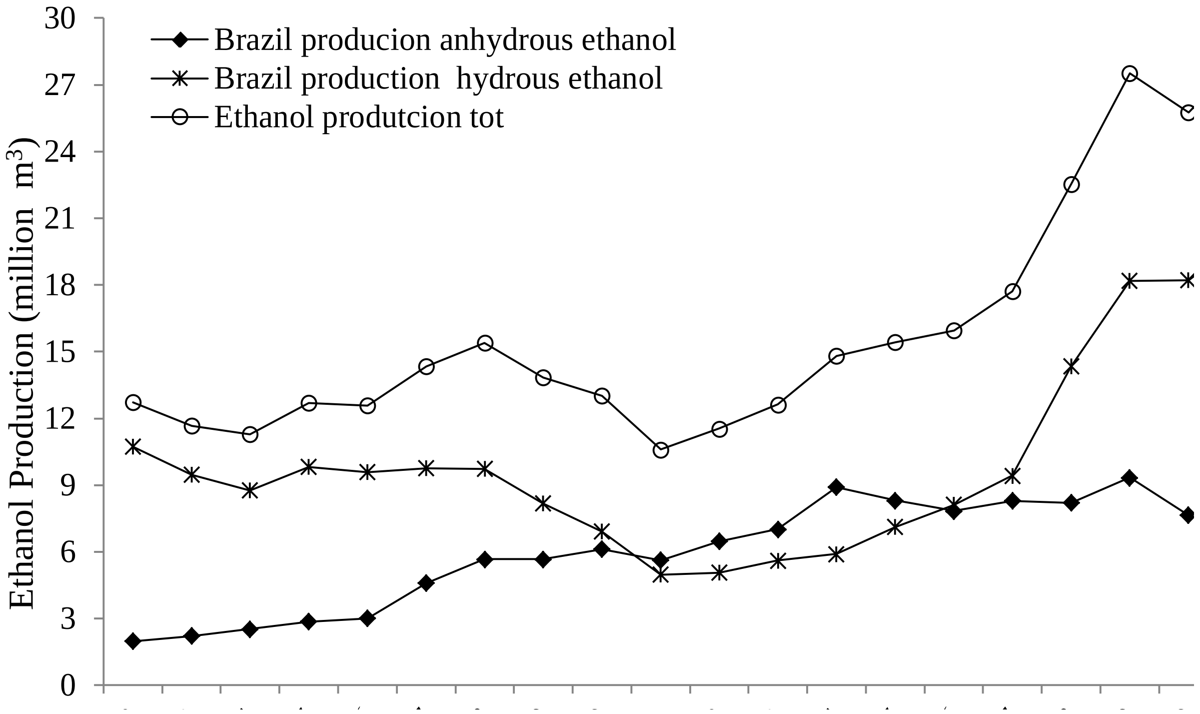
3. Results

Brazil is the world's largest producer of sugar cane, Brazilian mills in the harvest 2009/10 sued 604.514 million tons (Figure 1), with estimates for the harvest 2010/11 season to process 651.514 million tones [3].



** Projection for the harvest 2010/11*
Fig. 1. Sugar cane processed by mills in Brazil for sugar and ethanol.

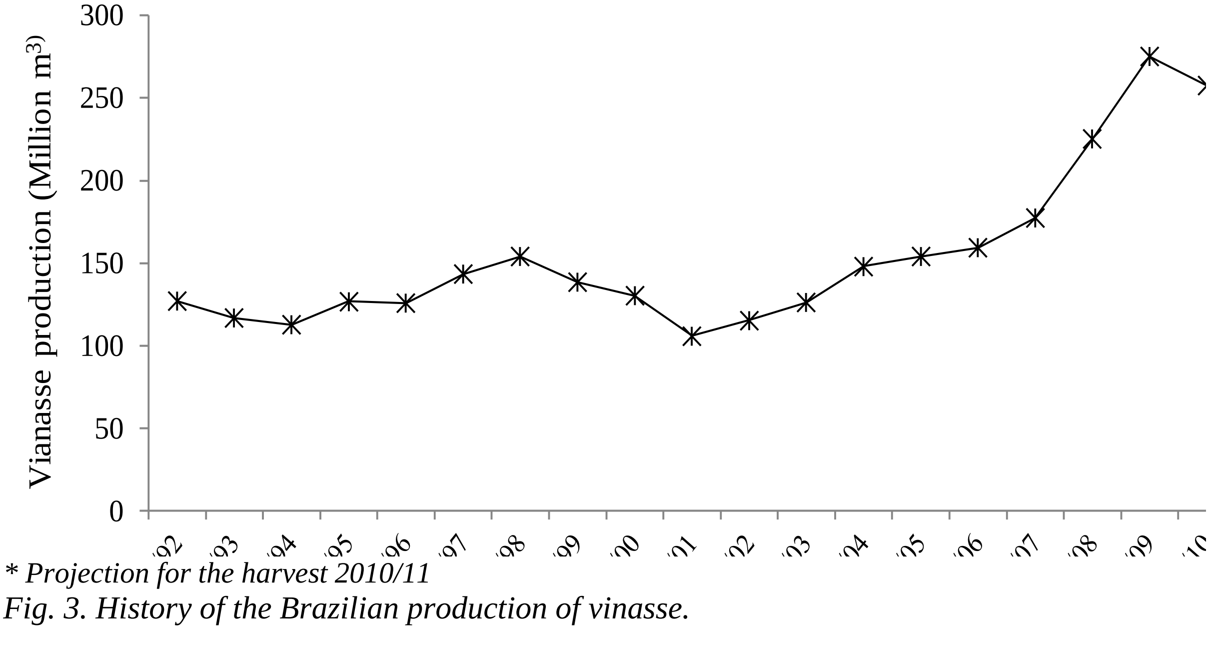
Recent years have seen average growth of 14.6% per annum on the amount of sugar cane processed in Brazil, from 229.22 million tons in the harvest 1991/92 to 604.51 million tons in 2009/10, with growth forecast to 1 billion tons by 2015, up almost 50% over the 2009/10 crop, increasing production of ethanol and sugar and generating more effluent.



** Projection for the harvest 2010/11*
Fig. 2. Comparative history of Brazilian ethanol anhydrous, hydrated and total production

Looking at Figure 2, it appears that, in the harvest 2009/10 ethanol production was 25.8 million m^3, being 70.7% (18.2 million m^3) with ethanol and 29.3% (7.6 m^3) of anhydrous ethanol. Recent years was seen huge increase in ethanol production, mainly hydrated for use as fuel in car engines that run on ethanol or flex fuel. Also according to the data the average productivity of ethanol was 90 L t^{-1} of sugar cane, a little above the average that is 85 L t^{-1} [3].

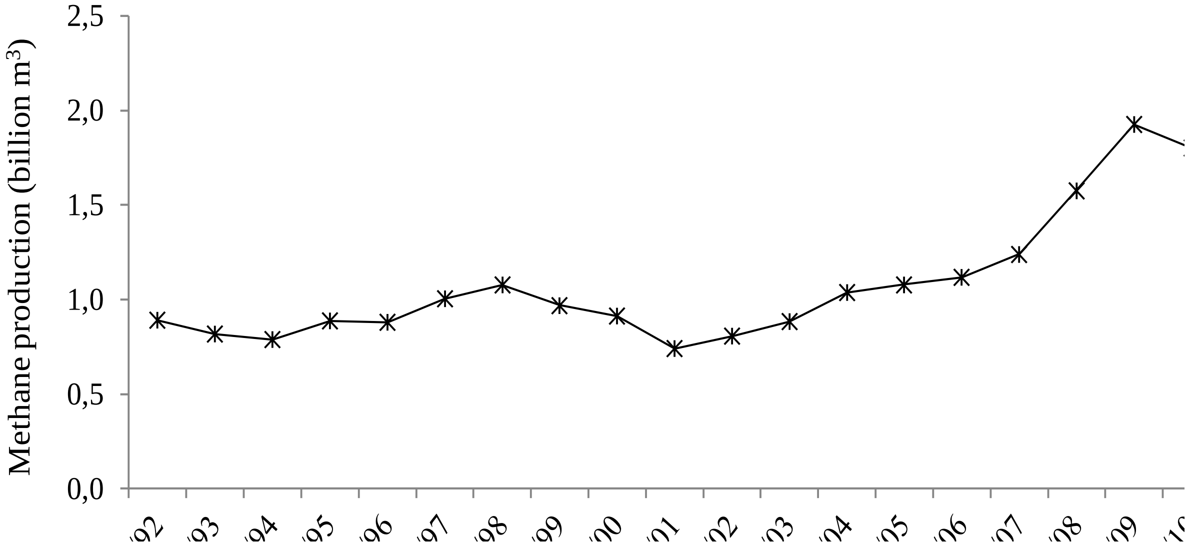
In Figure 3, can be observed the potential production historic of vinasse in Brazil from the production of ethanol, whereas to produce one liter of ethanol are produced on average 10 liters of vinasse.



** Projection for the harvest 2010/11*
Fig. 3. History of the Brazilian production of vinasse.

According to literature data, it was found that for every liter of ethanol production, results in an average of 10 liters of vinasse. The potential for production of vinasse in Brazil in the harvest 2009/10 was 257.63 million of m^3 (Figure 3), for the harvest 2010/11 the forecast is a production of 284.17 million m^3, an increase of 26 million m^3 compared the previous harvest.

Figure 4 presents the potential for methane production from vinasse in Brazil, considering that the whole stillage was treated by anaerobic digestion in UASB reactor type.

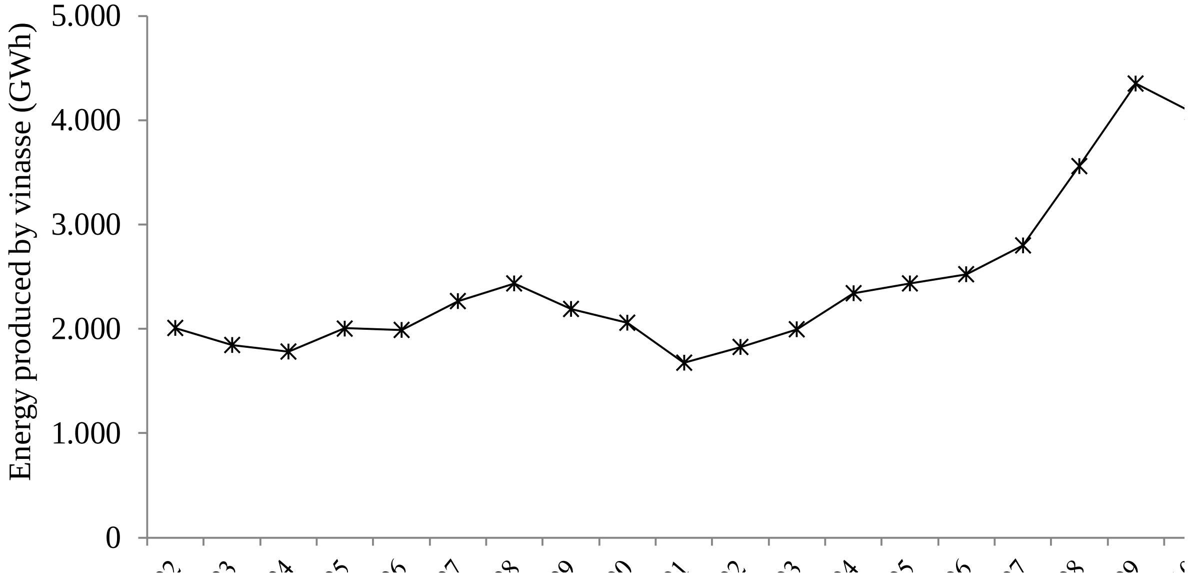


** Projection for the harvest 2010/11*

Fig. 4. History of the potential production of methane from the digestion of vinasse

The potential for methane production in the harvest 2009/10 would be 1.81 billion m^3 (Figure 4) for 2010/11 forecast of 1.98 billion m^3, considering that the whole stillage produced by plants was transforming into methane gas, which could be burned in engines to generate mechanical energy or thermal energy, and transformed into electrical energy.

Figure 5 shows the historical potential of generating electricity from the burning of biogas from the digestion of vinasse in UASB reactors, using internal combustion engines.



** Projection for the harvest 2010/11*

Fig. 5. History of the potential for electric energy production by vinasse.

The historical potential for generating electric power from the stillage (Figure 5), if it was all treated in digesters and the biogas gotten burned for power generation. If added all the production of the last 20 years, we would have a potential to generate 50,700 GWh of electricity.

For a production of 605 million tons of processed cane sugar in Brazil in the harvest 2009/10, using the anaerobic digestion process, we obtain a potential to produce approximately 1.4 billion m^3 of methane, would amount to 4.075 thousand GWh of electricity, equivalent to about 5% of the generation of the Itaipu plant, the world's largest hydroelectric dam, which generated during the year 2009 produced 91 thousand GWh, almost 20% of Brazilian electricity , which totaled to 466.16 thousand GWh in 2009.

3.1 Commercialization of energy produced

In the 2009/10 cane crop, the potential value received by throughout the production of energy, sold at a price of US$ 79.41 MWh (MWh price paid by system auctions conducted by ANEEL), generating revenues of US$ 323.6 million for the plants, by the production of 4.075 GWh of electrical energy.

3.2 Case study

The following table (Table 2) presents a case study of a sugar and ethanol located in the State of Parana, Brazil. The facility has an area of approximately 6,000 ha of planted area, between owned and leased areas and a producing 580 m^3 of alcohol/day.

Outcome of case study of an ethanol plant

Parameter	Indicator	Unit
Vinasse production	5,800	$m^3\ day^{-1}$ (241.67 $Nm^3\ h^{-1)}$
Methane gas production	40,600	$Nm^3\ d^{-1}$ (1691.6 $Nm^3\ h^{-1)}$
Power generation	91,752.28	kWh day^{-1} (91.75 MWh day^{-1})
Produced energy monthly	2,752.57	MWh $month^{-1}$
Monthly price from the sale of energy	218,586.32	US$ $month^{-1}$

The plant produces 5,800 m^3 daily stillage, which is used in fertigation of planting areas of the plant. Itself this stillage was used to produce methane gas ode through the process of anaerobic digestion in UASB reactor, would have a potential to generate 91.75 MWh day^{-1}, or 2.75 thousand MWh $month^{-1}$. If this energy was marketed at prices current (US$ 79.41 MWh) would generate revenues of US$ 218,586.32 month for the plant, beyond diversify their revenues.

4. Discussion and Conclusions

For this study, was used a potential of producing 10 liters of vinasse per liter of ethanol, the literature speak that to each liter of ethanol are produced 10 to 15 liters of vinasse [11], other authors argue that in producing 1 liter of ethanol produces a quantity minim than 10 liters of vinasse [12].

With respect to COD from stillage, the literature says that every m^3 of ethanol generates 200 to 500 kg of COD, in study was considered a minimum quantity of 200 kgCOD m^{-3} ethanol. From the amount of COD was estimated production potential of methane [13], [2].

The calorific value of biogas is variable and is in the range from 22.500 to 25.000 kJ m^{-3}, admitting the methane with about 35,580 kJ m^{-3}. This means a recovery from 6.25 to 10 kWh m^{-3} [14]. Due to the high concentration of methane in the biogas and consequently your potentially flammable, the main applications are in generating heat, cold and power [11].

Studies show that for the harvest 2004/05, the potential for producing electricity using the biogas produced by digestion of vinasse in motor-generators, internal combustion was 9.292 TJ $year^{-1}$ (2.6 TWh $year^{-1}$), representing 0.75% of national consumption of electricity in the year 2003 [5], data similar to those found in this work, where for the harvest 04/05 identified a potential to generate 2,43 GWh.

Lamo has built a prototype plant for the demonstration, consisting of a production unit (reactor of 120 m^3), purification, compression and use of biogas. This plant produced gas fuel at levels up to 0.35 m^3CH4 $kgCOD^{-1}$removed [15], agreeing with data of Cabello [16], that working with Ralf (fluidized bed reactor) also reached this relation.

Granato and Silva [2] performed a case study in a distillery with capacity to produce 600 m^3 day^{-1} of ethanol, as a result of digestion of stillage generated, they obtained a production of 75,600 Nm^3biogas day^{-1}. Considering a gas turbine efficiency of 35%, production would be 6,540 kWh of electrical energy alternative.

The stillage represents an important potential for renewable energy generation in Brazil, being a residue of ethanol production, which can generate energy and still be used as an important source of fertilizer for crops, in addition, your treatment will reduce environmental risks their application in nature.

Acknowledgements

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Electricity generation from biogas of poultry slaughterhouse biomass in Matelandia – Brazil

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Abstract: Brazil has great potential for biomass production. There are several processes to convert biomass into energy, among these is the biological conversion of organic carbon into methane. This work aimed to estimate the production of biogas in a poultry slaughterhouse in Matelandia state of Paraná, Brazil, by the IPCC methodology. The poultry slaughterhouse slaughter 140,000 poultries a day and generates a wastewater FLOW OF 3,360 $m^3.d^{-1}$. Electricity consumption by the industry plant is about 3,600 $MWh.month^{-1}$. The treatment system used in industry is the physical and biological process, and the pre-treatment consists of a static sieve and a flotation equipment, followed by stabilization ponds. Two anaerobic ponds were covered with a geomembrane of High Density Polyethylene and was installed a gas meter to measure the flow rate of biogas production. The biogas generation potential estimated can reduce 3.89% of the electricity consumed.

Keywords: *Bioenergy, Anaerobic digestion, Wastewater, IPCC.*

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1. Introduction

In the past decades, the consumption of meat chicken in many countries has been on the increase. As a result of the growing poultry industry, poultry slaughterhouses are producing increasing amounts of by-products and wastes[1].

The production and export of chicken meat perform an important role in the Brazilian economy. According to the ABEF - Brazilian Association of Chicken Producers and Exporters, in 2009, Brazil was among the international reach first place in the export sector and third in world production of chicken meat, behind the United States and China. The southern region of Brazil has an important role in the achievement of these data, because it focuses on the major poultry production and consequently the processing industries of chicken meat, accounting for approximately 75% of national production. The State of Paraná is the largest producer of chicken meat from Brazil, exporting in the year 2009 a total of 954,653 5 tonnes of chicken meat[2].

The interest in recovering the biogas generated by stations for sewage treatment, urban solid waste landfills, residue of sugar cane, by the biodigestion of the vinasse, livestock manure anaerobic digestion and poultry slaughterhouse wastewater associated with its energetic use and managing these residues, have been discussed in Brazil[3].

Anaerobic digestion is a biological process that occurs in the absence of oxygen, where organic matter is degraded and transformed in gaseous mixture called biogas. The biogas composition is highly variable depending on various aspects like the characteristics of biomass and environmental conditions offered. The average composition of biogas has the following values: CH_4 (50-75%), CO_2 (25-50%), N_2 (0-10%), H_2 (0-1%), H_2S (0-3) and O_2 (0-2)[4].

Wastewater as well as its sludge components can produce CH_4 if it degrades anaerobically. The extent of CH_4 production depends primarily on the quantity of degradable organic material in the wastewater, the temperature, and the type of treatment system. With increases in temperature, the rate of CH_4 production increases. Below 15°C, significant CH_4 production is unlikely because methanogens are not active and the lagoon will serve principally as a sedimentation tank. However, when the temperature rises above 15°C, CH_4 production is likely to resume[5].

This paper objectives to evaluate the potential for methane production in a poultry slaughterhouse by the IPCC methodology, and the potential for generating electricity from the energy use of the methane produced in anaerobic digestion process.

2. Methodology

2.1. *Water consumption and wastewater characteristics in poultry slaughterhouses*

The according to the sanitary requirements related to processing and industrialization of meat, the demand for water in this activity is high, it can be considered an average consumption of 25 a 50 L[6], 25 L[7,8] ou 17 L a 20 L by poultry slaughtered[9].

It is recognized that minimising water consumption and contamination has wide reaching environmental benefits. Increasing the volume of water used automatically affects the volume of waste water which has to be treated at either an on-site or a municipal waste water treatment plant. Water makes contact with a carcass or any animal by-product, whether during production or cleaning, contaminants such as fats or blood are entrained and these increase the burden on the waste water treatment plant. In many cases the water used is hot, so energy will have been used to heat it. Also the fats can melt in hot water and then become more difficult to separate from the water[5].

The references of wastewater characteristics available in the literature described in Table 1, have several values due different water consumption by poultry slaughtered, operational practices, size of the industry, collecting the effluent at different points, among others.

Table 1: Characteristics of wastewater poultry slaughterhouse

References	**COD ($mgO_2.L^{-1}$)**	**BOD ($mgO_2.L^{-1}$)**
AGUILAR, et al., 2005[10]	5,400	2,760
CHAVEZ, et al., 2005[11]	7,333	5,500
DORS, 2006[12]	6,720	4,434
MARQUES, 2007[13]	4,325	3,346
DE NARDI, et al., 2008[14]	6,880	-
AMORIM, et al., 2008[15]	3,102	-
MATSUMURA & MIERZWA, 2008[16]	9,115	4,593

2.2. *Characterization of the case study*

The industrial plant slaughter 140,000 $poultry.d^{-1}$, generating a flow of wastewater from 3.360 $m^3.d^{-1}$, resulting in 24 $L.poultry\ slaughtered^{-1}$.

The wastewater treatment system use in the industry is compound by categories pre-treatment, primary and secondary through the physical and biological processes. Pre-treatment consists of a static sieve to remove solids, the primary treatment in flotation equipment for the physical process for removal of oils and greases and secondary treatment is the arrangement of two biodigesters in parallel, an aerated pond with aeration sub- surface endowed with aerators and 6 also air vents and a facultative pond.

The main physical and chemical characteristics of wastewater are COD average Biodigester influent: 3,390 ± 1,275 mg L^{-1} and COD average Biodigester effluent: 1,205 ± 300 mg L^{-1}.

Measurements of water consumption were made by water meters installed at seven points of the production process, which resulted in consumption values by sector.

The industry in question has a demand of 3,360 $m^3.d^{-1}$ accounting for water consumption in all productive sectors, from receipt of the birds, washing trucks, bleeding, scalding, evisceration, cooling room, cuts, water sanitation cleaning equipment and industrial plant, boiler until the dispatch of meat.

Electricity consumption from the poultry slaughterhouse is 3,600 $MWh.month^{-1}$, resulting in approximately 1.07 $kWh.poultry\ slaughtered^{-1}$.

2.3. *Estimate of the methane potential production*

The principal factor in determining the CH_4 generation potential of wastewater is the amount of degradable organic material in the wastewater. Common parameters used to measure the organic component of the wastewater are the Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Under the same conditions, wastewater with higher COD, or BOD concentrations will generally yield more CH_4 than wastewater with lower COD (or BOD) concentrations[5].

Considering the IPCC Guidelines for National Greenhouse Gas Inventories – Chapter 6: Wastewater Treatment and Discharge, was used following the methodology to account the methane production potential in poultry slaughterhouse in Matelandia, Paraná, Brazil.

Emissions are a function of the amount of organic waste generated and an emission factor that characterises the extent to which this waste generates CH_4.

Three tier methods for CH_4 from this category are summarised below:

The Tier 1 method applies default values for the emission factor and activity parameters. This method is considered good practice for countries with limited data.

The Tier 2 method follows the same method as Tier 1 but allows for incorporation of a country specific emission factor and country specific activity data. For example, a specific emission factor for a prominent treatment system based on field measurements could be incorporated under this method. The amount of sludge removed for incineration, landfills, and agricultural land should be taken into consideration.
For a country with good data and advanced methodologies, a country specific method could be applied as a Tier 3 method. A more advanced country-specific method could be based on plant-specific data from large wastewater treatment facilities.

This paper follow the Tier 2 method.

Step 1: Estimate total organically degradable carbon in wastewater (TOW) for industrial sector i.

$$TOWi = Pi \bullet Wi \bullet CODi \qquad (1)$$

Where:
TOWi = total organically degradable material in wastewater for industry *i*, kg COD/yr
i = industrial sector
Pi = total industrial product for industrial sector *i*, t/yr
Wi = wastewater generated, m^3/t product
CODi = chemical oxygen demand (industrial degradable organic component in wastewater) $kg.COD.m^{-3}$

Step 2: Select the pathway and systems according to country activity data. Use Equation 2 to obtain emission factor. For each industrial sector estimate the emission factor using maximum methane producing capacity and the average industry-specific methane correction factor.

$$EFj = Bo \bullet MCFj \qquad (2)$$

Where:
EFj = emission factor for each treatment/discharge pathway or system, $kgCH_4$ /kg.COD
j = each treatment/discharge pathway or system
Bo = maximum CH_4 producing capacity, $kg.CH_4$/kg.COD
MCFj = methane correction factor

Good practice is to use country and industry sector specific data that may be available from government authorities, industrial organizations, or industrial experts. However, most inventory compilers will find detailed industry sector-specific data unavailable or incomplete. If no country-specific data are available, it is good practice to use the IPCC COD-default factor for Bo (0.25 kg CH_4/kg.COD).

2.4. *Electricity Generation Potential*

The estimate electricity generation potential by the biogas produced was calculated following this equation:

$$P_{el} = \frac{PCI_{CH4} * MJ * P_{CH4} * \eta_{el}}{kWh * 1000 * 100}$$

Onde:
P_{el}: Electricity generation potential $MWh.year^{-1}$;
PCI_{CH4}: Methane Calorific value: 50 $MJ.kg^{-1}$ [17];
$\frac{MJ}{kWh}$: Unit conversion factor: 0,2778;
η_{el} : Electricity Generation System Efficiency: %.

3. Results

The methane generation potential is 515,963 $kgCH_4.year^{-1}$, equivalent 1.414 $kgCH_4.d^{-1}$. Considering a electric generation efficiency of 30% for the motor, the methane generation can produce 1,681 $MWh.year^{-1}$, or 4.61 $MWh.d^{-1}$.

4. Conclusion

The biogas produced by the anaerobic digestion process can reduce 3.89% of the electric energy consumption at poultry slaughterhouse.

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Economic evaluation of an industrial biogas system for production of gas, electricity and liquid compost

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Abstract: Iran is on the verge of elimination of energy subsidies. This means a sudden increase in prices such as gas, electricity, etc.... On the other hand, the different means of the different means of energy production is a great concern for human being. Amongst all different methods of energy production, renewable energy is paid more and more attention due to the least consequences concerning the diverse climate change effects. However, the economic factors are also important in order to bring a project into reality. In this paper, the potential of biomass energy in an industrial scale is investigated under this great change on national policies. Then the economic analysis of an industrial biogas system in a rural area near the province of Tehran, the capital of I.R.I., as a case study is illustrated .In this process several products will be produced such as organic compost by anaerobic fermentation of agricultural and organic wastes, liquid fertilizer, Methane and Carbonic gases, electricity and heating. The results of economical evaluation shows that the use of methane-fired generators for the production of electricity is economical because of the high amount of biogas production. So, the revenue gained from produced electricity is more than produced compost. Also, in the process of biogas production, the huge amount of Carbonic gas will be produced which can be used after purification in industry. The result show a promising future for the use of bio gas, specially under new policies of zero energy subsidies for households , commercial, and public use.

Keywords: *Biogas, Economical evaluation, Renewable energy.*

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1 Introduction:

Biogas is a renewable energy source which is produced on the basis of organic waste from the agriculture, food trade industry and households. Furthermore, biogas can be extracted from sludge in the wastewater treatment plants and from landfill sites [1].

Biogas is produced in the process of anaerobic digestion. Anaerobic Digestion is process whereby organic waste is broken down in a controlled, oxygen free environment at certain temperature by using bacteria naturally occurring in the waste material [1,2]. Biogas can be extracted from landfill sites by using collection pipes and wells, which uses vacuum to collect the gas. For the gas production from organic waste, sewage sludge and manure, a hermetical digestion tank is needed. Biogas is composed of approximately 50 to 70 % methane (CH4), 30 to 40 % carbon dioxide (CO2), as well as water vapor and a small quantity of nitrogen (N2), sulfur (S) and other trace compounds. Biogas has the same characteristics as the natural gas, which allows using it in the same appliances [2,3]. But its calorific value can be up to two times lower than natural gas. The collection of biogas actually removes pollution from the atmosphere. If the gas is emitted to the air, it would contribute to the global warming as methane is one of greenhouse gases. The impact of methane emissions on global warming is 21 times bigger than that of CO2 emitted during the burning of biogas [2]. There are many biogas plants all over the world, mainly in USA, India, Mexico, Africa, but as well in Denmark, Sweden, Germany and Austria. It is used for heat production and cogeneration of heat and power, alternatively as well as vehicle fuel in the public transportation [3].

2 Potential of Biomass energy in Iran

Considering, the availability of all types of Biomass resources in Iran, Power Ministry did a research to evaluate the potential to use biomass for renewable energy. This research was conducted in 1976 and conclusions are as follow [4]:
1- Quantity of accessible Animal Waste in Iran is 74.95 million tons(MT); Biogas could be produced by this amount is 8668 Million cubic meter(MCM) and energy equivalent this biogas is 193299TJ. (TJ=10^{12} J)
2- Quantity of accessible Urban Waste in Iran is 10.6 MT: Biogas could be produced by this amount is 1645.7 MCM.
3- Quantity of accessible Biogas from Urban Waste Water in Iran is 98.85 MCM/day. (Waste Water specifications are: 160 Litter per capita per day and BOD per capita is 33-40 gr/d.c)
4- Quantity of accessible Methane from Industrial Waste Water in Iran is 167.67 MCM/year. Energy equivalent this quantity is 6153TJ per year. (This Waste Water is from Big Food Industry in Iran.)
5-Total gross energy potential from Agricultural and Wood Waste is 411.9 PJ from 3285.5 MCM Methane and 33.95 MCM Ethanol which could be produced [4].

3 Availability of industrial biogas plants in Iran:

In Iran, presently two main industrial biogas plants are exist which include Mashhad Landfill Power Plant and Saveh Biogas Plant [5,6].

3.1 Summary of Mashhad Landfill Power Plant:

The first Landfill-Gas (LFG) power generation project was initiated in Mashhad, the second largest city in Iran, located on the north east part of Iran, through a memorandum of understanding between “Renewable energy Organization of Iran (SUNA)” and “Waste Recycling and Processing Organization of Mashhad Municipality (WRPO)”. Based on the mentioned memorandum, SUNA took the responsibility of preparing technical investigations and tender documents and follow-up the electricity purchase contract between Mashhad LFG power plant and Ministry of Energy. Investment for power plant and commissioning was accepted by WRPO. Feasibility studies, conceptual design and tender documents preparation were consequently allocated to Renewable Energy Department of NRI [5].

The first phase of this project, included design criteria for engineering landfills and gas extraction systems and transmission lines, introduction to energy conversion and power generation technologies for LFG, field investigations and measurement methods and monitoring of LFG. The next phase was feasibility study for installation of power generation unit in Mashhad Landfill, in which, estimation of landfill gas theoretical yield for Mashhad municipal solid wastes, LFG generation modeling and gas flow prediction for long term periods, evaluation of confident power capacity for Mashhad Landfill, technical assessment of power generation equipment for LFG and introduction of more appropriate commercial generating sets for utilization of LFG in Mashhad Landfill, were performed. In the third phase, economical studies, three alternatives were selected on the base of feasibility study results. These alternatives were assessed as economical aspects and finally, installation of generating sets near the guard room of Mashhad Landfill, which is located near to irrigation station and a 20kV line, was selected as the most useful option for utilization of the whole gas which can be collected through the existing gas extraction systems. The generated electricity in this unit will be sold to power network at an average price of 0.61 dollars per kWh [4,6].

The phase of conceptual design included: pipeline design for LFG transmission to central gas station, gas blower station, gas treatment process, foundation and structure of generating house, power generation unit arrangement and grid interconnection system plus protection and confidential instruments. Technical characteristics and tender documents were consequently prepared on conclusions [6]. The contract for construction and start-up of Mashhad Landfill power generation unit will be as an Engineering Procurement Construction (EPC) contract. The results of this project shows:

- Pipeline and collection systems were designed on the basis of 13 years useful operation period of a biogas fueled generating set, and LFG generation modeling results, for average gas flow rate of 550 Nm3/h and maximum gas flow rate equal to 660 Nm3/h. A minimum power capacity of 435 kW is expected to be achievable until the end of 2018 by existing gas extraction systems [6].
- The power capacity can be increased to at least 715 kW if Mashhad municipality develop the gas extraction systems to recent buried layers of solid wastes which are dumped in period of 2004-2006.
- Generating sets with LFG fueled internal combustion engines are the best option for Mashhad Landfill, furthermore, a list of qualified manufacturers of these equipment, has been presented in the project documents.
- Economical assessment results showed the best alternative is the installation of power generating unit in near of Landfill irrigation station.

A case study with capacity of 400 kW (due to capacity of commercial models) will have the generation cost of electricity relevant to discount rates of 8%, 12% , 16% and 20% equal to: 293, 320, 350 and 0.39 dollars per kWh, respectively [5,6].(It should be noted for the exchange of Rls rate to dollar, one dollar was considered as 10000Rls.)

- LFG power plant interconnection with regional power grid is feasible through the existing 20kV line in Mashhad Landfill. Electrical circuit drawing and single-line diagram for connection to 20kV network were obtained and presented in project documents [8,9].

3.2 Summary of Saveh Power Plant:

The city of Saveh is in the central province, 150 km from Tehran with a population of 120,000. It has a Semi-arid climate and the temperature during different seasons of the year fluctuates within the range of –10°C to 40°C. In order to establish the Bio-gas power plant in this city, the usable pollutants in Saveh were studied and they were divided into four groups: Household garbage, sludge of sewage treatment, slaughter house waste water and sludge of leaching pit [3]. Through statistical studies, separation operation, sampling and executing physical, and chemical tests, quantity and quality specifications of each of the four types of pollutants were determined. The results are shown in the following tables[6]:

Table 1: MSW Specification[4]

Parameters	**Quantifies**
Average garbage / day	78.3 tons
Household garbage/ day	58.7 tons
Organic material of garbage /day	38.2 tons
Total solids (15%)/ day	5.73 tons

Table 2. Specification of sewage treatment sludge[4]

Parameters	Quantifies
Annual average of sludge	10000 tons
Daily average of sludge	27.4 tons/day
Total solids (1.002%)/ day	274.54 kg/day
Volatile solids/ day	5.73 tons

Table 3: Specifications of the Slaughterhouse sludge[4]

Parameters	Quantifies
Annual average of slaughterhouse waste water	4380 m^3
Daily average of slaughterhouse waste water	12 m^3
Total solids (0.508%)/day	60.96 kg
Volatile solids/day	51.39 kg

Table 4: Specification of leaching pit sludge[4]

Parameters	Quantifies
Annual average of discharged sludge from household wells	5000 tons
Daily average of discharged sludge of household wells	13.7 tons
Total solids (1%)/ day	137 kg
Volatile solids/day	83.57 kg

After determining the quantity and quality of each pollutant separately, anaerobic digestion situation, and the production of Bio-gas from combination feed including above mentioned pollutants, considering the existing real relations in the city in anaerobic reactor at 35 degree centigrade was investigated in a semi-industrial anaerobic reactor.
This reactor is metallic and has a volume equal to 10 cubic meters. In order to control the heat, it is completely isolated and in order to heat up the contents and create suitable heating conditions, the reactor is equipped with an internal coil and a sludge evacuation pump is also installed to mix the content. The reactor has been designed in a way that is the capable of operating both continually and dis- continually (batch). (Fig.1)

In order to study the anaerobic digestion of these feeds on a continuous basis, determining the stoppage time of the material in reactor becomes necessary. Thus, at first, the situation for producing gas in the related reactor on dis- continuous basis was studied. By investigating the volume of daily gas production and the speed of production during the dis-continuous period and the related curve, the stoppage time was determined to be 20 days and for continuous studies the 20 days stoppage was also agreed[8].

Fig.1. Anaerobic metallic digestion reactor with 10m^3 volume

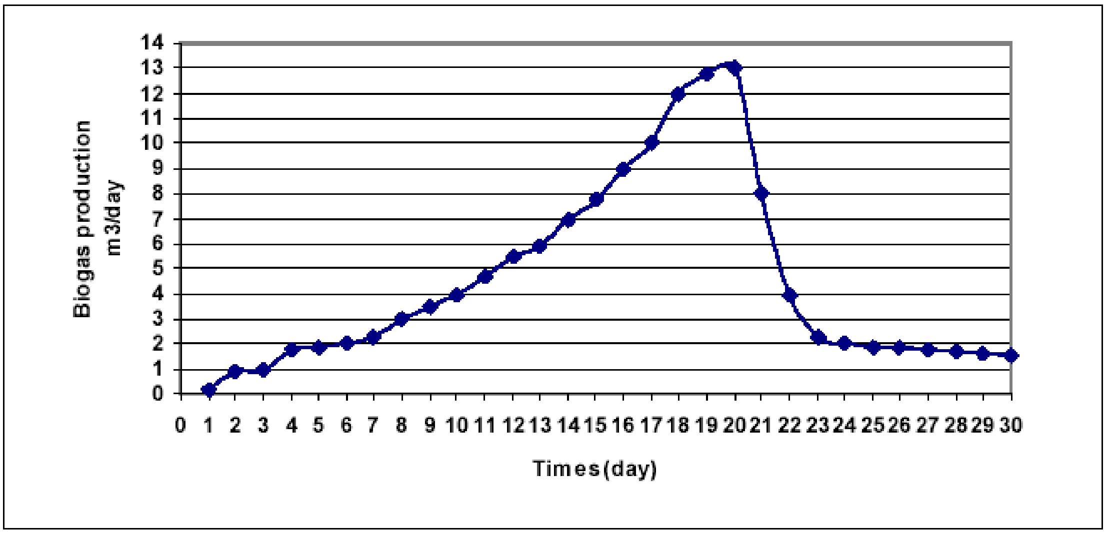

Fig.2. Bio-gas production curve in dis-continuous loading at 35°C[3].

Studies during the continuous loading of combination feed including the four groups of urban pollutants with actual existing recording in the city of Saveh shows that for each kilogram of total solid as input, 500 liters of Bio-gas is produced in anaerobic digestion process. Thus on the basis of scientific studies carried out in Saveh Bio-gas power plant, the operation can be summarized as follows:

Table 5. Summary of operation and technical specifications of Saveh power plant[4]

1	Amount of bio-gas produced for every kilogram of dried input/ day	500 liter/kg of total Solid
2	Percentage of T.S in combination feed entering reactor, including four types of pollutants	6.794%
3	Amount of daily input to the power plant	91.3 ton/day
4	Amount of Total Solids as input/day	6202.5 kg/day
5	The most suitable stoppage time in 35°C	20 Days
6	Total volume of Bio-gas produced/day	3101 m^3/day
7	Amount of Fertilizer produced / day	2500 kg/day
8	Extracted water suitable for agricultural irrigation	31025 m^3/year

4 Methodology:

This paper provides a case study for an industrial biogas system to be built on Eshtehard industrial city near the province of Tehran. Since, more than 40% of husbandries and also an accountable number of settled livestock farming are located in this region, therefore it is possible to collect a total volume of five thousand cubic meters of feedstock per day to feed the system for production of gas, electricity and liquid compost. For feasibility study of this plan, the economical evaluation is considered based on the cost benefit analysis of this project. To calculate the capacity of the system the following assumptions were made:

- The amount of biogas production is equal to 100-160 cubic meter from each ton of organic wastes which can be produced about 170 kwh of electricity and 340 kwh of heating energy.

- Each 10 cubic meters of biogas can be produced about 15 kw of AC electricity and 35000 kcal of heating water
- Each unit of biogas can produced about 25-30 cubic meter of organic fertilizer per day in 55-60°C during 15 to 20 days.
- Each cubic meter of organic compost weights 0.7 ton and the weight of 25-30 cubic meters of produced compost is equal to 17.5 or 21 ton.

5 Results:

Whereas a lot of husbandries and settled livestock farming are located at Eshtehard region, the amount of substrates for feeding the biogas system could be very high. The estimated amount of substrates at this region is presented at table 6.

Table 6.The estimated amount of substrates at Eshtehard region

Type of substrate	Existing amount	Unit
Cattle dung	219000	tons
Chicken dung	87600	tons

For design and installation of this project, different parameters such as the total capital cost, number of persons who can be involved in this project, total area for project installations, the amount of electricity, water and energy consumption were calculated for the implementation of this project.

- The required area for biogas unit installation is equal to 136,000 square meter at Eshtehard industrial region which is located near to the more than 40% of husbandries and also an accountable number of settled livestock farming of the country
- Total capital cost is assumed as 22.8 million dollars
- The total number of persons for this project include 103 persons as a producer and 43 persons as a supporter
- The power of consumed electricity is equal to 259 kwh of total 5950 kwh of electricity which is produced by the biogas unit. Total production capacity of products is presented in table7.

Table7. Total production capacity of products

Type of product	Amount of production(per hour)	Amount of production (per year)	Unit
Electricity	5950	52,122,000	kwh
Carbonic gas	2.36	20,673.6	ton
Heating	11900	104,244,000	kwh
Cattle dry compost	7.98	69,934	ton
Chicken dry compost	3.193	27,959	ton
Liquid compost	58.8	515,288	Cubic meter

It should be mentioned, from the total amount of produced electricity, 250 kwh consumes for the biogas system and the rest can be delivered to grid electrical network. Also, the produced dry compost which contain 35% humidity can be packed for domestic consumption.

- The annual amount of consumed water is equal to 342144 cubic meter which can be used for agricultural land after an anaerobic fermentation process.

- The annual amount of consumed energy is equal to 1,569,000 litres of gasoil for combustion of electrical generator and 21,900 litres of gas for the vehicles during the installation of plant

Based on the mentioned characteristics, the following economical parameters were calculated for the presentation of economic analysis of this project. The calculate amount of these parameters were shown in table8.

Table8.Economical evaluation of this project based on financial calculations

Financial parameter	Estimated cost (Dollars)
The amount of fixed investment	22 million Dollars
The amount of investing turnover	0.85 million Dollars
Total amount of investment	22.9 million Dollars
Actual cost of products in final capacity	0.36 Dollars per kwh of electricity 87.5 Dollars per ton of Carbonic gas 26 Dollars per ton of Cattle dry compost 65 Dollars per ton of chicken dry compost 3.5 Dollars per cubic meter of liquid compost
The amount of total sale in final capacity	13 million Dollars
Annual return of investment in final capacity	3.4 million Dollars
Return investment time	3.3 years
Rate of return	0.22 %
Per capita investment	0.17 million Dollars

It should be noted for the exchange of Rls rate to dollar, one dollar was considered as 10000Rls.

As the above table illustrates, the time for capital cost return is equal to 3.3 years and the amount of earnings after this time is about 3.9 million dollars.

6 Conclusions:

The aim of this project is the conversion of low-value organic wastes to organic compost with high value at industrial scale based on anaerobic fermentation. The anaerobic digestion has numerous advantages rather than aerobic digestion. The most advantages include:

- The value of the produced compost is so high rather than traditional fertilizer. For example by the use of this compost the production of agricultural crops such as corn and tomato can be increased respectively up to 49% and 35%.
- Elimination of pathogenic bacteria, viruses, agents and odour in anaerobic digestion
- The huge amount production of methane and carbon dioxide gases. Methane gas can be used to produce electricity with the use of methane burner.

Calculation indicates that it is possible to produce 5950 kw electricity which 250 kw should be consumed for the process itself. This system can produce 2.36 tons of gas, 58.8 cubic meters of liquid compost, 11 tons of dry compost and equivalent of 11900 kwh of heat per hour. The results of economic analysis shows that this project can be beneficial and economical in a short time period. Finally, with consideration of economical, environmental and social issues, the promotion of this types of industrial biogas system can be an attractive project at regional and national level.

For accelerating the execution of this kind of projects in Iran and similar developing country, the following recommendations are suggested:

- As discussed, the elimination of energy subsides help the rapid development of this kind of renewable energy systems. The government can encourage the use of these systems by setting the purchase policy for the electricity production from these systems. To do so, some technical steps should be carried out to make this action possible.
- It is necessary to implement some policies to encourage the private sector participation in this issue.
- It is necessary to imply some policies to increase the awareness of decision makers, especially managers, authorities and experts about the benefits and advantages of this kind of energy.
- The CDM mechanism was not brought into account in this study. However, the implementation of CDM mechanism can help to have even a better outlook using this type of energy system.

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Development of an anaerobic hydrogen and methane fermentation system for kitchen waste biomass utilization

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Abstract: Utilization of kitchen waste as biomass resources has been of growing importance in urban areas of Japan. Present-day standards have set much sterner target recycling rates especially for kitchen waste from food industry, e.g. restaurants and food retail dealers. Aiming at high-efficiency energy recovery from kitchen waste, we have developed a two-step anaerobic fermentation system for generating hydrogen and methane. Bio-hydrogen is produced in the initial fermentation step by thermophilic microbiota mainly consisting of *Clostridium* species. Then, residues such as organic acids are converted into bio-methane in the second methane fermentation step. By proficiently combining these two fermentation steps, high system efficiency can be achieved. Optimum operating conditions have been found in the laboratory test of hydrogen fermentation operated over 300 days using artificial kitchen waste.

Keywords: *Biomass, Methane fermentation, Hydrogen fermentation*

Nomenclature

TS Total solid	*%*	*COD Chemical oxygen demand*	*mg/L*
VFA Volatile fatty acid	*mg/L*	*HRT Hydraulic retention time*	*days*

1. Introduction

Energy from biomass is the promising renewable energy. In Japan, “Biomass Japan broad strategic view" was determined in December 2002. The concrete target value of greenhouse gas discharge reduction was set to develop the recycling society. We are demanded to plan maximum profit utilization of biomass. In particular of them, it needs great amount of energy as oil and gas to incinerate sewage sludge and kitchen wastes which content much water. Great amount of energy as oil and gas is particularly required to incinerate sewage sludge and kitchen wastes, which contain much water. The realization of fermentation technology recovering energy from biomass reduces CO_2 emission from the garbage disposal. H_2 produced from biomass (Bio-H_2) is especially expected as one of the important energy sources in the future plan of hydro-energy. We know bacteria fermenting carbohydrates as glucose and cellulose. The bacteria make organic acids in their metabolic process. H_2-CH_4 fermentation is known as an efficient energy recovery system because organic acids can be used for substrate of fermented methane. Methane fermentation is available for many carbonic wastes, however, HRT is long. Therefore, pre–treatment to oxidize carbonic wastes in the fermentation process is needed to shorten HRT. Some trial tests have been conducted to apply H_2 fermentation as pre-treatment for acceleration of energy generation.

