# 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].

Triglycerides + 3 $CH_3OH$ -→ Glycerol + FAME (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.

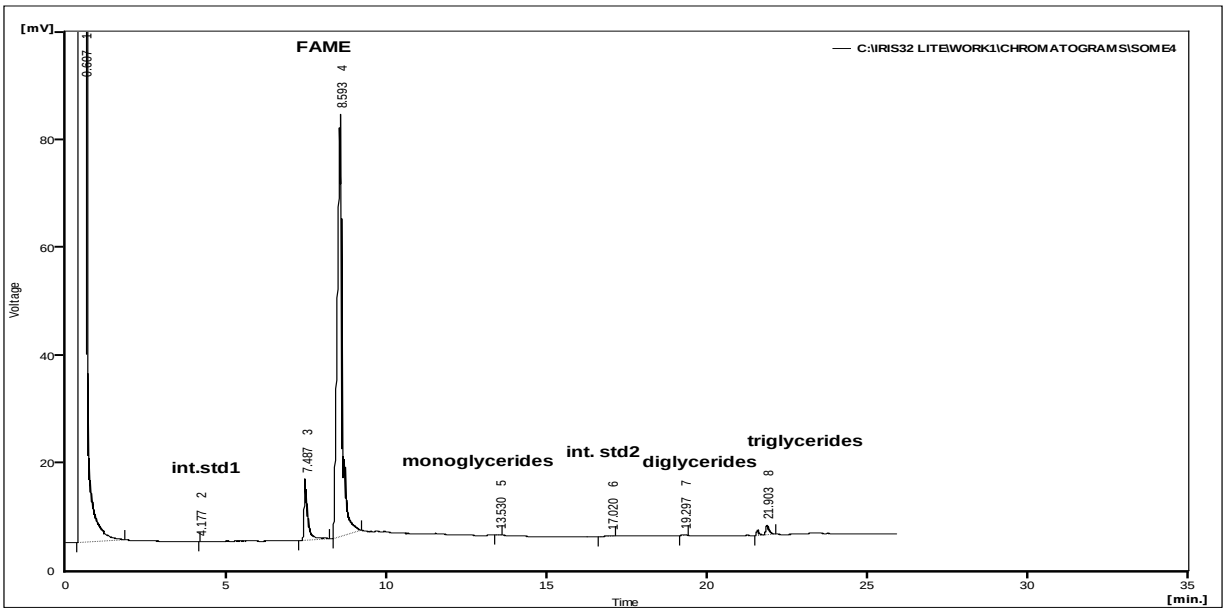


*Fig. 1. Soy-FAME Gas Chromatogram*

## 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.

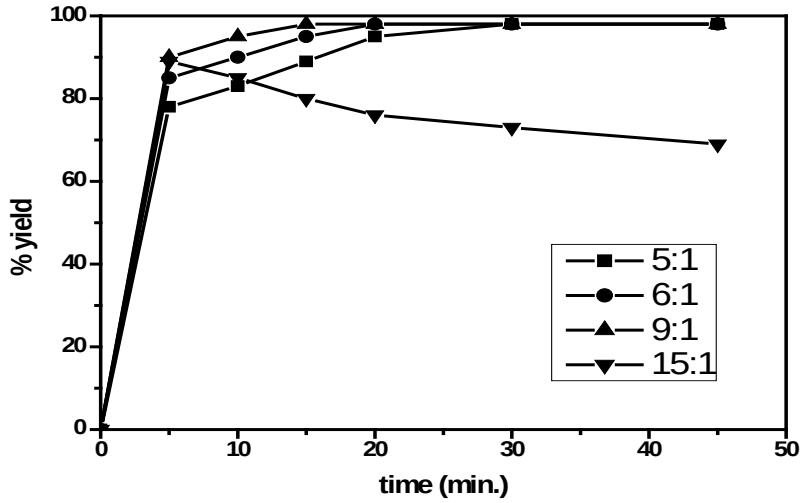


*Fig. 2. Percentage yield of soy-FAME at varied methanol-oil molar ratios and different interval*

### *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.

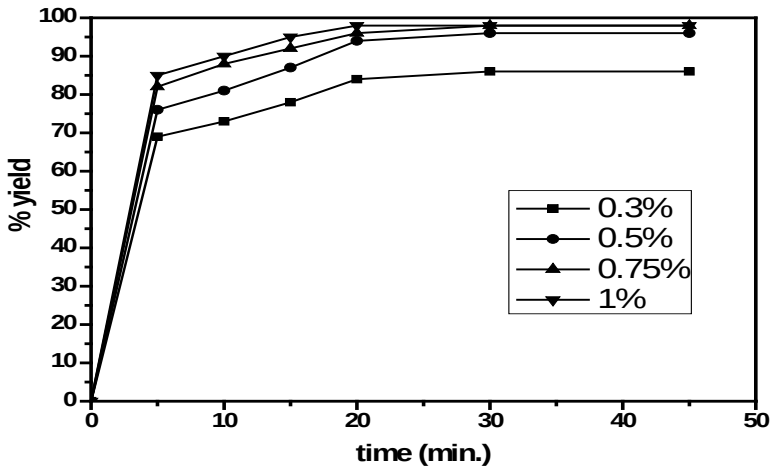


*Fig. 3. Percentage yield of soy-FAME at varied catalyst concentrations and different time intervals*

### *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.

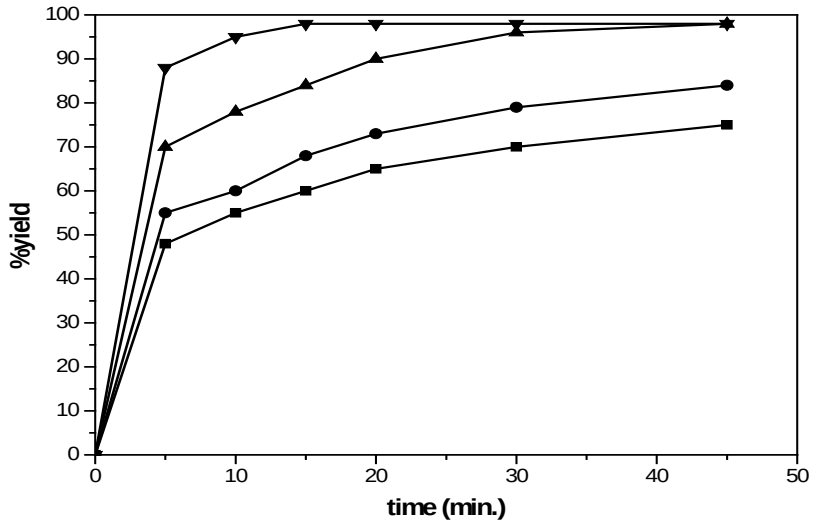


*Fig. 4. % yield of soybean oil methyl ester at varied temperature and different time intervals*

### *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 $130^0$C. 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.