2. Materials and methods

2.1. Materials

Our research is aimed for the realization of efficient recycle and disposal system. We used artificial kitchen wastes as the substrate in our lab. In the pilot plant, the kitchen waste discharged from our canteen and dog foods are made use of raw materials. The composition and contents of substrates in the laboratory test are as follows. (Table1, 2, 3) The ratio of carbon and nitrogen is about 15. It is slightly lower than ideal condition for CH_4 fermentation. Table4 shows materials in the pilot plant. These materials are diluted and regulated the ratio of total solid. (Table5)

Table 1 *Composition of the material as artificial kitchen waste in the laboratory test*

	Shredded vegetable	Minced meat	Boiled fish	Cooked Rice
Weight ratio (wt %)	86.7	3.3	3.3	6.7

Table 2 *Contents of the material as artificial kitchen waste in the laboratory test*

Content	Water	Protein	Oil	Carbohydrates	Ash
Weight ratio (wt %)	77.8	4.4	2	15	0.8

Table 3 *Ratio of elements of the material as artificial kitchen waste in the laboratory test*

Element	C	H	N	S	O	Ash
(%)	45.5	7.3	3.2	0.1	41.2	2.7

Table 4 *Composition of the material for the plant test*

	Kitchen waste	Dog food
Weight (kg)	20	12

Table 5 *TS in the diluted materials*

	Laboratory	Pilot plant
TS (%)	7.5	6.5

2.2. Methodology

2.2.1. H_2-CH_4 fermentation

The metabolism of H_2–CH_4 fermentation is as follows. Bacteria generate H_2 on two pathways concerning glucose as carbohydrate in kitchen waste. Much hydrogen can be generated from glucose in the pathway (1). The generation rate of hydrogen is 4mol / 1mol-glucose, and that of acetic acid is 2mol / 1mol-glucose.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH \quad (1)$$

$$C_6H_{12}O_6 \rightarrow 2H_2 + 2CO_2 + CH_3CH_2CH_2COOH \quad (2)$$

In the case of CH4 fermentation, acetic acid and H2 are the substrate for generating CH4. There are 3 main pathways as follows. 70% of Bio-CH4 is generated as the deconstruction of acetic acid in the pathway (3), and about 30% of Bio-CH4 is generated in the pathway (4). The pathway (5) is a rare case.

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (3)$$

$$4H_2 + CO_2 + H_2O \rightarrow 4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \quad (4)$$

$$4HCOOH \rightarrow CH_4 + 3CO_2 + 2H_2O \qquad (5)$$

When we develop high-efficient H_2-CH_4 fermentation system, the pathway (1) and (3) should be activated.

A pre-treatment process is generally adopted in commercial plants to promote the methane fermentation.

In the process, carbohydrate is converted to organic acetic acids in the following pathway (6). The acetic acids are equivalent to 3mol methane / 1mol-glucose.

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \qquad (6)$$

Table 6 shows estimated calorific values of generated bio-H_2 and bio-CH_4. H_2-CH_4 fermentation is more efficient than Acidizing-CH_4 fermentation to recover energy.

Table 6 *Calorific values of generated biogas on two pathways*

	Calorie [kJ/ mol-glucose]
Acidizing – CH_4 fermen.	2405
H_2 fermen. - CH_4 fermen.	2570

Representative bacteria of H_2 fermentation include the Clostridium genus of the obligate anaerobe, and Escherichia coli of the facultative anaerobic bacterium. These bacteria have a weak property in concentration of organic acids, especially lactic acid. Acid generation bacteria are cultured in medium temperature and prefer neutrality to acidity not in thermal and aciditic environment. Therefore, it is most important to look for H_2 generation bacteria with thermal and high acidity tolerance. The microbiota named OF-1 we use in this research was collected from soil samples. In addition, it can be cultured in high temperature as 60°C and acid atmosphere as pH 5.5. OF-1 includes the bacteria saccharifying cellulose and thermophilic bacteria generating H_2.

2.2.2. Test equipment

The outline of test equipments in the laboratory is indicated in Fig.1. The volume of H_2 fermenter (ABLE & Biott Co.,Ltd., Japan) is 1L and the effective volume is 600cc. Dilution materials adjusted to TS 7.5% are crushed by a food processor. The crushed dilution materials and additional minerals, e.g. Ni and Co, were thrown into the fermenter. The additional minerals have a role to promote the methane fermentation. NaOH is used as pH control chemical. The residue of H_2 fermentation is used as materials for CH_4 fermentation. CH_4 fermener (PRECI Co.,Ltd., Japan) has a carrier which is pumice stone. An operation of feeding materials and pulling up fermentation liquid is in the atmosphere.

The pilot plant flow is shown in Fig. 2. Kitchen wastes from our canteen are classified and crushed. They are mixed with crushed dog food and water. The materials are diluted to TS 6.5%. The lower TS than laboratory test depends on a feeding ability of a pump. pH was adjusted to be 5.5 by $Ca(OH)_2$. A feeding and pulling up is anaerobic operation. Other experimental conditions are written in Table7.

The devices for analyzing the materials, biogas and fermentation liquid are as follows. Calorific values of materials are measured by a calorie meter EA6320 (Parr Instrument

Company, U.S.). Elements are analyzed by an elemental analyzer Vario EL Ⅲ（Elementar Americas, Inc. U.S.) . An absorption meter DR2800 (Hach Company, U.S.) measures COD. Biogas analysis is used by a gas chromatography GC-8A (Shimazu Corporation, Japan). Fermentation liquids are analyzed by a liquid chromatograph HPLC-20AD (Shimazu Corporation, Japan).

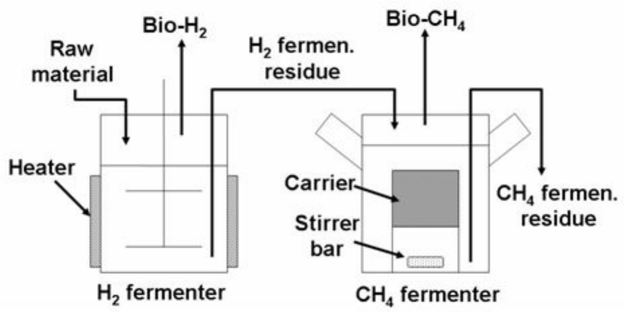


Fig. 1 Schematic diagram in the laboratory

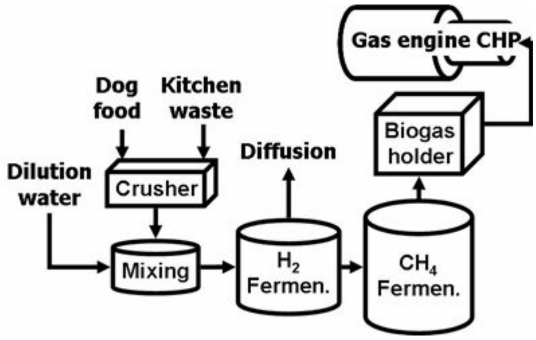


Fig. 2 Plant flow

Table 7 Experimental conditions

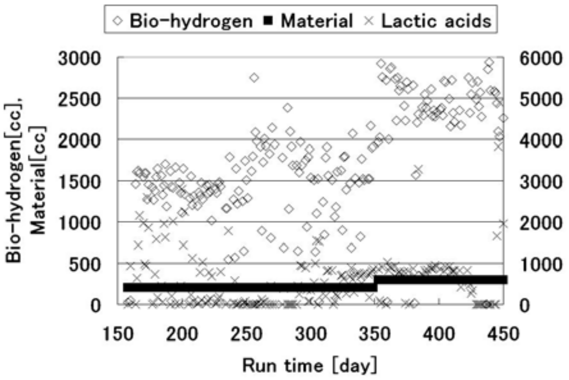
Equipment	Laboratory		Pilot plant	
Fermentation	H_2	CH_4	H_2	CH_4
Material	Artificial kitchen waste	Residue of H_2-fermen.	Kitchen waste Dog food	Residue of H_2-fermen.
Feed		1 feed / day（5days / week）		
HRT (days)	4.2, 2.8	14	4.2, 2.8	14
Volume	600cc	800cc	$0.4Nm^3$	$4Nm^3$
Temp. (˚C)	60	55	60	55
pH	5.5(Controlled)	7(Uncontrolled)	5.5(Controlled)	7(Uncontrolled)
Carrier	×	○	×	○
Stirring	Stirrer	Magnetic stirrer	Stirrer	Stirrer Circulation pump
Varied sludge	OF-1 (Microbiota from soil)	Sludge of high temp. CH_4 fermen.	OF-1 (Microbiota from soil)	Sludge of high temp. CH_4 fermen.

3. Results

3.1. Laboratory test

Figure 5 shows the time variation of bio-H_2 volume. The stable and successive operation over 300 days was achieved. On the 350th day, the amount of feedstock was changed. Though HRT was shortened from 4.2 to 2.8 days, the condition of H_2 fermentation was well maintained and the stable running could be continued. But it is too difficult to realize shorter HRT. Because the feeding was once a weekday, in the perspective of only weekday, HRT is calculated as only 2 days. In the short HRT, H_2 fermentation became unstable. The determined feeding on weekday made the fluctuations of bio-H_2 in the all run time. In beginning of the week, bio-H_2 reduced and increased in weekend. The bands of fluctuation in the amount of bio-H_2 became smaller as HRT shortening.

Though the materials and reactors were not sterilized, the density of lactic acid was under 2000 mg/L almost all the run time. A contamination was almost avoided since the operation temperature is high. H_2 generation bacteria OF-1 has heat resistance, however, concentrated metabolites harm it. Figure 4 shows the relation between the density of lactic acid and the generated bio-hydrogen. The decrease in H_2 was caused by the increase in the lactic acid. In this case we fed materials including large amount of lactic acid. The density control of lactic acid under 10000mg/L is needed for efficient H_2 fermentation.



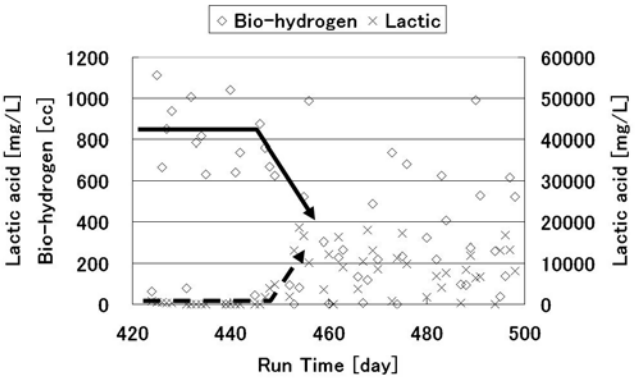
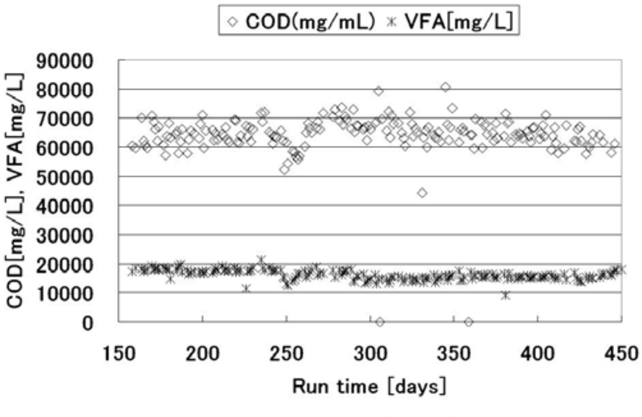


Fig.3 Generated bio-hydrogen

Fig.4 Increased lactic acid

Figure 7 shows the time variations of COD and VFA in the residue of H_2 fermentation. The residue of H_2 fermentation was a good substrate for methane fermentation since the residue contained much organic acids and the density of COD is suitable. The residue feeded into CH_4 fermenter generated biogas including CH_4 of 60%. The energy recovery efficiency from biomass to bio-H_2 and bio-CH_4 is shown in Fig.6. The efficiency is the average value in one month. The efficiency was nearly 80 %, which was almost all derived from the generation of bio-methane. In this experimental condition, feeding and pulling up was operated in the atmosphere, therefore it is severe circumstances for anaerobic bacteria.



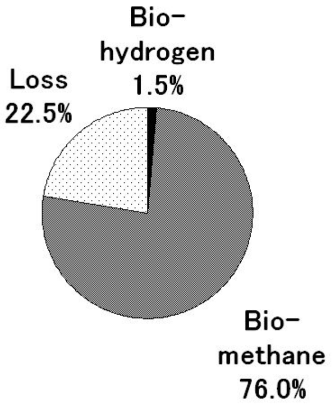


Fig. 5 COD-VFA in the residue of H_2 fermen.

Fig. 6 Energy recovery in the laboratory

3.2. Pilot plant test

H_2-CH_4 fermentation was carried out in the pilot plant. Figure 7 shows the time variation of the generated bio-hydrogen. Stable operation continued over 150 days though the material injection was sometimes stopped. Kitchen wastes from the canteen were used in the pilot plant. Therefore feedstock was involved large amount of organic acids. Measured Lactic acid was about 1000 - 5000 mg/L in materials and 2000 – 8000 mg/L in the residue of H_2 fermentation. The lactic acid density in the pilot plant test was higher than that in the laboratory test. The increased lactic acid affected H_2 fermentation in the pilot plant compared with the results of the laboratory test. The concentration of lactic acid over 10000 m g/L prevents the generation of bio-H_2. In the pilot plant, the density of lactic acid was scarcely kept under 10000 mg/L.

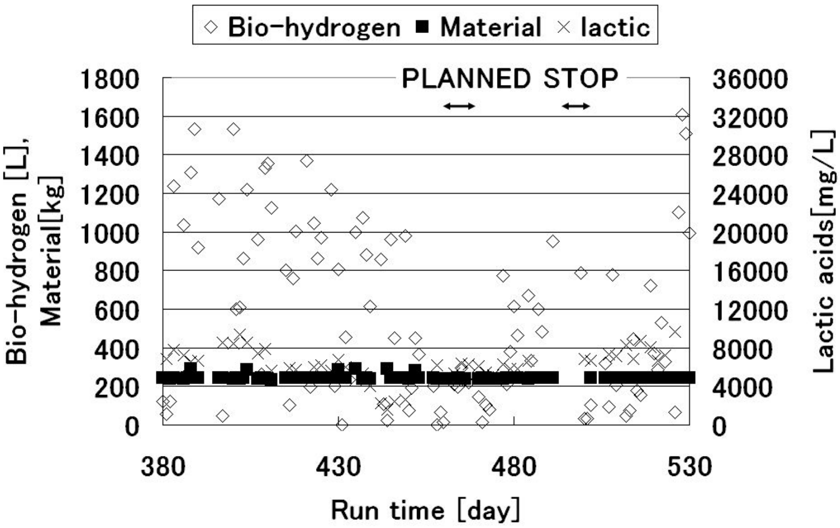


Fig. 7 Bio-hydrogen in the pilot plant

The residue of H_2 fermentation was sent into the CH_4 fermenter. The amount of bio-methane is indicated in Fig.8. Bio-CH_4 was stably produced during the operation period.

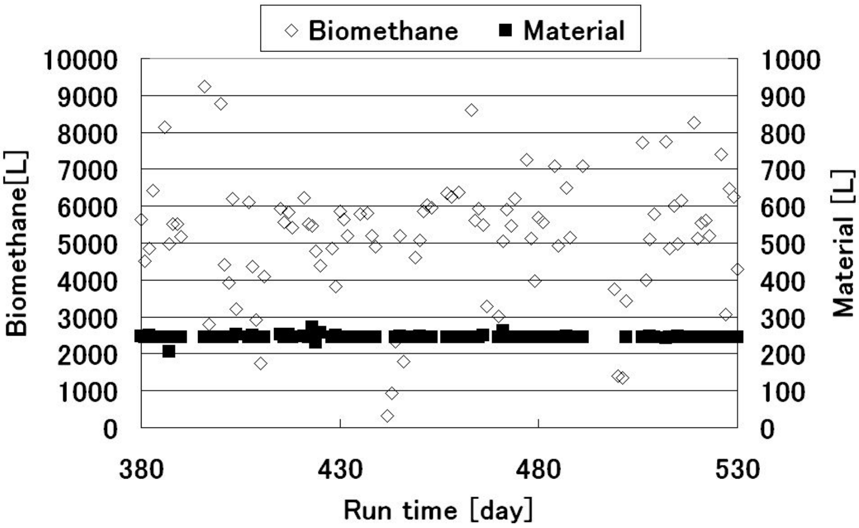


Fig. 8 Bio-methane in the pilot plant

Figure 9 shows the progress of energy recovery from materials in this pilot plant test. Almost all converted energy was the bio-methane as well as the laboratory test. The energy recovery efficiency was kept about 80 % during the operated period. I In the same plant, another test was carried out, in which the oxidization was pretreated instead of the H_2 fermentation. Figure 10 compares the recovery efficiency when the different pretreatment was conducted. Though the real kitchen wastes included lactic acid concentration and had contamination, the equal energy recovery was achieved.

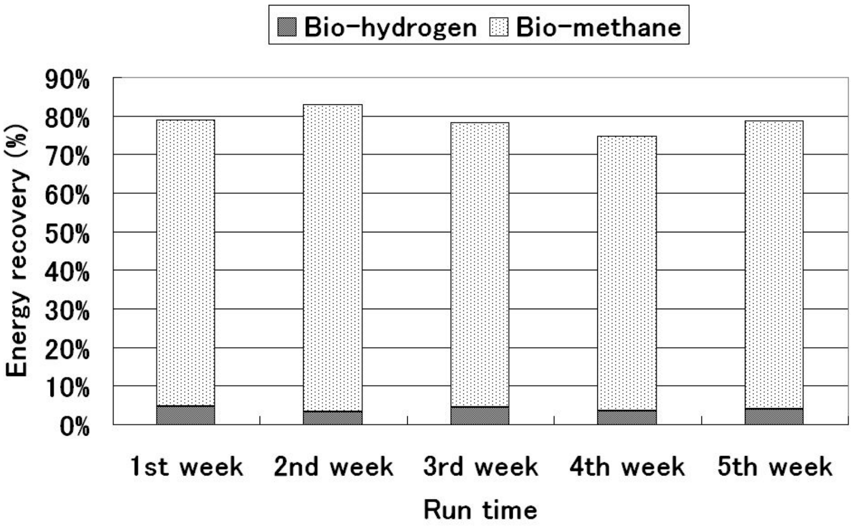


Fig. 9 Energy recovery

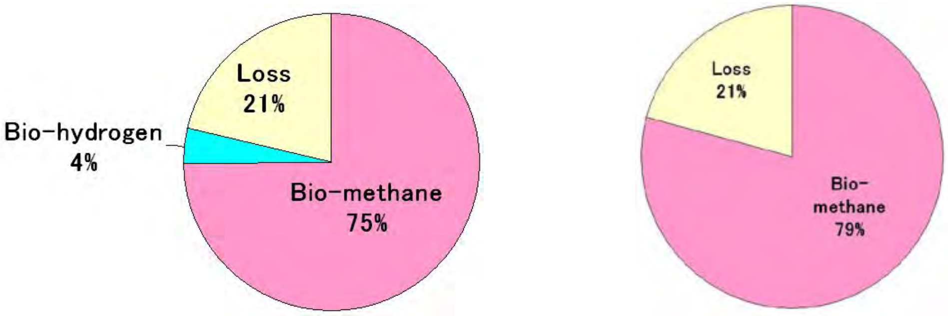


Fig. 10 Comparison of recovery efficiency
(Left: H2-CH4 fermentation, Right: Acidizing – CH4 fermentation)

4. Conclusions

OF-1 is determined to generate H_2 in the environment which is high temperature and acidic. The stable operation in the H_2 – CH_4 fermentation system was developed. Though metabolites generated by H_2 fermentation harm the H_2 generation bacteria itself, the running was stably kept due to high temperature operation and shortened HRT. The operation was stably conducted in 300 days in the laboratory and 150 days in the pilot plant. The residue of H_2 fermentation was found to be good substrates for CH4 fermentation. The energy recovery efficiency in H_2 – CH_4 fermentation was about 80 %. The efficiency value was equivalent to that of the acidizing – CH_4 fermentation.

Future plan is aimed for increasing bio-H_2 from the biomass consisted of cellulose. OF-1 includes cellulose decomposition bacteria. We will consider the possibility of disposing kitchen wastes with the biomass consisted of cellulose.

Acknowledgement

This research depends on the collaborative investigation with Toho Gas Co., LTD, and Mie University. I thank the concerned members.

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An environmental assessment of the production of biodiesel from waste oil : two case studies

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Abstract: The UK transport sector is currently responsible for 30% of UK CO_2 emissions. Therefore, the use of biofuels is explored. As the CO_2 released when energy is generated from biomass is generally balanced by that absorbed during the fuel's production it is often regarded as a 'carbon neutral' process. However, there are impacts associated with bioenergy production, including, for example, the growth and transportation of feedstock. One way to overcome these is to use a waste oil feedstock. Whilst there will not be enough waste oil to meet all our fuel demands, some firms in the UK have started to use their waste catering oil for transport. Collection and conversion is often done on a small scale and a number of methods are used for the processes. Therefore, the associated environmental impacts are variable. The environmental impact of the production and use of biodiesel from waste oil based on two case studies has been assessed. The impacts associated with the use of fossil fuels and climate change gas production is lower than that of the production of conventional fossil fuel diesel. The biggest impact within the process is associated with the use of methanol and the waste oil collection.

Keywords: *Biofuels, environmental life cycle assessment, waste oil.*

1. Introduction

Climate change and energy security have become major concerns in recent times and many countries have agreed, under the Kyoto Protocol, to reduce emissions of greenhouse gases. One of the ways in which this is being done is through the pursuit of bio-energy. As the carbon dioxide (CO2) released when energy is generated from biomass is generally balanced by that absorbed during the fuel's production it is often regarded as a 'carbon neutral' process [1]. However, there are impacts associated with various stages of bio-energy production, including, for example, the boiler production and transportation of feedstock.

Bio-energy is unique amongst renewable energy in that it is not immediately dependant on the weather (unlike, for example, wind and solar). However, it is also unusual in that it requires a feedstock of often bulky materials which can limit its capacity and the geographical extent of its supply chain [2]. The production of this feedstock can also be associated with environmental consequences, with some citing rising food prices and land use conflict as an unwelcome side effect of its use. This is due to the land required to grow specialist biomass crops such as miscanthus or oilseed crops. One way to overcome the issues associated with "land squeeze" is to use waste oil to produce bio-fuels. This study examines two such systems. Both use waste oil to produce bio-diesel. One system works on a fairly small scale, and the other on a larger scale. Life Cycle Assessments (LCA) of the systems have been undertaken in order to examine their environmental costs and benefits.

LCA is an environmental management tool which examines the environmental burden of a product or system over its entire life, from production, through use and on to disposal or recycling. The energy and materials used, pollutants or wastes released into the environment as a consequence of a product or activity are quantified over the whole-life cycle from "cradle-to-grave". Two case studies were selected and a truncated LCA was undertaken. Data for the collection of the waste oil and its conversion into biodiesel were determined and analysed. Impacts associated with the previous life of the oil were not considered; nor were impacts associated with the biodiesel's use in vehicles after conversion. These data are then examined with regard to a number of environmental impacts. The embodied energy and greenhouse gas emissions are calculated for both systems and are compared with the production of biodiesel from virgin rapeseed oil and the energy output when used.

2. Methodology

The methodology of LCA has been standardised via Society of Environmental Toxicology and Chemistry (SETAC) guidelines subsequently codified in ISO Standards [3&4]. There are four main stages in the LCA process: Goal Definition, Inventory, Impact Assessment and Improvement Assessment and Interpretation. These are described below;

- **Goal definition** is the stage in which the scope of the project is outlined. Here the study boundaries are established and the environmental issues that will be considered are identified.
- The **inventory** is where the bulk of the data collection is performed. This can be done via literature searches, practical data gathering or through the use of software. Most commonly, a combination of the three is adopted.
- **Impact assessment** is where the actual effects on the chosen environmental issues are assessed. This stage is further subdivided into three (or four) elements: classification, characterisation, (normalisation) and valuation.
    - **Classification** is where the data in the inventory are assigned to the environmental impact categories. In each class there will be several different emission types, all of which will have differing effects in terms of the impact category in question.
    - A **characterisation** step is therefore undertaken to enable these emissions to be directly compared and added together. This step yields a list of environmental impact categories to which a single number can be allocated.
    - These impact categories are very difficult to compare in terms of relative impact and so the **valuation** step is employed so that their relative contributions can be weighted. This is subjective and difficult to undertake and many studies omit this step from their assessment. The LCA ISO standards state that it should not be used in any comparative or decision making study.
        - Instead of, or as well as, **valuation** many people employ **normalisation** as an intermediate step. Normalisation allows a degree of comparison between data types by determining the relative contribution of the calculated damage to the total damage caused by a reference system. Within this research the LCA impact assessment method, EI99 was used. It is a damage-oriented method, which considers, by means of damage factors, the effects of the emitted or used substances in three damage categories: human health, ecosystem quality, and resources (both fossil and mineral). Within this report the data have been normalised with respect to the average emissions or damage within Europe. In order to give a more comprehendible number this is then divided by the amount of people within Europe. Because the normalisation step compares the emissions or damage generated by a particular system with those generated at a European or global level the result of a normalisation step are dimensionless. Within this paper the normalisation method proposed and used in the methodology Eco-Indicator 99 has been followed [5]
- **Improvement assessment** is the final phase of an LCA in which areas for potential improvement are identified and implemented.

LCA requires all the energy inputs, raw materials inputs, emissions to air, soil and water, and waste to be examined at every stage of the life of the product or system. It is a simple, elegant idea, but it can become convoluted in practice [6].

3. The Case Studies

Two case studies have been examined and produced; these have both followed on from previously funded research [7&8]. Details about the composition, use and performance of the systems, together with information about feedstock sourcing, were obtained from the case study companies. This was done through a combination of visits, emails, phone conversations and augmentation of the data gathered from the previous case studies [8].

Data for the production of the materials used to produce the systems were calculated using generic life cycle inventory data. Where possible the EcoInvent database [9] was used. Where data required some geographical amendments (for example, changing to the UK electricity mix) this was done. Some estimation was made in the material composition of the systems, but generally there was detailed information about their size, weights, and composition. In general it was assumed that virgin materials, for example steel and rubber, were used in the production of the systems. However, where specific alternative information was available, for example the large tanks in the case studies had been reclaimed and were being reused, this was modelled accordingly and not all of the environmental impacts associated with the production of these units were allocated to this life cycle.

The first case study is based on a small company based in the south west of England, UK. Used cooking oil is collected from pubs, hotels, restaurants and schools in the local area; some is also delivered by customers who purchase their biodiesel. Where collected, a flat bed truck which runs on their own product is used. They make 220,000 litres per year, using a system that they have built and designed themselves. The company sells the biodiesel on site.

The second case study is a larger business with the capacity to produce 1,000 litres per hour, utilising automated control systems as far as possible. The processing site is also in the south west of England, UK, and the system was purchased from a UK manufacturer. The company purchases their oil from national oil collectors. The oil is delivered in 30,000 litre loads and is brought in by the company’s own oil tanker which collects the oil from the collectors. After the biodiesel has been produced, the tanker is used to haul the biodiesel out of the plant, which means that the tanker avoids empty journeys. The tanker runs on 100% biodiesel. Much of the biodiesel is sold to haulage companies; some is sold on site to local customers. The company produces approximately 3 million litres a year. The processes followed for both case studies are shown in Figure 1.

4. Results

4.1. System Production

Within both case studies, much of the equipment has been hand made or assembled and so, whilst these case studies are a good example of local businesses, the results from this may not be indicative as an average of the whole industry. Some parts of the equipment have been re-used, for example the large holding tank was originally an old printers’ ink tank. It is possible that this is due to cost, but also that those involved with making a product such as biodiesel are interested in the re-use of products for their environmental benefits. Therefore, whilst the re-use of materials does in some way make each system unique; it is possible that many companies will use re-cycled and re-used materials.

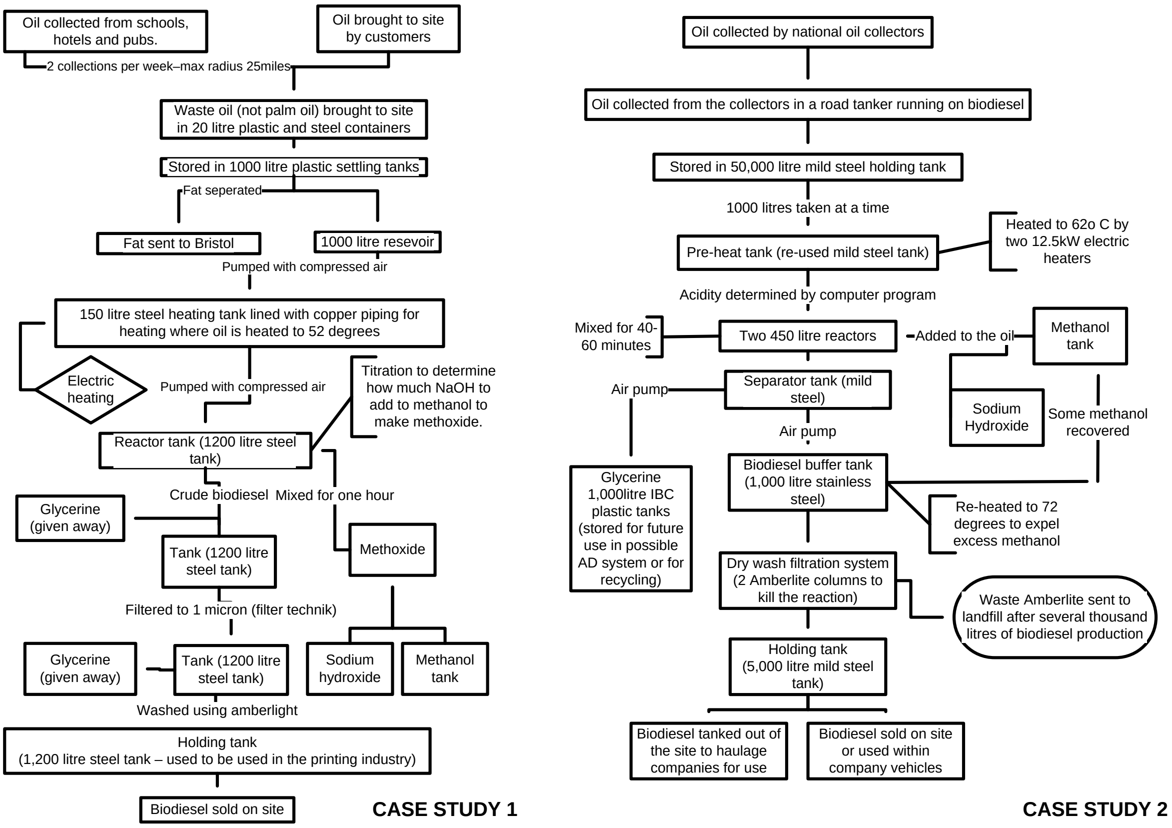

Figure 1. Waste oil collection and biodiesel production processes.

A fair way to determine the allocation of environmental burden to a re-used product is difficult. If a product is used once then all of the burdens must be attributed to that one use. If it is certain that the product will be recycled then any benefit associated with the recycling, eg any reduction in the amount of virgin material used, can be attributed to the product during the recycling stage. However, where there is no knowledge of the full life cycle of a product, for example, how many times it will be used and for what period of time, it is more difficult to attribute environmental burdens to its different life cycle stages. However, it is known that many of the tanks used have been bought second hand and so have therefore had a previous life. This previous life should be allocated some of the burdens. It is not acceptable to attach none of the environmental burdens to the second use of the system, as there is clearly a good second hand market for these tanks. Therefore, it is proposed that half of the environmental impacts associated with the production of these re-used tanks are attributed to this system.

Figure 2 shows the normalised data for the production of both systems. This includes all the components within the system. In case study 1 there are in total six 1000 litre plastic tanks, one 150 litre steel tank, four 1,200 litre steel tanks, one 25,000 litre steel tank and one 100 litre plastic tank. The production of the larger tanks (unsurprisingly) has the biggest impact. Within the second case study the predominant impacts are shown to be attributed to fossil fuel use, mineral depletion and the production of respiratory inorganics (Figure 2). Similarly to the first case study these are due to the production of steel, which is one of the largest material components of the system. Note the differing scales on the y axis – whilst case study two system production has a larger production impact it is a larger system that can produce more fuel, therefore at this stage the figures should not be compared against each other in terms of scale, but they do show where differences in production impact occur.

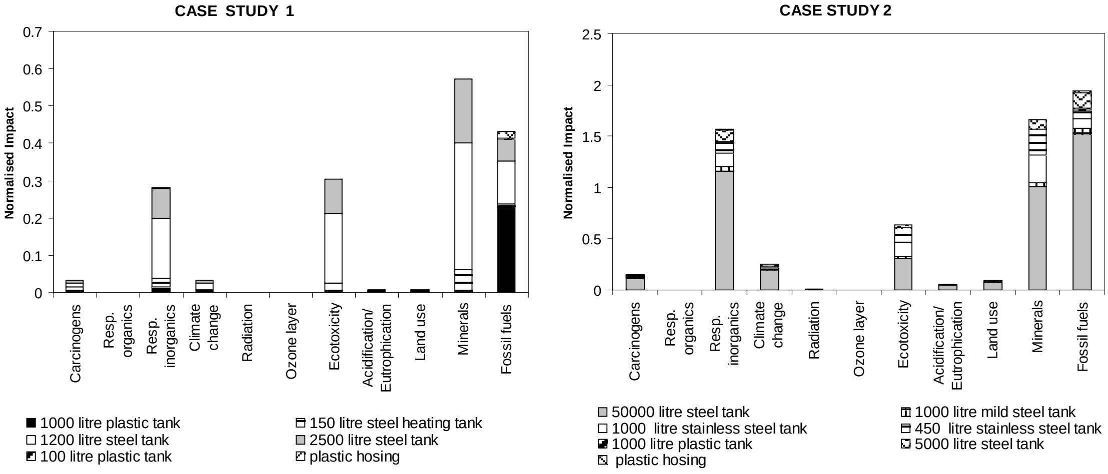

Figure 2. Normalised data for the production of the two systems; this shows the entire production systems and is not a comparison based on the final functional unit.

4.2. Production of the biodiesel

In order to determine the impact of the production of the fuel the production of the system, the use of electricity and any other consumables – such as the washing and filtering system and the collection of the oil etc, must also be examined. Specific data for the trade marked washing and filtering system used in case study 1 were not available and so this has been estimated using a generic ionic resin (of which the trade marked system is one). With used oil, there is a variation in the conversion rate from approximately 98% - 60% if the oil supplied is bad.

For the first case study, once the oil has been collected or delivered it is stored in an Intermediate Bulk Container (IBC) in the yard. From there it is pumped to a 150 litre heating tank in the building, where the oil is heated to 52ºC by electricity. It is then pumped to a reactor tank where a titration test determines the necessary quantities of methanol and sodium hydroxide needed to create a complete reaction process. The chemicals are mixed in a small methoxide tank and passed into the reactor tank. The reaction takes about one hour after which the liquid is pumped to a holding tank, which used to be a printers' ink tank. The glycerine settles to the bottom overnight and is then pumped to 150 litre tanks outside. The biodiesel then passes through a 1 micron filter to a further holding tank during which most of the particulates are removed. Further filtration then takes place via a resin filter system. The biodiesel is then stored in a final tank from which it is dispensed to customers through a metered pump. The glycerine made as a by-product of the process is given away (Figure 1).

In the second case study the oil delivered by the tanker is pumped into a 50,000 litre holding tank. From this, 1000 litres at a time are pumped into a pre-heat tank. This heats the oil to 62^{o}C using two 12.5kW electric heaters. To this is added methanol and methalate (the control systems automatically add the specified amounts) and the oil is then mixed for between forty and sixty minutes (Figure 1).

From the reactor tanks, the liquid is pumped into a separator tank where most of the glycerine falls to the bottom as the liquid flows continuously over flow plates. This means that there are no filters that need to be changed periodically in this stage of the process. The glycerine is pumped out of the bottom of the tank and currently is stored for possible future use in anaerobic digestion systems or other forms of recycling. This potential use has not been modeled here, as it held no commercial value to the companies. The biodiesel still contains some methanol and glycerine, and the next stage involves heating the liquid to 72°C in a buffer tank. The methanol evaporates at 68°C and by then re-condensing the vapour in the exhaust pipe, some of the methanol is captured and then re-cycled.

Glycerine causes problems if it is found within biodiesel and the reaction can continue after this stage, so in order to stop the reaction the liquid is then pumped through a washing and filtration process. The filters are the same as in the first case study and contain a polymeric resin that absorbs sodium and fats and attracts glycerol to the outside of the polymer beads. The system can filter 14 litres per minute and the columns can process 300,000 litres of biodiesel before they need to be emptied. The waste is inert and is sent to landfill.

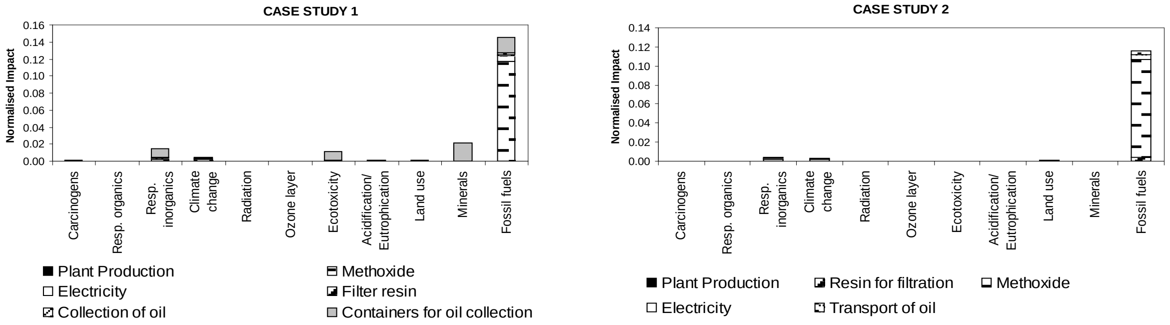

Figure 3. Normalised data for the production of 1000 litres of biodiesel using the two systems

Figure 3 shows the normalised data for the production of 1000 litres of biodiesel. Both plants are assumed to have a working life of ten years. In both cases the use of fossil fuels is the largest impact; predominantly associated with the production of methoxide, this finding is consistent with other publications in this area, for example Morais et al [10]. This is because methanol is made from either natural or coal gas. Methanol can be produced from a number of sources, and so it might be possible to reduce the impact of the methoxide by purchasing methanol that has not been made from fossil fuels. Another option would be to recover some of the methanol. This is done in case study 2; resulting in a slightly lower impact (see again the differing values on the y axis). Within case study 1 the use of the small steel and plastic collection containers also has a visible impact. These containers have been re-used, and so only half of their production impact has been allocated to them. The remaining impact is considered to be attributable to their first life.

4.3. Disposal of the Systems

No disposal options have been modelled for the plants as it is not possible to determine how they will be disposed of at this time. If the plant were to be recycled and any benefits were associated with this at the end of its life, the impact of the plant production would be reduced. However, as the plant production has a relatively small impact in the life cycle impacts, this would not have as significant effect as any change in the production methods of the methanol or a change in the collection system.

4.4. Energy and Green House Gas Emissions Analysis

There is little point producing biodiesel if it uses more energy in its production that it can produce when it is in use. Therefore the embodied energy of the biodiesel has been calculated. This has been calculated using the same processes and boundaries shown in the previous parts of the paper and includes the energy required to produce the systems, collect the waste oil and process it into biodiesel. In order to produce one litre of biodiesel with the first case study process approximately 11 MJ of energy are required, and for the second case study the figure is slightly lower at 8MJ. The difference between the two systems is predominantly due to the different scales of the systems and the way in which the oil is collected. By comparison, the energy content of diesel is approximately 38MJ/litre and the energy content of biodiesel is approximately 37MJ/litre [1]. Published ranges of embodied energy of bio-diesel from rapeseed varies; but is approximately 15MJ/L [11] to 30MJ/L [1&6]. Therefore, the production of the biodiesel from waste oil requires significantly less energy than that from rapeseed, and also provides much more energy than it requires in its production.

The total greenhouse gas emissions (GHG) have been calculated for both systems using IPCC 100 year time horizon data. The production of one litre of biodiesel generates 343g and 228g CO_{2eq} from case studies one and two respectively. Much of the GHG result from the use of the methanol and also from the collection of waste oil process. Compared to published literature these results are high. Alternatives suggest values from 87g/litre [12] to 343g/litre [11]. The differences primarily occur due to differing boundaries and allocation procedures. For example, in many cases the glycerine is used, therefore some of the burden can be and is attributed to that. As the glycerine was not used in either of these cases no burden was allocated to it. Also, the boundaries selected here do not attribute any impact to the initial production of the oil before it becomes waste. However, there are also differences that can be attributed to the producers examined; larger, more commercial producers may produce biodiesel more efficiently.

5. Discussion and Concluding Remarks

A significant impact in both of the biodiesel production systems is the use of methanol. This is due to the methanol production process which uses natural gas or coal gas. An alternative method for its production is through the gasification of a range of renewable biomass materials, such as wood and black liquor from pulp and paper mills. However, this is not as common as its production from fossil fuels. One way in which both companies could reduce their impact would be to source methanol produced from these more renewable sources.

Both systems use materials and parts that have been used before. This brings some interesting issues associated with how the burdens should be divided between the product's current use and any previous or future uses. Within any life cycle system, if an individual component is to be used two or three times then each use would be allocated half or a third of its environmental burden. However, these products have been used in completely different situations and how the burden is allocated for this is more difficult. It is unrealistic to say that the second use should have all of the burdens, as it has already fulfilled one function elsewhere. However, the second use cannot be ignored and be said to have no burden as the product clearly has a market value and therefore has been sold. It is not known whether the product has had one or two previous lives, or if it will be further used after being used in these systems. Therefore, the burden has been divided by two in order to simulate two lives for these products. As the impact of these products is small during the life time of the system, this is not a significant issue.

However, this does raise inconsistencies with the way in which the oil has been treated and modeled. Within this system the oil used has been treated as a waste. That means that no environmental burdens have been allocated to it for its production or transport to the place of its original use. Within this study the boundaries have been set at the point where the oil becomes no longer useful to its owner and is collected by the waste carrier. Often this oil is free of monetary cost to the collector, who then adds value to it by collecting it and delivering it in bulk to a second user. Previously much of this oil would have found itself as waste. Sometimes energy might have been recovered from it, sometimes not. As a waste product, it is acceptable to decide that all the production impacts are associated with the first use.

However, if this becomes a commercial product, is this method still acceptable? At this point within an LCA these issues become more philosophical than scientific. The impacts still happen, so one is only then deciding to whom or what the impact is attributed. The allocation of such burdens is an area of ongoing research within the life cycle community.

In order to improve the two systems in question less methanol use, or methanol produced from renewable sources, would improve the environmental performance of the biodiesel. In addition, a more efficient collection system would improve the process. For any further studies using the data produced, the issues associated with the system boundaries and environmental burden allocation must be noted.

Acknowledgements

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Feasibility of Jatropha oil for biodiesel: Economic Analysis

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Abstract: *Jatropha curcas L.* (also called the physic nut) is found to be a potential alternative source of renewable energy since its cultivation and oil extraction contribute to sustainable development, poverty alleviation, combating of desertification and women empowerment in developing countries. The jatropha seeds after three years of cultivation have an oil yield between 1-4 tonnes and 2.5-12 tonnes per hectare when rain fed and irrigated respectively. The Operational and maintenance costs for the oil extraction are minimal, and can be estimated at approximately 10 – 15% of the capital cost per year. In Ghana, for instance, in 2010, whilst the cost of jatropha oil and kerosene were estimated to be US$0.085/liter and US$1.23/liter respectively, the cost of biodiesel from jatropha oil and petroleum diesel were also estimated at US$0.99/liter and US$1.21/liter respectively. This indication gives jatropha oil the best 'candidate' for 'green kerosene' and biodiesel in diesel engines and particularly in multi-functional platforms (MFPs) used agro-processing/industrial applications in rural areas of Ghana. This paper presents a comparative technical feasibility of jatropha oil as fuel and biodiesel in MFPs. It also presents the findings from a study carried out in Ghana with respect to the promotion of jatropha oil as a fuel in rural areas of Ghana.

***Keywords**: Jatropha, Crude oil, Renewable energy, Biodiesel*

1. Introduction

Jatropha curcas L. has various socio-economic benefits which makes it more economical when cultivated on commercial scale. A hectare of jatropha plantation is reported to yield 2.5-3.5tonnes of seeds in the third year and increases sharply to 5000-12,000 tonnes per hectare from the sixth year onwards [1]. Like other vegetable oils, jatropha oil can be used directly in modified diesel engines for automobile applications in Europe, North America and some other parts of the world. It is however found from researches that the neat jatropha oil can be used to run the engines in mini-vans for rural transportation, haulage trucks, farm tractors and other agricultural machinery, but may require little modification [10]. According to Achten et al., 2008, at full output, hydrocarbon emission level using neat jatropha oil was observed to be 532ppm against 798ppm for fossil diesel, NO level was 1163ppm against 1760ppm and smoke was reduced to 2.0 Btu against 2.7 Btu [2]. In the northern part of Ghana, women engaged in shea butter production, use jatropha oil in place of diesel the MFPs comprising shea butter press, dehuller and the mill. Since it's quite cheaper to use jatropha oil in these MFPs, commercial cultivation of jatropha and subsequent extraction of the oil for such purposes are done in the rural northern Ghana to empower women in the area of job creation. To enhance and improve the viscosity of jatropha oil, this study assesses the feasibility of the oil for biodiesel instead based on the Ghanaian production conditions. In the rural areas where jatropha plantation and extraction are done, the drying of the seeds are done by spreading the fruit on the ground or a dark-coloured mesh net to dry in the sun. Solar and forced air dryers offer faster drying capabilities. According to research performed at the Kwame Nkrumah University of Science and Technology (KNUST) in Ghana, a fabricated 500 kg tent dryer suitable for small scale applications [3] was about US$2000 but may be costly for rural folks. This research work considered drying in the sun to minimize cost. From the roots to the seeds of the plant are numerous uses which solve some of the socio-economic problems of most people in the rural sectors of the world. The oil extracted from jatropha can be used as a substitute for kerosene without any further processing. This is more economical compared to kerosene from crude oil, which are used for rural electrification. Moreover, the raw oil is used by most rural folks for soap making which ease them of most economic problems. Jatropha farming is labour intensive thus providing job for many people in the rural areas. This paper assesses the potential of local production of biodiesel in remote areas of Ghana where jatropha plantation is done in commercial scales and used for other purposes other than biodiesel production. Since every economy is driven by the quantum of energy produced, utilized and destroyed in a particular section of the economy, the sustainability of energy systems needs to be analysed critically to allow room for improvements, process and material optimization.

Sustainability of any industrial process design comprises three main parts namely social, economic and environmental aspects. The economic indicator is based on the costs of purchasing material and energy, employing labourers, and other product prices [4] [12]. This paper focuses on the economic feasibility of biodiesel production from *Jatropha curcas L.* considering the processes from jatropha farming, through oil extraction to biodiesel production. Each unit process contains different inputs and outputs of which some have more than one alternative. Each alternative carry different values in terms of costs and to make a more proper renewability analysis in terms of economy, each production unit needs to be quantified accordingly. The economic analysis is done to compare the various alternatives for getting the final product, biodiesel. This paper assesses the cost benefits of biodiesel produced from *Jatropha curcas* considering all the processes from jatropha farming to biodiesel purification, and present the results in monetary units. Data in this research were obtained from literature [5] [9] and situations in Ghana as well as some parts of the world where jatropha is grown on commercial scale. The economic analysis of any project can only be done based on the estimates from the investments required and the cash flows. The actual cash flows achieved in any year will be affected by any changes in raw material costs and other operating costs, which may also dependent on the sales volume and price of the products [6] [13].

2. Methodology

The traditional method of producing jatropha biodiesel in the northern parts of Ghana were analysed and compared to those employed in modern technologies worldwide. In this work, the criteria used to determine the economic viability of jatropha oil for biodiesel production include the total capital cost, the total production cost, profitability and sensitivity assessments. There are currently no tax credits or subsidies for renewable energy production in Ghana and so no consideration of it in this work.

2.1 Total capital investment

This is the amount of money that must be supplied or required to finance the purchasing of equipments as well as its auxiliary parts, spare parts, construction of the plant and the acquisition of items necessary for plant operation. The total capital investment comprises the fixed capital, i.e. investment needed to supply all production facilities as well as supply of construction overheads and plant components that are directly or indirectly related the biodiesel process from jatropha; and the working capital, i.e. the amount of money needed to start the project. This is normally estimated as 0.15times the Fixed Capital Investment [6]. Total capital cost may include costs of land, equipment and installations, building and construction costs.

2.1 Total production Investment

The total production investment involves the cost needed to run the project including marketing of the product. This generally consists of the variable cost, fixed costs and general expenses. Variable cost consists of direct and indirect costs. Generally, variable cost may include costs of raw materials, utilities, miscellaneous materials, shipping and packaging which are negligible in this work because the biodiesel processor is fabricated locally in Ghana. Fixed costs also include the cost of maintenance, operating labour, supervision, plant overheads, capital charges, Insurance rates and Royalties [6]. General expenses are made up of administrative costs, engineering and legal costs, office maintenance and communications, distribution and selling cost [7].

2.3 Profitability analysis

The methods used in estimating the profitability of the project are Rate of Return on Investment (ROR), pay back period, break even point, discounted Cash Flow Rate of Return (DCCFRR) and the net present/future value [5].

2.4 Sensitivity Assessment

Sensitivity analysis is a way of examining the effects of uncertainties in the forecast on the viability of a project. This is achieved by the most probable values for various factors which establish the base case for the analysis. The cash flows and criteria of performance used are calculated assuming a range of error for each of the factors in turn [6].

2.5 Process Description and Assumptions

Fig. 1 shows the system boundary for the jatropha cultivation, oil extraction and biodiesel production.

2.5.1 Jatropha curcas farming

A case study of Jatropha curcas cultivation in Gbimsi, a village located in the northern part of Ghana was used. Organic fertilizer used for the cultivation is assumed to be produced from the seed cake through composting [8], in which the energy input is considered negligible. Labour work was assumed to replace diesel fuel consumed by the machines used in cultivation, i.e. one labour hour is approximately equivalent to 0.8 liters diesel [6]. Many researchers have argued that jatropha plant can succeed without irrigation and therefore does not compete for water or displace food production from prime agricultural land [14]. However, Ariza-Montobbio et al. reports that irrigation makes a big difference to yields, and even with irrigation the yields are so much lower than those reported from experimental plots [11]. For this study, on the other hand, irrigation of the jatropha plant was considered as done in Ghana. Harvesting of fruits starts from the 2nd year of plantation, where seed yield would have increased.

2.1.2 Jatropha oil extraction

Solvent (hexane) extraction, mechanical screw press and manual ram press are the most used methods but this work employed the mechanical screw press. The oil cake generated after oil extraction can be used as organic fertilizer for jatropha cultivation. For mechanical screw press extraction 77% oil content is obtained after extraction [6]. The screw press is locally fabricated.

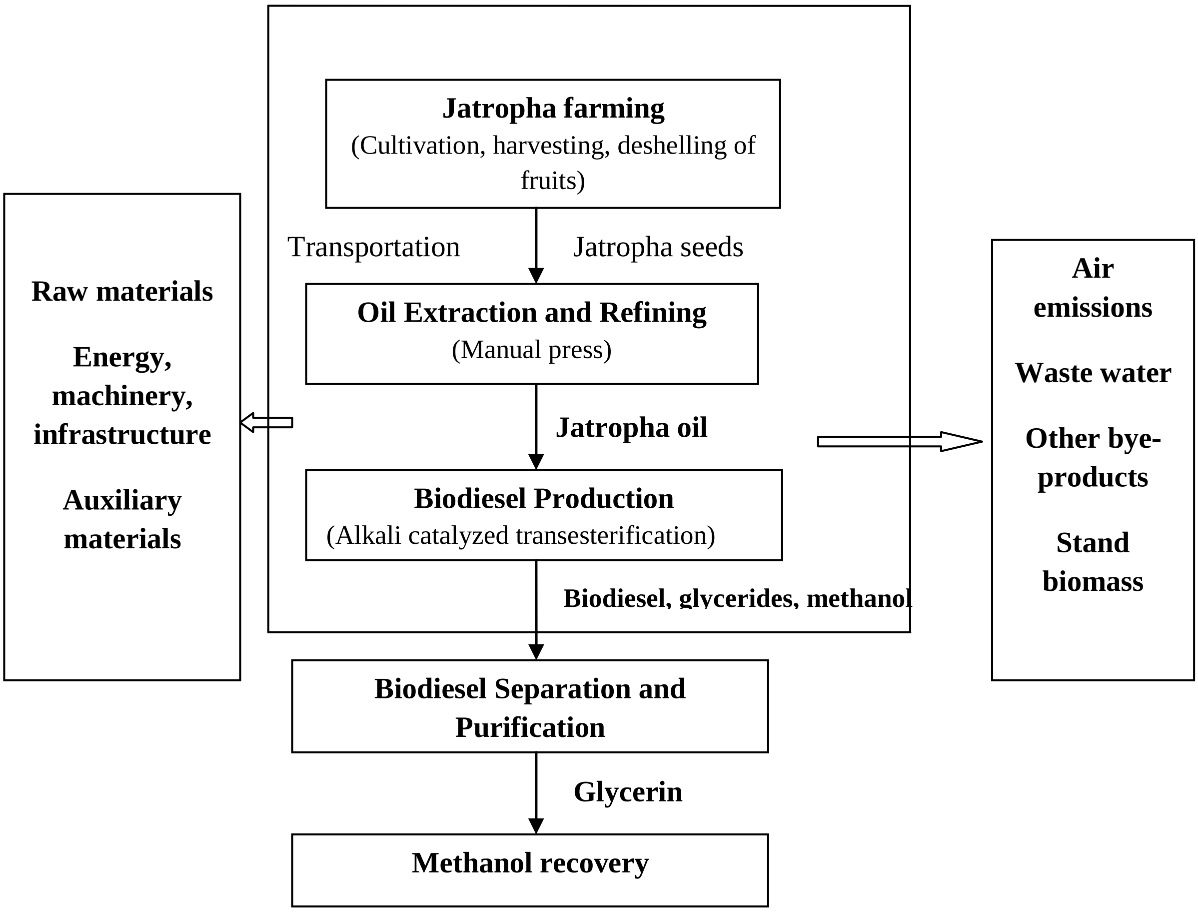

Fig. 1 Process flow diagram of biodiesel production from jatropha curcas L.

2.1.3 Jatropha biodiesel production

1 tonne of biodiesel output (apprx. 1136l) was chosen for the material balance. Alkali-catalyzed transesterification is used. All results were estimated under conditions in Ghana, and some data obtained from literature [9].

Three scenarios (Cases 1-3) were considered for jatropha oil cost at various economic conditions of Ghana, to obtain and estimated cost of the biodiesel as well as profit.

Case 1 shows present economic conditions of Ghana but estimated high cost of jatropha oil
Case 2 shows present economic conditions of Ghana but reduced cost of jatropha oil
Case 3 shows slightly reduced present economic state of Ghana yet reduced jatropha oil cost.
These three cases were chosen based on present and future cost of living in Ghana.

3. Results and Discussion

Assuming holidays and days for maintenance, the plant will work for 230 days/year

Table 1. Estimation of Fixed Capital Investment (FCI)

Item	Quantity	Estimated cost, US dollar
Land	0.67ha	496.7
Irrigation Pump	1 Hp	168
Mechanical Screw Press	1.5 tonne capacity	1000
Biodiesel Reactor	1.5 tonne capacity	11,944.41
Other land area for work	0.405ha	299
TOTAL		**13908.11**

Total Capital Investment (TCI) = FCI + Working Capital (WC) = **16362.48USD**
WC = 0.15TC

Table 2. Estimation of Total Production Cost (TPC)- Variable costs

Item	Quantity	Estimated cost, US dollar
Organic fertilizer	30kg	0
Pesticides	0	0
Cultivation Total Cost		**0**
Irrigation water	147680 l	147.68
Jatropha seeds	3.5 tonne	1750
Diesel	10.91 l	12.2
Extraction Total Cost		**1909.88**
Process water	3408 l	3.408
Methanol	227.5 l	49.98
Electricity	120kWh	14.4
Catalyst	0.082 tonne	82
Biodiesel production Total		**149.79**
TOTAL		**2059.67**

Table 3. Estimation of Total Production Cost (Fixed cost and General Expenses)

Item	Factor	Estimated cost, US dollar
Maintenance cost	0.05FCI	695.41
Operation labour	-	705.14
Administration	0.02TPC	41.19
Miscellaneous	0.1Maintenance	13.9
TOTAL		**1455.64**

Source: (Sinnot et al, 1985)

3.1 Profitability analysis

Based on the following assumptions and the estimates made in Tables 1 to 3, Table 4 was developed with the help of software for modeling the cost of an industrial plant.
Production capacity is 1136 litre for 8hour shift
The number of 8 hour shifts per day is 1
Yield of biodiesel is assumed to be 0.93

Table 4. Profitability Assessment Results of a Biodiesel Production Plant from Jatropha oil

Item	**Unit**	**Estimated cost, US dollar excluding VAT**		
		Case 1	**Case 2**	**Case 3**
Jatropha oil	per litre	2.5	0.18	0.18
Methanol	per litre	0.22	0.22	0.25
Labour cost	per week	76	76	350
Rent	per month	50	50	50
Insurance	per year	2500	2500	2500
Interest rate	percent	12	12	12
Biodiesel plant	per tonne	13849	13849	13849
Catalyst	per litre	0.006	0.006	0.006
Duty on biodiesel	per litre	0	0	0
VAT rate	percent	14	14	14
Water	per litre	0.001	0.001	0.002
Electricity	per kWh	0.120	0.120	0.120
Overheads costs	per year	4,762	4,762	4,762
Overheads costs	per litre biodiesel	0.018	0.018	0.018
Labour costs	per litre biodiesel	0.013	0.011	0.062
Water cost	per litre biodiesel	0.002	0.002	0.015
Electricity cost	per litre biodiesel	0.015	0.015	0.004
Estimated Biodiesel cost	per litre	2.779	0.383	0.339
PROFIT		**-89.42**	**803.03**	**409.91**

Source: Cash flow calculations from data collected for this work **[6] [15]**

Case 1 which also shows the conditions for maximum profits (almost at breakeven) resulted in a loss after the cash flow analysis. The loss per day is minimal recorded as -89.42 US Dollar. In this case, we assumed higher cost for jatropha oil at the present Ghana's economic status, and a higher biodiesel cost was estimated after cash flow calculations. For the second case where the cost of jatropha oil was similar compared to cost on the international market, maintaining minimal conditions, profit was observed at 803.03 US dollar per day. For case 3, profit was observed on extreme conditions i.e. the prices of jatropha oil maintained as that of the international market whilst biodiesel cost was kept low, yet there was a marginal profit of 409.91 US dollar per day. No scenario was created for harsh economic conditions because the three cases showed profitable and feasible results.

These results therefore show that the project which produces 1tonne of biodiesel per day is viable economically (except in case 1 where there was a loss) and if the plant's capacity is increased profit per day will also increase even when biodiesel price is kept as low as US$0.339. Jatropha plantation for biodiesel is worth a project considering the economic analysis with conditions and assumptions made in this report. In the northern part of Ghana where jatropha is grown on large scale, the oil after extraction is used mainly on multifunctional platforms where the oil is used purposes for fueling engines of machines which otherwise may be used manually. For instance in the northern part of Ghana, the oil is used to power the mechanical screw press instead of using diesel which is environmentally unfriendly when burnt.

Multifunctional platforms have been introduced in Ghana for such purposes to empower women especially. From the analysis, the cost of jatropha oil is much cheaper at

0.18USD/litre compared to that of biodiesel at 0.3-2.7USD/litre. It therefore presents a much more economical sense currently to use biodiesel oil from jatropha in diesel engines instead of using for producing biodiesel. However, it is still viable to go into biodiesel production using jatropha oil as detailed in the results of this work. Table 5 shows the comparison of prices between petroleum diesel, jatropha oil, gasoline and biodiesel from jatropha oil in Ghana from the year 2000 to 2010.

Table 5. Comparative prices of jatropha oil, kerosene and biodiesel in Ghana

Product	**Estimated cost, US dollar/litre**		
	2005	**2008**	**2010**
Jatropha oil	0.154	0.191	0.085
Kerosene ex-refinery	0.92	0.85	0.87
Kerosene ex-pump	0.83	0.77	1.23
Jatropha Biodiesel	1.54	1.02	0.99
Diesel ex-refinery	0.56	0.90	1.12
Diesel ex-pump	0.78	1.01	1.21

Source: Energy Commission, Ghana and TradingEconomics.com [16]

4. Conclusion and Recommendation

Biodiesel produced from jatropha oil is assessed to be feasible economically when the seeds are cultivated on large scale. In Ghana where jatropha plantation is done on commercial basis for multifunctional platforms in rural areas, jatropha oil is more economical to use compared to jatropha biodiesel. It is however viable to produce jatropha oil and further processing it when the oil is in large quantities. As reported by other studies in India, Mali etc, jatropha oil produced on commercial basis is less costly hence biodiesel production from this oil is feasible especially in MFPs which can keep the engines for a long time. Therefore, if 1tonne of biodiesel can be produced from jatropha at quite a minimal cost, then on commercial basis, when this quantity is normalized to a desired capacity, marginal profit will be reported after payback time of not more than three years. For better efficiency of diesel engines, biodiesel from jatropha is however preferred to raw jatropha oil especially in MFPs.

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Novel Production Of Biofuels From Neem Oil

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Abstract: Biodiesel production is a valuable process which needs a continued study and optimization process because of its environmentally advantageous attributes and its renewable nature. In India Neem tree is a widely grown crop, termed as Divine Tree due to its wide relevance in many areas of study. The present study is intended to consider aspects related to the feasibility of the production of biodiesel from neem oil. This report deals with biodiesel obtained from neem oil which are mono esters produced using transesterification process. The optimum conditions to achieve maximum yield of biodiesel were investigated at different temperatures and with different molar ratio of neem oil and methanol. The temperature increases yield of methyl ester at 55 ^{0}C and a molar ratio of 1:12 were found to be beneficial. From the obtained results it was apparent that the produced biodiesel fuel was within the recommended standards of biodiesel fuel. The fuel properties of biodiesel including kinematic viscosity and acid value were examined. The engine power and pollutant emissions characteristics under different biodiesel percentages were also studied. Experiments demonstrated that the biodiesel produced using neem oil could reduce smoke and Carbon monoxide emissions, significantly while the Nitrogen oxide emission changed slightly. Thus, the ester of this oil can be used as environment friendly alternative fuel for diesel engine.

Keywords: *Biodiesel, Transesterification, Methyl ester of neem oil, Emissions*

1. Introduction

Vegetable oils have become more attractive in the recent past owing to its environmental benefits and the fact that it is made from renewable resources. Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel. Oils derived from vegetable and microbial sources may in course of time become as important as petroleum and the coal tar products of present time [1]. Recent increases in petroleum prices and due to uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines [2].

Neem (*Azadirachta indica*) is a tree in the mahogany family Meliaceae which is abundantly grown in varied parts of India. The Neem grows on almost all types of soils including clayey, saline and alkaline conditions. Neem seed obtained from this tree are collected, de-pulped, sun dried and crushed for oil extraction. The seeds have 45% oil which has high potential for the production of biodiesel [3]. Neem oil is generally light to dark brown, bitter and has a rather strong odour that is said to combine the odours of peanut and garlic. It comprises mainly of triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature and in order to emulsify it in water for application purposes, it has to be formulated with appropriate surfactants.

Neem oil also contains steroids (campesterol, beta-sitosterol, stigma sterol) and a plethora of triterpenoids of which Azadirachtin is the most widely studied [4].This study is intended to consider aspects related to the feasibility of the production of biodiesel from neem oil in an attempt to produce biodiesel using the abundantly grown tree naturally as the use of vegetable oils for engine fuels seems insignificant at present day scenario. Neem oil will become a potential supplier of Biodiesel in future. Biodiesel is a mono alkyl ester (methyl or ethyl ester) of long chain fatty acids derived from renewable lipid of neem oil. Biodiesel thus obtained can be used in any compression ignition (diesel) engines without the need of modification and is therefore a good substitute for diesel fuel. The first documented commercial production of rapeseed oil methyl esters is reported to be in 1988 [5]. It possesses several distinct advantages over petro-diesel in following safety, biodegradability and environmental aspects [6].

This present study is intended to consider aspects related to the feasibility of the production of biodiesel from neem oil. The variables affecting the yield and characteristics of the biodiesel made were studied. The obtained results were analyzed and compared with conventional diesel fuels.

2. Methodology

Neem oil was obtained commercially. Chemicals such as Sodium hydroxide, Methanol, Sulphuric acid, Phosphoric acid were purchased from Merck. All the chemicals used were of analytical reagent grade.

2.1. Experimental Setup of Transesterification Process

Biodiesel fuel blend can be conventionally prepared by using alkali or acid as catalyst.100gm of refined neem oil is mixed with 12gm of alcohol and 1gm of sodium hydroxide (NaOH) which acts as catalyst. The experiments were conducted in a manner similar to Soxhlet extraction apparatus [7].This mixture is taken in a 500ml round bottomed flask .The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w. Using magnetic stirrer and heater equipment the above mixture is thoroughly mixed and maintained at a temperature of 50-55 ^{0}C for two hours. The mixture is now allowed to settle for 24 hours at which two separate layers are obtained. The top layer will be methyl ester of neem oil (fatty acid methyl ester (FAME) i.e, .biodiesel) and the bottom one glycerin. Using a conical separating funnel the glycerin is separated at the bottom. To separate the FAME (fatty acid methyl ester) from glycerol, catalyst (NaOH) and methanol, washing was carried out with warm water. Further water and methanol will be removed by distillation. Then the NaOH, Glycerol, methanol and water was treated with phosphoric acid for neutralizing the catalyst. Finally glycerin is obtained as a byproduct in case of alkali transesterification process. Fig.1. shows the experimental set up of the process.

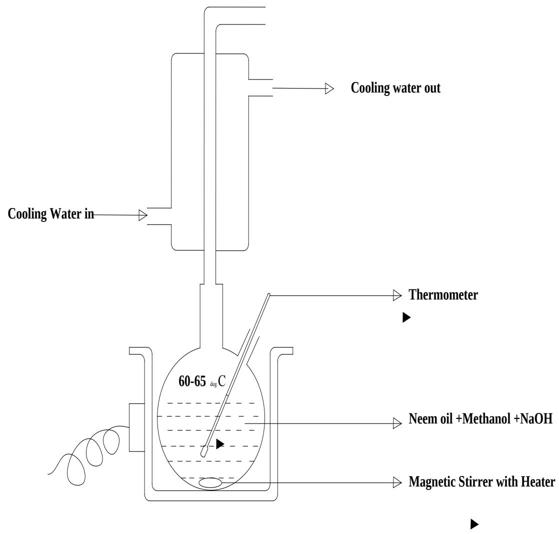

Fig.1. Experimental set-up

Acid catalyst production is the second conventional way of making the biodiesel. The most commonly used acid is sulfuric acid. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day obtaining the final product [8].

2.2. Distillation of Crude Biodiesel

The crude biodiesel was composed of FAME and methanol. FAME was purified by a distillation system. It was provided with an evaporator and an internal condenser. Feed (0.2 L/h) was let in using a jacketed glass vessel equipped with a flow regulation valve, where the temperature was maintained at 40^0C.The discharge of distillate and residue was done in glass flasks. The vacuum system was composed of a mechanical pump and a diffusion pump. The heating of the evaporator was provided by a jacket. The yield of the purified biodiesel (FAME) was calculated by from the ratio of the mass of the purified biodiesel to that of the crude biodiesel. Biodiesel was distilled from the crude biodiesel at evaporator temperatures of 40, 50, 60, and 70 °C. Other conditions for distillation were maintained at evaporator vacuum to be 1.0 Pa, the condenser temperature at 40 °C.

3. Results and Discussion

The raw neem oil has high moisture content and contains other impurities. In order to remove the moisture and impurities from the neem oil it has to be refined. The purification process can be accelerated tremendously by boiling the oil with about 20 % of water. The boiling should continue until the water has completely evaporated (no bubbles of water vapor anymore). After few hours the oil then becomes clear**.** This refined neem oil is taken as raw material for transesterification process. If the neem oil is having 6% free fatty acid content alkali transesterification process seems to be better option otherwise acid transesterification process is carried out. Since the free fatty acid content was observed to be 5.7 in weight percentage alkali transesterification process was carried out. The refined neem oil was checked before doing transesterification process and properties are tabulated in Table 1.

Table 1. Properties of Neem oil

Properties	Quantity	Fatty Acid	Weight %
Moisture content (wt %)	0.4	Oleic acid	51.3
Free Fatty Acid Content (wt %)	5.7	Palmitic acid	17.8
Refractive Index	1.47	Linoleic acid	14.7
Gum Content (wt %)	0	Steric acid	14.4
Iodine Value	80	Arachidic acid	1.6
Density(kg/m3)	1024	Myristic acid	0.03

3.1. Transesterification process at different molar ratios of methanol and neem oil-alkali catalyst

Different molar ratios of methanol and neem oil were taken for studying the yield percentage. The mole ratio of 1:12 was found to be efficient compared to lower or higher molar ratios where the conversion was around 83%. On further increase in the methanol it leads to a saturation curve as shown in Fig.1 , 1: 12 molar ratio were taken for further studies. Temperature effects were conducted on transesterification process (Fig.2). As the temperatures increases, the yield of methyl ester also increases to a maximum of 92% which was at 55^0C.If the temperature reached a v alue beyond 60^0C the yield started decreasing drastically.

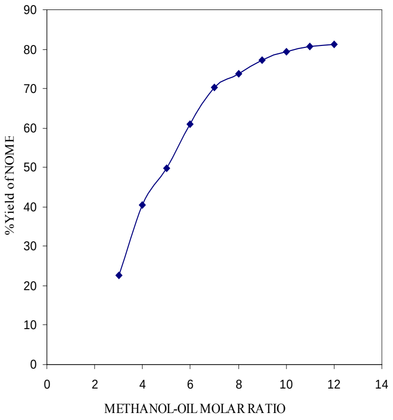

Fig.2. Different molar ratio of methanol and oil

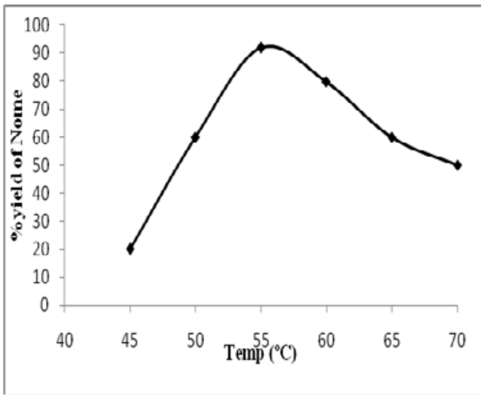

Fig. 3. Effect of temperature

Table 2. Comparison of Biodiesel obtained from acid, alkali catalysts and Commercial Diesel

PROPERTIES	**NOME (ACID CATALYST)**	**NOME (ALKALI CATALYST)**	**DIESEL FUEL**
Viscosity at 40 ^{0}C (cP)	5.3	4.9	6.8
Density at 15 ^{0}C (g/cc)	0.78	0.81	0.8
Heating value(Mj/kg)	39.1	39.4	44.5
Cetane number	46.0	46.0	51.0
Carbon mass (wt %)	76.7	76.7	86.8
Hydrogen (wt %)	12.1	12.1	13.1
Oxygen (wt %)	11.15	11.15	0.00
C/H ratio	6.33	6.33	6.63
Sulphur (wt %)	≤ 0.004	≤ 0.004	0.042
Total glycerin (%)	0.027	0.03	-
Free glycerin	0	0.00	-

3.2. Properties of NOME

The comparison of properties between neem oil and diesel are tabulated in Table 2.Testing was done to study the properties of the neem oil after undergoing transesterification process and properties of neem oil methyl ester is tabulated in Table 2. The cetane number was found to be 46 which are in par with commercially available diesel. Sandun Fernando et al., stated that the cetane number for biodiesel should be a minimum of 47[9]; as high cetane number could lead to engine performance problems. Glycerin result measures the amounts of unconverted and partially converted fats and oils which are in comparison in both the catalysts. The neem oil properties were compared with the normal diesel fuel. The sulphur content of NOME was found to be less than 0.004. Compared to diesel it is very less. So neem oil is found to be nontoxic.

3.3. FTIR results of nonesterified and esterified neem oil

The FTIR test of nonesterified and esterified neem oil is carried out using MATSEN equipment. The IR spectra of neat esterified and nonesterified neem oil show (Fig.4 & Fig.5) the pronounced functional groups which indicate the presence of alkanes and lesser extent of aromatics and polyaromatics groups, with a clear absence of phosphorous and sulfur. The IR spectra of the esterified neem oil also show that they contain significant amount of esters. The esterified neem oil contains little amount of water and this water was removed by heating the oil before using in the engine. The comparative frequency ranges of IR-spectra, their corresponding functional groups and indicated compounds were performed by Nurun Nabi et al. [10].

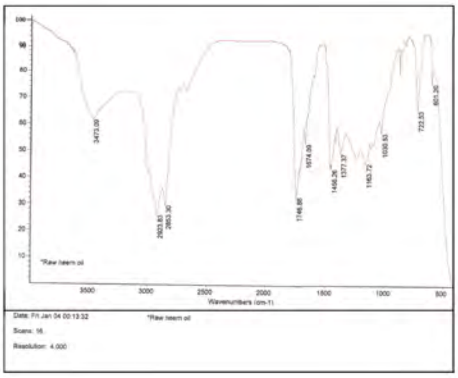

Fig.4. IR Spectra of Esterified neem oil

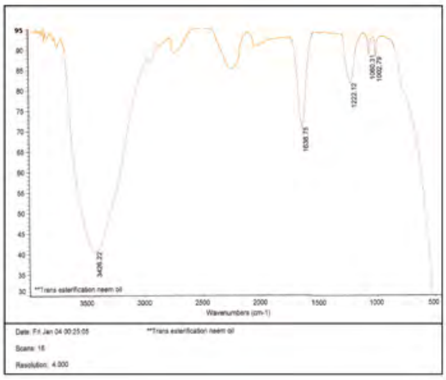

Fig. 5. IR Spectra of non Esterified neem oil

3.4. Distillation of Crude Biodiesel

The yield of purified biodiesel increased as the evaporator temperature increased from 40 to 70 °C, the yield increased from 55.45% ± 0.5% to 63.67% ± 0.25%. However, the color of the final products changed from being colorless to light yellow when the evaporator temperature increased. Distillation was introduced as an alternative practice for biodiesel production via two ways. One method was to remove the FFAs from the feedstock with a high acid value to a very low extent, so the base-catalyzed transesterification was easy to perform. The other method was to purify FAME at 50−80 °C from the crude biodiesel from low-quality feedstock to meet a high biodiesel standard. Distillation was also employed to remove FFAs from acidic neem seed oil at 60°C for the production of biodiesel.

3.5. Analysis Of Exhaust Emissions With Neat Diesel Fuel And Diesel Neem Oil Blends

3.5.1. Effect of engine speed on brake thermal efficiency

In order to study the effect of Brake thermal efficiency, the speed of engine was operated at various levels ranging from 500-1500rpm. In this study, four cylinders IDI diesel engine was used as a test engine. The test engine specifications as reported by them were injection time 20^o CA BTDC and pressure of 120 bar.

An increase in the engine speed of upto 1050 rpm the Brake thermal efficiency increased as also the fuel consumption. Beyond 1050rpm there was a slight decrease in Brake thermal efficiency even with higher fuel consumption. This is an indication of low calorific value with an increase in fuel consumption. At 1050rpm, there was high Brake thermal efficiency indicating complete combustion of fuel hence further studies were carried out at this rpm.

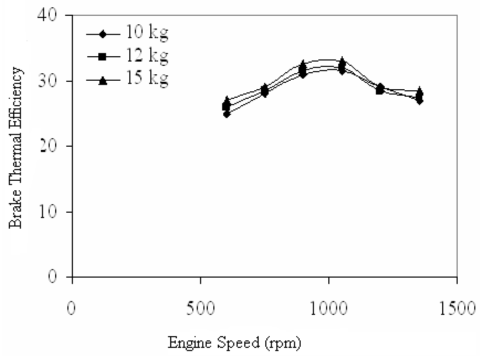

Fig.6. Brake Thermal efficiency

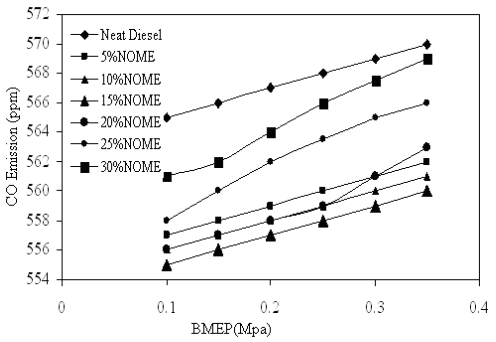

Fig. 7. Carbon monoxide emission

3.5.2. Carbon monoxide emission

The carbon monoxide emissions of the Neem oil methyl ester and various other blends of biodiesel were found at the rated engine speed of 1050 rpm for different Brake Mean Effective Pressure (BMEP). The result shows (Fig.7) carbon monoxide emissions are found to be increasing with increasing BMEP. This is typical with all internal combustion engines, since air fuel ratio decreases with increase in load. The engine emits more CO using diesel as compared to that of biodiesel blends under all BMEP conditions. With increasing biodiesel percentage CO emission level decreases up to 15%blend, increasing the percentage of NOME in diesel more than 15% CO emission is increases. Biodiesel itself has about 11.15 % oxygen content in it. This helps for the complete combustion. Reports show that the carbon monoxide emissions emerging from the biodiesel will lower the overall load and speed ranges up to 51.6% [10].

3.5.3. NO_X emission

The NO_X emission characteristics with respect to various BMEP's at various blends of Neem oil was found. The result shows (Fig.8) the diesel fuel is having lower NO_X emission and blended Neem oil is having higher NO_X emission. Compared to conventional fuel the NO_X emission is increased by 5% with the blend of Neem oil. The presence of oxygen in NOME helps to produce more amount of NO_X The impact of fuel injection also play a role in the higher NO_X emissions in the NOME. The NOx variations were less than 8%, which is consistent with most published results [11].

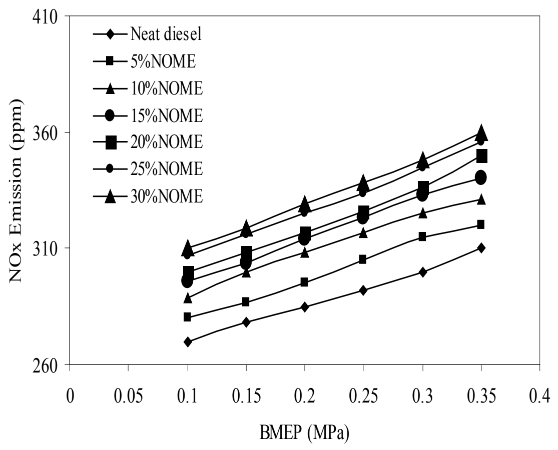

Fig.8. No$_x$ Emission

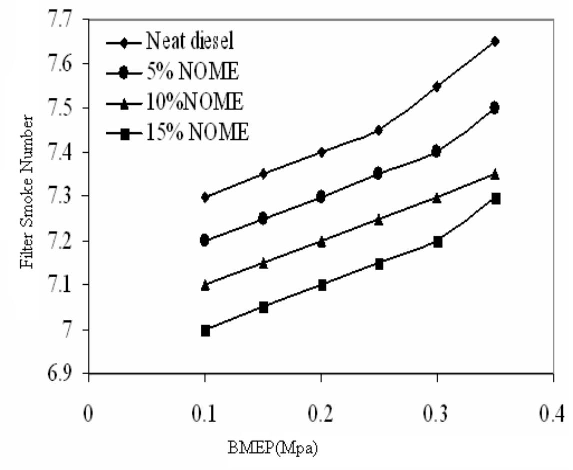

Fig. 9. Smoke emission

3.5.4. Smoke emission

Fig.9 represents filter smoke number with respect to different BMEP. The filter smoke number with respect to different BMEP was analyzed for various blends of fuel. The results confirm that filter smoke number for biodiesel blend to be lower for NOME than that of the diesel fuel. 15% blend show low smoke number contributing to the factor that lesser amount of unburnt hydrocarbons is present in the engine exhaust emission**.** Previous researchers *showed* the visible smoke emerging from the biodiesel over all load and speed ranges are lower by 13.5% to 60.3% [12].

4. Conclusion

Studies have been made using neem oil, a novel feedstock of obtaining biodiesel which is renewable in nature. The effect of methanol to oil molar ratio and acid & alkali catalyst transesterification were analyzed. The exhaust emissions of neem oil blended biodiesel are studied. Compared with conventional diesel fuel, diesel exhaust emissions including smoke and CO were reduced, while NO_X emission was increased with the diesel-NOME blends. The reductions in CO and smoke emissions and the increase in NO_X emission with Diesel – NOME blends may be associated with the oxygen content in the fuel. More than 15% NOME-diesel blends created poor atomization tendency and incomplete combustion in engine. So the engine exhaust emission level is increased. The ester of this oil can be used as environment friendly alternative fuel for diesel engine creating a greener environment in the future.

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Characterization of Waste Frying Oils Obtained from Different Facilities

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Abstract: Biodiesel cannot economically compete with petroleum-based diesel fuel because of its high cost problem. This problem may be solved with the use of low cost feedstocks in biodiesel production. Waste frying oils are one of the low cost feedstocks. However, the feedstocks' properties to be processed must be controlled in detail prior to transesterification reaction, since the physical and chemical properties of the feedstock significantly influence biodiesel production reaction as well as fuel properties. Frying oils which are used in various facilities in different conditions (such as frying temperature, time, and kind of food) have significantly different physico-chemical properties. Therefore, in this study, 30 different waste frying oil samples (14 from fish restaurants, 5 from fast-foods, 5 from hospitals, 4 from pastry shops, and 2 from restaurants) were collected and their density, viscosity, total polar material, water content, acid value, iodine value, peroxide value, and heating content were determined and compared to each others. The correlations between the total polar material content (which has to be legally determined to monitor frying oil's degradation level) and density, viscosity, acid value and water content were remarkable. The usage of peroxide value to decide the quality of an oil was misleading.

Keywords: *Biodiesel, Low cost feedstock, Waste frying oil, Characterization.*

1. Introduction

One of the most important and critical parameters which are effective in social and economical development of a country is energy. Energy consumption is steadily increasing each passing day as a result of rising world population, technological developments and living standards. At the present day, about 90% of the world's total energy needs are met by fossil fuels and 45% of these fossil fuels is petroleum (petroleum's share is supposed to rise to 58% in 2030) [1, 2]. Although petroleum is the most of energy sources used in the world, its reserves originate from some regions. Thus, the world's many countries such as the USA and European Union (EU) countries have to import their energy requirements. In Table 1, daily petroleum production and consumption amounts of some countries are seen.

Table 1. The petroleum production and consumption amounts of some countries [3]

Country	Petroleum Consumption (barrel/day)	Petroleum Production (barrel/day)
USA	18,690	9,056
EU	13,680	2,383
China	8,200	3991
India	2,980	879
Russia	2,850	9,932
Germany	2,437	157
France	1875	71
Turkey	580	53
Greece	414	7

As seen in Table 1, the USA which has the largest industry in the world can produce only the half amount of its petroleum consumption. Situation of EN countries which are poor in terms of fossil fuels is worse. These 27 countries can only produce about 17% of the consumed amount with their own resources. As the result of increased dieselization, diesel fuel (D-2) is the most consumed oil-based engine fuels, and this share is rising progressively each passing year. For example, in Turkey, about 7.4 million tons of D-2 was consumed, while gasoline consumption was only 2 million tons in the year of 2009 [4].

When we consider the pessimistic situation explained above, the importance of alternative diesel fuel which is renewable, sustainable, green (not causing global warming and acid rains) and producible with domestic sources is evidently understood.

Biodiesel which is defined as fatty acid alkyl monoesters derived from feedstocks such as vegetable oils and animal fats is one of the most important renewable energy sources. It has many superior properties over D-2 including renewability, lubricity, biodegrability, exhaust emission etc. Increasing environmental concerns and the need for energy independence have led to the biodiesel market. The global biodiesel market is expected to grow from $8.6 billion in 2009 to $12.6 billion in 2014 [5]. The EU is the biggest biodiesel producer in the world. As seen in Table 2, annual production of 27 EU countries increased from 3.20 million tons in 2005 to 9.04 million tons in 2009 which means the increase is about 3 times.

Table 2. EU biodiesel production and capacity amounts [6]

Year	Annual Production (million tons)	Annual Growth (%)	Annual Production Capacity (million tons)	Annual Growth (%)
2005	3.20	65.0	4.23	88
2006	4.90	54.0	6.07	43.50
2007	5.74	16.8	10.29	69.55
2008	7.70	35.7	16.00	54.49
2009	9.04	16.6	20.91	30.69

However, this must be remembered that these figures have been essentially attained through governments' economic stimulations and subsidies which were enforced in accordance with EU directive (2003/30/EC) and this has led to serious tax losses. Biodiesel cannot economically compete with D-2 because of its high cost. As biodiesel is usually obtained from high quality food-grade vegetable oils, the biggest reason of the high cost problem is feedstock cost which approximately accounts for 70 – 90% of the total cost of biodiesel production [7, 8]. This problem may be solved with the use of low cost feedstocks in biodiesel production. Waste frying oils are one of these low cost feedstocks. Compared to neat vegetable oils, the cost of waste frying oils is anywhere from 60% less to free, depending on the source and availability [9]. With this decrease in the feedstock cost, the great difference between the prices of biodiesel and D-2 can be lowered to an acceptable value.

2. Waste Frying Oils as Biodiesel Feedstock

In Europe, a total of about 17 million tons vegetable oils are annually consumed and this amount raises approximately 2% each passing year [10]. It is clearly understood from this figure that there are very big amounts of waste frying oil resources. However, there is no comprehensive study carried out on the waste frying oil potential of the EU countries and very little portion of this waste oil can be collected. When waste frying oils are poured into kitchen sink; they block drains in the course of time, and cause the sewerage not to be used by catching other waste materials in the sewerage system. Thus, they damage waste water treatment plants and raise processing costs. According to a study performed in USA, 40% of the sewerage system blockages are caused by the waste frying oils poured into kitchen sink [10]. Moreover, waste frying oils have eco-toxic properties. If they are spilled onto ground, they will contaminate the soil and so damage plants.

Waste vegetable oils usage in the production of animal feed has been forbidden by European Commission since 2001 because of bovine spongiform encephalopathy (mad cow disease). In addition, these waste oils and fats have not been used in soap production since they may cause health problems. Thus, waste oils and fats can only be used as feedstock in the production of biodiesel. Furthermore, by using waste frying oils as feedstock in biodiesel production, in addition to their positive influence in reducing the final cost of biodiesel, serious environmental pollution problems causing from these waste oils can be eliminated. However, the physical and chemical properties of the feedstock significantly influence biodiesel production reaction as well as fuel properties. Because of this, in order to obtain fuel quality biodiesel, the feedstocks’ properties to be processed must be controlled in detail prior to transesterification reaction.

3. Chemistry of Frying Process

During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Three essential degradation reactions occurs under these conditions are:

- Hydrolysis causing from the moisture content of fried food. This reaction produces free fatty acids (FFA), mono- and diglycerides.

- Oxidation causing from the contact with oxygen. Reaction products are oxidized momomeric, dimeric and oligomeric triglycerides and volatile materials such as aldehydes and ketones.

- Polymerization causing from these two reactions, and high temperatures. This reaction produces dimeric and polymeric triglycerides with ring structure [11-13].

Because of these degradation reactions mentioned above, a number of physical and chemical changes occur in frying oils including increase in viscosity, density, FFA content, total polar material (TPM), polymerized triglycerides, and decrease in smoke point, the number of double bonds, etc. If the frying process is continued, these materials will undergo further degradation and finally the oil will not be appropriate for frying. The frying oil has to be discarded.

Since all degradation products are of polar character, TPM content of frying oil is a good indicator of its degradation level. Thus, in many countries, TPM content of frying oil has been legally accepted as the limit value to decide discard it or not. For example, in Turkey, TPM content of frying oil must not exceed the top level of 25%. In addition to TPM, as the oil deteriorates, some changes in its physical and chemical properties occur. For instance, during frying, oil’s double bonds are ruptured and so its fatty acid composition changes, FFA level and saturation degree increase [14, 15]. The change in the fatty acid composition influences some oil properties such as iodine value, viscosity, density, heating content. Thus, these properties can also be used to monitor the quality of the frying oil.

4. Methodology

Waste frying oils which are used in different conditions (such as frying temperature, duration, the type and shape of the fryer, kind of food etc.) have significantly different physico-chemical properties. In this study, in order to decrease this difference, after classifying the facilities producing waste frying oils into categories, 30 different waste frying oil samples (14 from fish restaurants, 5 from fast-foods, 5 from hospitals, 4 from pastry shops, and 2 from restaurants) were collected and their density, kinematic viscosity, TPM, water content, acid value (AV), iodine value (IV), peroxide value (PV), and heating content were determined and compared to each other. It must be pointed out that, at the end of the project which is carried out with the collaboration of Izmit Municipality, totally, 150 waste frying oil samples will be collected from 7 different sectors and also, in addition to the physico-chemical properties mentioned in this article, saponification value, cetane index and smoke points of all samples will be determined.

The procedures used in the determination of AV, PV, and IV are AOCS Cd 3a-63, AOCS Cd 8-53, and TS EN 14111, respectively.

Samples were coded according to their origins. Namely, FR means waste frying oil sample obtained from fish restaurants, FF means waste frying oil sample from fast-foods, H means from hospitals, PS means from pastry shops, and R means from restaurants.

5. Results and discussion

All results determined are shown in Table 3. When the waste frying oil samples obtained from fast-foods are examined and compared to each other, it is seen that FF1 has the TPM content of 30% and exceeded the top limit of 25%. Moreover, in addition to TPM, water content, PV and AV of this waste frying oil was the highest. Its AV (17.85 mg KOH/g) was more than twice of that of FF5 which was the second highest. FF4's TPM content (24.5%) was close to the top limit value. In addition, density and viscosity values of this sample were the highest. Its viscosity was 6.95 mm^2/s higher than that of the second highest viscosity. It was a reasonable result that the peroxides values of FF1 and FF4 which had the highest TPM contents were almost same (50.61 and 50.42 meq/kg). However, among the samples obtained from fast-foods, FF4's AV (1.78 mg KOH/g) was the lowest and its IV (95.38 $gI_2/100g$) which is the indicator of unsaturation level was the highest. Whereas its iodine value was expected to be low as the result of destruction of double bonds, the result was not in this expectation. As the heating content increases with saturation, the highest heating content (39741 kJ/kg) belonged to FF5 which was the most saturated sample having an IV of 52.17 $gI_2/100g$.

Among the samples collected from hospitals, TPM content of H1 (29%) was the highest and higher than the top limit. Again, the result of the same sample had the highest density, viscosity, water content and lowest iodine value. However, high TPM level which is the indicator of massive deterioration made us think that its peroxide value would be the highest, but it was in the third order among the waste frying oils from hospitals with the value of 20.82 meq/kg. This may be explained by splitting of hydro peroxides which form during the first stage of the oxidation, in the course of time. AVs of the samples were closer to each other and all of them were lower than 1 mg KOH/g.

*Table 3. Data obtained from waste frying oil samples**

1	2	3	4	5	6	7	8	9
FF1	0.9237	42.28	1657.00	17.85	85.53	50.61	30.0	39223
FF2	0.9194	39.81	1310.30	3.74	82.29	33.78	16.0	39259
FF3	0.9183	42.37	441.76	2.64	66.48	36.84	15.5	39090
FF4	0.9273	51.44	1059.30	1.78	95.38	50.42	24.5	39007
FF5	0.9207	44.47	1181.90	8.62	52.17	19.05	19.5	39741
H1	0.9311	47.24	1208.7	0.52	97.30	20.82	29.0	38925
H2	0.9231	34.80	956.78	0.93	119.81	7.75	13.5	39650
H3	0.9273	39.91	1050.70	0.50	124.28	26.65	23.0	39322
H4	0.9242	34.81	1021.30	0.65	126.90	10.74	15.5	39498
H5	0.9231	35.18	785.31	0.25	121.13	28.41	14.0	39689
PS1	0.9238	39.89	710.03	0.56	141.26	55.92	16.0	39632
PS2	0.9237	34.28	533.75	0.39	124.09	93.94	12.0	40336
PS3	0.9232	32.85	568.52	0.22	126.54	74.22	16.0	39466
PS4	0.9223	33.79	566.53	0.17	120.86	200.38	11.5	39276
R1	0.9219	34.34	530.05	0.37	109.19	85.17	18.0	39270
R2	0.9216	34.64	556.44	0.63	108.26	20.69	13.0	39399
FR1	0.9264	40.52	1200.10	5.25	112.57	43.42	20.0	39344
FR2	0.9269	39.86	1089.50	0.36	128.84	42.51	22.0	39404
FR3	0.9248	36.94	753.37	0.49	122.29	49.05	16.5	39492
FR4	0.9252	37.12	714.90	0.41	122.99	52.05	20.0	39449
FR5	0.9238	35.99	817.73	0.28	121.71	44.46	17.0	39519
FR6	0.9236	35.61	966.50	0.29	127.07	46.64	16.0	39556
FR7	0.9241	34.89	915.33	0.75	118.83	53.77	15.5	39367
FR8	0.9243	37.74	669.46	0.32	120.70	31.43	16.0	39518
FR9	0.9238	35.58	1024.10	0.34	108.58	25.39	17.0	39449
FR10	0.9238	36.37	732.64	0.43	124.37	21.72	16.5	39652
FR11	0.9233	33.74	670.11	0.29	120.70	39.74	17.0	39624
FR12	0.9239	34.85	713.93	0.41	124.48	34.24	15.5	39562
FR13	0.9249	38.14	827.15	0.41	124.33	40.49	16.5	39465
FR14	0.9262	41.60	1017.80	0.48	119.72	48.31	19.5	39474

*1;Company Code, 2;Density (g/cm^3 @ 15 °C), 3;Viscosity(mm^2/s @ 40 °C), 4;Water Content (ppm), 5;Acid Value (mgKOH/g), 6;Iodine Value (gI$_2$/100g), 7;Peroxide Value (meq/kg), 8;Total Polar Material (%), 9;Heating Content (kJ/kg)

Within the waste frying oils from pastry shops, the one which had the highest density, viscosity, water content, AV, and TPM was PS1. However, this sample had the lowest PV (55.92 meq/kg) and the highest IV (141.26 gI$_2$/100 g). Normally, low PV and high IV are attributed to slight oxidative degradation. However, this oil was one of two samples which had the highest TPM content. This situation made us think that the degradation reactions which had increased the TPM content of the oil caused from hydrolysis and polymerization rather than thermal oxidation. High water content and AV can be interpreted as the result of hydrolysis. PS4 which was the first waste frying oil in terms of PV (106.44 meq/kg higher than the second one) had the lowest TPM content (11.5%) and it was amazing.

In this study, 2 samples were collected from restaurants. When we examine the results of these samples, it was seen that their density and viscosity values were almost the same. R1 had higher values than R2 in terms of PV (the difference is 64.48 meq/kg) and TPM content (the difference is 5%). This showed us that this frying oil was subjected to more degradation reaction. However, IVs of these two oils were almost same. Whereas, it was expected that R1 had the lower IV due to higher oxidation reaction leading to splitting of double bonds.

Among the waste frying oil samples obtained from fish restaurants, FR1's AV of 5.25 mg KOH/g was 7 times higher than that of second oil. The AVs of other 13 samples were less than 1 mg KOH/g. The density, viscosity, water content and TPM amounts of this oil were within the highest ones.

FR2 which had the highest TPM content (22%) was within the first three samples in terms of density, viscosity and water content. One of the most remarkable results among waste frying oils obtained from fish restaurants was that all the heating contents were almost the same. The difference between the highest heating value (39624 kJ/kg) and the lowest heating value (39344 kJ/kg) is only 0.7%.

6. Conclusions

According to the results, at first, it must be strongly emphasized that waste frying oils are very heterogeneous feedstock for biodiesel production in terms of physico-chemical properties and must be characterize in detail prior to biodiesel production.

When waste frying oils were compared to each other, it was seen that, in general, fast-food origin waste frying oils' viscosities, water contents and AVs were higher and iodine values were lower than those from other sectors. The most suitable feedstocks were from pastry shops in terms of TPM, AV, and water content. The densities of all the samples were generally close to each other.

The correlation between TPM, density, viscosity, AV, and water content were remarkable. Heating contents of the samples were almost the same. In addition, the measurement of PV as an indicator of oil quality was misleading.

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Ethanol production by *Mucor indicus* using the fungal autolysate as a nutrient supplement

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Abstract: To develop a cost-effective fermentation medium, fungal extract (FE) of *Mucor indicus* biomass, which is a by-product of fermentation processes, was evaluated as a nutrient source for ethanol production by the fungus. Autolysis as a natural process of self-digestion of fungal cells was used to release the nutrients in surrounding medium leading to the production of the FE. Glucose consumption and ethanol production were followed using several media made with different concentrations of FE as nutrient supplementation replacing either yeast extract (YE) or whole nutrient. According to the results, 5 g/L YE could be successfully replaced with 5 g/L FE, resulting in higher ethanol yield (0.46 g/g) and productivity (0.69 g/L.h). Yield of glycerol production, the major byproduct of fermentation, was also increased by supplementation of the FE.

Keywords: *Bioethanol; Fungal extract; Autolysis; Mucor indicus.*

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1. Introduction

Amongst all liquid biofuels, bioethanol is widely recognized these days as a promising renewable and environmentally friendly source of energy. It is an alternative fuel with the recognition that the global crude oil reserve is finite, and its depletion is occurring much faster than previously predicted [1]. Recently, saprophytic zygomycetes strain *Mucor indicus* (formerly *M. rouxii*) has been identified as an ethanol-producing organism, capable to grow aerobically or anaerobically on a number of different carbon sources including hexoses and pentoses with yield and productivity in the same order as *Saccharomyces cerevisiae* [2]. Furthermore, the interest in the potential utilization of fungal biomass zygomycetes as a valuable product is increasing due to the structural composition of cell walls [3]. Ethanol production by fermentation of natural feedstocks usually requires the use of complex growth supplements, such as yeast extract (YE) [2, 4]. The high cost of YE and other commercial nutrients is a limitation to its application in industrial processes, including the fermentation of biomass to ethanol. Thus, it is desirable to develop media that are likely to perform well in conditions that are representative in microbial fermentation. Several studies have concentrated on the use of yeast autolysate as effective nutrients in wheat fermentations and ethanol production [5, 6]. Fungal biomass as a by-product of fungal fermentations can be used as a source of nutrients for microbial fermentations. This can be achieved by disintegration and releasing materials hydrolyzed in-to assimilable monomers to produce a fungal autolysate as a nutrient-rich solution containing such as amino-acids, peptides, phosphorus and carbohydrates. Cell autolysis as an economical method is the natural degradation process, which starts after the exhaustion of major nutrients and reserves [7]. The objective of the present study was to develop a low-cost and suitable fermentation medium based on the utilization of filamentous fungus biomass, *M. indicus*, as a nutrient source for production of ethanol with the same fungal strain.

2. Materials and Methods

2.1. Microorganism strain and media

The fungus *M. indicus* 22424 CCUG (Culture Collection University of Göteborg, Sweden) was used in all experiments. The fungus was cultivated on agar slants containing (g/L):

glucose monohydrate, 40; peptone, 10; and agar 20 at pH 5.5±0.1 and 32±0.5°C for 5 days, where the fungus grew to form a cotton-like mycelium and spores. The agar slants were stored at 4°C until use.

2.2. Fungal spore germination

The batch cultivations were carried out in 500-ml cotton-plugged conical flasks with 300 ml working volume containing glucose monohydrate (40 g/L), supplemented with (per liter): 5 g YE, 7.5 g $(NH_4)_2SO_4$, 3.5 g K_2HPO_4, 1 g $CaCl_2 .2H_2O$, 0.75 g $MgSO_4.7H_2O$ at pH 5.5±0.1. The flasks were incubated at 32±0.5°C and 180 rpm for 30 h, which provided initial biomass for further fungal autolysis.

2.3. Fungal autolysis

The produced biomass (fungal cells) from the fungal germination were recovered and separated from the liquid broth by filtration under aseptic conditions and washed at least three times with sterile distilled water to remove any residual nutrients. The clean solids were then re-suspended in sterile distilled water to achieve a concentration of 50 g/L fungal biomass. The fungal suspensions were then placed in 250 ml glass vessels immersed in a temperature-controlled shaking water bath. The initial pH was adjusted to 5.2±0.1 using either 10% sulfuric acid or 1 N sodium hydroxide. The autolysis was carried out at 55±1°C and 120 rpm for 72 h. After autolysis, the suspension was centrifuged for 15 min at 4°C and 4500 rpm, and the supernatant was designated as autolysate of fungal cells. The solubilized cell constituents in autolysate of fungal cells resulting from the autolysis were referred to as “FE”.

2.4. Ethanol production

The fermentation experiments were carried out anaerobically in 120 ml glass bottles with 50 ml working volume, containing 40 g/L glucose monohydrate and different media supplementation (Table 1) in 50 mM sodium citrate buffer with pH 5.5±0.1. The media were sterilized by autoclaving at 121°C for 20 min, and then inoculated with 1.0 ml of a suspension containing $4.5(\pm0.5) \times10^5$ spores of *M. indicus*. The fully nutrient medium containing YE (5 g/L) supplemented with mineral salts (g/L): $(NH_4)_2SO_4$, 7.5, K_2HPO_4, 3.5, $CaCl_2.2H_2O$, 1, $MgSO_4.7H_2O$, 0.75. Table 1 shows the type of supplementation corresponding to the various media assayed. All fermentations were performed in a shaking incubator at 32±0.5°C with the agitation speed of 180 rpm for 72 h. The fermentation samples were stored at -20°C before metabolite analysis.

2.5. Analytical methods

For determination of the amount of materials released from the cells into the surrounding liquid phase during autolysis (FE), 10 ml of autolysate of fungal cells after autolysis process was separated and dried in an oven at 55±1 °C until constant weight was achieved. The liquid samples from fermentations were analyzed by high performance liquid chromatography (HPLC), which was equipped with UV/vis and RI detectors (Jasco International Co., Tokyo, Japan). Glucose, ethanol, glycerol were analyzed on an Aminex HPX-87H column (Bio-Rad, Richmond, CA, USA) at 60ºC with 0.6 ml/min eluent of 5mM sulfuric acid. All components were detected on RI chromatograms. All experiments in this work were duplicated and the averages of two replications are presented.

3. Results

3.1. Effect of the supplementation of fungal extract on ethanol production

M. indicus was produced in the fully supplemented medium containing 40 g/L glucose monohydrate and other nutrient components, and the produced fugal cells were recovered by filtration and were subjected to fungal autolysis process. To verify the potential of FE as an alternative nutrient supplementation replacing YE, a series of experimental fermentations were performed at two concentrations (2.5 and 5 g/L) of FE (Table 1).

Table 1. Results of ethanol production by M. indicus in different media.

Nutrient Supplementation	Maximum ethanol volumetric productivity (g/L h)	$Y_{E/S}$[b] (g/g)	$Y_{Gly/S}$[c] (mg/g)	Terminal time (h)[d]
YE (5 g/L), mineral salts[a]	0.67	0.45	47.3	24
YE (5 g/L)	0.37	0.43	46.4	48
FE (2.5 g/L)	0.34	0.39	43.3	72
FE (2.5 g/L), mineral salts	0.53	0.40	42.0	36
FE (5 g/L)	0.54	0.43	45.1	36
FE (5 g/L), mineral salts	0.69	0.46	49.0	24

[a] Mineral salts supplementation (g/L): $(NH_4)_2SO_4$ (7.5), K_2HPO_4 (3.5), $MgSO_4.7H_2O$ (0.75), $CaCl_2.2H_2O$ (1)

[b] Maximum ethanol yield on consumed glucose.

[c] Maximum glycerol yield on consumed glucose.

[d] Time needed for total consumption was defined as the period between addition of glucose and its exhaustion to concentration below 0.5 g/L.

To establish a basis for comparison, a fermentation run was carried out in a fully supplemented medium (YE (5 g/L) and mineral salts). The results showed that, glucose was rapidly consumed and mainly converted to ethanol (Fig. 1a and b), reaching a maximum yield of 0.45 g/(g glucose) and a volumetric productivity of 0.67 g/L h in less than 24 h cultivation under anaerobic conditions. Glycerol was the most important byproduct of the fermentation with maximum yield of 47.3 mg/g glucose (Table 1). As can be seen from Table 1, *M. indicus* gave the ethanol yield of 0.43 g/g and low productivity with the supplementation of only 5 g/L YE (Table 1). A preliminary experiment was carried out using 2.5 g/L of FE as unique supplementation (Table 1). As a result, the low glucose consumption indicated the existence of nutrient limitation in the medium and the maximum ethanol concentration was reached after a relatively long reaction time (about 72 h). However, the experiment with supplementation of 2.5 g/L FE gave a poor performance in ethanol production because of nutrient limitation in fermentation media relative to YE or whole nutrient supplementations.

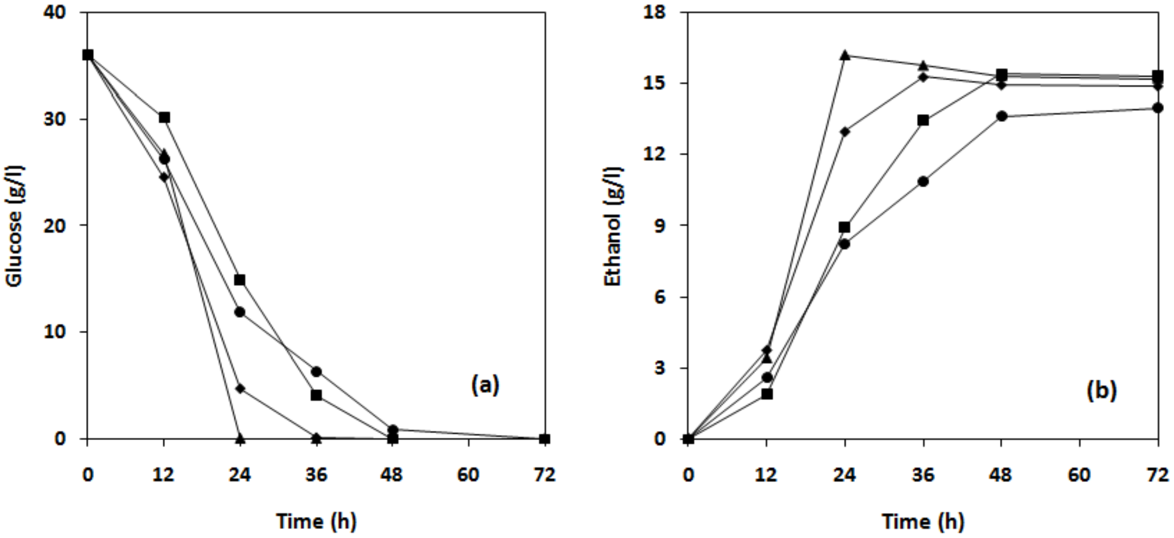

Fig.1. Effect of the supplementation of fungal extract on glucose assimilation (a) and ethanol production (b). The symbols represent of supplementation of YE (5 g/L) (■); YE (5 g/L) with mineral salts (▲); FE (2.5 g/L) (●) and FE (5 g/L) (♦).

In this direction, an additional experiment performed in order to increase the nutrient concentration with 5 g/L FE of *M. indicus* as unique supplementation (Table 1). Compared with 5 g/L YE, 5 g/L FE resulted in a higher ethanol yield with a maximum of 0.43 g/g. However, the low glucose consumption indicated the existence of nutrient limitation in the medium. As a result, the maximum yield and productivity of ethanol in this medium was still lower than the fully supplemented medium (Table 1).

3.2. Evaluation of fungal extract for media supplementation replacing yeast extract

The possibility of supplementing of FE (2.5 g/L) in the fermentation media with combination of mineral salts (Table 1) was assessed in an additional experiment to overcome nutrient limitation. According to Table 1, addition of the mineral salts provided a gradual increase in ethanol yield and volumetric productivity in comparison with addition of only 2.5 g/L FE. However, it was comparatively low due to result obtained in a fully supplemented medium. Considering that a deficit in mineral salts with 5 g/L FE supplementation could be partially responsible for the prolonged fermentation time, additional experiment was prepared by adding the mineral salts presented in the full nutrient medium. As a result of this modification, the bioconversion to ethanol was further improved and showed results closely related to the ones observed for the fully supplemented medium (Fig. 2a and b), with a maximum ethanol yield and productivity of 0.46 g/g and 0.69 g/L h in less than 24 h, respectively. The maximum glycerol yield of 0.49 mg/g was achieved at this condition. It came, therefore, to the conclusion that autolysis of *M. indicus* biomass as a valuable by product from ethanol fermentation could be used as a microbial nutrient source for further fermentation with supplementation of 5 g/L FE replacing 5 g/L YE.

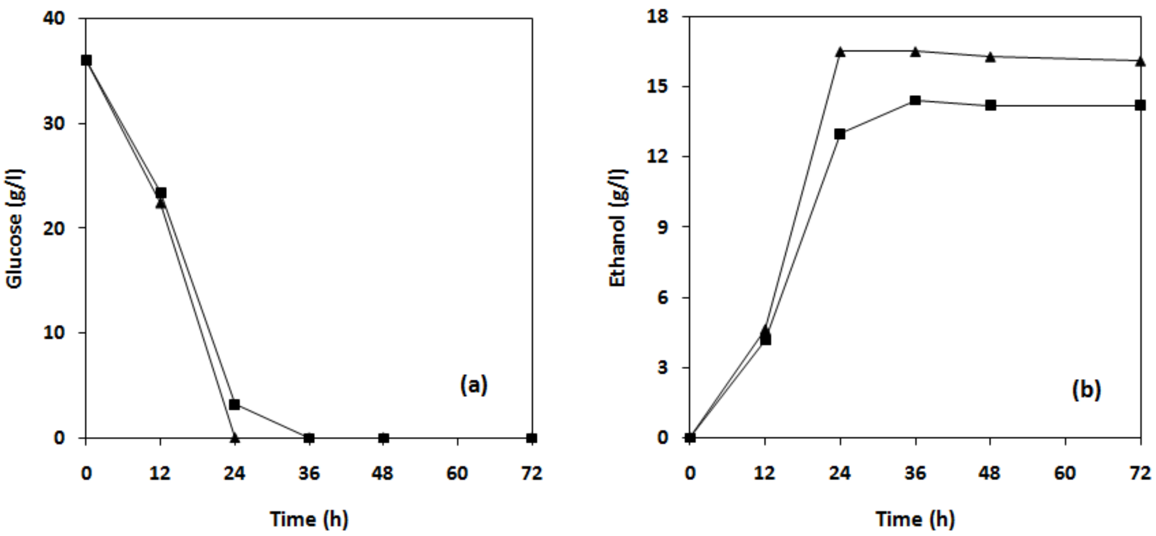

Fig.2. Effect of the supplementation of fungal extract with combination of mineral salts on glucose assimilation (a) and ethanol production (b). The symbols represent of supplementation of FE (2.5 g/L) with mineral salts (■); FE (5 g/L) with mineral salts (▲).

4. Discussion

The main purpose of the current work was the fermentative production of ethanol by the filamentous fungus, *M. indicus*, using a fungal autolysate as a low-cost complex nutrient solution. *M. indicus* is a fungus that has recently been identified as a candidate for industrial production of ethanol [2, 4]. Considering the similarity of chemical components between *M. indicus* and yeasts, it might be assumed that the fungal extract might be a feasible alternative to yeast extract as a nutrient source for fermentation media. Thus, the fungal cells of *M. indicus*, as a by-product of fermentation processes, were then subjected to autolysis to produce nutrient supplements for the following fermentations by similar fungus *M. indicus*. Therefore, the autolysis of the fungal cells biomass produced during fermentation may be considered as a suitable replacement for YE. Thus, the natural enzymatic process of fungal autolysis under oxygen starvation conditions was used in order to disrupt *M. indicus* cells and release various nutrients into the surrounding liquid. On the other hand, this process could be applied as an effective approach to nutrient regeneration/ production due to its simplicity [7]. In this study, autolysate of fungal cells, referred to as FE resulted in high performance in ethanol production. Media containing FE (5 g/L) replacing YE as nutrient source led to high-yield and high-volumetric productivity of ethanol. In addition high-yield of glycerol was obtained in FE concentration (5 g/L) relative to fully supplemented medium. This demonstrates clearly that the FE of *M. indicus* contains sufficient essential nutrients for the ethanol fermentation.

5. Conclusion

The biomass of *M. indicus* can be used as a nutrient source for ethanol production by this fungus. Autolysate of the fungal cells could successfully replace the major nutrients which are necessary for the fermentation.

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Yeast adaptation on the substrate straw

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Abstract: Bioethanol production of lignocellulosics is technologically analyzed, but requires further investigations concerning yield optimization and economic efficiency. One important aspect is to obtain an ideal yeast strain for the fermentation process, which should possess the ability of a stable conversion of C5- and C6-sugars, resistance/tolerance against inhibitory compounds, temperature, ethanol, sugar and industrial stability. The use of genetically-modified microorganisms is reported. Problems with the stability of the microorganisms and public concerns with regard to/about the use of genetically-modified organisms led us to seek other strategies. For this purpose, several yeast strains were adapted to the mentioned characteristics using specific natural adaptation and systematic selection.

For improved utilization of xylose, several yeast strains have been cultivated on xylose-minimal agar for various generations. Yeast strains have been adapted to grow in ascending concentrations of wheat straw hydrolysate medium. Furthermore, several yeast strains have been bred at increased temperatures, with enhanced ethanol and sugar concentrations.

Some xylose- as well as hydrolysate-adapted yeast strains show an increased fermentative competence. A few of the thermally adapted yeast strains represent an enhanced fermentative capacity at higher temperature (42°C). Various yeast strains are tolerant concerning 8-12 % of ethanol and 400-450 g/l of glucose. Some significant improvements concerning ideal yeast strain could have been reached. These improvements offer new possibilities for further optimization.

Keywords: *Lignocellulosic remnant straw, Ideal yeast strain, Natural adaptation, Systematic selection, Bioethanol*

1. Introduction

Economic production of bioethanol using lignocellulosic biomass involves quantitative fermentation of cellulosic as well as hemicellulosic fraction, which contains xylose as major sugar component in agricultural remnant materials [1]. By use of the yeast strain *Saccharomyces* only C6-sugars can be converted to ethanol, but not C5-sugars [2]. If the pentoses were also converted, ethanol yield could be increased significantly.

In the literature, numerous approaches are described where due to genetic engineering the pentose phosphate pathway in yeast cells (especially in *Saccharomyces cerevisiae*) is modified, so that the yeasts are able to convert xylose into ethanol, reviewed in [3]. Anyway, during longer application in the laboratory, the stability of recombinant yeast strains is not guaranteed, moreover, global acceptance concerning GM-organisms is another serious problem [4]. Therefore, development of non-GM yeast strains, capable of utilizing and converting xylose efficiently for production of bioethanol, using natural selection and breeding would be advantageous. When lignocellulosic biomass (e.g. straw) is pretreated (with Steam Explosion), substances, such as phenols, hydroxymethylfurfural (HMF), furfural and organic acids are generated. Those substances inhibit yeast cells, resulting in a highly constrained growth and ethanol production.

The majority of fermenting yeasts generally have limited osmotolerance and thermotolerance, with an optimum temperature ranging from 30 to 37°C [5]. Therefore, the development and use of osmotolerant and thermotolerant yeast strains, capable of growing and fermenting with good yields at temperatures above 40°C would be advantageous, especially with regard to

simultaneous saccharification and fermentation (SSF) [6]. Yeast growth and fermentation at high initial sugar concentrations and high temperature not only minimizes contamination chances, reduces cooling costs, has faster fermentation rates, but also facilitates the attainability of high ethanol concentrations, therefore reducing subsequent distillation costs.
Ethanol is known to act as an inhibitor to yeast cells, inducing loss of cell viability and inhibition of both yeast growth and different transport systems [7]. Thus, ethanol tolerant yeast strains are beneficial, in order to achieve high fermentation efficiency and finally a high yield of ethanol.

Summing up, the ideal yeast strain for bioethanol production of lignocellulosic biomass (e.g. straw) should possess the following characteristics: stable conversion of C5 and C6-sugars, resistance against inhibitory compounds, tolerance concerning temperature, ethanol as well as sugar and industrial stability. In this paper, we demonstrate that various yeast strains could have been adapted to the mentioned characteristics using specific natural adaptation and systematic selection.

2. Methodology

2.1. Microorganisms

The following microorganisms have been used: *Kluyveromyces marxianus (DSM 5418), Kluyveromyces marxianus (DSM 5420), Kluyveromyces thermotolerans (DSM 3434), S.C.BUT8, S.C.BUT4, Candida utilis, S.C.BUT3, Rhodotorula, Kluyveromyces lactis (DSM 4909), osmophilic yeast strain, Saccharomyces cerevisiae, Malaga, white wine yeast strain, Pichia stipitis, Pachysolen tannophilus (DSM 70352)* and *industrial baker´s yeast (S.C.BUT2).*

All yeast strains, used for adaptation, were grown in YGC medium at 30°C and maintained at 4°C on YGC agar plates. *Pichia stipitis* and *Pachysolen tannophilus (DSM 70352)* are maintained on Xylose agar plates.

2.2. Media

YGC medium (yeast extract 5 g/L, glucose 20 g/L, chloramphenicol 0.1 g/L) was routinely used as growth and testing medium. Agar plates have been prepared by adding agar 15 g/L. Xylose medium (urea 6.4 g/L, KH_2PO_4 1.2 g/L, Na_2HPO_4 0.18 g/L, yeast extract 10 g/L, xylose 50 g/L, chloramphenicol 0,1 g/L) was used as xylose-growth medium. Xylose agar plates have been prepared using yeast extract 10 g/L, peptone 20 g/L, xylose 20 g/L, agar 20 g/L, chloramphenicol 0.1 g/L. Xylose minimal-medium (DIFCO® yeast nitrogen base without amino acids 6.7 g/L, xylose, 50 g/L, chloramphenicol 0.1 g/L) was used as xylose-adaptation minimal medium [8].

Agar plates have been prepared by adding agar 18 g/L. Hydrolysate adaptation medium was prepared, similar to [9], by adding xylose 15 g, glucose 30 g, yeast extract 1.5 g, peptone 3 g, KH_2PO_4 2 g, $(NH_4)_2SO_4$ 1 g and $MgSO_4$-$7H_2O$ 0.5 g in 1 L of 10 – 30 % (dry substance) pre-fabricated straw hydrolysate (described in chapter 2.3), the pH was adjusted to 5.0 ± 0.1. In normal straw hydrolysate (10 % dry substance), the average xylose yield accounts for about 15 g/L and average glucose yield accounts for about 30 g/L. With increasing hydrolysate concentrations (dry substances of up to 30 %), glucose and xylose input amounts were reduced in adaptation media. Adaptation media have been finished by sterilely filtrating.

2.3. Preparation of wheat straw hydrolysate

With pretreated, dried and grinded straw, a 10 to 30 % suspension has been produced, using citrate-buffer solution (acetic acid 9.6 g/L, pH 5.0 ± 0.1). Suspension has been enzymatically solubilised at a temperature of 50 °C for 96 hours. After hydrolysis, suspension has been filtered and further used in hydrolysate adaptation media.

2.4. Determination of sugars, ethanol, organic acids, furans, xylitol

For precise sugar and ethanol analytics, as well as for determination of HMF, furfural and xylitol, HPLC from Jasco and BioRad AMINEX® HPX 87H with ultra-pure water as eluent, RI detection has been used. For precise organic acids analytics, as well as for lateral validation of sugar-, HMF-, furfural- and xylitol-concentrations, HPLC from Agilent Technologies, Varian Metacarb 87 H with 5 mM H_2SO_4 as eluent, UV 210 nm and RI detection has been used.

2.5. Xylose-solution for fermentation

Xylose solution was produced using xylose, 125 g/L, filled up with citrate buffer solution. After sterilely filtrating, a fermentation nutrient solution has been added. pH-value has been adjusted to 6.3.

2.5.1. Fermentation nutrient solution

Fermentation nutrient solution has been prepared using DIFCO® yeast nitrogen base without amino acids 85 g/L, urea 113.5 g/L, peptone 328 g/L.

2.6. Glucose-solution for fermentation

Glucose-solution was produced using glucose 140 g/L, filled up with citrate buffer solution. After autoclaving, $(NH_4)_2HPO_4$, $CaCl_2$-$2H_2O$, KH_2PO_4 and $MgSO_4$-$7H_2O$ have been added, pH-value has been adjusted to 4.6.

2.7. Adaptation of yeast strains on xylose as sole carbon source

Selected, analyzed yeast strains have been streaked constantly on xylose-containing agar plates (rich medium) for several generations (approx. 15 passages). Those yeast strains have been adapted to grow on Xylose-minimal agar. Yeast strains have been streaked again constantly on that minimal agar for several generations (currently passage 50).

2.8. Fermentation analyses with xylose-adapted yeast strains

Fermentation analyses with xylose-adapted yeast strains have been conducted, using xylose liquid medium as yeast growth medium and xylose solution for fermentation, including the fermentation nutrient solution, pH 6.3. Fermentation has been practised aerobically and anaerobically at 30 °C for 168 hours. As positive control, not adapted yeast strains have been cultivated in YGC-medium and used in fermentation process with identical parameters.

2.9. Adaptation of yeast strains on wheat straw hydrolysate

Selected yeast strains have been cultivated in ascending concentrated hydrolysate adaptation media. Adaptation of yeast strains has been conducted at 30°C. Simultaneously, several yeast strains were cultivated additionally at higher temperatures (up to 41°C). Therefore, increased inhibitor-resistant yeast strains with a higher temperature tolerance could be achieved.

2.10. Fermentation analyses with wheat straw hydrolysate-adapted yeast strains

Fermentation analyses with hydrolysate-adapted yeast strains have been conducted, using hydrolysate adaptation medium as yeast growth medium. Fermentation has been conducted using pre-fabricated and concentrated straw hydrolysate (60 % of straw dry substance) at 30°C for 168 h. As positive control, not adapted yeast strains have been cultivated in YGC-medium and used in fermentation process with identical parameters.

2.11. Adaptation of yeast strains on increased temperatures

Several yeast strains have been streaked on YGC agar plates and incubated at increasing temperatures up to 42 °C. *Kluyveromyces marxianus* has been bred at temperatures up to 45°C. Thermotolerant yeast strains have been tested additionally in a fermentation approach at higher temperatures.

2.12. Determination of alcohol and sugar tolerance

Yeast strains have been grown in YGC medium at 30°C for 24 hours and inoculated into YGC medium plus different ethanol concentrations (ranging from 0-13 %). Yeast cell concentrations have been determined using spectrophotometer (OD 600 nm) after incubation at 30°C. Sugar tolerance of yeast strains have been tested after growth in YGC medium, including different concentrations of glucose (up to 450 g/L). Yeast cell concentration was determined using spectrophotometer (OD 600 nm) after incubation at 30°C. Sugar tolerant yeast strains have been tested additionally in a fermentation approach using glucose solution with different glucose concentrations (up to 450 g/L) at 30°C for 168 hours.

3. Results

3.1. Fermentation analyses with xylose-adapted yeast strains

Several xylose-adapted yeast strains (about 50 passages) produced slightly increased ethanol yields, especially during aerobic fermentation process. Using xylose-adapted *Pichia stipitis* (passage 48) in the aerobic fermentation process, a significant increase in ethanol production with 4.6 %vol. could be observed (table 1 and 2).

Table 1. Ethanol yields after aerobic and anaerobic fermentation of xylose-solution, including fermentation nutrient solution, with non-adapted control yeast Pichia stipitis.

Control yeast *Pichia stipitis*	Fermentation condition	EtOH [% vol.]	remaining xylose [g/L]	xylitol [g/L]
	aerob	3,4	34,5	2,5
	anaerob	2,1	73,4	2,4

Table 2. Ethanol yields after aerobic and anaerobic fermentation of xylose-solution, including fermentation nutrient solution, with Pichia stipitis, adapted on xylose as sole carbon source.

Xylose-adapted *Pichia stipitis*	Fermentation condition	EtOH [% vol.]	remaining xylose [g/L]	xylitol [g/L]
	aerob	4,6	19,7	14,4
	anaerob	4	19,1	16,2

3.2. Adaptation of yeast strains on wheat straw hydrolysate medium

Yeast strains have been adapted successfully to ascending concentrations of wheat straw hydrolysate medium. Both, at 30 °C and also at increased temperatures (up to 41°C), yeast growth in straw hydrolysate medium is successful.

3.3. Fermentation analyses with wheat straw hydrolysate-adapted yeast strains

Fermentation approaches with hydrolysate-adapted yeast strains have been conducted using concentrated wheat straw hydrolysate (with 60 % of dry substance) (table 3). Fermentation approaches have shown that some adapted yeast strains have increased resistance concerning existent inhibitory compounds (table 4).

Table 3. List of sugars, organic acids and furans, contained in concentrated wheat straw hydrolysate (with 60 % of dry substance).

Components of concentrated hydrolysate	[g/L]
Glucose	140.3
Xylose	55.8
Acetic acid	9.9
Formic acid	1.2
Propanoic acid	1.1
Hydroxymethylfurfural	0.3
Furfural	0.2

Table 4. EtOH-yields [%vol.] after fermentation of concentrated wheat straw hydrolysate, using adapted yeast strains and non-adapted control yeast strains.

Adapted yeasts	EtOH [%vol.]	Control yeasts	EtOH [%vol.]
S.C.BUT3	4,8	*S.C.BUT3*	0,7
S.C.BUT8	4,2	*S.C.BUT8*	2,9
S.C.BUT4	4,6	*S.C.BUT4*	0,7

3.4. Adaptation of yeast strains on increased temperatures

Several yeast strains show very good growth on YGC-agar plates at temperatures up to 42°C, except *Saccharomyces cerevisiae*, which is only able to grow well at 30°C. Exclusively, *Kluyveromyces marxianus* can grow at a temperature up to 45°C.

3.5. Analysis of fermentative capacity of different yeast strains at increased temperatures

Several yeast strains have been tested in a fermentation process, using glucose-solution for fermentation at 40°C. As positive approach, several yeast strains have also been tested in a fermentation process at 30°C. Most of the yeast strains produced similar ethanol yields during fermentation at 30°C (between 5.3 and 7.2 %vol.) and 40°C (between 4.7 and 6.1 %vol.). Only a few yeast strains show a significant collapse concerning fermentative capacity at 40°C.

3.6. Determination of alcohol tolerance

Several yeast strains have been tested concerning growth in YGC medium, including ascending concentrations of ethanol (0-13 %). Yeast cell density has been examined using spectrophotometer (OD 600 nm) after incubation at 30°C. Using 11 % of EtOH in the growth medium, several yeast strains still have good cell density (60 %, 74 %, 58 %, 61 %, 60 % and 75 %, respectively). With 13 % of EtOH, only one yeast strain has 61 % cell density. Only 3 used yeast strains have low ethanol tolerance (2-4 % EtOH).

3.7. Determination of sugar tolerance and fermentative competence

After analysis of yeast cell growth in YGC medium with ascending glucose-concentrations, several yeast strains have been tested additionally in a fermentation process, using glucose solution with different concentrations of glucose at 30°C for 168 hours. Almost all yeast strains have produced high ethanol yields after fermentation with increased glucose-concentrations (up to 450 g/L glucose). Best results have been reached using two special types of yeast.

4. Discussion

Lignocellulosic raw materials contain 5-20 % of the pentose sugars xylose and arabinose [10]. Microorganisms, able to ferment xylose are found among bacteria, yeast and filamentous fungi [11]. However, natural xylose-fermenting yeast strains, such as *Pichia stipitis*, *Candida shehatae* and *Pachysolen tannophilus* [12] are known to produce low ethanol yields and to re-assimilate the produced ethanol [13]. However, *Pichia stipitis* is known as one of the better yeast strains, able to ferment xylose. During anaerobic fermentation conditions a large portion of xylose is converted to xylitol therefore ethanol yield is accordingly low. Low levels of oxygen are important in the conversion of xylose into ethanol, so that cell viability and NADH balance are maintained.

Agbogbo et al. [14] have tested *Pichia stipitis* in fermentation approaches on various glucose and xylose mixtures. Maximum ethanol concentration with 100 % of xylose (60 g/L) was 24.3 ± 0.34 g/L, which corresponds to about 3.03 %vol. We have successfully adapted many yeast strains to grow on xylose-minimal medium, according to Attfield and Bell [8], who have demonstrated the development of non-GM yeast strains (*Saccharomyces cerevisiae*), capable of efficiently growing on xylose.

In our study, xylose-adapted yeast strains, regularly bred on xylose-minimal agar for several generations, produced slightly increased ethanol yields, especially during aerobic fermentation process. Using xylose-adapted *Pichia stipitis*, a significant increase in ethanol production after aerobic fermentation process of about 35 % can be observed (ethanol yield of 4.6 %vol., see table 1 and 2). Also within anaerobic fermentation process, using xylose-adapted *Pichia stipitis*, an increase in ethanol production of 90 % can be observed (ethanol yield of 4 %vol., see table 1 and 2). All xylose-adapted yeast strains show good tendency of getting adaped to convert xylose to ethanol, but also with a high production of xylitol as by-product. However, yeast strains will be further cultivated on xylose-minimal agar, as well as in xylose-liquid medium and fermentative capacity concerning increased xylose conversion will be regularly analyzed.

The most widely studied yeast strains for ethanol fermentation using wheat straw hydrolysate as feedstock are *Pichia stipitis* [9], *Kluyveromyces marxianus* [15], native as well as recombinant strains of *S.cerevisiae*. Best ethanol yields have been obtained with the native non-adapted *S.cerevisiae* with 31.2 g/L, which corresponds to about 3.9 %vol. [16]. However, those yeast strains are hindered during fermentation process by inhibitory compounds, generated during pretreatment and hydrolysis of lignocellulosic biomass [17]. Bjorling and Lindman [18] reported, that *Pichia stipitis* is completely inhibited during fermentation by using a medium, containing 3.9 g/L acetic acid, known as an inhibitory component in hydrolysates. In his study, Nigam [9] has improved fermentation performance by adapting xylose-fermenting yeast *Pichia stipitis* on higher concentrations of acetic acid. The addition of 5 g/L acetic acid in hydrolysate medium significantly inhibited sugar utilization and ethanol production. Maximal ethanol yield with inhibitor-adapted yeast culture was 14.5 g/L, which corresponds to about 1.8 %vol. In order to adapt yeast strains to inhibitory compounds in the hydrolysat, several yeast strains, used in our study, have been successfully bred in ascending concentrations of wheat straw hydrolysate medium at 30 °C and also at increased temperatures (up to 41 °C). Fermentation approaches have shown that some hydrolysate-adapted yeast strains have increased resistance concerning existent inhibitory compounds. Fermentation has been conducted in pre-fabricated wheat straw hydrolysate, containing among glucose and xylose, 9.9 g/L acetic acid, 1.2 g/L formic acid, 1.1 g/L propanoic acid, 0.3 g/L hydroxymethylfurfural and 0.2 g/L furfural.

The adapted yeast strain *S.C.BUT3* produced an ethanol yield of 4.8 %vol., whereas the not adapted control yeast only 0.7 %vol. Also the adapted yeast *S.C.BUT8* yielded an increased ethanol concentration of 4.2 %vol. (not adapted control yeast only 2.9 %vol.). By use of adapted *S.C.BUT4*, an ethanol yield of 4.6 %vol. could be reached, the not adapted control yeast only produced 0.7 % vol. (see table 4).

A serious problem concerning simultaneous saccharification and fermentation (SSF), which appears as a promising alternative among all processes for bioethanol production from lignocellulosic biomass is the different optimum temperatures for saccharification (45 - 50 °C) and fermentation (25 - 30°C) [6]. The majority of fermenting yeasts generally have limited osmotolerance and thermotolerance, with an optimum temperature ranging from 30 to 37°C [5]. In our study, we could thermally adapt several yeast strains to grow at temperatures up to 42°C, *Kluyveromyces marxianus* is able to grow at a temperature of 45°C. Fermentation approaches at 40°C provided good ethanol yields (up to 6.1 %vol).

Ethanol is known to be an inhibitor to yeast cells, inducing amongst others loss of cell viability which results in less efficient fermentation process and thus to reduced ethanol yield. The receipt of highly ethanol tolerant yeast mutants is very difficult, isolation requires long-term selection techniques in continuous culture [19]. In our study, numerous yeast strains have been tested concerning growth in YGC medium, including ascending concentrations of ethanol (0-13 %). Using 11 % of EtOH, several yeast strains have good cell viability. With 13 % of EtOH, one yeast strain has still 61 % cell density. Fermentation at high initial sugar concentrations provides high ethanol concentrations, which reduces subsequent distillation costs. After analysis of yeast cell growth in YGC medium with ascending glucose-concentrations, used yeast strains have been tested additionally in a fermentation process, using glucose solution with different concentrations of glucose at 30°C for 168 hours. Several yeast strains have produced high ethanol yields after fermentation with increased glucose-concentrations (up to 450 g/L glucose).

5. Conclusion

The ideal yeast strain for bioethanol production of lignocellulosic biomass has not been produced yet, because the mentioned requirements could not have been combined completely into one ideal yeast strain. However, some significant improvements with regard to the ideal yeast strain could have been reached. These improvements offer new possibilities for further optimization.

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Thermodynamic analysis and potential efficiency improvements of a biochemical process for lignocellulosic biofuel production

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Abstract: This paper presents a thermodynamic analysis of a biochemical process for the production of bioethanol from a lignocellulosic feedstock. The major inefficiencies in the process are identified as: i) the combustion of lignin for process heat and power production and ii) the simultaneous saccharification and fermentation process. As lignin is not converted to ethanol and lignin has a high value of chemical exergy, the overall efficiency of the biochemical process largely depends on how the lignin is utilized. We therefore consider integrating a source of low temperature heat, such as waste heat or low-enthalpy geothermal heat, into a biochemical lignocellulosic biorefinery to provide process heat. This enables the lignin-enriched residue to be used either as a feedstock for chemicals and materials or for on-site electricity generation. Our analysis shows that integrating low temperature heat source into a biorefinery in this way represents an improvement in overall resource utilization efficiency.

Keywords: *Bioenergy; biorefinery; geothermal energy; process heat; integrated approach.*

Nomenclature

Ex	*exergy* .... $MJ\cdot s^{-1}$
P	*electric power* .... $MJ\cdot s^{-1}$
η	*efficiency* .... *[-]*
δ	*exergy loss for heat transfer* .... *[-]*
subscript	
bio	*biomass*
ch	*chemical*
geo	*geothermal*
HT	*heat transfer*
ph	*physical*
proc	*process*
prd	*product*
wstprd	*waste product*
SN	*sink*
SR	*source*
0	*dead state*

1. Introduction

Increasing the percentage of liquid transport fuel from renewable biomass sources is an important opportunity in the move towards a more sustainable energy system. Recent political and research and development trends show a clear move towards lignocellulosic feedstocks for these biofuels [1]. Lignocellulosic feedstocks mitigate competition for land and water used for food production, increase biomass production per unit of land and reduce the inputs needed to grow the biomass [2-4].

A key challenge for biofuel production systems is to develop efficient conversion technologies which are able to compete economically with fossil fuels. The biorefinery concept [5, 6], where a range of high-value co-products are produced in addition to commodity fuel products, attempts to achieve increased efficiency by making full use of biomass feedstocks [5, 7-9]. Due to the potential cost reductions from this strategy, biorefineries are seen as a key step towards the commercial implementation of biofuels [5].

A large percentage of the lignocellulosic biorefinery concepts that have so far been proposed are based on a biochemical conversion platform where the polysaccharides in lignocellulosic material are converted to liquid fuel using enzymes [10, 11]. In these systems it has been proposed that the lignin by-product and other extractives can be used for higher value uses such as the production of high-value chemicals and materials [5, 7] or on-site electricity production [12].

One of the major impediments to the lignocellulosic biorefinery concept is that the liquid fuel production from lignocellulosic biomass is a very energy intensive process [5, 11, 13, 14]. Current integrated biorefinery concepts use the lignin-enriched residue as a fuel to meet process energy demands, reducing the possibility of higher-value uses of lignin. A potential option to overcome this is to introduce an external source of low-enthalpy heat, such as geothermal or waste heat, to meet the process heat demand and thereby leave the lignin-enriched residue available for higher-value uses.

As with other energy technologies, thermodynamic analysis provides a powerful tool to guide technology selection and research efforts towards more efficient biofuel production systems. Conventional energy analysis based only on the first-law of thermodynamics cannot be used reliably for these purposes as it does not embody second law constraints on energy conversion and erroneously treats all energy types as equal [15].

Exergy analysis is a convenient method of carrying out thermodynamic analysis of complex systems and has been applied to a wide range of different processes, including; energy technology, chemical engineering, transportation and agriculture [16]. A number of authors have recently applied exergy analysis to biofuel production process [17-26]. While a number of exergy analyses of thermochemical pathways exist [18, 19, 22, 23] applications of exergy analysis to biochemical pathways are limited [20, 24, 25].

In paper we present an updated synthesis of our previous work [25, 26] on applying exergy analysis to identifying the inefficiencies in a biochemical process for producing biofuel and evaluating the potential efficiency gains from integrating low-enthalpy heat into the process. The analysis is based on the National Renewable Energy Laboratory (NREL) process [11] for producing ethanol from a lignocellulosic feedstock.

2. Methodology

2.1. Exergy analysis

Unlike energy, exergy is exempt from the law of conservation. Every irreversible phenomenon causes exergy losses leading to the reduction of the useful effects of the process or to an increased consumption of the original energy source. The main aim of exergy analysis is to identify and quantify the causes of this thermodynamic imperfection in the process under consideration. The methodology of exergy analysis is presented by Szargut et al. [15] and the general approach to applying exergy analysis to biofuel production processes are given in Lu et al. [19] and Prins et al. [21]. One of the major difficulties in applying exergy analysis to biochemical process for biofuel production is that a number of components are not present in standard exergy tables [15]. In our previous work [25], a table of exergy values for these components and the methods used to calculate them are presented.

2.2. The biochemical production process

Several process models for the production of ethanol from biomass have been reported in the literature [11, 13, 14]. In particular, in a NREL publication Wooley et al. [11] have described in detail the overall process for ethanol production from wood chips via a process of simultaneous scarification and co-fermentation (SSCF). They considered a process that on average converts about 44.44 kg/s of biomass to 5.52 kg/s of ethanol. The process utilizes lignin enriched by-products to meet process heat demand. The model showed that such a plant can produce more energy than required for process demands. The model includes an integrated power plant capable of producing 44 MW of electricity (33 MW for internal use and 11 MW for export). Piccalo and Bezzo[14] have developed an optimized system by applying pinch analysis to the original system described by Wooley et al. [11]. The analysis presented here is based on this optimized system. An overview of the process is shown in Fig 1.

Following Piccalo and Bezzo [13], the base case considered here processes 160 metric Ton of wet chip per hour, where the composition of the wood chip is cellulose: 22.2%, xylan: 9.9%, arabinan: 0.4%, mannan: 2%, galactan: 0.1%, acetate: 2.4%, lignin: 14.4%, ash: 0.5%, and moisture: 47.9%.

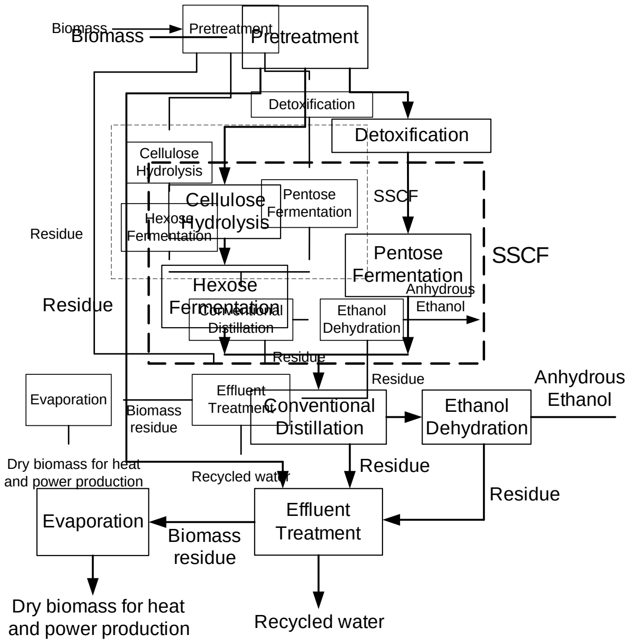

Fig. 1. Process diagram of ethanol production from lignocellulosic biomass

2.3. The efficiency of biochemical production process

One of the key parameters that can be evaluated in an exergy analysis is the overall thermodynamic efficiency. The thermodynamic efficiency of a system is defined as [15]:

$$\eta = \frac{Exergy\ of\ useful\ products}{Input\ Exergy} \qquad (1)$$

In the current case, the overall efficiency of ethanol production via the biochemical process described in section 2.2 can be written as

$$\eta = \frac{E_{X,Fuel} + P_{net} + E_{X,lignin\ residue}}{E_{X,Biomass} + \sum E_{X,ch} + E_{X,low\ temp}} \qquad (2)$$

Here, $E_{X,Biomass}$ is the input chemical exergy of biomass, $\sum E_{X,ch}$ is the sum of the chemical exergies of all input chemicals to the process, $E_{X,low\ temp}$ is the exergy of a potential low temperature heat source supplied to the system, $E_{X,Fuel}$ is the chemical exergy of the fuel,

$E_{X,lignin\ residue}$ is the exergy of the lignin-enriched residue and P_{net} is the net electricity produced by the system. To evaluate the efficiency of the NREL process described in section 2.2 we put $E_{X,low\ temp} = 0$ and $E_{X,lignin\ residue} = 0$.

Exergy analysis can also be used to evaluate thermodynamic losses in each unit process of the system. The exergy balance [27] applied to the system boundary of a unit operation of a process gives

$$\sum_{in} E_X = \sum_{out} E_{X,prd} + \sum_{out} E_{X,wstprd} + I \qquad (3)$$

where $\sum_{in} E_X$ is the total input exergy flow, $\sum_{out} E_{X,prd}$ is the total output exergy flow in the products, $\sum_{out} E_{X,wstprd}$ is the total output exergy flow in the waste products from the unit process and I is the exergy destruction due to internal irreversibility. The last two terms in the exergy balance represent the total exergy loss associated with the unit process. For an irreversible process $I \neq 0$ and Eq. (3) expresses the fundamental property that, unlike energy, exergy is not conserved.

2.4. *Efficiency improvements by integrating a low temperature heat source*

One possibility for improving the efficiency of biofuel production is to integrate a low temperature heat source to meet process heat demands. We consider three discrete cases and calculate the corresponding efficiencies. Here we assume that the internal electricity demand is met from the combustion of lignin-enriched residue. The rejected heat from lignin combustion can also be used to meet all the low temperature heat demand (150 ºC or less).

The highest quality steam required for the biorefinery process is 192ºC (saturated at 13 bar). This steam demand can be met from any suitable low temperature heat source. The energy required for the highest quality steam is about 46 MW (or 17.6 MW of exergy). We could meet this heat demand by using an external 210ºC heat source in the biofuel production system, thus integrating heat and biomass resources in a single process. An alternative use for this steam is in an independent power plant. Assuming a typical binary cycle power plant first law efficiency of 15% [28] we can get about 6.9 MW of electricity from this same heat source. In this work we would like to compare the overall resource efficiency of the integrated vs. independent use of the two resources. We consider 3 cases:

Case 1

This represents the base case, here we operate the biorefinery and the low temperature heat source independently, with the low-temperature heat being used in an independent power plant. The overall efficiency can be calculated from Eq. (2) where, $E_{X,Biomass}$ = 454.8 MW, $\sum E_{X,ch}$ = 12.3 MW, $E_{X,low\ temp}$ = 17.6 MW, $E_{X,Fuel}$ = 147.1 MW, P_{net} = 17.9 MW and $E_{X,lignin\ residue}$ = 0 MW. For the biorefinery we use the system described in Section 2.2.

Case 2

Here we integrate the heat source into the biorefinery to meet the high-temperature heat demands (in the biochemical process) and combust the available lignin-enriched residue to produce additional power. The overall efficiency is calculated from Eq. (2) with $E_{X,Biomass}$ =

454.8 MW, $\sum E_{X,ch}$ = 12.3 MW, $E_{X,low\ temp}$ = 17.6 MW, $E_{X,Fuel}$ = 147.1 MW, P_{net} = 22 MW and $E_{X,lignin\ residue}$ = 0 MW.

Case 3
In this case we meet internal electricity demand from lignin combustion and leave any additional lignin for some higher value use. The overall efficiency is calculated from Eq. (2) with $E_{X,Biomass}$ = 454.8 MW, $\sum E_{X,ch}$ = 12.3 MW, $E_{X,low\ temp}$ = 17.6 MW, $E_{X,Fuel}$ = 147.1 MW, P_{net} = 0 MW and $E_{X,lignin\ residue}$ = 45.8 MW.

3. Results

3.1. Exergy analysis of the biofuel production process

The efficiency of the standard NREL process [11] is calculated to be 34% using Eq. (2). Fig. 2 (b) provides a breakdown of the exergy losses in various unit operations of the production process. For comparison we have also provided a breakdown of the energy losses in Figure 2 (a). It is clear from the figures that heat and power production is the major contributor to both energy and exergy losses. The second, third and fourth largest contributors to energy loss are evaporation, distillation and dehydration and the pre-treatment & detox processes, respectively. Unlike the energy losses, the second, third and fourth largest contributors to exergy losses are SSCF, SSCF seed and pre-treatment processes, respectively. Feed handling and lignin separation have similar levels of contribution to energy and exergy losses (less than 1%).

3.2. Efficiency improvements by integrating a low temperature heat source

The calculated overall efficiency for case 1 is 34.0% which is considered as the base case here. If we integrate the low temperature heat source to the biorefinery (case 2) efficiency becomes 35%. Although, the overall improvement is only 1%, there is a significant improvement in low temperature heat utilization. In particular, an additional 4.1 MW of electricity is generated which represents a 40% gain in electricity generation from the same low temperature heat source. The overall efficiency for case 3 is 40%. Fig. 3 presents a Grassman diagram of case 3, showing the exergy flow through the various stages of the system.

4. Discussion and conclusion

The difference in the breakdown of energy and exergy losses in the system presented in Fig. 2 emphasises the importance of exergy analysis. While both the energy and exergy analysis show that heat and power production is the major loss, there is a significant difference for most of the other unit processes. This difference arises from the fact that first law analysis (energy) treats all forms of energy to be the same, whereas exergy analysis takes into account the available work in different forms of energy. For example, although evaporation, distillation and dehydration are associated with large energy demands, this demand can be met with low temperature heat sources (low exergy sources). In contrast, the SSCF and SSCF seed processes consume very little heat (low exergy) but require a significant amount of electricity (high exergy). A thermochemical process involving gasification and Fisher-Tropsch synthesis was found to have a similar overall efficiency of biochemical process [22]. A more detailed comparison is presented in [25].

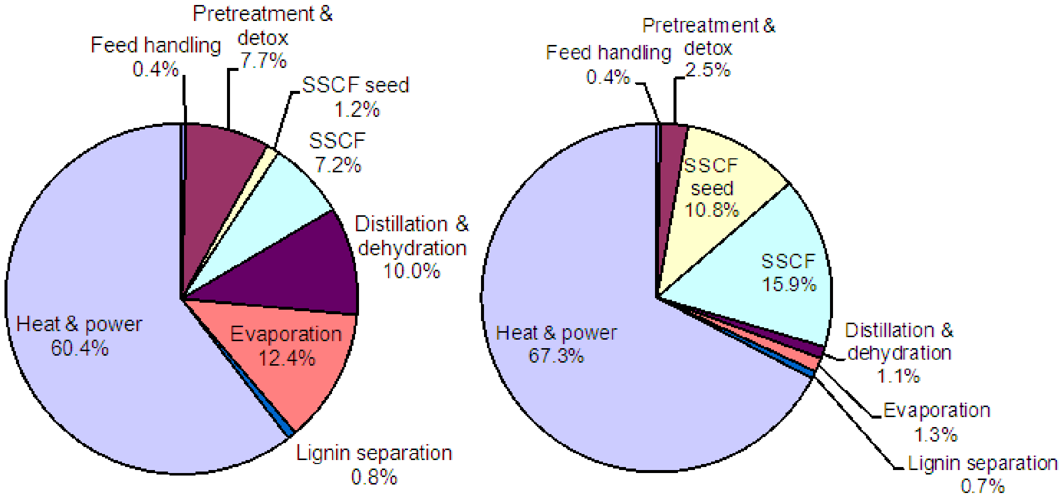

Fig. 2. Breakdown of energy (a) and exergy (b) losses for a biochemical process of biofuel production from lignocellulosic feed stock.

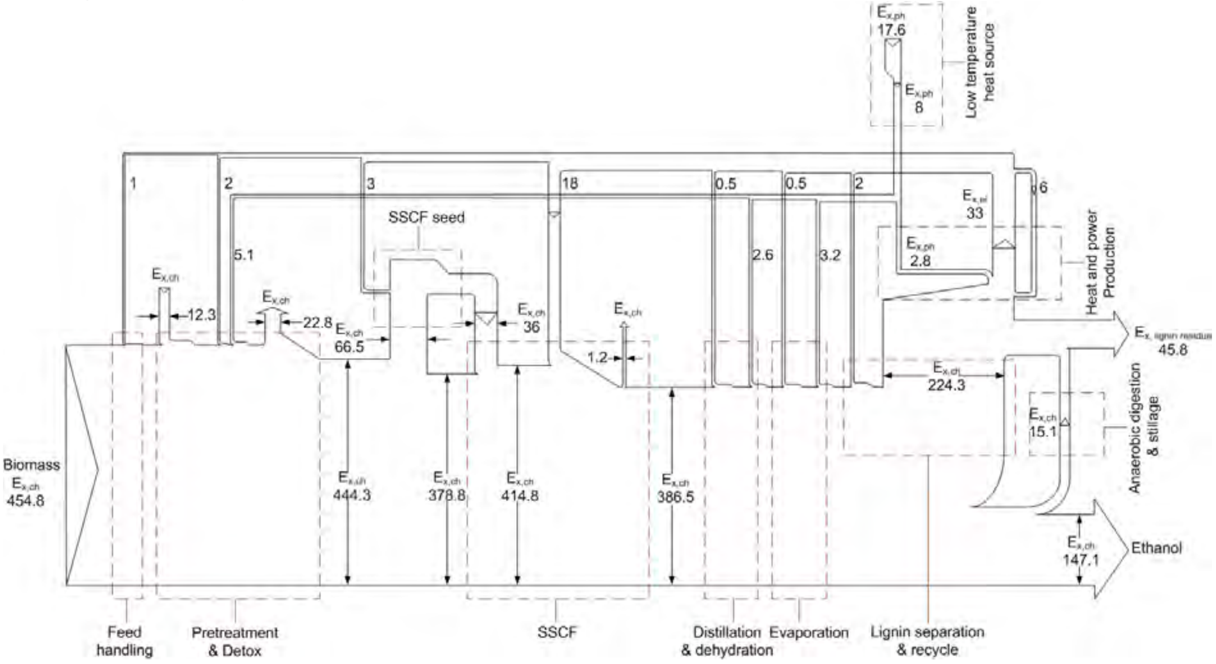

Fig. 3. Grassman diagram for an ethanol and lignin-enriched residue production process where the 192ºC heat demand is met from low temperature heat source and the remaining internal electricity demand is met from lignin combustion

There are two main reasons that heat and power generation is the largest area of exergy loss in the process. Firstly, due to the inherent inefficiency of combustion, much of the chemical exergy in the lignin is lost. The Carnot efficiency places limits on the ability of future technologies to improve this efficiency. Secondly, the direct reduction in temperature from the combustion temperature (815 ºC for lignin) to that of the process heat (200 ºC) leads to a further loss of exergy. The exergy loss due to entropy generation associated with heat transfer to a cooler medium can be easily deduced from the Carnot efficiency [15]

$$\delta_{HT} = \frac{T_0}{T_{SN}}\left(\frac{T_{SR}-T_{SN}}{T_{SR}-T_0}\right) \qquad (7)$$

where all temperatures are in Kelvin. From Eq. (7) the exergy loss due to entropy generation associated with heat transfer from 815ºC to 200ºC with ambient temperature of 25ºC is calculated to be 49% of the original exergy, whereas if we meet the heat demand from low temperature heat source of 210ºC, the exergy loss due entropy generation associated with heat transfer becomes only 3% of original exergy. This explains the improvement in efficiency by integrating a low-enthalpy heat source to meet the process heat demand.

Producing co-products or usable by-product can also change the efficiency of the system significantly. For instance, gypsum and ammonium acetate (4.8 MW, 16.8 MW equivalent of exergy, respectively) are produced in the detox process. If we can recover and utilize even 50% of these two wastes/by products, the overall efficiencies for case 1, case 2 and case 3 increase to 35%, 37% and 42%, respectively.

In summary, this analysis shows that, in essence, the lignin enriched residue is too valuable from a thermodynamic perspective to be combusted for process heat. This is therefore a thermodynamic justification for the biorefinery concept which proposes making the most out of the biomass by using the lignin-enriched residue as a feedstock for higher value products. For current technologies, to support this concept requires a source of low-temperature heat to meet process heat demands. Using a heat source with a temperature very close to that of process heat demand reduces the losses incurred by this approach. Potential sources of this heat are waste heat and geothermal. Overall, this process of integrating low-enthalpy heat and thus leaving the lignin enriched residue available for higher value uses can lead to significant improvements in overall efficiency of a biochemical biofuel process. This analysis also showed that if we can recover and utilize some of the key wastes and by-products, the overall efficiency increases due to the large exergy content in these chemicals.

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Co-production of electricity, heat and biocoal pellets from biomass: a techno-economic comparison with wood pelletizing

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Abstract: Hydrothermal carbonization (HTC) is an artificial coalification process which converts raw biomass into a coal-like product, biocoal. Biocoal has a higher energy density than the original biomass and is easier to transport, store and process. Hence, HTC is recently promoted as an upgrading technology, especially for wet biomass. For HTC to become a commercial technology, it is essential to identify applications which offer technical or economic advantages over conventional biomass processes. This paper presents a process design where HTC is integrated with wood-fired combined heat and power production (*HTC-CHP*), and compares it to standalone HTC (*HTC-sep*) and to wood pelletizing integrated with CHP (*WP-CHP*). The respective plant designs are modeled with Aspen Plus and an economic analysis is performed using investment costs from literature. The overall efficiency of electricity, heat and wood or biocoal pellet production is very close in all considered cases. When biodegradable waste is available at zero cost, the production costs of biocoal pellets are similar to those of wood pellets. If wood chips are used as an HTC feedstock, the production costs are 32–38% higher. The average cost of CO_2 avoidance is highest for the standalone HTC plant, due to the auxiliary consumption of natural gas and electricity.

Keywords: *hydrothermal carbonization, biocoal, biomass, wood pellets*

1. Introduction

Co-firing with coal has been identified as one of the least expensive and most efficient technologies for converting biomass to electricity [1]. This gives rise to a demand for biofuels with a uniform quality and high energy density, which can be processed in the fuel handling and combustion equipment of existing coal-fired power plants. Since most raw biomass falls short of these requirements, upgrading technologies, which improve the properties of biomass for transport, storage, combustion and gasification, have become of interest. The most established upgrading technology today is wood pelletizing, whereby wood is dried, milled and pressed into pellets of a defined form and size. Several technologies which convert biomass into a more coal-like product through chemical processing are currently being developed, but not yet commercialized. While torrefaction and fast pyrolysis have been mainly applied to dry wood and straw, hydrothermal carbonization (HTC) does not require prior drying and has been successfully tested with a wide range of biomass including wood, straw, cut grass, municipal waste, digestate, and bark mulch in laboratory scale experiments [2,3].

To achieve a high overall energetic efficiency of 80 to 90% (HHV basis), efficient heat recovery within an HTC plant is required [4]. However, complex heat recovery might not be attractive due to operability issues and cost. This paper presents a process design in which the need for a complex heat recovery design within the HTC process is eliminated by integrating the HTC process with wood-fired combined heat and power production (CHP). Steam for the HTC reactor is bled from a steam turbine extraction, while low temperature heat from the cooling of the HTC reaction products is used for district heating and for combustion air and water preheating for the CHP process. This integrated design is compared to a stand-alone HTC plant and to wood pelletizing, also integrated with CHP, in relation to energetic efficiency and production costs. Poplar wood chips from short rotation coppice and biodegradable waste are considered as feedstocks for the HTC process.

2. Hydrothermal carbonization as an upgrading technology for biomass

HTC is an artificial coalification process which takes place in pressurized water at 200 to 250°C at or above saturation pressure and is slightly exothermic. Oxygen is removed from the feedstock through the formation of water and CO_2, thereby increasing the carbon content and higher heating value (HHV). HTC renders gaseous and dissolved byproducts containing CO_2, carbon monoxide, organic acids, phenol, furfural and hydroxymethylfurfural [5,6]. Minerals contained in the biomass are partly dissolved in the aqueous phase [7]. By destroying the cell structure of the biomass and removing oxygen-containing functional groups, HTC makes the product hydrophobic [8] and facilitates mechanical dewatering, which is much less energy intensive than thermal drying. Previous simulation studies show that for fresh wood with 50 to 60% moisture (wet basis), pre-treatment with HTC before combustion could increase the overall energetic efficiency compared to the combustion of the untreated wood by 5 to 12 percentage points, given that dissolved organics losses are limited to 5% (by weight) and that mechanical dewatering yields 70% dry matter content [4]. In laboratory scale dewatering experiments, a dry matter content of 57 to 68% was achieved for biocoal from biodegradable waste [9].

Fig. 1 presents a flow diagram for a continuous HTC plant. The heat recovery scheme is adopted from a pilot plant for the hydrothermal treatment of peat [10]. The biomass is mixed with recycled process water to create a pumpable slurry, and then preheated in several stages by mixing with steam recovered at different temperature levels from the product depressurizing. Only direct heat exchange is employed at temperatures greater than 100°C because (carbonized) peat slurry was found to cause fouling and clogging problems within heat exchangers [11]. The additional steam required to reach the reaction temperature is produced by a natural gas boiler. The product is mechanically dewatered, dried to a moisture content of 10% (w.b.) and pelletized. Low temperature drying uses steam at 100°C to heat up the drying air. The gaseous byproducts from the HTC reactor are co-combusted in the natural gas boiler. We described a similar plant design in detail in [4].

The need for a complex heat recovery scheme within the HTC process can be eliminated by integrating the HTC process with a CHP plant using wood chips as a fuel, as shown in Fig. 2. Steam for the HTC reactor is taken from the steam turbine. The biocoal slurry is depressurized in two steps. Some of the recovered steam is used to preheat the biomass slurry to 90°C and to supply the biocoal dryer. The remainder of the steam, plus heat from the waste water, gaseous byproducts and biocoal slurry cooling are used to generate steam at 0.2 MPa for the deaerator, for the combustion air and make-up water preheating, and for district heat production.

3. Methodology

The standalone HTC plant (*HTC-sep*) and the integrated plant design (*HTC-CHP*) described above are modeled with *Aspen Plus V7.1*, a simulation package which calculates material and energy balances for a given flowsheet of a steady-state chemical process. A stand-alone CHP plant (*CHP-sep*) and a CHP plant integrated with wood pelletizing (*WP-CHP*) are also modeled for comparison. The design of *CHP-sep* and *WP-CHP* corresponds to the integrated CHP process (marked by grey underlay in Fig. 2), without flow streams A, B, G, F, and H. In *WP-CHP,* additional steam is extracted at 0.12 MPa for drying the wood to a water content of 10% before milling and pelletizing. Based on the simulation results, raw material and auxiliary energy demand are obtained, and plant equipment is sized. Investment costs for the plant equipment are estimated, and the annual levelized product costs are calculated for each simulation case. Poplar chips from short rotation coppice with a water content of 50% (w.b.) are used as a fuel for the CHP plant and as the raw material for the HTC and wood pelletizing. For the *HTC-CHP*, a second case is analyzed, with biodegradable waste as the HTC feedstock. All HTC simulation cases have an input of 11.15 MW_{HHV}, requiring either 4 t/h wood or 8.6 t/h biodegradable waste.

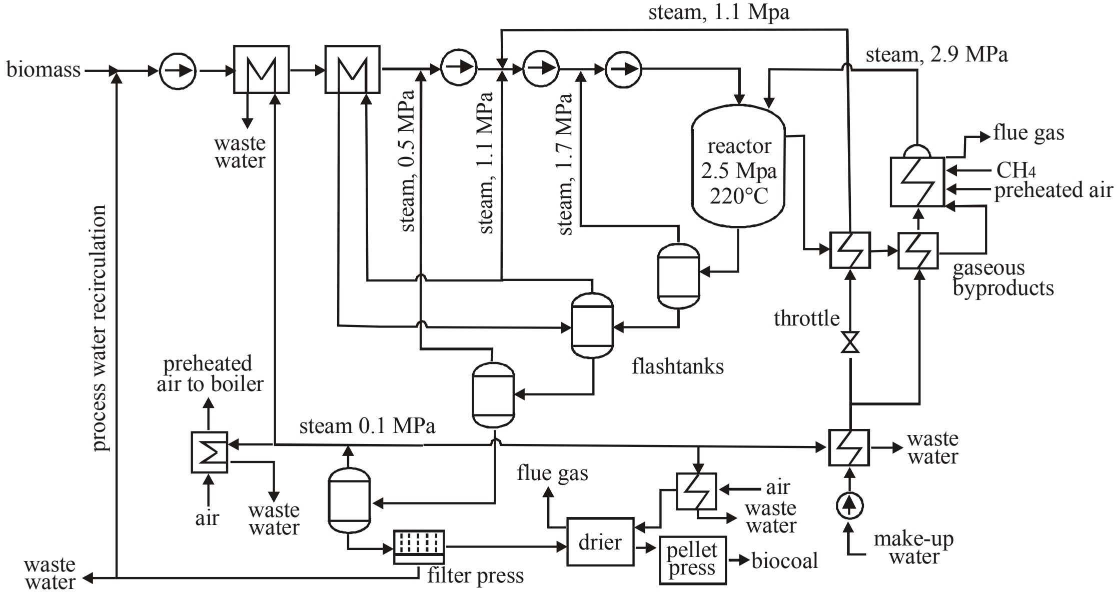
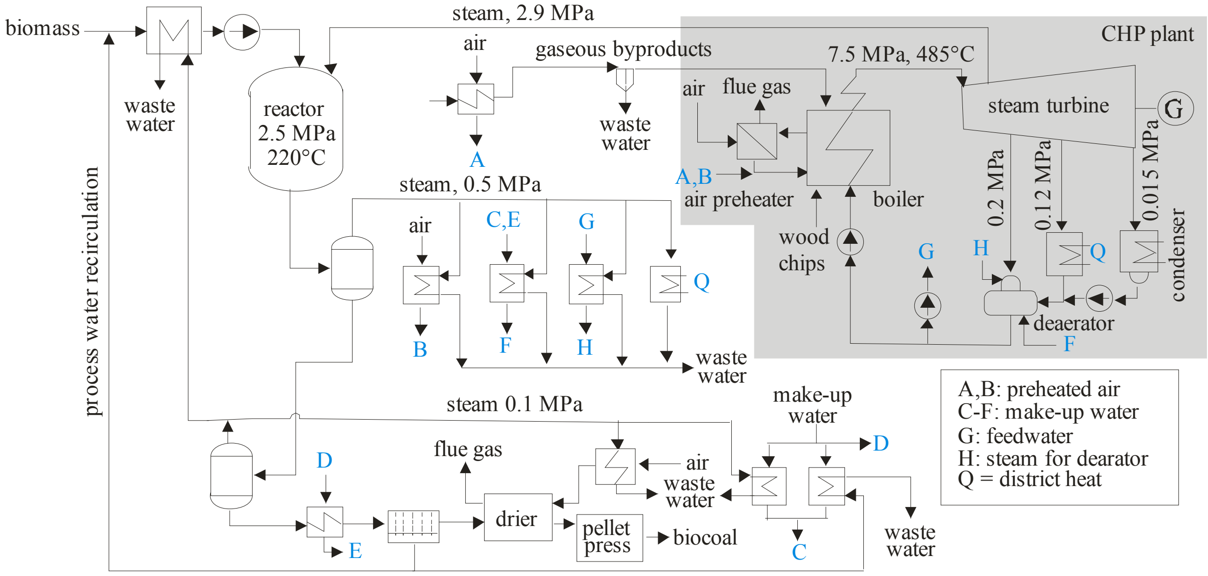


Fig. 1. Flow diagram of a stand-alone HTC plant (HTC-sep) with staged heat recovery.



A,B: preheated air
C-F: make-up water
G: feedwater
H: steam for dearator
Q = district heat

Fig. 2. Flow diagram of an integrated HTC and CHP plant (HTC-CHP).

3.1. Modelling assumptions

The operation of each plant is simulated for an average day within and outside the heating season, a cold winter day of -10°C with maximum heat load and frozen biomass, and a hot summer day of 30°C. The district heat load is taken to be 1.0 MW outside the heating season, 15.7 MW on the average winter day and 20.7 MW at capacity. Outside the heating season, the boiler runs at approximately 40% capacity, and the steam not used for district heating (7.0 MW) is discharged to the condenser. For the biomass upgrading processes, an availability of 80% is assumed, due to maintenance requirements and fluctuation in biomass supply.

The HTC reactor is modeled as a black box, with yields and composition of the biocoal and byproducts based on experimental data using poplar wood and straw at 220°C with a residency time of 4 hours [12] and on published data [13]. The composition (wt%, d.b.) of biomass and biocoal is given in Table 1. Mass yields (d.b.) are 70.3% to 70.9% for the biocoal from wood and 71.9% for the biocoal from waste. Dissolved organic byproducts account for 10.1% of the feedstock dry mass. The solid matter content is assumed to be 15% at the slurry pump inlet and 60% after mechanical dewatering with a filter press. Since biocoal is brittle, it is assumed that it can be fed directly to the pellet press without prior milling.

Table 1. Characteristics of wood, biodegradable waste, biocoal and dissolved organics.

	wood	waste	biocoal (wood)	biocoal (waste)	dissolved organics
Carbon	49.75%	38.60%	63.68%	48.54%	40.52%
Hydrogen	6.08%	5.30%	5.65%	4.27%	5.36%
Oxygen	42.85%	36.10%	29.47%	21.96%	54.12%
Ash	1.32%	20.00%	1.21%	25.23%	—
HHV (d.b.) (MJ/kg)	20.07	15.58	25.81	19.18	—
Water content (w.b.)	50%	70%	10%	10%	—

3.2. Economic analysis

Module costs for the plant equipment are estimated based on vendors data (for the wood pelletizing equipment) and literature. For the biomass upgrading processes, overdesign (safety) factors of 10-20% are applied. All components in contact with the biomass or biocoal slurry are stainless steel. Costs are converted to 2009 €. The total capital investment (TCI) comprises the total module costs plus fees and contingencies (15% of module costs), offsite costs (land, ancillary buildings, site development, utilities), working capital and start-up costs. The investment annuity is calculated with an economic plant life of 15 years and an interest rate of 7.0% p.a. Constant money values are used with real escalation rates of 0.5% p.a. for natural gas and purchased electricity, and 0.3% p.a. for wood chips and bituminous coal. Annual levelized costs for auxiliary energy, raw materials, and operation and maintenance are calculated with the constant escalation levelization factor (CELF).

The costs for the wood chips from short rotation coppice are calculated including cultivation and harvest, transportation and seasonal storage. It is assumed that the standalone HTC-plant is located in the centre of the cultivation area and that wood chips are stored onsite. The transport distance is calculated relative to the biomass demand under the assumption that 10% of the surrounding area is used to grow short rotation coppice. The location for the CHP plant would be selected based on district heat demand rather than biomass supply, and the seasonal storage of biomass has to be off-site. Therefore, an additional truck reload and transport of 100 km are assumed in this case. Biodegradable waste is assumed to be available at zero cost, including delivery to the HTC plant.

The total annual levelized revenue requirement (TRR) in €/a of the *HTC-CHP* plant equals the production costs of the three products, namely electricity, district heat and biocoal pellets. Assuming that specific revenues for district heat and electricity are the same for all plant designs, the specific cost of the biocoal pellets ($c_{pellets}$) in €/GJ can be calculated according to Eq. (1), where W is the net annual electricity production in GJ/a, c_w the renumeration for electricity feed-in from the CHP plant in €/GJ, and $Q_{pellets}$ is the annual pellet production in GJ/a. The specific costs of wood pellets in *WP-CHP* are calculated in the same way.

$$c_{pellets} Q_{pellets} = (TRR_{HTC-CHP} - TRR_{CHP-sep}) - c_w (W_{HTC-CHP} - W_{CHP-sep}) \qquad (1)$$

The cost of CO_2 avoidance is calculated with Eq. (2), assuming that the upgraded biofuel substitutes bituminous coal, that no additional investment at the power plant is required and that efficiency is not affected. $c_{pellets,LHV}$ and $c_{bit.coal,LHV}$ are the specific costs in €/GJ_{LHV}, and $e_{pellets}$ and $e_{bit.coal}$ the specific emissions in t CO_2 per GJ_{LHV} for the respective fuels.

$$c_{CO2} = \frac{c_{pellets,LHV} - c_{bit.coal,LHV}}{e_{bit.coal} - e_{pellets}} \qquad (2)$$

4. Results

In the following, the standalone HTC and CHP plants, *HTC-sep* and *CHP-sep*, are treated as one system with two separately located plants for the purpose of the economic analysis, in order to better identify the effects of the integration.

4.1. Technical performance

Low ambient temperatures lead to a higher energy demand for preheating the drier air and the biomass. At 5°C, the natural gas demand in *HTC-sep* is 13% higher than at 15°C, at -10°C with frozen biomass it is 50% higher. At +30°C, a surplus of heat (191 kW) has to be discharged to the environment, for which coolers are required. Annual energy balances for the analyzed cases are given in Table 2. The overall efficiency on an HHV (LHV) basis of *HTC-sep* is 81.1% (92.9%). The electrical efficiency of *CHP-sep* is 16.3% (20.1%), and the energetic efficiency 53.4% (65.8%). The overall energetic efficiency, where the sum of biofuel energy (HHV), net electricity and district heat is the product and the raw biomass is the fuel, is very close in all considered cases — it ranges from 60.8% when biocoal is produced from wood to 59.7% when biocoal is produced from waste.

Table 2. Annual energy balances (on HHV basis).

		HTC-sep	CHP-sep	HTC-CHP wood	HTC-CHP waste	WP-CHP
Inputs						
Biomass (upgrading)	(GWh/a)	75.14	—	75.14	75.14	75.14
Biomass (combustion)	(GWh/a)	—	224.65	232.60	233.88	255.17
Natural gas	(GWh/a)	7.68	—	—	—	—
Net electricity consumption	(GWh/a)	1.16	—	—	—	—
Products						
Net electricity Production	(GWh/a)	—	36.69	35.47	34.60	39.51
District heat	(GWh/a)	—	83.33	83.33	83.33	83.33
Upgraded biofuel	(GWh/a)	67.72	—	68.24	66.54	75.14

The HTC process receives 21.7 GWh/a from the CHP plant, of which 75% is returned at a lower temperature level, resulting in a net import of 5.4 GWh/a. This leads to an increased demand for boiler fuel wood chips for *HTC-CHP* compared to *CHP-sep*. Using biodegradable waste instead of wood for the HTC increases the steam flow by 14%. The wood pelletizing requires 15.7 GWh/a of steam, resulting in a 10% higher consumption of boiler fuel wood chips compared to *HTC-CHP*. Since the turbine extraction in *WP-CHP* is at a lower pressure, additional electricity is produced in co-generation. The yield of upgraded biofuel is higher for *WP-CHP*, since in the HTC reaction, part of the biomass is converted to heat and byproducts.

4.2. Economic analysis

Wood chip costs including transport and storage result in 3.86 €/GJ for *HTC-sep*, with a land requirement of 1710 ha of short rotation coppice and an average transport distance of 9 km. For *CHP-sep*, *HTC-CHP* and *WP-CHP*, wood chips costs are 4.48 to 4.50 €/GJ, due to the larger catchment area, and additional transport from the seasonal storage site to the plant.

Table 3. Economic results.

		HTC-sep, CHP-sep	HTC-CHP wood	HTC-CHP Waste	WP-CHP
Investment costs					
HTC reactor	(k€)	1206	1133	1176	0
Slurry pumps, flash tanks, screw feeder	(k€)	754	460	491	0
Filter press	(k€)	846	799	951	0
Drying, milling, pelletizing	(k€)	1496	1495	1728	2595
Heat exchangers, product coolers	(k€)	740	735	825	0
Auxiliary boiler	(k€)	141	0	0	0
Waste water treatment	(k€)	245	288	419	0
Biomass sizing, metal/plastic screening	(k€)	0	0	218	0
Upgrading plant, total module costs	(k€)	5427	4910	5807	2595
CHP plant module costs	(k€)	17313	17717	17674	18633
Total capital requirement (TCI)	(k€)	30819	30600	31586	28733
Levelized costs					
Carrying charges [1)]	(k€/a)	3698	3672	3789	3448
Operation & maintenance [2)]	(k€/a)	1733	1517	1720	1145
Wood chips	(k€/a)	4763	5077	3858	5449
Electricity and natural gas [3)]	(k€/a)	276	0	0	0
Total revenue requirement	(k€/a)	10470	10265	9367	10041
Revenues electricity [3)]	(k€/a)	2936	2837	2768	3161
Revenues district heat [4)]	(k€/a)	4248	4249	4248	4248
Production cost upgraded biomass	(k€/a)	3286	3178	2351	2632
Specific cost upgraded biomass	(€/GJ_{HHV})	13.48	12.94	9.81	9.73
Specific cost upgraded biomass	(€/GJ_{LHV})	14.32	13.74	10.47	10.57
CO_2 avoidance cost [5)]	(€/t CO_2)	135.14	115.75	81.28	82.36

[1)] Annuity plus tax and insurances (1% of TCI)

[2)] Operating labour requirement estimated based on plant equipment. Plant operators: 27.63 €/h, biomass yard workers: 20.75 €/h. Material costs: 10% of module costs for high wear components, 2% for other components.

[3)] Energy prices: natural gas: 6.31 €/GJ_{HHV}, purchased electricity: 22.22 €/GJ, electricity revenues: 22.22 €/GJ

[4)] Calculated from *CHP-sep*

[5)] Coal price: 2.69 €/GJ_{LHV}, emission factor for purchased electricity in *HTC-sep*: 641.3 kg CO_2/MWh_{el}

The results of the economic analysis are shown in Table 3. The equipment costs for HTC are about twice than that for wood pelletizing. The higher complexity of the HTC plant compared to wood pelletizing also leads to a higher labour requirement and operation and maintenance costs. The integrated plant design saves 10% on the equipment cost for HTC, mostly related to biomass pressurizing, flash tanks, heat exchangers and the omission of the auxiliary boiler. However, this is offset by higher investment in the CHP plant, which needs a higher capacity due to the additional steam production. The investment for HTC utilizing biodegradable waste is 18% higher than that for the plant using wood, due to higher biomass and biocoal mass flows and additional metal and plastic contaminant screening equipment.

Product costs of the upgraded biomass range from 9.73 €/GJ (175.7 €/t) for wood pellets to 13.48 €/GJ for biocoal produced in the standalone HTC plant. Despite the higher cost of wood chips due to transportation logistics, integration with the CHP plant leads to a slight decrease in biocoal cost. Biocoal pellets produced from biodegradable waste are comparable to wood pellets, assuming zero cost for the biodegradable waste. The cost for CO_2 avoidance when the biofuel is used to substitute bituminous coal is lowest for the biocoal from waste. For *HTC-sep*, only 90% of the CO_2 is avoided due to consumption of natural gas and electricity from the grid, while in the integrated cases, the HTC energy requirements are completely covered by biomass, resulting in zero direct emissions (supply chain emissions aside). The product costs are strongly dependent on the cost of the biomass, which contributes 32% of the annual cost in *HTC-sep*, and around 50% for the integrated plants.

5. Further technical considerations

While wood pelletizing is an established technology, there remains significant uncertainty about some technical aspects and the economics of the HTC plant, because there are no commercial-scale HTC plants yet in operation. Data for the HTC reaction is currently based on laboratory-scale batch experiments. Optimization of the design and operating parameters of the HTC plant might yield higher efficiencies. Key technical issues include biomass pressurizing and the dissolved organics. The dissolved organics result in a substantial energy loss and require waste water treatment. However, the quantity and composition of dissolved organics from laboratory scale experiments may not be representative for a continuous HTC process with process water reflux. In the analyzed plant designs, 21 600 to 68 400 m^3 per year of waste water are generated. That said, experiments on aerobic and anaerobic degradation are reported to indicate good degradability [9]. Low-boiling organics might evaporate in the drier and necessitate remedial treatment of the drier exhaust for VOC emissions.

Regarding product quality, biocoal pellets from wood have a higher calorific value than wood pellets. Biocoal pellets from biodegradable waste are likely to have a higher ash content, resulting in a lower calorific value. The quantity and composition of mineral matter in the biocoal is a consideration for combustion applications. In particular, ash melting temperature, flue gas cleaning requirements and corrosion need to be examined in greater detail. If biocoal is co-fired with coal, sulfur in the biocoal should not be an issue, since coal-fired power plants are equipped with desulfurization. However, the gaseous phase from the HTC of biodegradable waste was found to contain significant amounts of H_2S [13], which could prove more problematic. For biocoal to become a commodity fuel, quality standards regarding ash, sulfur and heavy metal content need to be developed and implemented to avoid damage to combustion equipment and the environment.

6. Conclusions

Hydrothermal carbonization (HTC) is an artificial coalification process which is being promoted as an upgrading technology for high moisture biomass. Under the economic assumptions made in this paper, biocoal pellets from biodegradable waste can be produced at a cost of 9.8 €/GJ_{HHV} when the waste is available at zero cost. This is comparable to the cost of wood pellets. The economics of HTC from biodegradable waste would be further improved if the HTC operator is paid for the disposal of the waste. When wood chips are used as a feedstock for HTC, the pellet costs are 30% higher. This raises the question whether the application of HTC can be justified for biomass that can be easily pelletized without further pretreatment. Since the biocoal pellets produced by HTC are closer to coal, they might be better suited than wood pellets for co-firing in existing coal-fired power plants. Regarding plant design, integrating HTC with a CHP-plant eliminates the need for a complex heat recovery scheme within the HTC-plant and thereby aids operability. The modeling in this paper relied on laboratory scale data and simulation. Operational data from HTC pilot plants is needed to reduce uncertainty regarding conversion efficiency, availability and investment costs.

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Effect of atmosphere on torrefaction of oil palm wastes

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Abstract: Torrefaction is a low temperature treatment for lignocellulosic biomass at lower temperatures between 473 K and 573 K under an inert atmosphere, which has been found to be effective not only for improving the quality of lignocellulosic solid fuels, such as their energy density and shelf life, but also to make them useful as a feedstock for further decomposition such as gasification and liquefaction. Although more than ten papers on this subject have been published in the last several years, in all of these studies, the atmosphere has been inert (nitrogen). When we try to utilize waste thermal sources, such as flue gas from boilers for torrefaction, the gas contains some components other than nitrogen such as oxygen, carbon dioxide and water vapor. The most serious problem is thought to be the existence of oxygen in the gas. In this study, torrefaction of Malaysian oil palm wastes was carried out in a fixed bed tubular reactor under oxygen/nitrogen flow at a temperature range of 494 to 573 K, in order to clarify the effect of oxygen on torrefaction of lignocellulose. The effects of torrefaction conditions such as atmosphere, temperature and time, on the torrefaction behavior were investigated. The lignocellulosic biomass wastes utilized were mesocarp fiber and kernel shell of oil palm, which are typical agricultural wastes in Malaysia.

Keywords: *Torrefaction, Oil palm waste, Lignocellulose, Oxygen*

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1. Introduction

One of the promising renewable energy sources is biomass, which can be utilized as solid, liquid or gas fuels. Specifically, lignocellulosic biomass residues are attracting interest worldwide because they are non-edible. Due to their availability in Malaysia, oil palm wastes are considered as the best among all biomass wastes [1]. In 2008, Malaysia was the second largest producer of palm oil with 17.7 million tonnes, or 41% of the total world supply, while Indonesia was the world's largest producer of palm oil with 19.3 million tonnes of oil, or 45% of the total world supply [2]. In 2008, productive oil palm plantations in Malaysia covered 4.5 million hectares, a 4.3% increase from the figures in 2007, which stood at 4.3 million hectares [3]. The types of biomass produced by the oil palm industry include empty fruit bunches (EFB), mesocarp fiber, kernel shells, fronds and trunks. EFB, mesocarp fiber and kernel shells are either utilized or discarded at palm oil mills. Similarly, the rest, fronds and trunks are either utilized or discarded at plantations. The amount of each type of biomass is summarized in Table 1. Since the current primary energy supply in Malaysia is about 70 Mtoe (million tons of oil equivalent), the total oil palm biomass energy potential of 17 Mtoe may be able to contribute considerably to the decrease in consumption of fossil fuels (natural gas, coal and oil). In order to utilize biomass wastes efficiently, the following drawbacks about biomass compared to fossil fuels must be properly solved:
(1) Higher energy consumption during collection
(2) Heterogeneous and uneven composition
(3) Lower calorific value.
(4) Quality decay by biodegradation.

There are a few options to solve some of those problems; the major ones are pelletization, liquefaction and gasification of biomass. Pelletization includes the following processes: drying, chipping, grinding and pelletizing of lignocellulosic biomass. Though pelletization is the least expensive option, there are some problems associated with it; lower heat value and quality deterioration by moisture (pellet disintegration, moss growth and bioorganic decomposition). In recent investigations, a low temperature treatment at 473 to 573 K under an inert atmosphere was found to be effective for improving the energy density and shelf life of the biomass. The treatment is called 'torrefaction,' and has been reported for wood and grass biomass over the past few years [4-16]. Arias et al. torrefied woody biomass (eucalyptus) at 513 to 553 K, and found that the grindability of the biomass was improved [5]. Prins et al. proposed a kinetic model of torrefaction [9], and reported the details of torrefaction mass balance [10]. Some papers have focused on the fuel quality [6] and the feedstock quality for gasification [4,7] of the torrefied lignocellulosic biomass. Uslu et al. focused on a comparison of torrefaction, fast pyrolysis and pelletization from the viewpoint of international bioenergy logistics [8]. Currently, experimental torrefaction studies are mostly conducted on woody and grass biomass; wood dusts [8], beech [4, 9, 10], eucalyptus [5], willow [6, 7, 9, 10], larch [9, 10], and canary grass [6]. Few academic papers have been found for torrefaction of agricultural lignocellulosic wastes, such as wheat straw [6, 9, 10], although they are among the most promising renewable resources, especially in Southern Asia. The authors have already reported on the torrefaction behaviour of three types of oil palm residue; empty fruit bunches (EFB), mesocarp fiber and kernel shell [17].

Table 1. Oil palm biomass wastes and their potential.

Site	Waste type	Generation rate		Plantation area or FFB processed		Annual generation	Moisture	CV (LHV, dry base)	Annual energy (dry base)	
						million t-wet/y	wt%	GJ/t	PJ	Mtoe
Palm plantation	Trunk	40	t-dry/ha-replantation/y	0.08	million ha-replantation	11	71	16.4	52	1.2
	Fronds	15				4.1	71	14.4	17	0.4
	Fronds	6	t-dry/ha-plantation/y	4.488	million ha-plantation in 2008	92.9	71	14.4	388	9.2
Palm oil mill	EFB	0.2	t-wet/t-FFB	85.71	million t-FFB processed in 2009	17.1	65	15.8	95	2.3
	Fiber	0.12				10.3	42	18.3	109	2.6
	Shell	0.05				4.3	17	18.5	66	1.6
	POME	0.6				51.4	-	-	28	0.66
Total									727	17.3

At palm oil mills in Malaysia, we may be able to utilize flue gas from the boilers as a thermal energy source for torrefying unutilized residues. Currently, in most of the palm oil mills, all the mesocarp fiber and part of the kernel shell generated at the mills are utilized as fuel for the boilers. EFB and most of the shell are not utilized. Specifically, EFB is simply incinerated without any thermal recovery due to its high moisture content. If it is possible to utilize the flue gas from the boilers for torrefying EFB, (1) a considerable quantity of energy can be saved in the process; and (2), EFB could be sold as a solid fuel. This makes the oil mill more economically viable. In this case, the problem is that no data are available to demonstrate if torrefaction can be carried out properly in the presence of oxygen, because flue gas from the boilers at palm oil mills contains oxygen. According to our survey, the oxygen concentration in the flue gas is around 13%. Based on this point of view, the authors have already studied and reported the effect of oxygen on torrefaction behavior of EFB [18]. In addition, recent developments in boiler technology have improved their efficiency considerably. If such updated technology is applied, boilers at oil mills will only consume part of the fiber generated at the mills. In the very near future, kernel shell and part of the mesocarp fiber, therefore, could be the source for torrefaction to produce solid fuel.

In this paper, torrefaction of mesocarp fiber and kernel shell residue was carried out in a fixed bed tubular reactor in the presence of oxygen in the range of 3 to 15 %, in order to answer the question above. The effects of torrefaction conditions, oxygen concentration, temperature and biomass size, on the mass and energy yields were investigated.

2. Experimental

2.1. Biomass samples

Mesocarp fiber and kernel shell were collected from an oil palm plantation at Bota in Perak, Malaysia in July, 2010. After drying at 378 K for 24 h, they were ground by a mechanical grinder. The ground powders were sieved into four fractions as shown in Table 2.

Table 2. Biomass size used in this study.

Range of sieve opening [mm]	Nominal average diameter [mm]
0.25-0.50	0.375
1.0-2.0	1.5
2.0-4.0	3.0
4.0-8.0	6.0

2.2. Torrefaction

Torrefaction of the biomass samples was carried out using a horizontal tubular type reactor made of stainless steel, with a 46 mm internal diameter. The entire set-up is illustrated in Fig. 1.

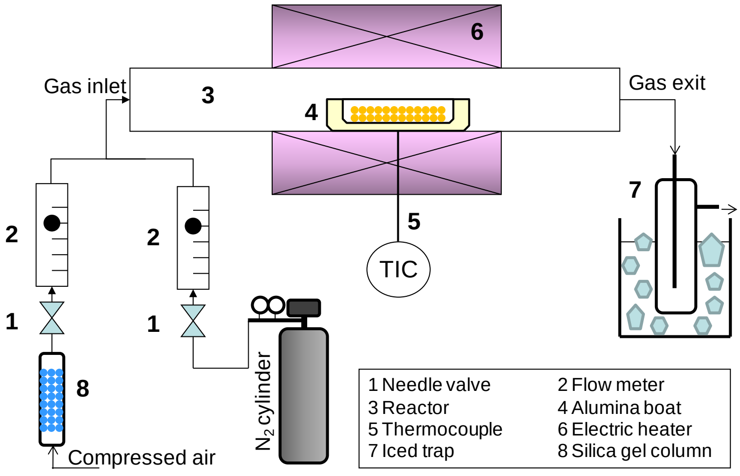


Fig. 1. Experimental apparatus used in this study.

A prescribed amount of biomass waste (1.6 g) was weighed, and put in a ceramic boat. The boat was placed at the center of the reactor. After flushing the reactor with torrefaction gas for 15 min, the temperature of the reactor was raised to different desired levels, *i.e.* 493, 523 or 573 K at a constant rate of 10 deg/min by an electric furnace surrounding the reactor. The temperature range (493 to 573 K) was chosen because selective decomposition of hemicelluloses occurs between 473 and 573 K. The reason for selecting the minimum temperature as 493 K is that we may not have a substantial torrefaction rate at less than 493 K. After 30 min of torrefaction, the heater was turned off and the reactor was left to cool down to an ambient temperature. The torrefied sample was then recovered, weighed and kept in an air-tight vessel till the characterization. Throughout the procedure described above, 0.1 L/min of torrefaction gas was flowed through the reactor. The concentration of oxygen in the gas was adjusted to 3, 9 or 15 %, in order to investigate the effect of oxygen concentration on torrefaction. During each torrefaction experiment, collection of volatile substances generated from the reactor was attempted by an iced trap as shown in Fig. 1. After all, no condensation was observed in the trap for all the runs.

2.3. Measurements

For all the eight samples used in this study, the mass and the calorific value were measured before and after torrefaction. The calorific value was measured using a bomb calorimeter, model C2000 series manufactured by IKA Werke. The calorific value from a bomb calorimeter is the high heat value (HHV), which includes the latent heat of the vapor emitted from the specimen. From the experimental results described above, the three parameters were calculated by the following three equations:

$$y_M = \frac{Mass\ of\ \ solid\ \ after\ torrefaction}{Mass\ of\ \ EFB\ used} \tag{1}$$

$$CV\ \ ratio = \frac{CV\ \ of\ \ solid\ \ after\ torrefaction}{CV\ \ of\ \ EFB\ used} \tag{2}$$

$$y_E = y_M \times CV\ \ ratio \tag{3}$$

Where y_M means the mass yield, CV means the calorific value, and y_E means the energy yield.

3. Results and Discussion

The biomass samples after torrefaction and their physical properties are listed in Tables 3 and 4. In this study, the calorific values of the untorrefied mesocarp fiber and the untorrefied kernel shell were 18.6 and 19.9 MJ/kg, respectively. Wahid reported 18.8 and 20.1 MJ/kg as the calorific values of mesocarp fiber and kernel shell [19]. The difference between this and other studies is surprisingly small, although the physical properties of biomass frequently depend on soil conditions and the harvesting season [20].

Table 3. Torrefaction results for fiber of 0.375mm.

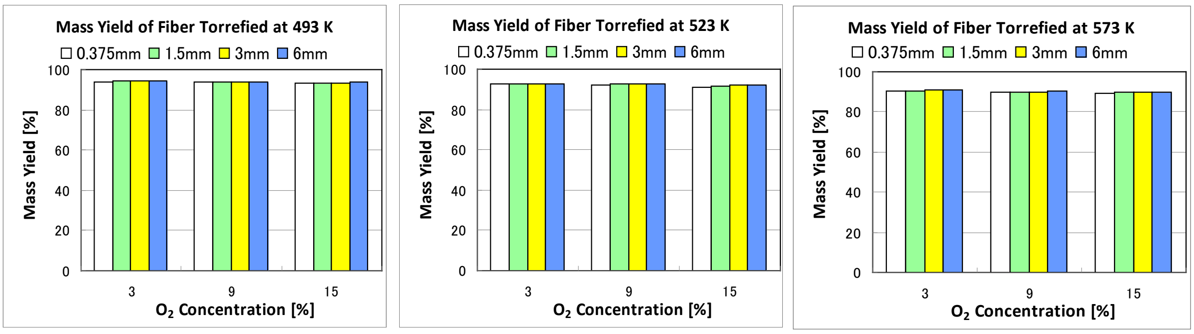
Temp [K]	O_2 conc [%]	Calorific value [MJ/kg]	CV ratio [%]	Mass yield [%]	Energy yield [%]
493	3	21.2	114.2	94.0	107.4
523	3	21.3	114.6	92.8	106.3
573	3	22.1	118.8	90.3	107.3
493	9	21.0	113.2	93.7	106.1
523	9	21.4	114.8	92.4	106.1
573	9	22.1	119.0	89.8	106.9
493	15	21.1	113.4	93.1	105.5
523	15	21.6	116.1	91.2	105.9
573	15	22.1	118.8	89.5	106.3

Table 4. Torrefaction results for shell of 0.375mm.

Temp [K]	O_2 conc [%]	Calorific value [MJ/kg]	CV ratio [%]	Mass yield [%]	Energy yield [%]
493	3	22.0	110.4	95.8	105.8
523	3	21.7	109.0	94.3	102.8
573	3	22.8	114.5	93.1	106.6
493	9	21.9	110.2	95.4	105.2
523	9	21.6	108.8	93.8	102.0
573	9	22.7	114.3	92.5	105.7
493	15	21.8	109.8	94.9	104.2
523	15	21.6	108.7	93.6	101.7
573	15	22.7	114.3	91.9	105.0

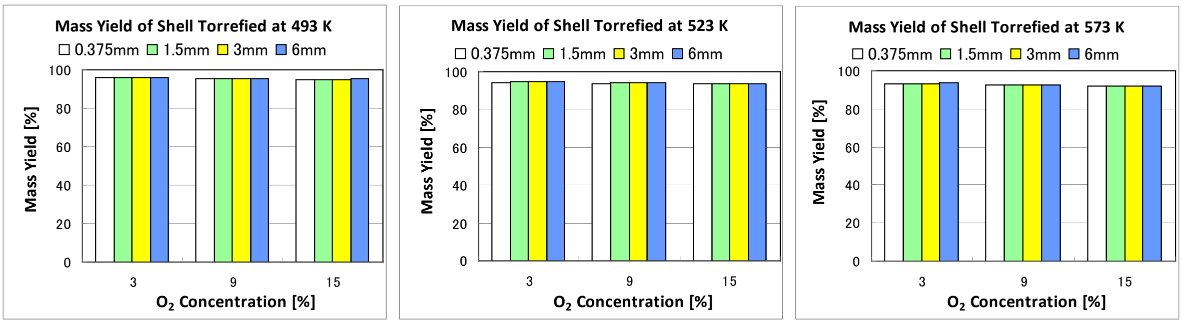
3.1. Effect of biomass size on mass yield

Figures 2 and 3 show the results of mass yield for mesocarp fiber and kernel shell, respectively. It is obvious that mass yield shows no significant dependency on particle size under the conditions of this study. Hereafter, the effects of temperature and oxygen concentration on the torrefaction results will be discussed. Also, the results are for 0.375 mm biomass unless otherwise noted in the text.



(a) (b) (c)

Fig. 2. Mass yield for mesocarp fiber.



(a) (b) (c)

Fig. 3. Mass yield for kernel shell.

3.2. Effects of temperature and oxygen concentration on mass yield

Figures 4 and 5 show the relationship between mass yield and temperature at oxygen concentrations of 3, 9 and 15 % for mesocarp fiber and kernel shell, respectively. The mass yield decreases with an increase in temperature. A similar tendency was reported in previous torrefaction studies [6, 11] as well as in our study on EFB torrefaction [18]. This tendency reflects the positive effect of temperature on the torrefaction rate. On the other hand, the mass yield slightly decreases with an increase in oxygen concentration as shown in Figs. 4 and 5. As we have reported already, for torrefaction of EFB, the mass yield decreased with an increase in oxygen concentration. EFB is found to be not as resistant to oxygen in the atmosphere as mesocarp fiber or kernel shell. When the mass yield of fiber is compared with that of shell, shell always shows a larger mass yield than fiber at any temperature.

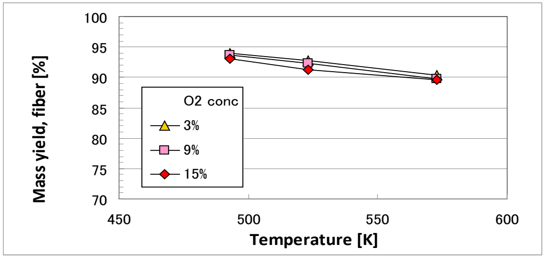


Fig. 4. Effects of temperature and O_2 conc. on mass yield for mesocarp fiber.

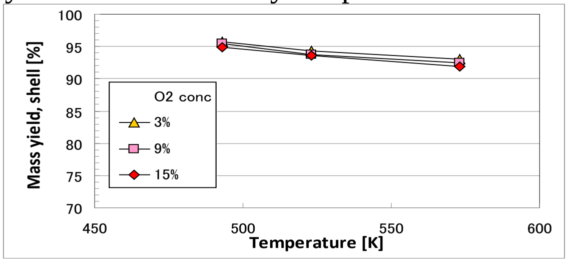


Fig. 5. Effects of temperature and O_2 conc. on mass yield for kernel shell.

This tendency may be attributed to the fact that shell contains 22.7 % hemicellulose, which is less than that of fiber, which contains 38.8 % hemicellulose [21].

3.3. Effects of temperature and oxygen concentration on calorific value

Figures 6 and 7 show the relationship between calorific value and temperature at oxygen concentrations of 3, 9 and 15 % for mesocarp fiber and kernel shell, respectively. The calorific value increases with an increase in temperature. This tendency has been reported in previous papers, in which wood and grass-type lignocellulosic biomass samples were used. It can be explained by the fact that the main gaseous products during torrefaction are water and carbon dioxide [4,10]. Surprisingly, the calorific value has little dependency on oxygen concentration in the range of 3 to 15%. This is the same tendency as what the authors already reported in a previous paper [18]. In that report, the authors proposed that EFB may undergo torrefaction and oxidation in parallel during torrefaction in the presence of oxygen, and these two reactions do not interact with each other. From the results as shown in Figs. 6 and 7, it is likely that the torrefaction mechanism of mesocarp fiber and kernel shell is similar to that of EFB.

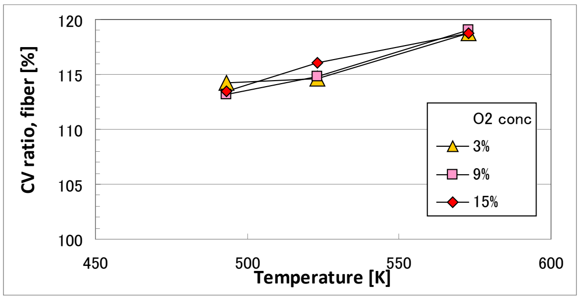


Fig. 6. Effects of temperature and O_2 conc. on CV ratio for mesocarp fiber.

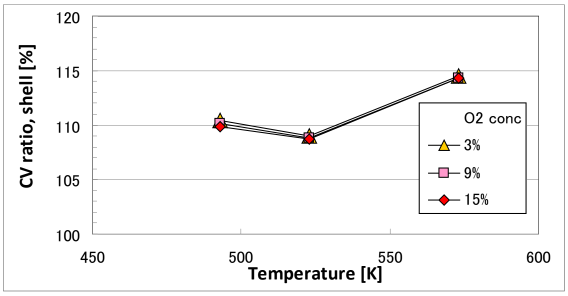


Fig. 7. Effects of temperature and O_2 conc. on CV ratio for kernel shell.

3.4. Effects of temperature and oxygen concentration on energy yield

Figures 8 and 9 show the relationship between energy yield and temperature at oxygen concentrations of 3, 9 and 15 % for mesocarp fiber and kernel shell, respectively. The energy yield is the key parameter to understand how much energy has been reserved after torrefaction. For both types of biomass, the energy yield slightly decreases with an increase in oxygen concentration. For mesocarp fiber, the energy yield has little dependency on temperature. From this result, when we focus only on the energy yield, it is recommended that mesocarp fiber be torrefied at 493 K. Sometimes, however, the calorific value itself does matter. In that case, the torrefaction temperature should be 573 K. For kernel shell, the energy yield shows a concave profile against temperature. This tendency is attributed to the fact that the energy yield is a product of the mass yield and the CV ratio; the former decreases with an increase in temperature, and the latter increases with an increase in temperature. Kernel shell shows a smaller energy yield value than that of fiber under the same conditions. From this fact,

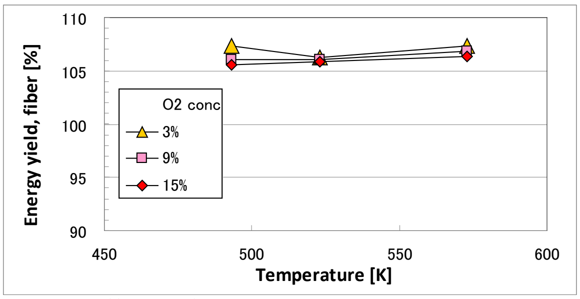


Fig. 8. Effects of temperature and O_2 conc

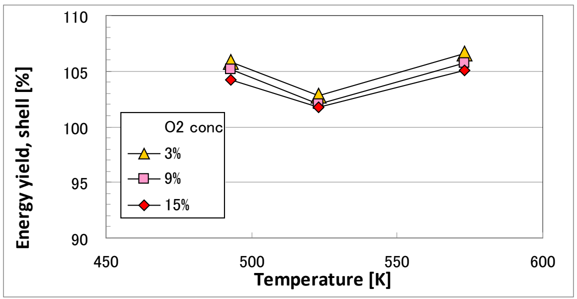


Fig. 9. Effects of temperature and O_2 conc

on energy yield for mesocarp fiber. *on energy yield for kernel shell.*

mesocarp fiber is more suitable than kernel shell as a feedstock for torrefaction.

4. Conclusion

Torrefaction of mesocarp fiber and kernel shell was carried out in the presence of oxygen in order to investigate the effects of various torrefaction conditions, *i.e.*, oxygen concentration (3, 9 and 15 %), temperature (493, 523 and 573 K) and biomass size (0.375, 1.5, 3 and 6 mm), on the mass and energy yields. The mass yield decreased considerably with an increase in temperature, and decreased slightly with an increase in oxygen concentration, but showed very little dependency on biomass size. In other words, the torrefaction reaction rate was affected only by temperature. The other two factors, oxygen concentration and biomass size, had no significant effects on the rate. The energy yield against temperature showed either a slight and steady increase profile or a concave profile. This rather complex behavior is due to the fact that energy yield is a product of the mass yield and the CV ratio; the former decreases with an increase in temperature, and the latter increases with an increase in temperature. The energy yield slightly decreased with an increase in oxygen concentration, but all the values fell between 105 and 108 % for mesocarp fiber and between 102 and 107 % for kernel shell. It is worthwhile pointing out that torrefaction in the presence of oxygen can be carried out without any significant problem, while the mass and energy yields slightly decrease with an increase in oxygen concentration from 3 to 15%. Since the flue gas from a palm oil boiler contains around 13% oxygen based on our survey described in the introduction, direct use of boiler flue gas to torrefaction will not deteriorate the quality of the torrefied biomass.

Acknowledgments

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Biofuels Production Process and the Net Effect of Biomass Energy Production on the Environment

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Abstract: Biomass is based on carbon. It is also the admixture of organic molecules that include hydrogen, oxygen, often nitrogen and small amounts of other atoms like alkali metals, alkaline earth metals and heavy metals. Better method of producing biomass for more energy production has the potential to replace fossil fuels. Converting biomass to liquid, gaseous or solid fuel depends on four main characteristics:
1) Platforms 2) processes 3) feedstock 4) products
Platforms are the most important feature in this classification; they are the key intermediate between raw materials and final products.
There are two main methods to convert biomass to liquid, gaseous or solid fuel: Biochemical and thermo chemical. Biochemical method is known as the sugar platform that is based on enzymatic hydrolysis and fermentation. Thermo chemical method depends on thermo chemical process. Methods that are in this category contain Direct Combustion Gasification and Pyrolysis.
Utilizing biofuels instead of fossil fuels due to a lot of reasons are preferred. They produce less CO_2 than fossils, they produce a little bit of brimstone and they do not produce pure C. Moreover, they can help to reduce greenhouse gasses and can save the environment from destruction. On the other hand, using such fuels help not only the nature to be more stable, but also to gain stable increment in future.
This article is seriously focused bio fuels production process and the net effect of biomass energy production on the environment, tools and combining methods to produce components that cover the mechanism of biomass energy production process and the unique performance of these parts. In this paper the development of biorefinery technologies and using renewable resources in national and international level is studied.
Of course it would be considered that producing more biomass for energy has the potential to pollute water resources and decrease food security.

Keywords: *Biomass energy production process, Bio fuels production process, Renewable energy resources.*

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1. Introduction

Changes in utilization of the Earth and combustion of fossil fuels are the worst mankind's effects on the Earth which have changed the cycle of carbon in the planet.
Combustion of fossil fuels enters huge amounts of carbon dioxide (CO_2) into the atmosphere. Biofuel is a kind of energy which is very important according to the following reasons:

1. Environmental concerns
2. for security reasons
3. Currency saving (frugality in foreign currency savings), social and economical issues related to rural sector and so on.

Biomass is a renewable energy resource which is produced from bio materials. Bio materials contain herbaceous reliquiae which are used for producing electricity and heat. Biomass is one of the most important factors in the economy of the world. If we use biofuels, cost of production will be reduced because of dramatic improvement in efficiency, paying attention to the environmental systems and development of rural places.

Biofuels are vegetable oil, Biodiesel, Bioethanol, bio methanol, Biogas, etc. Most of the biofuels, like ethanol are produced from corn, wheat or sugar beets. Biodiesels are usually produced from oil seeds. For example the amount of energy that can be gained from each m^3 of wood with moisture content of 60% is7GJ or the amount of energy that can be gained from each m^3 of new harvested herbaceous is 3GJ. Bio-ethanol is a suitable replacement for gasoline or it can also be used as its supplement. By using bio-syngas, Bio ethanol can be gained from the steam of biomass which is obtained from the reformed biomass process. Bio-methanol recovers easier from biomass than bio-ethanol. Biodiesel is an environmental friendly fuel and is a good replace for liquid fuels in diesel engines that can be used without change. Using herbaceous oils to make biodiesels has been significantly developed due to these reasons:

1. They produce fewer amounts of CO_2 and pollutant in comparison of fossil fuels in the time of combustion.

2. Ability of being renewable for bio diesel in comparison of conventional diesel fuel oil.

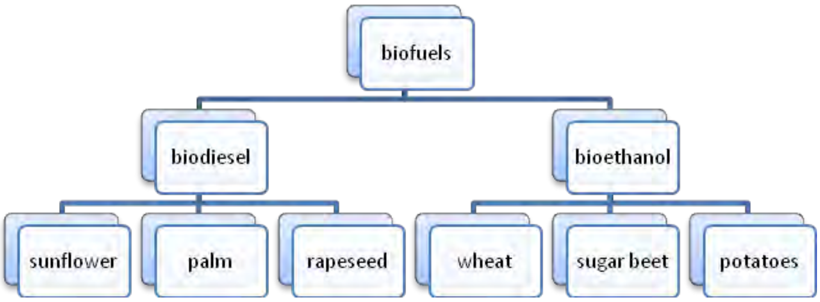

Fig.1. Resources of bioethanol and biodiesel

Technology of producing biomass energy in use of waste or plant matter to produce energy with lower level should be in a way that prevents production of greenhouse gases. [1]

In developed countries there are some modern and efficient technologies for converting bio-energy or at least such kinds of technologies are growing. Hence biofuels in industrialized countries compete with fossil fuels. [2]

Using of bio energy as a fuel of vehicles is getting more and more popular and it can get some portions of fuel market in future decades. In below, some advantages of using it are listed:

1. It helps to the structure of nature and stability of environment which is at risk.
2. Biofuel resources are accessible easily.
3. An economic frugality for consumers. [3]

1.1. How to get energy from biomass

So as to get energy from crude oil it must be refined in order to gain energy, processes must be done on biomass so that energy can be gained from it. Generally, the methods, processes and equipments that can be used to produce energy from Biomass are called Biorefinery. In fact Biorefinery is placed in front of refinery in oil and gas industry.

1.2. Biorefinery energy production methods

1. Sugar platform: This method is based on biochemical reactions and processes
2. Thermo chemical Platform: This method is based on thermo chemical processes

1.3. Sugar platform

In general in this method biomass converts into sugar or other fermented food. In the next steps the result of the material will be fermented by bacteria, yeasts and other microorganisms. Finally, because of processes which occur on the material, products like alcohol or other products that energy can be obtained from them is produced.

1.4. Thermochemical Platform

Methods that are in this category are:

1. Direct Combustion
2. Gasification
3. Pyrolysis

1.5. Direct Combustion

In fact the first people who produced biomass energy through the burning were early humans. This method is not very useful in terms of efficiency and productivity. In other ways through the biomass heating in the absence of oxygen or gas into liquid fuels, you can have high energy efficiency. Besides in comparison of Direct Combustion they have less pollution and higher economic efficiency.

1.6. Gasification

In this method biomass is heated in the absence of oxygen. The product is mixed with carbon monoxide and hydrogen, which is called Syngas. The outcome product will be synthesized with oxygen easily and can be used in turbines, boilers, etc. as a fuel.

As it was mentioned, using such kinds of fuels make not only high efficiency but also lower pollution.

1.7. Pyrolysis

Solid biomasses can be turned into liquid using chemical and catalysis methods. In method Pyrolysis like the method Direct Combustion, biomasses are heated in the absence of oxygen. These products, which are normally liquid, can be used as a fuel.

Now, this method is under research and study for a better environment.

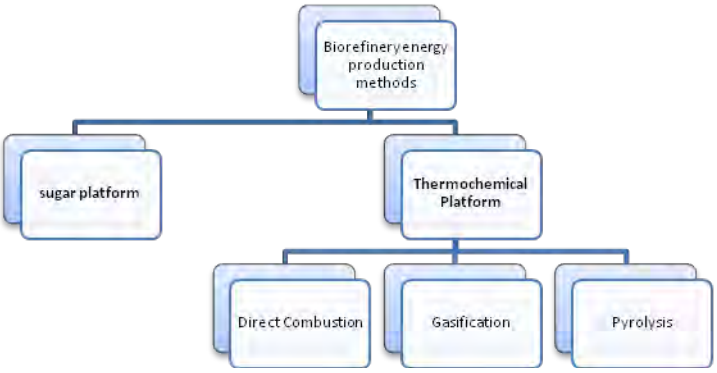

Fig.2. Flow Chart of Biorefinery energy production methods

2. Biofuels

2.1. Bioalcohols

Biofuels which are in forms of gas and liquid are mostly used in a 100% pure as a fuel for vehicles. They are also used, in some cases, with mixture of other fuels, For example, ethanol can be mixed with gasoline as15-20% alcohol by volume without any problem. [4]
Alcohol can be used as vehicles fuel according to the following:

1. Methanol (CH_3OH)
2. Propanol (C_3H_7OH)
3. Butanol (C_4H_9OH)
4. Ethanol (C2H5OH)

They are known as BIOALCOHOLS when they are obtained from land resources. Bio-ethanol contains about5% water. This compound can be purified by simple distillation and becomes as azeotropic mixture. Mixture of gasoline and ethanol is known as gasohol. Gasohol can even be as follow: 97% gasoline, 3% ethanol

However, this gasohol has higher percent octane compared with the previous. In general, this mixture can cause to reduce emissions of greenhouse gasses and some other pollutants. Of course, it should not been forgotten that ethanol evaporates easily and we know that its evaporation in hot weather causes pollution and produces greenhouse gas. Ethanol can be combined with gasoline easily without water. Hydrated ethanol includes not entire 2% of water volume. Mixture of gasoline- hydrated ethanol cannot be combined with diesel.

But we can use emulsion, to form diesohol. Bio ethanol is a petrol additive/substitute. It is possible that wood, straw and even household wastes may be economically converted to bioethanol.fig. 3. Shows ethanol production in different continents.

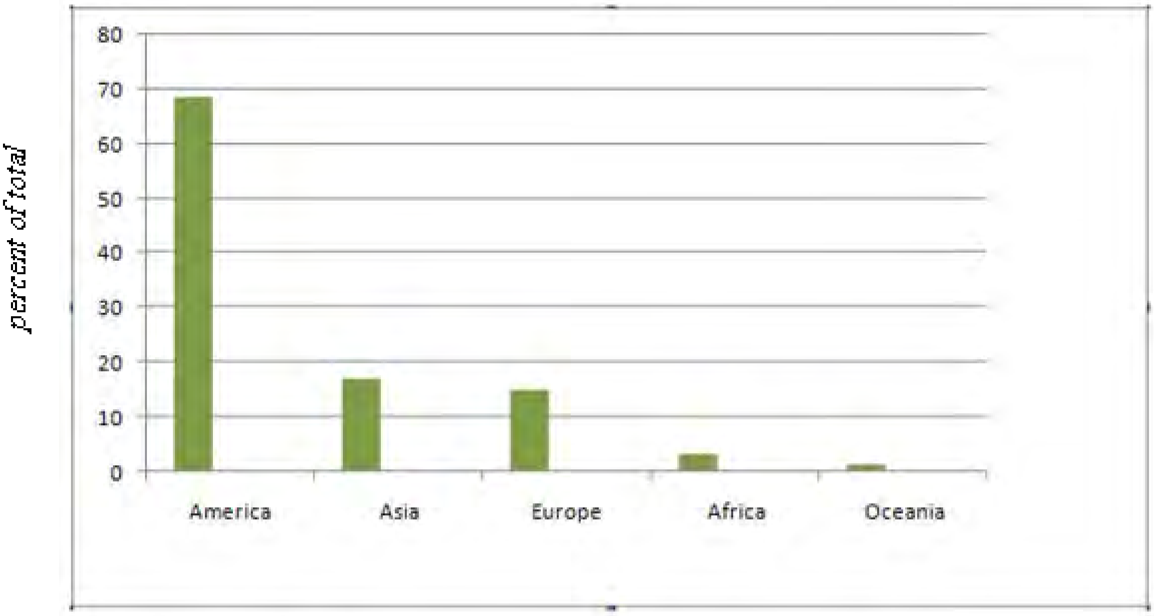

Fig.3. Ethanol in different continents

2.2. Biodiesel and Vegetable oils

Triglyceride chemical molecules with three molecules of fatty acid esters are joint to a glycerol molecule of herbaceous oils.

Herbaceous oils can be used as fuels for diesel engines; but they are more viscose than normal diesel fuels so they need to be reformed before they enter an engine.
There are different ways to reduce the viscosity of the herbaceous oils:
1-pyrolysis
2-Dilution
3-microemul-sifications
4-catalytic cracking
5-transesterifications

Process Pyrolysis has more benefits than Transesterifications. The components of the liquid fuels which produced in process Pyrolysis are resembled to the chemical components of the normal diesel petroleum fuel. Herbaceous oils can be turned into the maximum liquid and gas hydrocarbons using the processes pyrolysis، catalytic cracking, decarboxylation and deoxygenating. [5, 6]

Using herbaceous oils for making biodiesels, which is a renewable energy, introduces a new profitable way of using herbaceous oils. It means that this fuel produces lower pollutant in comparison of usual diesel which causes potential exhaustion. [7]

3. Conclusion

Biofuel, a pure fuel and a renewable energy, is obtained from biomaterials like herbal residue (corn, wheat, sugar beet and wood, straw, oilseeds, etc.). Biofuel is a good replacement for fossil fuels (non renewable) and with mentioning economical, safety and environmental reasons it is so crucial. Besides, it has more advantages than fossil fuels due to these reasons:

1- Frugality for users; Utilizing herbal residue and other agricultural products which have not been able to use by now.
2- Biofuels are renewable in comparison of normal diesel petroleum fuels.
3- They produce less amount of CO_2 in comparison of fossil fuels in the time of combustion.
4- They produce less pollutant which is a good help to the structure of nature and stability of environment which is at risk.
5- The resources of biofuels are available and their row materials are varied for producing biofuels.

A biofuel is produced in this way:

1- Thermochemical Platform (1.Direct Combustion 2.Gasification 3. Pyrolysis)
2 - Sugar platform

Biofuels which are in forms of gas and liquid are mostly used in a 100% pure as a fuel for vehicles. It is also used, in some cases, with mixture of other fuels.

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Simple extraction method of green crude from natural blue-green microalgae by dimethyl ether: Extraction efficiency on several species compared to the Bligh-Dyer's method

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Abstract: We proposed a simple, energy-efficient and environmental friendly method to extract green crude oil from microalgae by using dimethyl ether (DME). In this study, this method was tested on several species of natural blue-green microalgae. Consequently, the green crude was successfully directly extracted from high-moisture microalgae (78.2–93.4 % water content) with an extraction rate ranging from 9.9 to 40.1 % of the dry weight of the microalgae. The extraction yield of total green crude on these species by liquefied DME was compared to the widely-used Bligh-Dyer's method. The DME method almost achieved an extraction capacity approximately equivalent to the Bligh-Dyer's method. Furthermore, the dewatering properties of the proposed method on several species of wet microalgae, and the extraction efficiency were also investigated.

Keywords: *Biofuel, Blue-green microalgae, Extraction, Dimethyl ether.*

1. Introduction

Fossil fuel depletion and global warming issues have strongly motivated research on fuel production from biomass such as corps, animal fat, and micro algae [1]. Among these options, microalgae have attracted significant attention as a new generation biofuel resource [2]. Compared with terrestrial plants, microalgae have a high oil content and growth rate; mass algal cultivation can be performed on unexploited lands using systems supplied with nutrients, thus avoiding competition for limited arable lands [3].

In general, all type of microalgae biosynthesize oleic compositions. The oleic contents of many natural microalgae were approximately 20–50% of dry weight [3, 4]. The overall process related to microalgae biofuel include: species selection, microalgae cultivation, recovery of biofuel (the so-called green crude), and biofuel refining. Methods of microalgae cultivation have been widely studied [5, 6]. Green crude is basically recovered from microalgae by solvent extraction.

In the conventional process, the recovery of green crude from microalgae generally requires multiple solid-liquid separation steps. These processes involve drying, cell wall disruption, and solvent extraction; on a laboratory scale [7]. The extraction of green crude is usually performed with toxic organic solvents such as hexane, chloroform, and methanol, meaning these processes are highly energy-intensive and environmentally damaging [7]. In the lab-scale, green crude extraction with hexane normally carried out by soxhlet at 70 °C for 18 hours [4]. This long time of extraction and heating is drawback in the hexane extraction method. The most rapid and effective conventional extraction method for green crude is the Bligh-Dyer's method [8], which uses drying, cell disruption, solvent (chloroform-methanol) extraction, and evaporation of the solvent. This method has been indispensable and standard, not only for green crude extraction from micro algae but also the quantification of the crude oil from biological materials [9–11].

In the previous study, we proposed a simpler green crude recovery method, which combined drying, cell wall disruption, solvent extraction, and solvent evaporation in a single step [12].

By using liquefied dimethyl ether (DME) as an extractant, green crude was extracted directly from high-moisture natural microalgae without drying and cell wall disruption. This method was conceptualized from our previously established low-energy dewatering [13–16] and deoiling method [17–19], based on the following DME characteristics, namely (i) high affinity with oil and partial miscibility in water (ii) lower boiling point and stable pressure at normal temperature (iii) harmless and naturally decomposable [20, 21].

In the conventional method, the latent heat, sensible heat of water is lost since water should be evaporated in the pretreatment. The calorific value required for heating 1 g of water from 20°C to 100°C and for evaporating water at 100°C is 2,590 Jg^{-1}. Here, the initial moisture content of the micloalgae slurry is assumed to be 90.0% [12]. Therefore, the weight of water was 9 times of the dry weight of the micloalgae. Green crude content in micloalgae is also assumed to be 20% as we will describe later. In the green crude weight basis, theoretical heat loss is $2,590 \times 9 / 0.2 = 116,550$ Jg^{-1}. Moreover, the calorific value required for heating 1 g of chloroform-methanol mixture from 20°C to its boiling point (approximate 63°C) and for evaporating extraction solvent at 63°C is around 700 Jg^{-1}. This is assumed from average latent heat of chloroform (247 Jg^{-1}) and methanol (1,155 Jg^{-1}). Here, the final green crude oil concentration in the chloroform-methanol mixture is 3.3% which estimated from current study in the case of green crude content was 20%. Therefore, the weight of chloroform-methanol mixture was 29.3 times of the green crude weight. Therefore, the theoretical heat loss for evaporating the chloroform-methanol mixture is $700 \times 29.3 = 20,510$ Jg^{-1}. In addition, the energy consumed for cell disruption is unidentified and must be large. Therefore, the total required energy is roughly 137,060 Jg^{-1} and plus the unidentified part for cell disruption.

In contrast, in the proposed method, the energy required to remove 1 g of water is 1,109 J [13, 16]. As we will discuss later, extraction rate of green crude is faster than that of water. This implies that DME amount for extraction of green crude is less than that for removing of water. In other words, the required energy for extraction of green crude is less than water. Thus, the available calorific value for extraction of green crude oil from microalgae is less than $1,109 \times 9 = 9,981$ Jg^{-1}. Therefore, the proposed method is more energy efficient than the conventional method from the perspective of energy balance.

Considering both the need for sustainable energy and environmental concerns, this method was initially tested on a natural blue-green microalga (a species usually causing harmful algal blooms in human ecosystems) collected at Hirosawa Mere in Kyoto City, Japan [12]. By using dimethyl ether (293 K, 0.51 MPa) as an extractant, the green crude was successfully extracted from natural blue-green microalgae (91.0% water content) with a high extraction capacity of 40.1% of the dry weight of the microalgae. The extraction yield by liquefied DME was 99.7 %. The resulting green crude was further analyzed by GC-MS, and the result showed that the lipid substance was predominant chemical composition in the extracted green crude. The calorific value of the green crude was 45,790 J g^{-1}.

The practical application of this method will require fundamental research to evaluate its effectiveness for different types of algae. In this study, we investigate the extraction yield of green crude by liquefied DME on several natural blue-green microalgae and the results were compared to the Bligh-Dyer's method.

2. Methodology

2.1. Materials

The samples were five selected species of microalgae and two mixed-species of microalgae as follows. (i, ii) *Oscillatoria agardhii* NIES-595 and NIES-1263, collected in Northern Ireland, and Germany, respectively. The water contents of both microalgae were 85.0 %. (iii, iv) *Microcystis aeruginosa* ONC and GSK, collected in the main Okinawa island, Japan. The water contents were 93.4 and 91.1 %, respectively. (v) *Monoraphidium chlorophyta* GK 12. The water content was 78.2 %. (vi) Mixed-species (mainly *Cymbela*) collected at Lake Kanogawa in Ozu City, Japan. The water content was 93.0 %. (vii) The same sample used in the previous study [12]. Mixed-species (mainly *Microcystis*) collected at Hirosawa Mere in Kyoto City, Japan. The water content was 91.0 %.

2.2. Experimental apparatus and methods

The experimental apparatus was the same as that described in the previous study [12]. Briefly, a vessel used for storing liquefied DME (volume: 100 cm^3; TVS-1-100, Taiatsu Techno Corp., Saitama, Japan), a vessel as an extraction column (diameter, 11.6 mm; length, 190 mm; HPG-10-5, Taiatsu Techno Corp.) and a storage vessel for a mixture of DME, water and extracted crude oil (HPG-96-3, Taiatsu Techno Corp.) were connected in series. The microalgae sample was loaded into the lower half of the extraction column and the upper half was loaded with glass beads (of diameter between 0.71 and 0.99 mm; BZ-08, Asone Co., Inc., Osaka, Japan). Nitrogen gas (0.51 MPa) was supplied to flow through the extraction system. The DME flow rate was $10cm^3\ min^{-1}$, and the temperature was 293 K. The experiments were all performed three times independently and the data reported in this paper are the mean values with ± deviation.

2.3. Total crude oil content

The total crude oil content was determined using a widely-used gravimetric analysis based on Bligh-Dyer's method [8]. Briefly, 1g of the dried microalgae was mixed and homogenized with chloroform-methanol (1:1 vol/vol). An equivalent volume of distilled water was added to the microalgae and chloroform-methanol mixtures. Subsequently, the mixtures were transferred into a separatory funnel and agitated for 5 minutes. The mixtures separated into double layers of water-methanol and chloroform phases. The green crude dissolved easily in the low-polar chloroform phase. The green crude in the chloroform layer was separated from the separatory funnel and the separated chloroform was evaporated under reduced pressure.

3. Results and Discussion

3.1. Extraction of green crude from several microalgae

The extraction rate and yield of green crude on the blue-green microalgae by liquefied DME was examined. We would emphasize that the microalgae had high moisture and unbroken cell walls, in the extraction with sufficient liquefied DME. The extraction volumes achieved by liquefied DME and the Bligh-Dyer's method were respectively shown in Fig. 1. White expresses the green crude extraction rate by liquefied DME on the dry weight of the microalgae. Black expresses the results of the Bligh-Dyer's method. The superscript "^{a}" represents the extraction yield of the DME extraction method relative to the Bligh-Dyer's method.

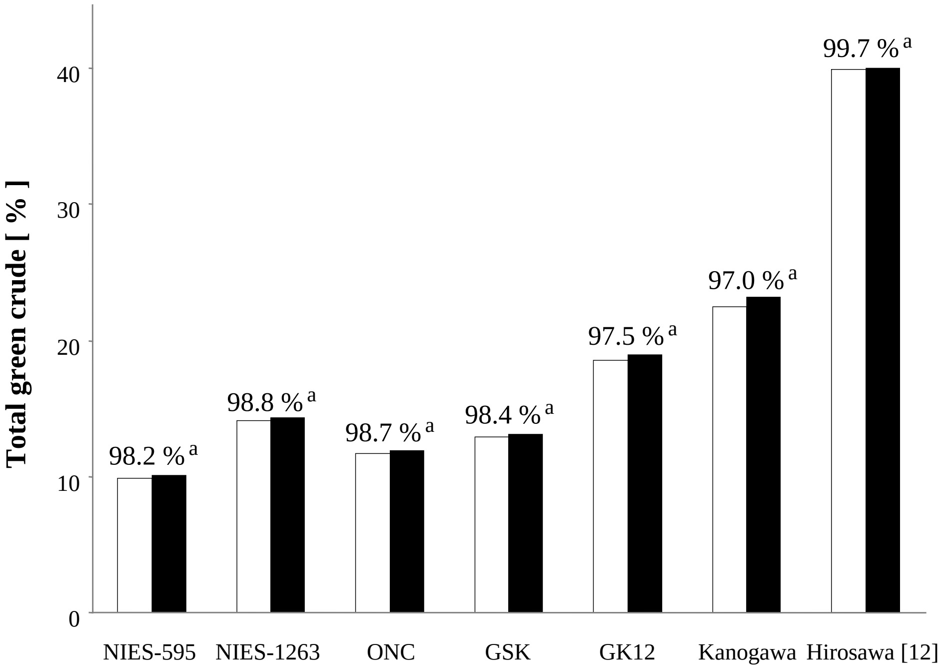

Fig. 1. Green crude extraction rate and yields on several microalgae.

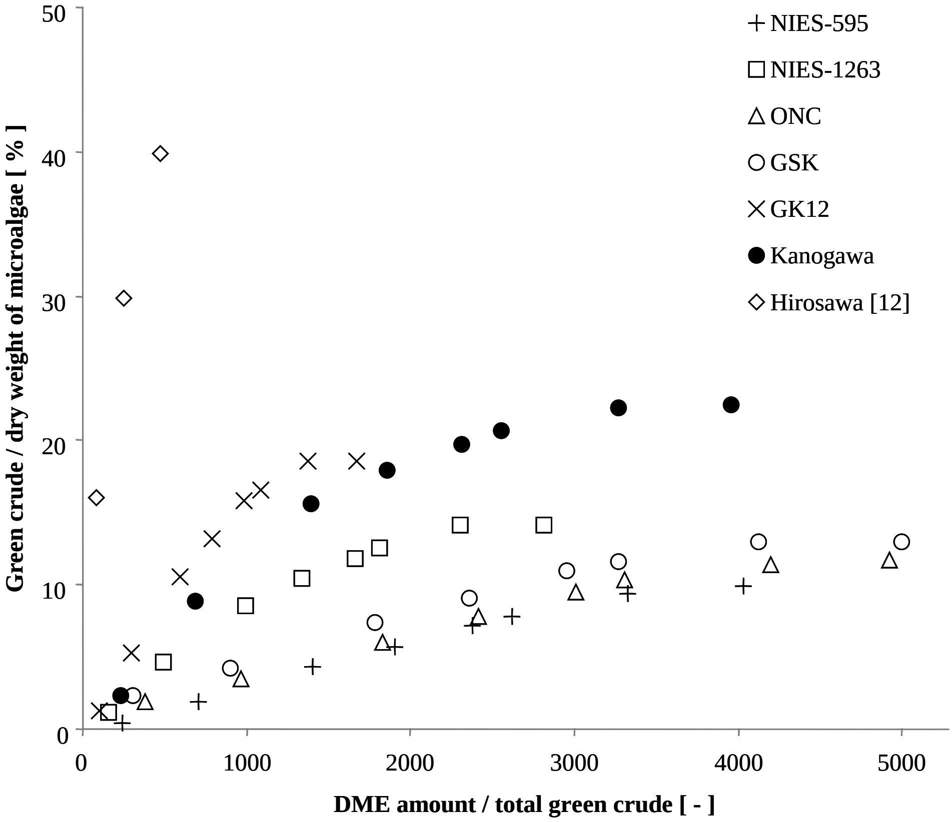

Fig. 2. Extraction of green crude from several microalgae by liquefied DME.

Both NIES-595 and NIES-1263 belong to *Oscillatoria agardhii*, but their extraction rates differ as 9.9 ± 1% and 14.0 ± 1%, respectively. Conversely, the extraction rates of ONC 11.0 ± 2% and GSK 12.0 ± 1.5 % are similar. The extraction rate of GK12 was 18.5 ± 2%. The extraction rate of the mixed-species of microalgae collected at Lake Kanogawa was 22.5 ± 1 %. The extraction rate of Hirosawa Mere showed the highest extraction rate of 40.1 ± 2 %.

The extraction yield of all species achieved more than 97.0 % of total crude oil as determined by the Bligh-Dyer's method. This implies that the DME extraction method provides comparable results to the Bligh-Dyer's method.

The extraction efficiency of green crude by liquefied DME on these microalgae was shown in Fig. 2. For each of the samples, the liquefied DME amount was converted into a ratio of the DME amount relative to total green crude, since the total green crude amount differed. In general, solvent is reused until the green crude concentration in the solvent increases sufficiently, whereupon the usual solvent ratio may apparently be much smaller. On the other hand, in this study, the liquefied DME was not reused after extraction, hence the liquefied DME ratio must be large.

The DME amounts required to reach equilibrium in the extraction of green crude in increasing order were Hirosawa < GK12 < NIES-1263 < Kanogawa < NIES-595 < ONC < GSK. This sequence almost corresponds with the total green crude amount.

3.2. Dewatering from several microalgae

The dewatering by liquefied DME on these microalgae was shown in Fig. 3. Since the water content also differed for each of the samples, the liquefied DME was converted into the ratio

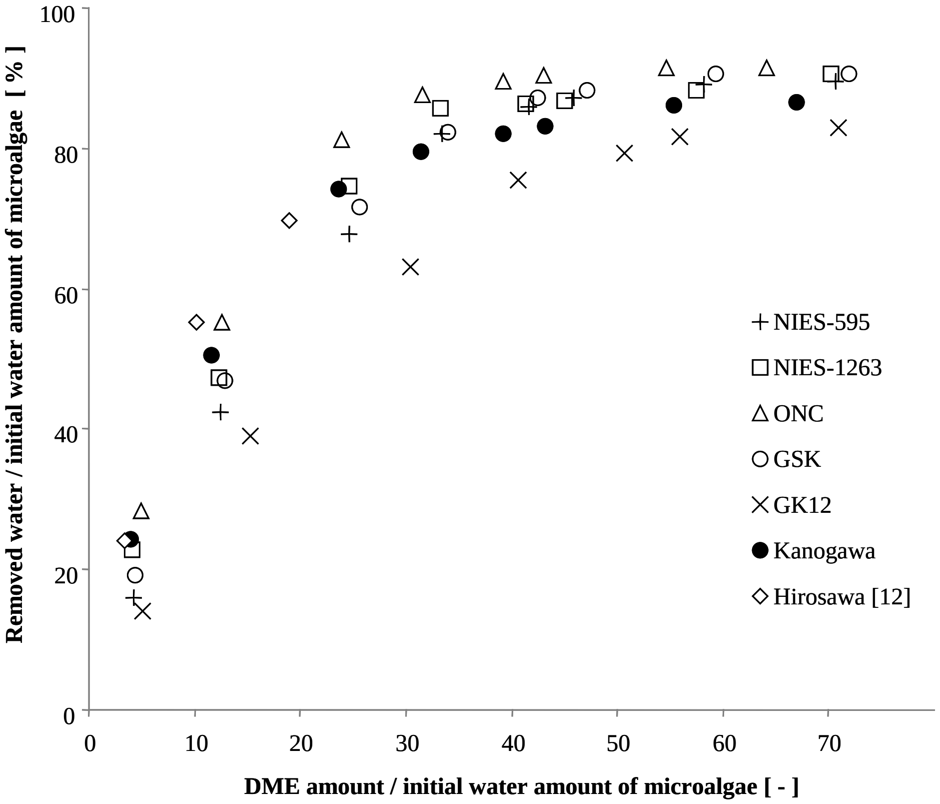

Fig. 3. Dewatering of several microalgae by liquefied DME.

of the DME amount relative to initial water content. By increasing the amount of liquefied DME, the water was extracted from the high-moisture microalgae together with green crude. Moreover, no obvious difference was observed in the dewatering for all samples. While green crude is confined in the microalgae cell wall, most of water exist outside the microalgae cell wall. This make a difference between the green crude extraction and the dewatering.

4. Conclusions

This study confirmed the direct extraction of green crude from several high-moisture natural microalgae by using liquefied DME. Moreover, the extracted amount was almost equal to the Bligh-Dyer’s method. Here it is notable that conventional methods are unable to directly extract green crude from high-moisture microalgae, and the cell disruption must be carried out before solvent extraction. The other advantage of this method is the dewatering effect. This method has the potential to reuse the removed water as microalgae broth. The materials in the removed water will be examined from the perspective of the water shortage crisis.

Acknowledgements

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Production of synthetic alcohol from syngas using $MoS_2/\gamma\text{-}Al_2O_3$

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Abstract: This study examined the transformation of the biomass gasification synthesis gas (syngas, CO and H_2) to liquid fuels and chemicals via the high pressure fixed packed bed (HPFPB). The $MoS_2/\gamma\text{-}Al_2O_3$ catalyst was packed in the packed bed (PB) to enhance the selectivity (S) and yield (Y) products. The effect of reaction temperature (T), pressure (P_{ST}), gas flow rate (Q_G) and H_2/CO (vol./vol.) ratio oon the system performance were investigated. Typical reaction conditions unless otherwise specified were as follows: T = 423, 473, 523 and 573 K, P_{ST} = 3 MPa, Q_G = 300 cm^3 min^{-1}, and mass of catalyst (m_S) = 30 g.

The main products include CH_4, C_2H_6 and C_2H_5OH (EtOH) that EtOH being the target product. The results indicate that with packing $MoS_2/\gamma\text{-}Al_2O_3$ catalyst in PB, the conversion of CO (X_{CO}) and alcohol production rate (R) are highly depended on T. At T = 573 K, X_{CO} = 8.19%, R of CH_4 (R_{CH4}) = 194.1 mg h^{-1} and selectivity of CH_4 (S_{CH4}) = 34.57%. For the production rate of C_2H_5OH (R_{EtOH}), the maximum R_{EtOH} of 134.25 mg h^{-1} takes place at T = 523 K while X_{CO} = 8.10% and S_{EtOH} = 51.98%. As T increase to 573 K, the EtOH is further decomposed into simple hydrocarbons (HCs) such as C1-C3 alkanes. Thus, for producing more alcohols and less alkanes, the optimal temperature condition is 523 K. For the case of varying H_2/CO ratio, the values of X_{CO} are about 7.55 to 8.32%) at 523 K with H_2/CO ratios of 1 to 4, indicating no significant variation. However, the optimal ratio of H_2 and CO to produce EtOH is 2 with maximum R_{EtOH} = 134.25 mg h^{-1} and S_{EtOH} = 51.98% while X_{CO} = 8.10%, R_{CH4} = 56.05 mg h^{-1} and S_{CH4} = 10.85%. Hence, increasing the H_2/CO ratio to 3 to 4 is not beneficial for the formation of EtOH. The results also show that a higher PST of HPFPB yields more products. For the EtOH production, the maximum R_{EtOH} (= 156.65 mg h^{-1}) occurs at P_{ST} = 3.6 MPa with corresponding S_{EtOH} = 51.16%, X_{CO} = 9.57%, R_{CH4} = 70.31 mg h^{-1} and S_{CH4} = 12.46%. Among various Q_G of 300, 450, 600 to 900 mL min^{-1} of HPFPB tested, the best X_{CO} is at Q_G = 300 mL min^{-1} with X_{CO} = 8.10%, R_{CH4} = 56.05 mg h^{-1} and S_{CH4} = 10.85%. Also, the maximum Y_{EtOH} take place at Q_G = 300 mL min^{-1} with corresponding S_{EtOH} = 51.98%. It shows that a low flow rate gives a longer residence time for reaction of the syngas and thus enhances the yield of products. However, there's no advance for S_{EtOH}.

For the production of EtOH from syngas, the Y_{EtOH}, S_{EtOH} and R_{EtOH} are key factors for the success of process. The results of this study shows that $MoS_2/\gamma\text{-}Al_2O_3$ catalyst can give satisfactory S_{EtOH} and R_{EtOH}, especially the Y_{EtOH} high selectivity.

Keywords: *Reforming of syngas; Synthesis of alcohol; $MoS_2/Al_2O_.$; catalytic synthesis; alcohol; alkane*

1. Introduction

Energy crisis has been a great concerned issue in recent years. With the continued climbing of crude oil price, studies on alternative energy become more and more essential. The use of biomass, such as agriculture residues and woody waste, to provide energy and chemicals is receiving increasing interest because these resources can supplement the existing supplies of raw materials while have less net environmental impact [1]. The biomass of agriculture and the biomass fibers of municipal solid waste (MSW) are among the suitable bio-energy sources that can be used for generation energy [1-2].

Gasification technologies have been developed for the possible replacement of traditional combustion technologies because of their higher power generation efficiency while lower environmental pollution [2]. Gasification is a thermochemical process yielding major product of synthesis gas (syngas) consisting of CO and H_2. Syngas can be used to produce hydrocarbons such as ethanol (EtOH) via Mo-based catalytic reaction and other high-value-added fuels via the Fischer-Tropsch process. Although the syngas has been also used as fuel gas, however, its storage, stabilization and transportation exhibit some problems. On the other hand, alcohols converted form syngas have high heating value with small volume and are stable as liquid phase. Moreover, the use of EtOH as a part of the automobile fuel offers the same chemical energy as that of gasoline. Besides, ethanol is a good additive for improving gasoline octane value and burning efficiency [3].

In this study, a high pressure fixed packed bed (HPFPB) with continuous flow was used to synthesize the syngas yielding alcohols. A $MoS_2/\gamma\text{-}Al_2O_3$ catalyst was packed in the bed to enhance the production. The MoS_2 based catalysts, such as K_2CO_3/MoS_2 and Ni-K_2CO_3/MoS_2, have been already verified as effective catalysts in the synthesis of mixed alcohols [4-7]. The distinct points of this study were the use of HPFPB and preparation method of MoS_2 on the $\gamma\text{-}Al_2O_3$ support with high surface of catalyst. The production rates (R), yield (Y) and selectivity (S) of alcohols and conversion of CO (X_{CO}) were examined and elucidated.

2 Materials and Methods

2.1 Preparation of $MoS_2/\gamma\text{-}Al_2O_3$

The MoS_2 was loaded on $\gamma\text{-}Al_2O_3$ pellet ($MoS_2/\gamma\text{-}Al_2O_3$). In preparation, about 30 g $\gamma\text{-}Al_2O_3$ (φ = 3 mm) were soaked in 200 mL solution containing 5% ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) with the adjustment of pH < 2 using nitric acid for adsorbing ionic Mo on the alumina surface for 12 h. It was then sintered at 773 K with N_2 for 3 h to form $Mo_XO_Y/\gamma\text{-}Al_2O_3$. The resulted $Mo_XO_Y/\gamma\text{-}Al_2O_3$ was further reduced and sulfurized in the mixed gas stream of H_2S/H_2 with volume ratio of 5/95 at 673 K for 2 h to produce $MoS_2/\gamma\text{-}Al_2O_3$ catalyst [8]. The $\gamma\text{-}Al_2O_3$, MoS_2 and $(NH_4)_6Mo_7O_{24}$ were supplied by First Chemical (Taipei, Taiwan), ProChem (Miaoli, Taiwan) and J.T. Baker (Phillipsburg, New Jersey, USA), respectively.

2.2 HPFPB system

The HPFPB system (Fig. 1) was carried out via continuous flow type operation. The synthesis reaction proceeded in a high pressure. Two packing materials of $MoS_2/\gamma\text{-}Al_2O_3$ and spherical glass beads were used and tested in the packed bed. The polar organic products such as alcohols and acids were collected by DI water (4 °C) in a condenser. The syngas was simulated with H_2/CO mole ratio of 2. The HPFPB system was operated under the conditions with mass flow rates of H_2 and CO (dmH_2/dt and $dmCO/dt$) of 1070.4 and 7492.8 mg h^{-1}, gas flow rate of syngas (Q_G) = 300 mL min^{-1}, temperature (T) = 423-573 K, mass of catalyst (m_S) = 30 g, flow rate (Q_G) = 300-900 mL min^{-1}, gas hourly space velocity (GHSV) = 600-1800 cm^3 $gcat^{-1}$ h^{-1}, and pressure (P_{ST}) = 1.5-3.6 Mpa (reading at 298 K).

2.3 Products analysis

The analyses of gaseous organic compounds were performed using the gas chromatography/flame ionization detector (GC/FID, 6890 GC, Agilent Technologies, Santa Clara, CA, USA) with AB-5 column (30m × 0.53mm × 5.00 μm, Abel Industries, Pitt Meadows, BC, Canada) to separate the organic products. A purge-and-trap sample concentrator (Model 4560, OI Analytical, College Station, TX, USA) was used to purify and inject liquid samples into GC/FID for analyses.

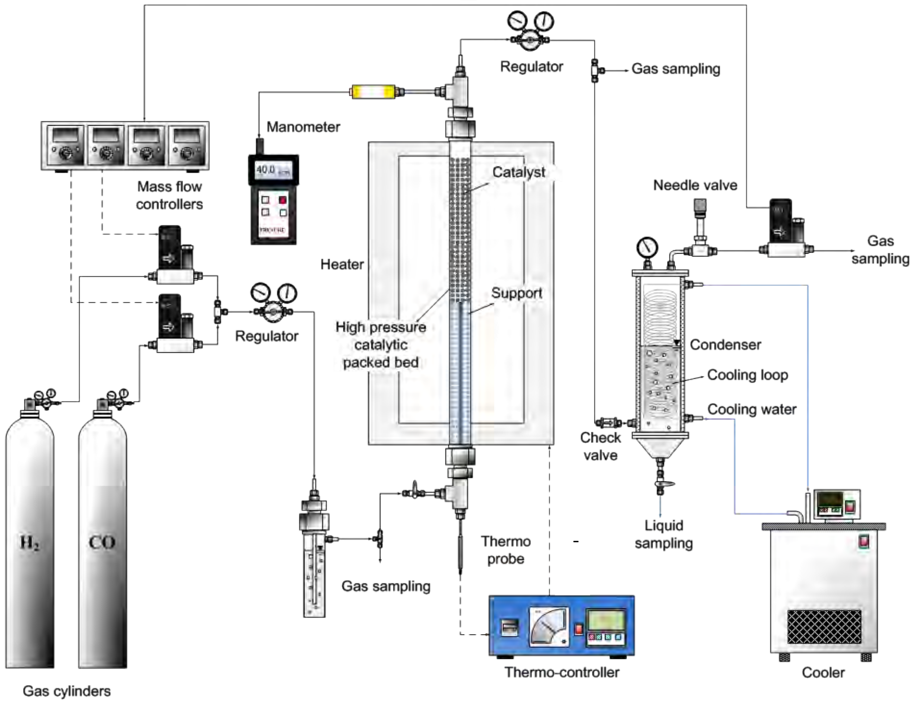

Fig. 1. Schematic diagram of HPFPB system.

3 Results and discussion

3.1 Properties of catalyst and support

The MoS_2/Al_2O_3 catalyst used is spherical with 3 mm diameter and bulk density of 3.2055 g cm^{-3}. The MoS_2 was loaded on the surface of porous Al_2O_3 pellet. The BJH (Barrett-Joyner-Halenda) average pore sizes obtained by adsorption and desorption are 70.404 and 57.841 Å, respectively, indicating mesoporous nature of catalyst. The corresponding BET surface area is 210.345 m^2 g^{-1}. The XRD (X-ray diffraction) spectrum of catalyst surface is shown in Fig. 2, exhibiting significant specific characteristics of MoS_2 at $2\theta = 14.5^\circ$, 39.6° and 60.18°.

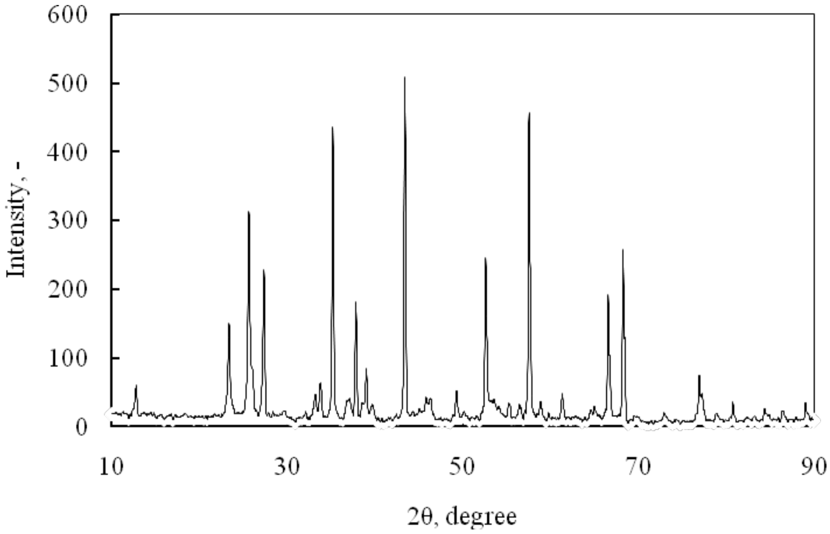

Fig. 2. XRD spectrum of MoS_2/Al_2O_3.

3.2 Effect of temperature

As shown in Fig. 3a, the production rate R of alkane via $MoS_2/\gamma\text{-}Al_2O_3$ synthesis increases with increasing reaction temperature, especially when T reaches 573 K. For the (b) alcohol products, the productions were not effected as the regular pattern as the increase T for the alkane products.

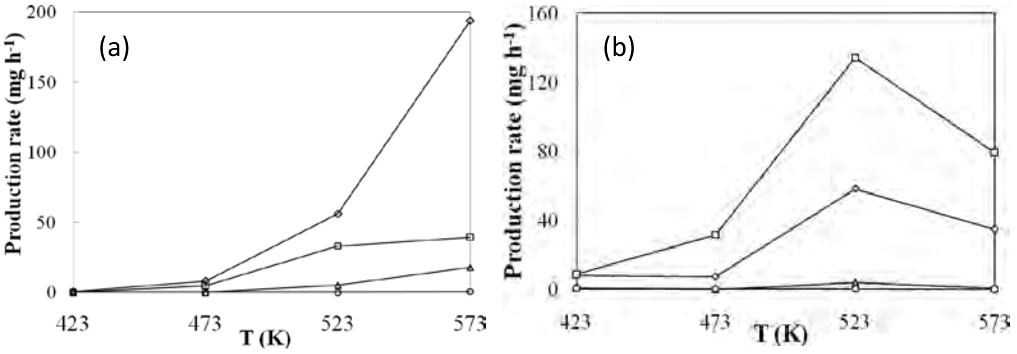

Fig. 3. Production rates of (a) alkane and (b) alcohol products at various temperatures via HPCPB-MoS_2 process. ◇, □, △, ○: C1, C2, C3, C4.

Table 1 illustrates the conversion of CO (X_{CO}) and selectivies (S) of synthesis products at the four different temperature conditions. Setting the reaction at the conditions of T = 473 K, P_{ST} = 3 MPa, $H_2/CO = 2$, Q_G = 300 cm^3 min^{-1}, and GHSV = 600 cm^3 $gcat^{-1}$ h^{-1}, the selectivties of synthesis products shows the highest forming favourable S_{EtOH} = 54.02% within four different temperatures and accompanies with lower forming S_{CH4} = 2.09%. Since X_{CO} is also a meaningful efficiency index, the best X_{CO} is 8.19% while the condition at T = 573 K.

Table 1. Conversion of CO and selectivities of products at various temperatures.

T	Conversion	Selectivity (%)								
(K)	(%)	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	MeOH	EtOH	PrOH	BuOH
423	0.59	1.19	0.74	-	-	31.12	16.69	36.43	6.53	7.30
473	2.09	6.88	8.06	-	-	22.50	6.38	54.02	0.30	1.86
523	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
573	8.19	34.57	14.06	9.58	0.48	6.28	6.21	28.28	0.39	0.16

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

At first appearance, the highest S_{EtOH} and the best X_{CO} seem to be well performances. In fact, they still could not represent the optimal condition because of theirs uncompleted well-performances which comparing these with the condition at T = 523 K. Setting the reaction T at 523 K is the optimal set point which not only yields more alcohol products, especially for higher S_{EtOH}, but also restrains the amount of alkanes formed.

3.3 Effect of H_2/CO ratio

Besides the temperature factor, the H_2/CO feed ratio is also a key adjustable variable affecting the conversion of syngas to ethanol or higher alcohols. The H_2/CO could be adjust to maximize S_{EtOH} and restrain methane forming that because methane is the most thermodynamically favored product, however, its economical value is less than alcohols [9]. The reactions of ethanol and methane are as the showing in following equations:

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \qquad (1)$$

$$\Delta H_r = -61.20 \text{ kcal/mol}; \Delta G_r = -29.32 \text{ Kcal/mol}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

$$\Delta H_r = -49.27 \text{ kcal/mol}; \Delta G_r = -33.97 \text{ Kcal/mol}$$

According the ratio of H_2/CO from the above equations, it is obvious to understand that higher ratio (eq. 2) is more favourable to produce methane than producing ethanol (eq. 1). As the shown in fig. 4, the productions present desired results which are higher production of alcohols accompany with lower production of alkanes when setting H_2/CO ratio as 2.

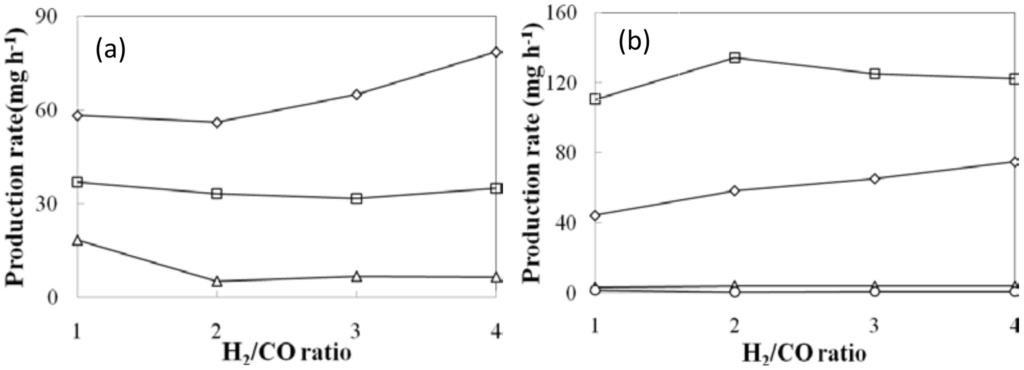

Fig. 4. Production rates of (a) alkane and (b) alcohol products at various H_2/CO ratios via HPCPB-MoS_2 process. ◇, □, △, ○: C1, C2, C3, C4.

Table 2. Conversion of CO and selectivities of products at various H_2/CO ratios.

H_2/CO	Conversion	Selectivity (%)								
	(%)	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	MeOH	EtOH	PrOH	BuOH
1	7.55	11.84	15.01	11.21	-	5.09	8.97	44.9	1.82	1.16
2	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3	8.01	12.67	12.34	3.94	-	6.97	12.69	48.73	2.13	0.53

4	8.32	14.67	13.05	3.67	-	6.52	13.94	45.57	2.05	0.53

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

Table 2 illustrates X_{CO} and S of synthesis products at the four different H_2/CO ratios. Setting the reaction at the conditions of T = 523 K, P_{ST} = 3 MPa, Q_G = 300 $cm^3\ min^{-1}$, and GHSV = 600 $cm^3\ gcat^{-1}\ h^{-1}$, X_{CO} is 8.10% and S_{EtOH} and S_{CH4} are 51.89% and 10.85%, respectively. In these conditions, MoS_2 catalyst shows obvious favour for EtOH and slight restraint for CH_4. For this reason, the results of the shown at $H_2/CO = 2$ are desired and acceptable even if the conversion of CO is not the highest performance.

3.4 Effects of pressure

Increasing pressure is equal to increase the providing raw materials and the equilibrium concentration of products from the hydrogenation of CO [1]. As the shown in fig. 5, both of the productions of alkane and alcohol products increase as the increasing reaction pressure. Therefore, the effects of reaction pressure appear as though Le Chatelier's Principle.

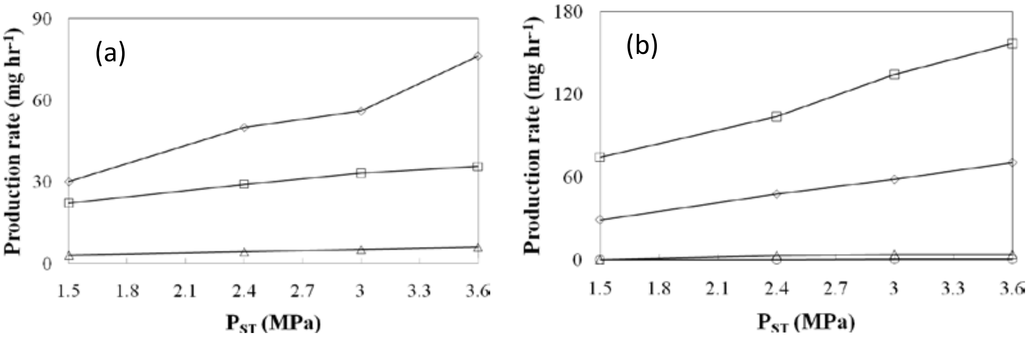

Fig. 5. Production rates of (a) alkane and (b) alcohol products at various pressures via HPCPB-MoS_2 process. ◇, □, △, ○: C1, C2, C3, C4.

Table 3. Conversion of CO and selectivities of products at various pressures.

P_{ST}	Conversion	Selectivity (%)								
(MPa)	(%)	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	MeOH	EtOH	PrOH	BuOH
1.5	4.6	11.84	15.01	11.21	-	-	9.93	50.92	2.47	-
2.4	6.48	12.05	14.04	3.08	-	7.27	11.29	50.00	2.27	-
3.0	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3.6	9.57	12.46	12.63	2.96	-	3.71	13.94	51.16	2.86	0.28

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

Table 3 illustrates X_{CO} and S of synthesis products at the four different reaction pressures (reading at 298 K). Setting the reaction at the conditions of T = 523 K, H_2/CO = 2, Q_G = 300 cm^3 min^{-1}, and GHSV = 600 cm^3 $gcat^{-1}$ h^{-1}. As the increased pressure in this study, there are only increasing effects for X_{CO} as the shown in table 3, however, the selectivities of both alkane and alcohol products are not affected by changing the reaction pressures.

3.5 Effects of flow rate

A high flow rate into the reactor gives a higher space velocity through the fixed catalytic bed, which is equivalent to change the volume of catalyst in the reactor. As the shown in fig. 6, increasing the flow rate also means more reactants input, enhancing the production rates for both of alkanes and alcohols.

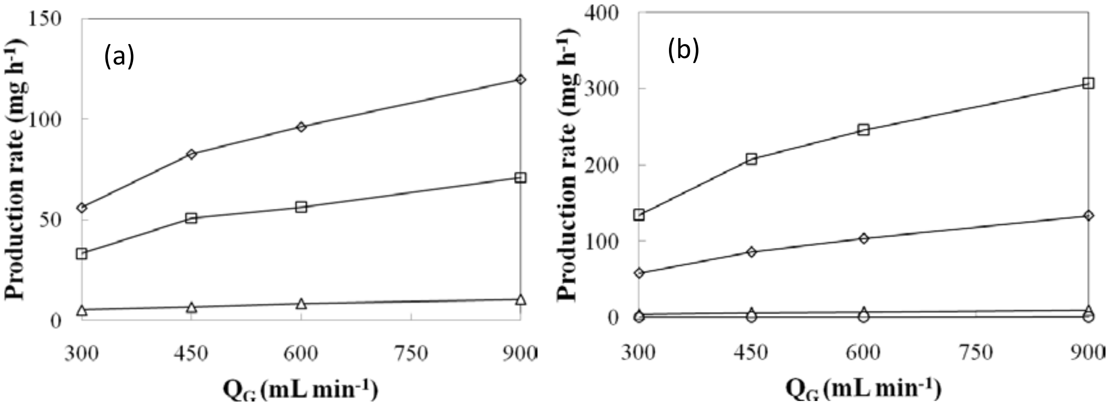

Fig. 6. Production rates of (a) alkane and (b) alcohol products at various flow rates via HPCPB-MoS_2 process. ◇, □, △, ○: C1, C2, C3, C4.

Table 4 illustrates the conversion of CO and selectivies of synthesis products at the four different flow rates. Setting the reaction at the conditions of T = 523 K, H_2/CO = 2, P_{ST} = 3 MPa, and GHSV = 300 cm^3 min^{-1}. As the shown in table 4, increasing the flow rate obviously decrease X_{CO} because the retention time is too small to finish more number of completed reactions. The increase of space velocity results in a slight decrease in selectivity of alkanes while an insignificant increase of alcohols in the reaction products. Besides, the effects of changing flow rate are similar with those of the changing of reaction pressures.

Table 4. Conversion of CO and selectivities of products at various flow rates.

Q_G	Conversion	Selectivity (%)								
(mL min^{-1})	(%)	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	MeOH	EtOH	PrOH	BuOH
300	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
450	5.44	10.54	12.95	2.52	-	7.54	10.91	52.91	2.37	0.26
600	4.83	10.41	12.18	2.70	-	7.82	11.16	53.14	2.34	0.25
900	4.12	10.25	12.14	2.68	-	8.38	11.39	52.50	2.40	0.26

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

4. Conclusions

In HPFPB system, the main organic products of alkane and alcohols of MoS_2/γ-Al_2O_3 catalytic synthesis are ethanol and methane, respectively. From the previous results shown, ethanol selectivity decreases at all temperatures when methane is the major product. For this reason, setting the reaction temperature at T = 523 K is the optimal set point which not only yields more alcohol products, especially for higher S_{EtOH}, but also restrains the amount of alkanes formed. Furthermore, it could increase S_{EtOH} versus CH_4 while setting the H_2/CO feed ratio as 2. C onsidering the effects of P_{ST} and Q_G, there are similar trends for both of alkane and alcohol products besides of the trend for the conversion of CO. Increasing the flow rate would decrease X_{CO} because the retention time is too small to finish more number of completed reactions.

Taken together, these observations suggest that setting the parameter as T = 523 K, H_2/CO = 2, higher pressure, and lower flow rate to reach the purpose of obtaining higher X_{CO} and outstanding S_{EtOH}.

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Thermal treatment of Rapeseed oil

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Abstract: The thermal decomposition of rapeseed oil lowered cetane value of the product through decarboxylation and decarbonylation. In this study the thermal decomposition in rapeseed oil was estimated with different temperatures (300 to 410°C) with or without hydrogen at 1 bar partial pressure. Initially, the reactor is loaded with glass pellets and then the rapeseed oil was fed into the reactor. At hydrothermal condition of 300 to 410°C, the formation of oxygenate groups (i.e. esters, acids and aldehydes) were 15 to 30%, while the rest contained thermally cracked hydrocarbons with excluded un-reacted feed. In residue oil, cyclic group formation was observed. The formation of acidic and aldehyde resulted in carbon dioxide and carbon monoxide in outlet gases. The hydroprocess of higher temperatures leaded higher cracking and cyclic groups with more dense and viscous residue oil.

Keywords: *Hydrodeoxygenation, Decarboxylation, Thermal conversion, Vegetable oil, Bio-fuels.*

1. Introduction

Recently, traditional oil refineries have started to hydroprocessing vegetable oil and fatty acids. Traditional renewable fuels were (1) fuel production based on a super critical process, (2) bio-ethanol technology and (3) production of FAME. All three fuel sources have received considerable attention over the past decade in order to achieve bio-refinery status. Apart from this research development, hydroprocessing was a friendly and suitable process for existing oil refinery concepts to include biomass as a co-feed. One big advantage is the factor of scale in oil refinery. The cost for processing is low per unit and the biomass can ride on this low cost of production and distribution of the products [1, 2]. During hydroprocessing, water is removed from the carboxylic group from tri-glycerol to give C_{18} hydrocarbon and propane, is known hydro-deoxygenation. The product had a high cetane value, low density and poor cold flow properties [3].

Thermal decomposition is unfavorable at deoxygenation mechanism. Usually, excess hydrogen partial pressure is needed for deoxygenation because of certain diffusion limitations over films. These limitations favored for thermal effect on carboxylic group to form CO_2 and CO. Thermal decomposition of the carboxylic group reduced to C_{17} and expelled CO and CO_2 in the gas phase, is known as decarboxylation/decarbonylation. Indeed, loss of one carbon at each hydrocarbon chain in decarboxylation resulted in a difference in the cetane value. Also, methylation and water-gas shift reaction (WGS) were evident as part of the catalytic thermal conversion [2- 4]. Eventually, the temperature around 300 to 360°C proved feasible for deoxygenation, and some researcher indicate it increases the decomposition [5, 6].

Much research on hydroprocessing could explain deoxygenation, thermal conversion, hydration and WGS reaction, but had trouble predicting the exact evaluation of the reaction path due to change in properties of vegetable oil during pre-heating [5-8]. Pre-heating in reactor is common technique for catalytic process. As a part on thermal effect of preheating, we focused only on the thermal effect to identify the modification in vegetable oil with hydrogen as co-feeding at ambient pressure and reinstate the result for future work on our catalytic process. During hydro deoxygenation, the vegetable oil has been subjected with hydrogen into reactor on concurrent flow. This assignment was to characterize the feed before introduce into Hydro deoxygenation catalytic process.

2. Experiment

The experimental setup consisted of a continuous reactor, a feed and product tank, a gas flow meter, pump, a gas chromatography and controllers. The major reaction conditions parameters were liquid hourly space velocity (LHSV = ml of liquid/g.cat*hr), gas hourly space velocity (GHSV= ml of gas/g.cat*hr), reaction pressure (bar) and reaction temperature (^{o}C). However, in our experiment, overall reaction conditions were adjusted with constant feed flow on the continuous reactor on a weight basis. The sample and gas outlet were collected under ambient atmospheric conditions. The reaction condition was stabilized through proportional–integral–derivative (PID) controllers. The samples were withdrawn subject to a manual time control and all samples were taken under a stabilized system.

2.1. Reactor

The experimental setup consisted of a feed tank, fixed-bed reactor, product tank, gas collector and dossier pump. The fixed-bed reactor was fixed with an electric furnace, connected with an instrumental controller to regulate thermal and pressure conditions. The vertical height of the reactor was 619.4 mm, excluding an external clump with bolt; the reactor was filled with 2 mm diameter glass pellets. The maximum temperature, taken at the middle of the reactor, was the indicated temperature point. There are another two more thermocouple connected at inlet and outlet on reactor to monitor the reaction temperature.

2.2. Analytical work

The gas outlet and liquid products from the reactor were analyzed with different gas chromatography equipment. The liquid analysis was performed according to ASTM D2887 using a gas chromatograph (GC) (Varian 3400) equipped with a packed column (OV101) and flame ionization detector (FID) with nitrogen as carrier gas. The outlet gas from the reactor was analyzed by the Clarus 500 GC online, which was connected with 600 link switch controllers; the signal was integrated to receive analytical data. Gas analysis consisted of the use of a thermal conductivity detector (TCD) to analyze CO, CO_2, CH_4 and H_2, as well as FID for hydrocarbons.

Elemental analysis of C, H and O was analyzed by Karlshamn Kraft AB. The ASTM D 5291 standard test method for instrumental determination of carbon, hydrogen and nitrogen in petroleum products and lubricants was used in our samples. Further, traces of nitrogen, sulphur and other metals in the sample were neglected and oxygen content was estimated from carbon and hydrogen content. The accuracy of the elemental analysis was ± 0.4 wt%.

The samples were analyzed with the Perkin–Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FTIR) to identify the internal change in processed vegetable oil. The liquid samples were placed between two plates in pure sodium chloride salt without any bubbles. The mid-infrared was used between wavelengths 400 and 4000 cm^{-1} to study the fundamental structure of the sample.

3. Results

The continuous reactor was heated to 350^{o}C temperature, after which vegetable oil was fed into the system. Initially, the feed was supplied for 48 h without any interruption to make sure the system was clean and to achieve a steady state. After this phase, the reactor conditions were changed systematically to obtain the samples for the appropriate conditions. The samples were collected on a weight basis at ambient pressure from a fixed feed rate of 200 ml/min over 19 h for each condition.

The rapeseed oil contains 7% stearic (18:0), 61.1% oleic acid (18:1), 20.9% linoleic acid (18:2) and the rest consisted of omega-3. At 300°C, 5.12 wt% of free C_{17}-COOH and 1 wt% of other hydrocarbons appeared in the products. In addition to C_{17}, there were traces of lighter hydrocarbon with less than 2 mol% and 10 mol% of CO in the gas phase (Figure 1). At 330°C, the carboxylic group increased to 8 wt% and 2 wt% of other products. Over 330°C, there was a steady increase of both - (COO) - and – (CO) – groups can be seen in Table 1, as well as some lighter hydrocarbons. The results of the thermal effect on (C=O)-O-C bond detachment had observed uniform distribution in gas chromatography.

Table 1. Rapeseed oil hydro-treatment at LHSV = 20 mln/min, 1 bar and H_2/oil = 10. R-(C=O)O refers to BP from 340 to 360°C while R-(C=O) refers to BP about 330°C.

Temp. (°C)	**R-(C=O)O** (wt%)	**R-(C=O)** (wt%)
300	5.12	0
330	7.95	1.9
350	6.55	2.65
370	8.43	3.99
390	11,56	3,64

High concentration of methane and ethane/ethane in the gas outlet were observed for lower temperatures. The dispersed gas in the liquid sample was not recoverable, so it was difficult to make mass balance for in and out of gas flow. Thus, we avoided dealing with the mass balance and instead just showed the concentration in the gas phases. The changes in flow of liquid in and liquid out were almost the same (variation of 0.01 to 0.05 wt%).

4. Discussion

In our study the carboxylic groups were mostly converted to free fatty acid and some traces of alcohol and aldehyde between 330°C and 350°C. This finding implies that the carboxyl groups were influenced by temperature and induced both decarbonylation and decarboxylation. However, there was less evidence of glycerol or glycol groups under these conditions. The gas phase contained CO as the main substitute (Figure 2). The CO outlet shows that the bonding of the carboxyl group was weaker than the C-C bond.

The carboxyl groups tended to detach above 350°C in high yield as acids, aldehyde, esters and paraffin. The concentration of carboxylic acid was doubled and paraffin concentration increased one- to three-fold for every 20°C rise in temperature. The product was distilled in simple distillation at a cut-off of 235°C, which removes water and lighter naphtha named distillate. The distillate had greenish appearance, with gasoline density and viscosity [9]. It had acidic compound. In figure 2 shows the FTIR result of distillate without water in it. Here, C=O groups identified in FTIR mainly of acids while the bottom product consisted of aldehyde and esters. The information in the figure proves that distillate had lighter hydrocarbon with acid group; these conclude that distillate mostly formed from C-C cracking. However, the esters and aldehyde groups had C-O-C- bond breaking, as was evident from the thermal impact.

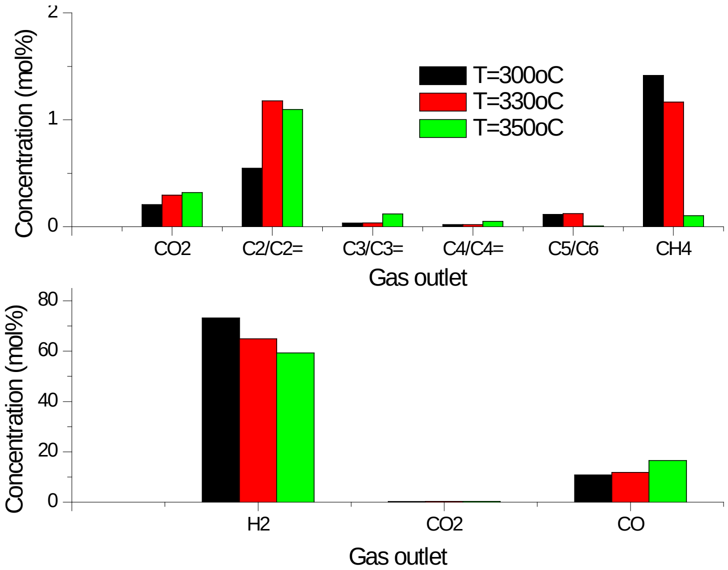

Figure. 1. Rapeseed oil hydro-treatment: gas outlet at LHSV = 20 mln/min, 1 bar and H_2/oil = 10.

At higher temperature (above 350°C) the oxygen content reduced between 10 and 12% into water, CO and CO_2. The distilled sample contained water from 0.04 to 0.1 wt%. The presences of water indicate that the hydroprocess was part in thermal reaction [10].

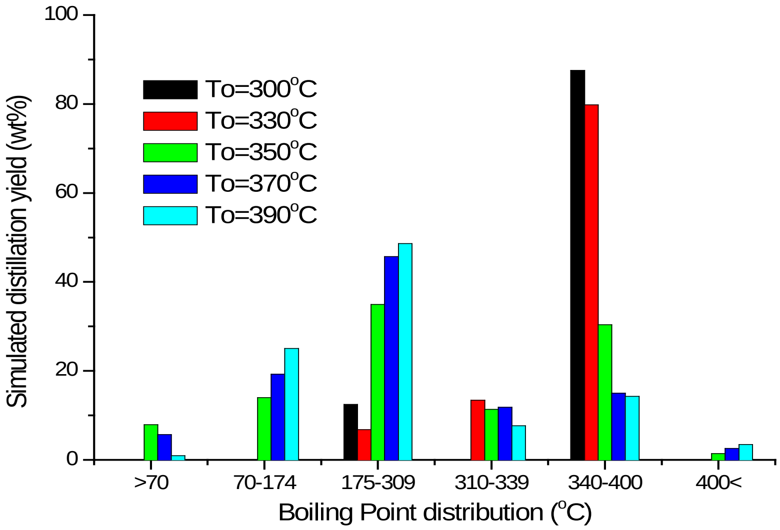

Figure 2. Rapeseed oil hydro-treatment at LHSV = 20 mln/min, 1 bar and H_2/oil = 10 excluding untreated rapeseed oil.

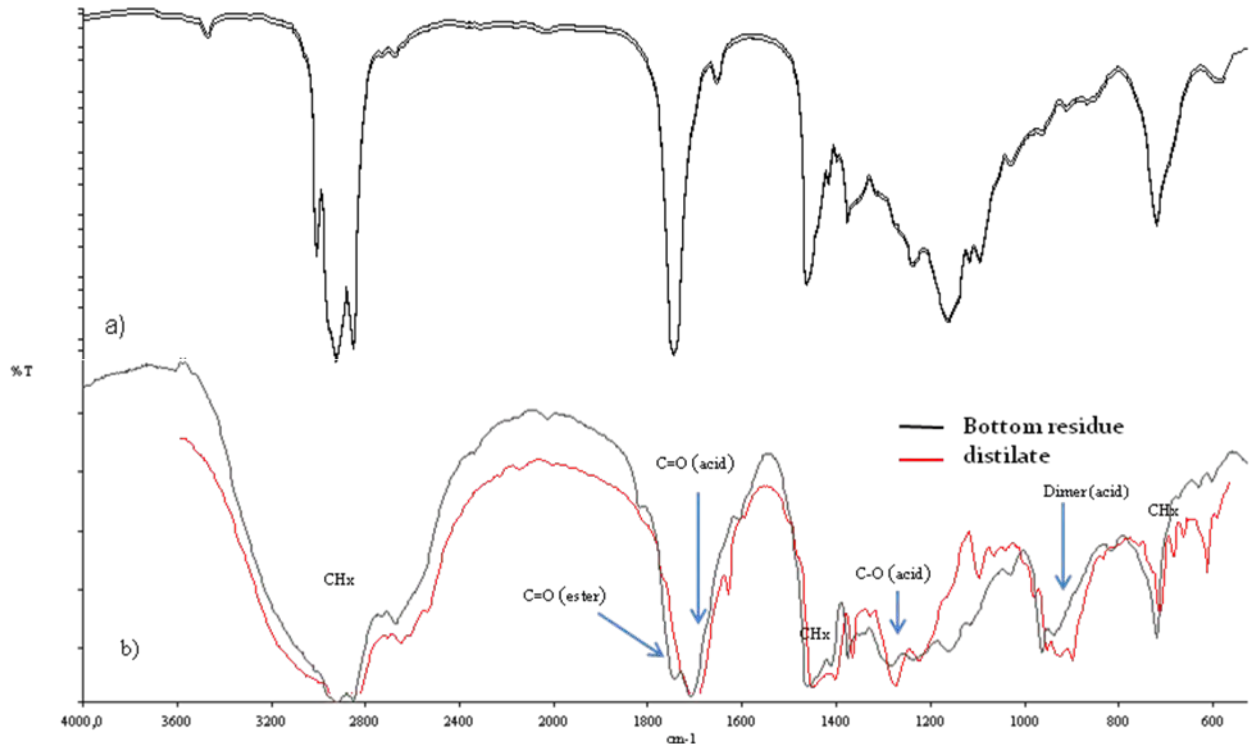

Figure 3. FTIR analysis for distilled product (LHSV = 20 mln/min, 1 bar, H_2/oil = 10 & T = 350 ^oC). (a) Rapeseed oil and (b) Simple distillation at a cut-off point of 235^{o}C.

5. Conclusion

The hydroxyl groups in triglycerides were found to be sensitive to temperature. The product variant in different temperatures was dependent on only CO and water outlet. Of the major gas outlets, CO dominated the composition at higher temperatures. Thermal cracking of C=C bonds between 300 and 350^{o}C, was minimal in this study. The condition between 330 to 360^{o}C indicates that CO formation has more dominant during thermal decomposition.

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Catalytic cracking characteristics of bio-oil molecular distillation fraction

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Abstract: The catalytic cracking characteristics of a bio-oil molecular distillation fraction using HZSM-5 were investigated. Properties of upgraded products and formation mechanism for gasoline components were discussed. The cracking products included 56.00wt.% upgraded liquid oil, 1.27wt.% coke and 42.73wt.% gas products. The conversion yield for components in bio-oil fraction was influenced by their cracking reactivity and their concentration. The cracking reactivity of phenols was strongly affected by the connected functional groups. Alkyl groups had a positive influence on phenols reactivity, while methoxy groups had a negative influence. Reactivity of typical phenols in bio-oil fraction followed the order: Phenol, 4-methyl-> Phenol, 4-ethyl-2-methoxy->Phenol> Phenol, 2-methoxy-. Expected gasoline components including ethylbenzene, p-xylene and benzene, 1-ethyl-3-methyl were detected in the upgraded liquid oil, which indicates liquid hydrocarbon fuels can be produced from bio-oil. A two-step reaction mechanism was proposed which successfully explains the formation routes for gasoline components. In the first step, dehydration and decarbonylation reactions generate H_2O, CO and CO_2. The cracking reaction produces free radicals including -CH_3, -CH_2- and -H. In the second step, these free radicals form gaseous and liquid hydrocarbons.

Keywords: *Bio-oil, Molecular Distillation Technology, Cracking, HZSM-5, Gasoline Components*

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1. Introduction

Supply security and price concerns for fossil oil have led to renewed interests in renewable energy resources as alternative feedstocks for the production of transport fuels. Biomass resources are among the most promising feedstocks because of their abundant reserves and carbon-neutral property. Fast pyrolysis technology is a key thermochemical process that can convert solid biomass waste into liquid bio-oil under atmospheric pressure[1-3]. Bio-oil has better fuel properties in terms of transportation suitability and energy density than solid biomass waste. However, it is only used as fuel in boiler[4, 5] but can not be directly substituted for fossil fuels because of its high viscosity and corrosiveness[6, 7]. Bio-oil refinement has become a key issue for its utilization as a high-grade transport fuel.

Catalytic esterification has been used to decrease corrosiveness of bio-oil by converting carboxylic acids into neutral esters. Carboxylic acid conversion of approximately 90% was achieved and the corrosiveness of bio-oil obviously decreased[8, 9]. Emulsification can be used to refine bio-oil by mixing diesel and bio-oil to produce a homogeneous fuel. Zhang et al. [10] studied the emulsification behavior of diesel and bio-oil using nonionic surfactants. The effects of HLB value, emulsifying temperature and time on emulsion stability were investigated. Wang et al. [11] compared the emulsification properties of different bio-oils and diesel combined at the same ratio(diesel/emulsifier/bio-oil was 92wt.% /3wt.% /5wt.%). Emulsion made from diesel and straw bio-oil showed the best stability. The corrosion properties of emulsions on four metals were measured at different temperatures by Lu[12]. Ikura et al. [13] determined the relationship between process conditions, emulsion stability and processing costs using bio-oil and No.2 diesel. Catalytic esterification and emulsification can improve bio-oil fuel properties to a certain extent, but they can not convert oxygenated bio-oil into pure liquid hydrocarbon fuels.

Among the technologies available for bio-oil upgrading, catalytic hydrogenation and catalytic cracking have been used to produce hydrocarbon fuels from oxygenated bio-oil. Oxygen in bio-oil was removed in the form of CO_2 and H_2O during catalytic hydrogenation[14, 15]. Hydrogenation process can only occur under high temperature and high hydrogen pressure, which limit its economic efficiency. By contrast, catalytic cracking technology is more economically efficient. It can produce liquid hydrocarbon fuels from bio-oil without consuming hydrogen. Adjaye et al. [16] investigated upgrading research of a fast pyrolysis bio-oil using different catalysts. Aromatic and aliphatic hydrocarbons were obtained. Gayubo et al. [17] produced olefins by catalytic transformation of crude bio-oil using HZSM-5. Besides, other researchers studied the cracking behavior of bio-oil using its model components[18, 19]. The key problem in catalytic cracking is the high coke yield, which leads to catalyst deactivation. Catalytic cracking research has mainly focused on crude bio-oil in recent years. The complex composition of crude bio-oil means that qualitative and quantitative analysis of its components is difficult. What more, the strong interaction between different components enhances the probability of coke formation. In the present study, the cracking behavior on HZSM-5 zeolite was investigated for a unique bio-oil fraction produced by molecular distillation technology.

2. Methodology

2.1. Experimental methods

HZSM-5(Si/Al=25) was used as the catalyst for cracking of a Bio-oil Middle Fraction (BMF) , which was obtained by molecular distillation using KDL5 equipment as described in our earlier papers[20, 21]. Cracking experiment was performed upon a fixed-bed reactor at 330 °C. The liquid hourly space velocity (LHSV) was 2 h^{-1} with a HZSM-5 volume of 2 ml. BMF was first vaporized in the pre-heater and then carried to the catalytic bed by a stream of nitrogen. After each run, catalytic bed was subjected to stripping with nitrogen for 40 minutes, with the aim of eliminating the reaction medium components that may remain adsorbed on the catalyst.

2.2. Catalyst characterization

Textural properties were determined by N_2 adsorption–desorption isotherms measured at 196°C below zero on a Quantachrom-Autosorb-1-C apparatus. HZSM-5 had a BET surface area of 283.97m^2/g, a pore volume of 0.07cm^3/g and an average pore size of 5.65nm. Coke deposition on the catalyst was measured during temperature-programmed combustion on a Mettler-Toledo TGA/SDTA851e thermogravimetric balance. Sample of approximately 15 mg was burnt at 30–650°C with an oxygen flow rate of 60 ml/min. The total coke weight was calculated according to the coke content and the total catalyst weight.

2.3. Analysis of liquid products

Liquid products were identified on a Trace DSQII system using a 30m×0.25mm×0.25μm Agilent DB-WAX capillary column. The oven was heated at 40°C for 1 min and then the temperature was increased to 240°C at 8 °C/min and held at this temperature. Data were acquired using Xcalibur software according to the NIST mass spectra library data base.

3. Results and discussion

3.1. Distribution of cracking products

Upgraded Liquid Oil (ULO), coke and gas products were obtained from catalytic cracking of BMF. ULO yield (Y_{ULO}) and coke yield (Y_{coke}) were calculated from Eq. (1) and (2). Yield of gas products (Y_{gas}) was calculated by difference.

$$Y_{ULO} = 100wt\% \times Weight_{ULO} \div Weight_{BMF} \tag{1}$$

$$Y_{Coke} = 100wt\% \times Weight_{Coke} \div Weight_{BMF} \tag{2}$$

Values for Y_{ULO}, Y_{coke} and Y_{gas} were 56.00 wt.%, 1.27 wt.% and 42.73 wt.%, respectively. Gas products accounted for large proportion. The coke yield was low, which means that cracking of bio-oil fractions is a feasible method for decreasing catalyst coking. Graca et al. [22] obtained a coke yield of 16 wt.% for cracking of a mixture of bio-oil and gasoil over ZSM-5. Adjaye et al. [23] obtained a coke yield about 22.5 wt.% for cracking of maple pyrolysis oil over HZSM-5 and silica-alumina catalysts. Thus, cracking of bio-oil fractions has obvious superiority over crude bio-oil in decreasing the coke yield.

3.2. Analysis of liquid products

Compounds in BMF and ULO were identified by GC-MS and quantified using peak area normalization method. The conversion yield was determined as a measure of reactivity during cracking, which was calculated by Eq. (3).

$$\eta_i = 100\% \times (C_{1i} - Y_{ULO} \times C_{2i}) \div C_{1i} \tag{3}$$

Where η_i represents the conversion yield of compound *i*. C_{1i} is its content in BMF and C_{2i} is its content in ULO. Y_{ULO} is the yield of ULO with a value of 56.00 wt.% in this experiment.

3.2.1. Cracking behavior of different compounds

Reactivity of different compounds is indicated by conversion yields. Typical compounds in BMF are listed from Table 1 to Table 3. The conversion yield of a compound during the cracking is determined by two main factors. The first is its cracking reactivity. Compounds with higher reactivity may have a higher conversion yield. The second is its concentration in BMF. Compounds with higher concentration may have a lower conversion yield because of catalyst deactivation. In Table 1, compounds with content below 1% had conversion yield of 100%. For example, 4-methyl-5H-furan-2-one and 2-furanmethanol were absolutely cracked. Three compounds had high content but were completely cracked. It indicated that they were very active during the cracking process. Combining with their concentration in BMF and conversion yields, the reactivity of these three compounds followed the order: Furan, 2,5-diethoxytetrahydro- > 2-Cyclopenten-1-one, 3-methyl- > 2-Cyclopenten-1-one, 2-hydroxy-.

Table 1 Compounds in BMF with the highest conversion yields

Compounds	Content (%)		η_i (%)
	C_1	C_2	
Heptane, 1,1-diethoxy-	3.41	0.44	92.77
Eugenol	1.24	0.07	96.84
4-Methyl-5H-furan-2-one	0.36	0.00	100.00
2-Furanmethanol	0.50	0.00	100.00
1,2-Ethanediol, monoacetate	0.72	0.00	100.00
2-Cyclopenten-1-one, 2-hydroxy-	1.28	0.00	100.00
2-Cyclopenten-1-one, 3-methyl-	1.52	0.00	100.00
Furan, 2,5-diethoxytetrahydro-	13.11	0.00	100.00

The conversion yields for compounds listed in Table 2 varied from 60% to 90%. Phenol derivates were the predominant chemicals in Table 2 and showed a clear cracking principle. Cracking activity of phenols was strongly affected by connected functional groups. Methoxy groups had a negative influence while alkyl groups had a positive influence on the phenols reactivity. Phenol had a conversion yield of 75.63%. This decreased to 59.87% when a methoxy group was attached, such as Phenol, 2-methoxy-. The conversion yield increased to 89.20% when a methyl group was attached, such as Phenol, 4-methyl-. When phenol derivates had alkyl and methoxy groups at the same time, their conversion yields were intermediate between phenol and Phenol, 4-methyl-. The cracking activity of different phenol derivates followed an order as: Phenol, 4-methyl-> Phenol, 4-ethyl-2-methoxy->Phenol> Phenol, 2-methoxy-.

Table 2 Compounds in BMF with moderate conversion yields

Compounds	Content (%)		η_i (%)
	C_1	C_2	
Phenol, 2-methoxy-	5.04	3.61	59.87
Ethanol, 2,2-diethoxy-	16.43	8.18	72.10
Phenol	1.45	0.63	75.63
Phenol, 2-methoxy-4-methyl-	4.98	2.02	77.29
2(5H)-Furanone	1.13	0.42	79.16
Phenol, 4-ethyl-2-methoxy-	1.14	0.36	82.31
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.56	0.57	87.55
Phenol, 2-methyl-	1.87	0.40	88.02
Phenol, 4-methyl-	1.61	0.31	89.20
2-Pentanone, 5,5-diethoxy-	3.02	0.54	89.99

Compounds in Table 3 had lower conversion yields than those in Table 1 and Table 2. Acetic acid, 2-Propanone, 1-hydroxy- and furfural were the most abundant compounds in Table 3. Subsequent to the cracking process, their contents in ULO increased. Content of acetic acid increased from 15.70% to 28.00%. This phenomenon can be well explained as follows. Compounds with high activity were cracked firstly, which generated gaseous hydrocarbons and micro-coke. The active surface of HZSM-5 catalyst was clogged by the micro-coke and deactivated. The cracking of the less reactive compounds, like acetic acid, was interrupted. Thus, the relative concentration of less reactive compounds in the upgraded liquid oil increased. The conversion yields of these compounds can be calculated by Eq. (3). The conversion yield of acetic acid was as low as 0.1%, followed by furfural (15.24%) and 2-Propanone, 1-hydroxy (26.85%).

Table 3 Compounds in BMF with the lowest conversion yields

Compounds	Content (%)		η_i (%)
	C_1	C_2	
Acetic acid	15.70	28.00	0.10
2-Cyclopenten-1-one	1.01	1.66	8.37
Furfural	3.11	4.71	15.24
2-Propanone, 1-hydroxy-	9.50	12.40	26.85
Butanoic acid, 2-methyl-	1.13	1.23	38.96
1-Hydroxy-2-butanone	0.97	1.03	40.47
2(5H)-Furanone, 5-methyl-	0.92	0.68	58.76

3.2.2. Identification of the gasoline components

Bio-oil is considered as one of the most promising substitute for fossil fuels. The most important issue involves the removal of bio-oil oxygen and its conversion to pure liquid hydrocarbons. Some liquid hydrocarbons and other new products were detected in ULO by GC-MS technology. Liquid hydrocarbons were listed in Table 4. The new products in ULO accounted for a total content of 29.74%, including liquid hydrocarbons, liquid ethers and esters. Besides liquid hydrocarbons, ethers and esters can be used as transport fuels or to produce emulsification fuels with gasoline and diesel. Aromatic hydrocarbons, such as toluene, ethylbenzene and benzene, 1-ethyl-3-methyl-, were produced during this cracking experiment. Elucidation the mechanism for formation of these aromatic hydrocarbons is very important for hydrocarbon fuels production from oxygenated bio-oil.

Table 4 Gasoline compounds in the ULO

Compounds	Content (%)	Compounds	Content (%)
Toluene	0.31	Benzene, 1,3-diethyl-	0.49
Ethylbenzene	0.55	Benzene, 1,2,3-trimethyl-	0.44
p-Xylene	1.69	Naphthalene, 1,4,6-trimethyl-	0.42
Benzene, 1-ethyl-3-methyl-	2.76	Naphthalene, 1,7-dimethyl-	0.50

3.3. Mechanism of aromatic hydrocarbons production

Transport fuel is the ultimate aim of bio-oil refinement. Liquid hydrocarbons were detected after cracking of BMF. Exploring the formation mechanism of liquid hydrocarbons was very important for selective enhancement of expected products. In earlier literatures[18, 19], researchers suggested reaction pathways for chemical groups such as acids, phenols and alcohols. But the exact formation mechanism of the liquid hydrocarbons was not proposed. Here, we proposed a two-step mechanism model to explain how the liquid hydrocarbons were produced from oxygenated bio-oil.

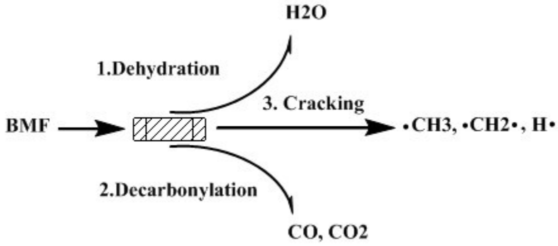

Fig. 1 The first step of the cracking mechanism

The first step is shown in Fig. 1 and it consists of three main reactions, dehydration, decarbonylation and a cracking reaction. Dehydration reaction produces a H_2O molecule, while decarbonylation reaction generates CO and CO_2 molecules. The cracking reaction results in free radicals including $-CH_3$, $-CH_2-$ and -H. All these free radicals participate in the second step to form liquid hydrocarbons.

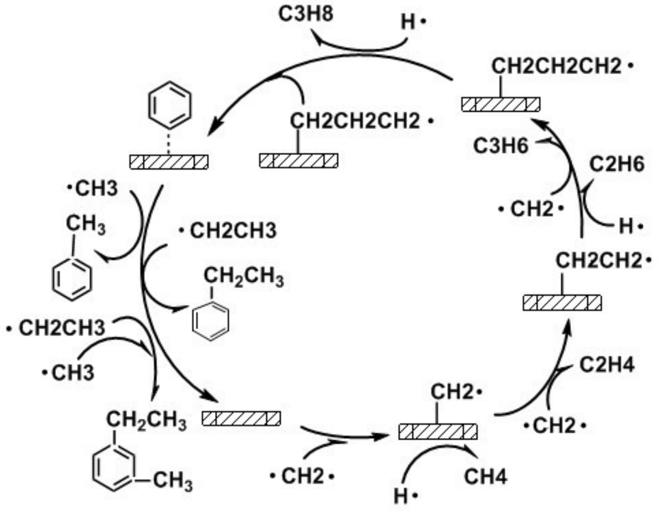

Fig. 2 The second step of the cracking mechanism

Fig. 2 gives a clear overview of the formation process for gaseous hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8) and liquid hydrocarbons (toluene, ethylbenzene and benzene,1-ethyl-3-methyl-). The reaction starts with adsorption of $-CH_2-$ on HZSM-5 catalyst surface. When another $-CH_2-$ group is adsorbed to the catalyst surface, the carbon chain becomes longer to form $-CH_2CH_2-$ group. Some of the $-CH_2CH_2-$ groups desorb to form ethylene (C_2H_4). Some of the $-CH_2CH_2-$ groups further adsorb on the catalyst surface to continue the cycle. Ethane (C_2H_6) is released when the adsorbed $-CH_2CH_2-$ groups are attacked by -H groups. The carbon chain increases to form $-CH_2CH_2CH_2-$ when an adsorbed $-CH_2CH_2-$ group is attacked by another $-CH_2-$ group. Propylene (C_3H_6) and propane (C_3H_8) are formed via the same mechanism as for ethylene and ethane. Adsorbed $-CH_2CH_2-CH_2-$ groups undergo an aromatization reaction to produce active benzene, which is further attacked by $-CH_3$ and $-CH_2CH_3$ groups to form liquid aromatic hydrocarbons. Another cycle is started by $-CH_2-$ group attacking the blank HZSM-5 catalyst surface.

4. Conclusion

A bio-oil fraction separated by molecular distillation technology was subjected to catalytic cracking for gasoline production using HZSM-5 catalyst. Gasoline components were detected in the upgraded liquid oil. A two-step mechanism model for gasoline components production was proposed.

The coke yield for cracking of the bio-oil fraction was only 1.27 wt.%, which was much lower than that for crude bio-oil. Compounds in bio-oil fraction were classified into three groups according to their conversion yields. Furan, 2,5-diethoxytetrahydro- was one of the most abundant components in bio-oil fraction, but was completely cracked. Reactivity of phenol derivatives was strongly affected by the connected functional groups. Methoxy groups had a negative influence on their cracking reactivity, while alkyl groups had a positive influence. The cracking activity of typical phenol derivates in bio-oil middle fraction followed an order as: phenol, 4-methyl-> phenol, 4-ethyl-2-methoxy->phenol> phenol, 2-methoxy-. Acetic acid and 2-propanone, 1-hydroxy- showed much lower cracking reactivity.

A two-step mechanism model was proposed according to the gasoline components detected in the upgraded liquid oil. Oxygenated compounds in bio-oil were subjected to dehydration, decarbonylation and cracking reactions in the first step. Free radicals including $-CH_3$, $-CH_2-$, and -H were involved in the second step to form gaseous hydrocarbons and liquid gasoline components (toluene, ethylbenzene and benzene, 1-ethyl-3-methyl- and etc.).

Acknowledgement

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Improvements in Bioethanol Production Process from Straw

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Abstract: An efficient production of sustainable, carbon-neutral, renewable fuels like bioethanol and biogas from straw and other agricultural by-products has to be developed to guarantee mobility. The scientific focus is the improvement of the bioethanol production using straw as an alternative energy source.

The ethanol production process is already established on a laboratory scale. The process involves the following steps - the pretreatment of straw with steam explosion and enzymatic hydrolysis. Subsequently, yeast ferments the obtained glucose to ethanol. Unfortunately, inhibitors such as weak acids, furans and phenolic compounds are generated during the pretreatment and hydrolysis process, thereby reducing the glucose concentration and ethanol yield.

Glucose concentration was raised up to 140 g/l and ethanol content up to 7% by means of optimization of the process (washing steps and recirculation). Diverse substances inhibit the fermentation and reduce the ethanol content. One washing step prior to hydrolysis clearly reduced the inhibitory substances.

The ethanol and glucose yield was improved due to optimization of the bioethanol production. Now an efficient procedure to reduce the inhibitors has to be established to plan a pilot plant.

Keywords: *bioethanol, lignocellulose, straw*

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1. Introduction

Due to climate change, dramatic fluctuations of the oil price, decline of oil and increased prices for foodstuffs it becomes more and more important to find alternatives like bioethanol produced from renewable lignocellulosic residues without competition to foodstuff.

The bioethanol production process of the 2nd generation involves the following steps: the pretreatment to open the three-dimensional structure from lignocellulose, alternatively chemical hydrolysis or enzymatic hydrolysis to obtain sugars and subsequently, yeast ferments the obtained sugars to ethanol.

However, the essential requirement in bioethanol fermentation is a highly concentrated sugar solution which leads to an increased product concentration and furthermore reduced purification costs. Unfortunately the agricultural lignocellulosic by-products solubilize at relatively low concentrations. Increasing the dry matter and fed-batch process overcome this problem. The final solids content could be raised up to 21 % during the hydrolysis process [1-3]. Using fed-batch process, where fresh substrate is successively fed into the hydrolysis reaction, final solids loading can reach amounts of up to 17 % [2, 3].

Thirty percent solid loading and a final sugar concentration of 20 % were reached with corn stover based on combined pretreatments and fed-batch process [4]. Pretreatment and hydrolysis of straw cause the formation of compounds (organic acids, phenols, furanes) inhibiting the fermentation through yeast [reviewed in 5].

In this study the bioethanol production from staw was investigated and improved. Several improvements, particularly one washing step before hydrolysis and recirculation strategy, were made. These improvements increase both sugar concentration and bioethanol yield up to 7 %.

2. Methodology

2.1. Pretreatment, hydrolysis, recirculation

For pretreatment the milled wheat straw was heated in steam explosion process at various temperature and conditions (120-200 °C, 5-60 minutes). The pressure was suddenly released and made the material accessible to subsequent enzymatic hydrolysis. The removal of potential inhibitors was conducted by a washing step prior to enzymatic hydrolysis. After washing, wheat straw has been dried and milled. The enzyme mixture Accellerase TM1000 from Genencor® has been used with enzyme activities of 775 IU cellulase (CMC)/g solids and 138 IU beta-glucosidase/g solids.

Suspensions with various dry substances (10-20%) have been produced with the pretreated straw in citrate buffer (50 mM, pH 5.0). The suspensions have been enzymatically solubilised (aerobically) at a temperature of 50 °C for 96 hours in a shaking incubator. The hydrolysis of pretreated straw (10 to 20 % solid) has been repeated three times in a recirculation process. After the first hydrolysis step (96 hours), suspension has been centrifuged and the hydrolysate has been used for the next hydrolysis step with fresh substrate (10 to 20 % solid). Then, the hydrolysate has been recirculated in a third step.

2.2. Determination of sugars, ethanol, organic acids, furans

For precise sugar and ethanol analytics, as well as for determination of HMF, furfural and xylitol, HPLC from Jasco and BioRad AMINEX® HPX 87H with ultra-pure water as eluent and RI detection has been used. The bioethanol yield has additionally been determined using a Anton Paar Alcolyzer Beer from DMA. For precise organic acids analytic as well as for HMF-, furfural-concentrations, HPLC from Agilent Technologies, the ion exclusion column Varian Metacarb 87 H with H_2SO_4 (5 mM) as eluent, UV-detection at 210 nm and a RI detector (Jasco) has been used.

2.3. Determination of phenols

Phenols have been determined as gallic acid equivalent, using folin-ciocalteu reagent [6].

2.4. Fermentation

Diverse salts were added to the wheat straw hydrolysate for the fermentation (di-ammonium hydrogen phosphat, 4.4 g/l, calciumchlorid 3 g/l, potassiumhydrogenphosphat 2.86 g/l, magnesiumsulfat 1.5 g/l. The pH-value has been adjusted to 4.6. Exclusively, a wild-type strain of *Saccharomyces cerevisiae* has been used. Fermentation process has been conducted at a temperature of 30 °C in a shaking incubator for one week.

3. Results

3.1. Straw pretreatment

Pretreatment of lignocellulose offer a rapid and efficient hydrolysis of cellulose [7]. Steam explosion is one possibility for removing lignin and hemicellulose as well as making cellulose accessible to subsequent conversion into monomers with enzyme [reviewed in 8-13].

3.2. Enzymatic batch and fed-batch hydrolysis

The glucose and xylose concentrations reached amounts of 64 g/L and 16 g/L after enzymatic hydrolysis with 20 % solids using unwashed straw, respectively. Due to a washing step prior to hydrolysis, glucose concentration could have been increased to 80 g/L. Xylose concentration has reduced from 16 g/L to 5 g/L after washing. Final glucose and xylose amounts after hydrolysis using unwashed and washed straw are shown in table 1 and 2.

Table 1: Sugar yield after the first hydrolysis with unwashed straw (10, 15 and 20 % solids).

	10 % solid	15 % solid	20 % solid
Glucose [g/L]	20	39	64
Xylose [g/L]	5	10	16

Table 2: Sugar concentrations after the first hydrolysis of washed straw (10, 15 and 20 % solids).

	10 % solid	15 % solid	20 % solid
Glucose [g/L]	31	52	80
Xylose [g/L]	2	3	5

3.3. *Recirculation strategies and fermentation*

Recirculation strategies have been developed, where the sugar solution of a first hydrolysis reaction is recycled to fresh straw and subsequent hydrolysis reaction.

For this approach, wheat straw has been pretreated with steam explosion. After the first recirculation step to fresh unwashed solids and subsequent hydrolysis (20 % solids, 2nd hydrolysis), glucose and xylose concentrations have reached 108 g/L and 28 g/L, respectively. Due to a washing step prior to hydrolysis, a glucose concentration of more than 116 g/L could have been reached. Xylose was removed to some extent during this washing step.

However, glucose concentration has been further increased by a second recirculation step to fresh washed solids and subsequent hydrolysis (20 % solids, third hydrolysis) to an amount of 143 g/L. After fermentation with *Saccharomyces cerevisiae*, an ethanol yield of 7.5 %vol. could have been produced.

In figure 1 a, b the final glucose concentrations after hydrolysis (10, 15 % and 20 %) and recirculation processes with unwashed and washed straw, as well as produced bioethanol yields after fermentation were demonstrated.

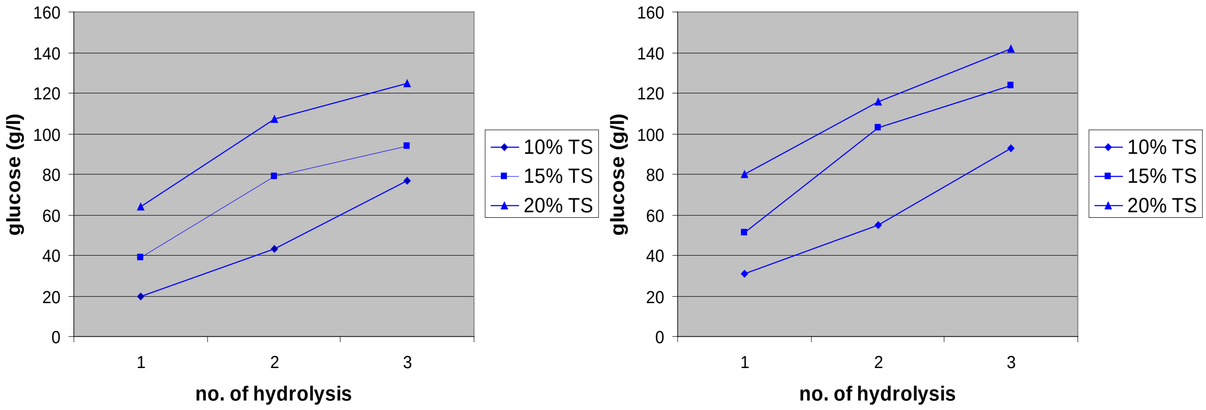

Fig. 1a: Final glucose concentrations after recirculation process (1st, 2nd, 3rd hydrolysis) with 10, 15 and 20 % solids loading of unwashed (left) and washed straw (right).

The hydrolyses from unwashed straw operated definitely superior to the hydrolyses from washed straw. Obviously the washing step reduced inhibitory compounds released during pretreatment and hydrolysis. However, even the sugar concentration from 2nd and 3rd hydrolysis with washed straw didn´t increase linear possible due end product inhibition.

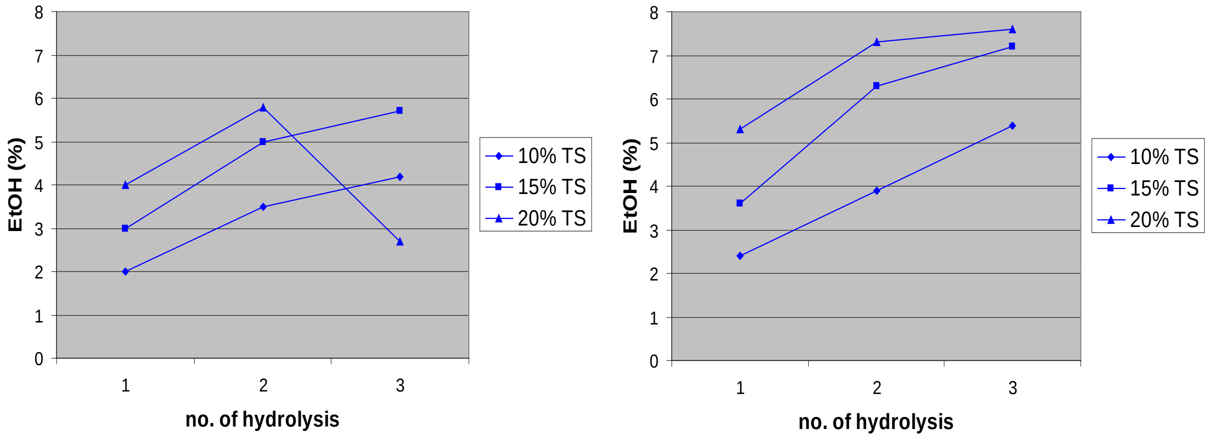

Fig. 1b: Produced bioethanol yields after fermentation of unwashed (left) and washed straw (right).

However, during pretreatment and hydrolysis of straw, groups of inhibitory compounds (phenols, organic acids, furanes) were generated, which had a negative influence on the ethanol-producing yeast. During recirculation procedures, the inhibitory compounds accumulate, resulting in a dramatic decrease of fermentative efficiency. The washing step before hydrolysis removed presumably the inhibitory compounds.

The concentration of diverse potential inhibitors was determined with HPLC analysis and phenol using folin-ciocalteu reagent (figure 2 and 3).

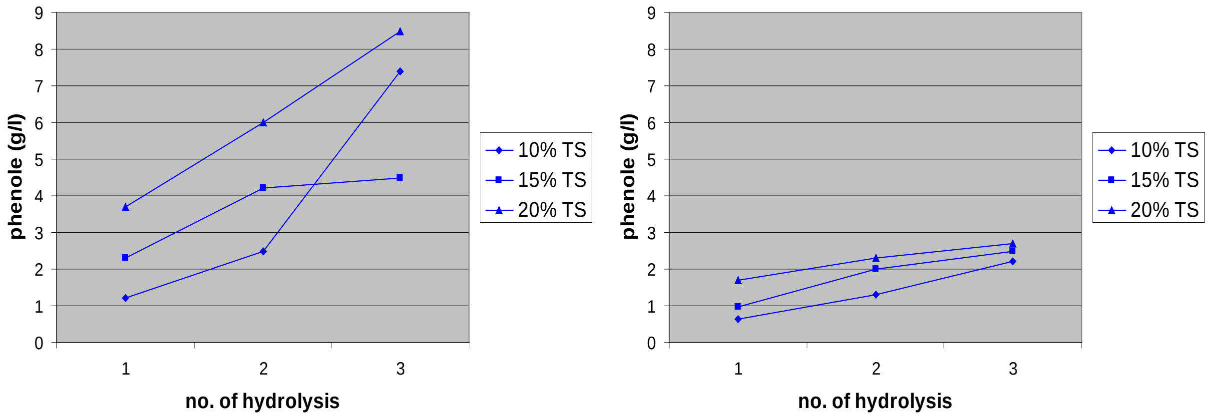

Fig. 2: Phenole concentrations after recirculation process (1st, 2nd, 3rd hydrolysis) with 10, 15 and 20 % solids loading of unwashed straw (left) and washed straw (right).

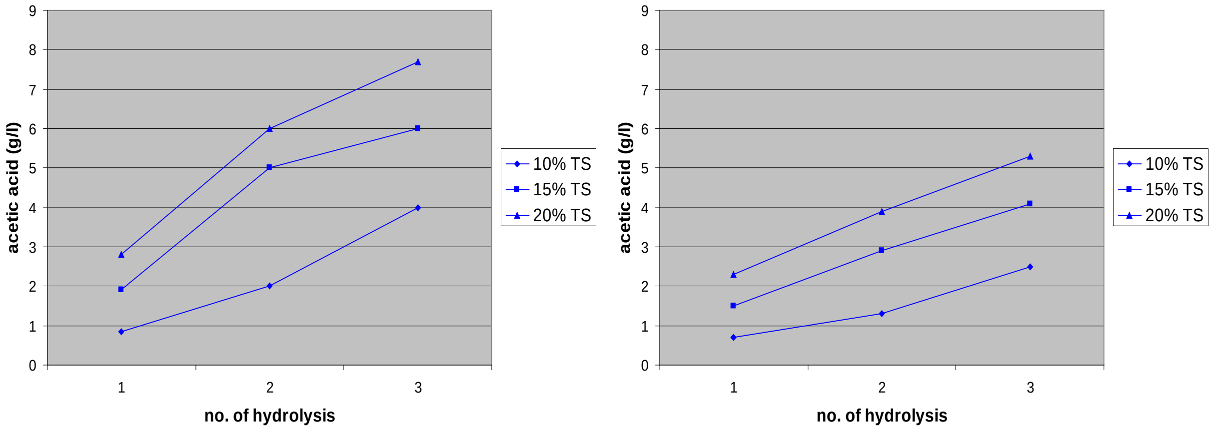

Fig. 3: Acetic acid concentrations after recirculation process (1^{st}, 2^{nd}, 3^{rd} hydrolysis) with 10, 15 and 20 % solids loading of unwashed straw (left) and washed straw (right).

A clearly reduction of potential fermentation inhibitors like phenol (figure 2), acetic formic acid (figure 3), propionic acid, HMF and furfural were detected between unwashed and washed straw (data not shown).

4. Discussion and Conclusions

An efficient bioethanol production requires an effective pretreatment, hydrolysis and fermentation resulting high sugar concentration and subsequent high ethanol yield without inhibitory compounds.

In this study one new strategy – recirculation – was chosen to raise the sugar and ethanol yield. Therefore steam exploded straw was washed, hydrolyzed and fermented reaching sugar concentration of 140 g/l and EtOH yield of about 7.5 %. A comparison with unwashed straw revealed that obviously the inhibitory compounds formed during pretreatment were removed through the washing step.

This washing step must be considered critically - a high water consumption and pollution – could be a tender point in the bioethanol production from straw. In the future the washing water can maybe purified through membrane technology and reused and/or fed in a biogas plant.

Unfortunately also xylose was removed through this washing step. At present xylose can not efficient ferment to bioethanol but maybe xylose could be used in another way for example as biopolymer. Therefore the recovery of xylose has to established to get more products from a bioethanol plant.

Furthermore the recirculation strategy must be improved – the actual sugar and bioethanol yield is two times lower than the theoretical value and is at the moment to inefficient for an industrial application. The cellulase activity during the hydrolyses was obviously reduced through end production inhibition and/or inhibitors. New enzyme and/or enzyme mixture can enhance the sugar yield.

In the future diverse improvements have to be done:

- particularly the inhibitory compound(s) or the combination of the inhibitory compounds have to be determined and
- an efficient reduction method of the relevant inhibitors has to be established
- and/or adapted yeast to the inhibitors has to be developed
- creation of product(s) from xylose.

In addition the cycle of materials must made to enable a cost-effective bioethanol production from straw. The energy for steam explosion step should be provided from a biogas plant and the fermentation remains fed in a biogas plant. The biogas remains should be manure the agricultural area.

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Improvement of enzymatic hydrolysis of rice straw by N-methylmorpholine-N-oxide (NMMO) pretreatment

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Abstract: "Food versus energy" analysis resulted in demanding raw materials which don't have conflict with food industries. The lignocellulosic materials are the most interested option, since not only these materials don't have conflict with food industries, but also there several economical and environmental advantages in those substrates for bioethanol production.
However, the lignocellulosic materials are recalcitrant to both acid and enzymatic hydrolysis. As a result, some pretreatment steps must be taken before hydrolysis. One of the most effective pretreatment methods is treatment with cellulosic solvent.
In this work rice straw, an agricultural residue which is mainly unused was pretreated with an industrial solvent, N-methylmorpholine-N-oxide (NMMO). The pretreatments were performed at 120°C for 1, 3,5 hours with 85% NMMO solution. The treated materials were then subjected to enzymatic hydrolysis by a mixture of commercial cellulase and glucosidase.
The results showed significant improvement on the enzymatic hydrolysis. Almost complete hydrolysis of the cellulose in the straw was observed after 5 h treatment with NMMO at ambient pressure and 120°C.

***Keywords**: pretreatment, NMMO, rice straw, enzymatic hydrolysis*

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1. Introduction

Nowadays different resources are applied for ethanol production in all over the world. The dominant of these resources are agricultural residue such as corn, sugar, starch, and lignocellulosic materials. Increasing growth of industrial ethanol production cause debates on "food & fuel" and afflicted the food industries [1]. Therefore, researchers are trying to find renewable resources that don't have conflict with food resources. Cellulosic wastes are the most possible option. The largest source for this purpose is lignocellulosic materials such as agricultural residue (bagasse, sugar cane stalk etc), forestry wastes (hard and soft wood), and municipal materials.

For a long time, researchers are aspiring to enhance digestibility of lignocellulosic biomass to convert cellulose to ethanol [2]. These materials are reluctant to enzymatic hydrolysis, as a result, conversion of them to ethanol consists of five main steps as shown Fig. 1:

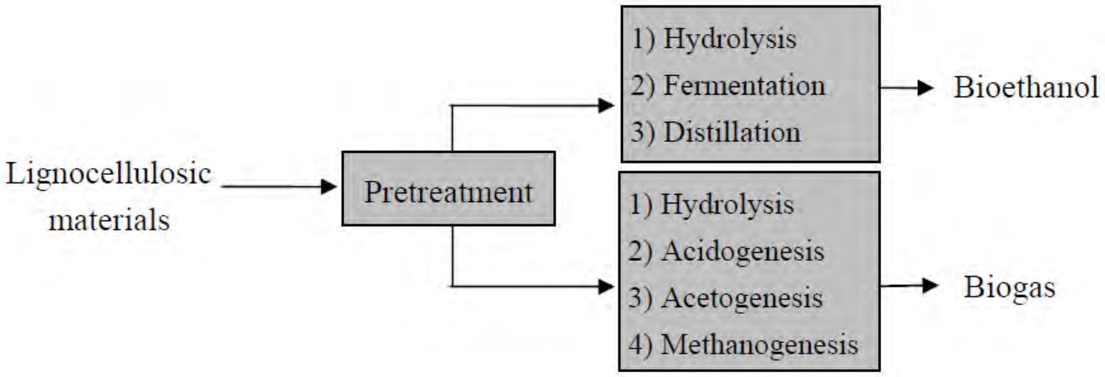

Fig. 1. Pretreatment of lignocellulosic materials prior to bioethanol prodyction [3]

Lignocellulosic materials consist of mainly three different types of polymers, namely cellulose, hemicelluloses, and lignin which are associated with each other [2].

Rice straw is one of the lignocellulosic waste materials could be found in the world. The estimation of annual production of rice by FAO is about 600 million tons per year in 2004. On the other hand, every kilogram of grain harvested is associated with production of 1-1.5 kg of the straw. It gives an estimation of global production of 600-900 million tons per year of straw. The ways of the disposition of rice straw are limited by the great bulk of material, slow degradation in the soil, harboring of rice stem diseases, and high mineral content. Field burning is the major practice for getting rid rice straw, but it increases air pollution and consequently affects the public health. Many counties in Western Europe have already banned open field burning and some other countries have considered it seriously [4].

Depend on the structure of lignicellulosic materials (the portion of these three polymers), the most effective pretreatment method could be selected. There are different kinds of pretreatment. The main categories are: physical pretreatment, chemical and physicochemical pretreatment, and biological pretreatment [3].

One of the chemical pretreatment methods is using solvent for solving the substrate and then regenerating the cellulose part by adding an anti solvent. N-methylmorpholine-N-oxide (NMMO) is among the nonderivatizing solvents which can dissolve cellulose by breaking the intermolecular forces. NMMO is one of the direct solvent for cellulose, which is nowadays applied in the industrial Layocell process. This process is one of the modern and environmentally friendly industrial fiber-making technologies with direct dissolution of cellulose without chemical derivatization. T he solvent does not produce toxic waste pollutants, and can be recycled with over 98% recovery. After dissolution in NMMO, cellulose can be regenerated by rapid precipitation with and anti solvent, which is usually water. The dissolution in NMMO can change the crystal structure of cellulose.

The treatment with NMMO has several advantages in comparison with other pretreatment methods such as conventional acid, alkali, and thermal pretreatments. Most of the other pretreatment methods change the composition of the substrates by e.g., removing hemicelluloses by dilute-acid or lignin by sodium hydroxide. However, NMMO keep the same composition as is reported in many researches. The NMMO process is performed in milder conditions, such as atmospheric pressure and lower temperature (<130°C) than for e.g., in dilute-acid, which results in less energy consumption of the entire process. In addition, no need for chemical neutralization and the possibility of more than 98% recovery of the solvent in industrial processes are other significant property of using NMMO. These properties in addition to the high amount of conversion of cellulose to ethanol which is presented here make the pretreatment with NMMO a good alternative for lignocellulosic ethanol production [5].

Different researchers have been working on the effect of NMMO on enzymatic hydrolysis of various substrates. As reported by Chai-Hung et al, the amount of reducing sugar released from sugar cane bagasse after 7 hr pretreatment in 100°C by NMMO was at least two times more than untreated sugar cane bagasse [6]. In another study, Shafiei et al have reported an increase about 75% and 50% in the yield of enzymatic hydrolysis of spruce and oak respectively after 3 hr NMMO pretreatment in 130°C in comparison with untreated substrates [5].

Because of all the mentioned reasons, the current study aimed at pretreatment of rice straw with NMMO.

2. Methodology

2.1. Raw materials and their analysis

The rice straw used in these experiments was obtained from Lenjan field (Isfahan, Iran). The original length was between 2 and 50 mm. It was partly screened to achieve a size of less than 0.8mm prior to the pretreatment. Its dry weight content was measured at 105°C for 24 h. The rice straw structure is reported by Karimi *et al* [4].

2.2. Pretreatment

The 85% NMMO solution was used for the pretreatment. The pretreatment performed in 200 ml Erlenmeyer flasks, where 1 g of rice straw (dry weight) was added to 19 g of the NMMO solvent and mixed every 15 min. Treatment was done in an oil bath at 120°C and for three different durations (1, 3, and 5 h). The pretreated rice straw was then regenerated by addition of 30 ml boiling deionized water, followed by vacuum filtration and washing until a clear filtrate appeared.

2.3. Enzymatic hydrolysis

NMMO-treated and untreated rice straw was subjected to 72 h enzymatic hydrolysis using 20 FPU cellulase and 30 IU β-glucosidase per gram cellulose [7]. Then the reminder solid was separated by centrifuge from the supernatant. The yield of enzymatic hydrolysis is defined as (grams of glucose released + grams of xylose released)/(grams of initial solid used for hydrolysis × 1.111). The dehydration factor (1.111) is used to convert cellulose chains to glucose monomers.

2.4. Analytical method

All the samples were analyzed by high-performance liquid chromatography (HPLC), equipped with UV/VIS and RI detectors (Jasco International Co., Tokyo, Japan). Glucose and xylose were determined by an Aminex HPX-87P column (Bio-Rad, Richmond , CA, USA) at 80°C. Deionized water was used as efluent at a flow rate of 0.6 ml/min.

3. Result and discussion

As shown in Fig.2, 3 h NMMO-treated substrate shows significant improvement in hydrolysis than 1 h NMMO-treated substrate and there is no significant change in the performance of NMMO after 5 h pretreatment in comparison with 3 h pretreatment. The glucose concentration in hydrolysate (liquid phase) after 24 h increase significantly by pretreatment, as a result, the rate of hydrolysis improve radically. The rate of hydrolysis (concentration after 24 h) increases about 100% after even 1 h treated straw in comparison with untreated straw and the concentration of glucose increases about 400%. All of these show significant improvement in enzymatic digestibility of rice straw after being treated with NMMO. That's because of destruction of intermolecular interactions.

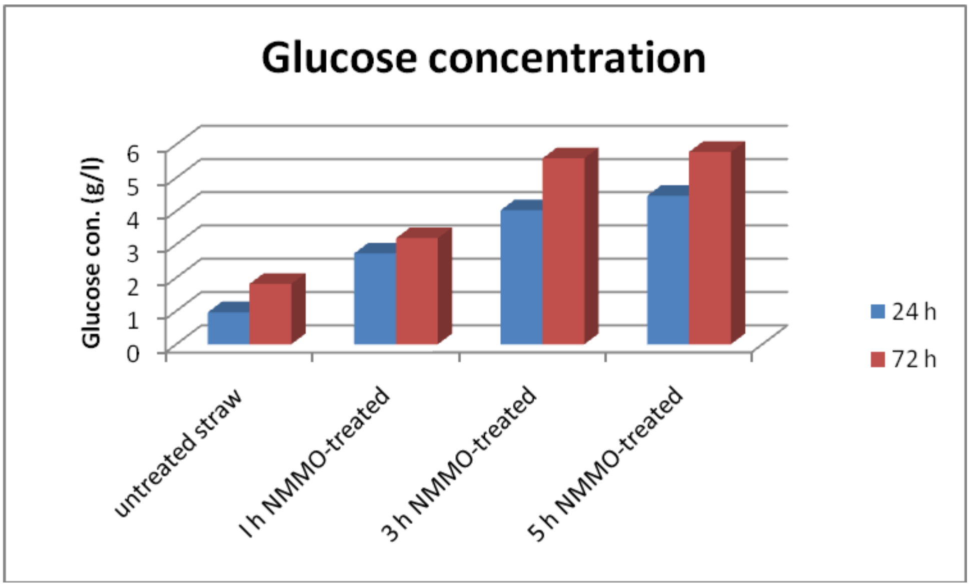

Fig. 2. Glucose concentration in hydrolysate during enzymatic hydrolysis

As shown in Fig. 3, xylose concentration increases, too. The xylose concentration by 5 h treatment increases about 500% after 72 h hydrolysis, moreover, the rate of hydrolysis increases by 300%. These results show undeniable superiority of NMMO over other solvents.

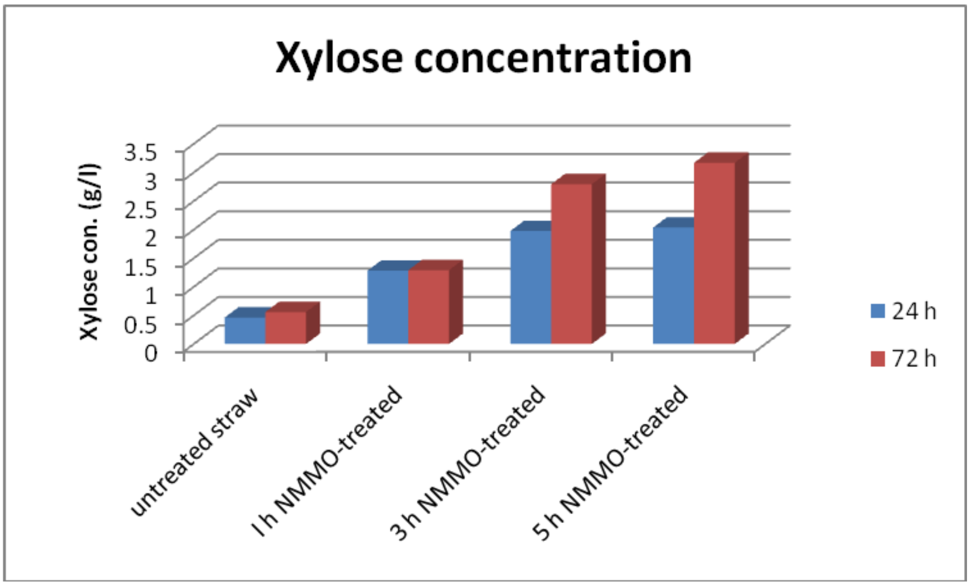

Fig. 3. Xylose concentration in hydrolysate during enzymatic hydrolysis

As shown in the last figure (Fig. 4.), the total sugar yield increases from 23.69% (untreated straw) to 84.42% (5 h NMMO-treated straw). This means an outstanding improvement in terms of industrial process.

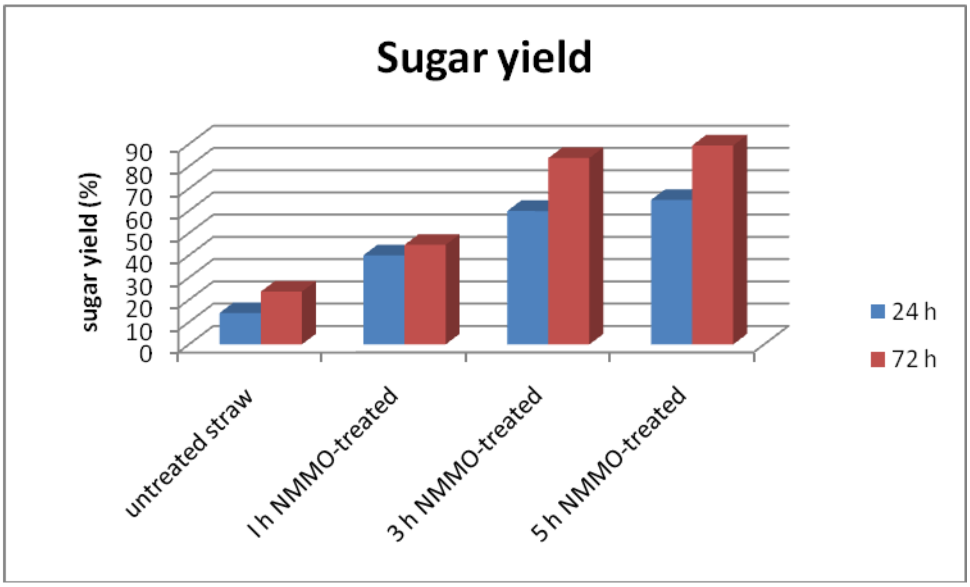

Fig. 4. Total yield of sugar during hydrolysis

4. Conclusion

Treatment with NMMO would be one of the promising ways for preparing rice straw for ethanol production. Having the capacity of being recovered and then reused, NMMO is a good alternative solvent for cellulose. As discussed above in atmospheric pressure and 120°C after 5 hr pretreatment the yield of about 90% could be achieved after 72 hr enzymatic hydrolysis of rice straw.

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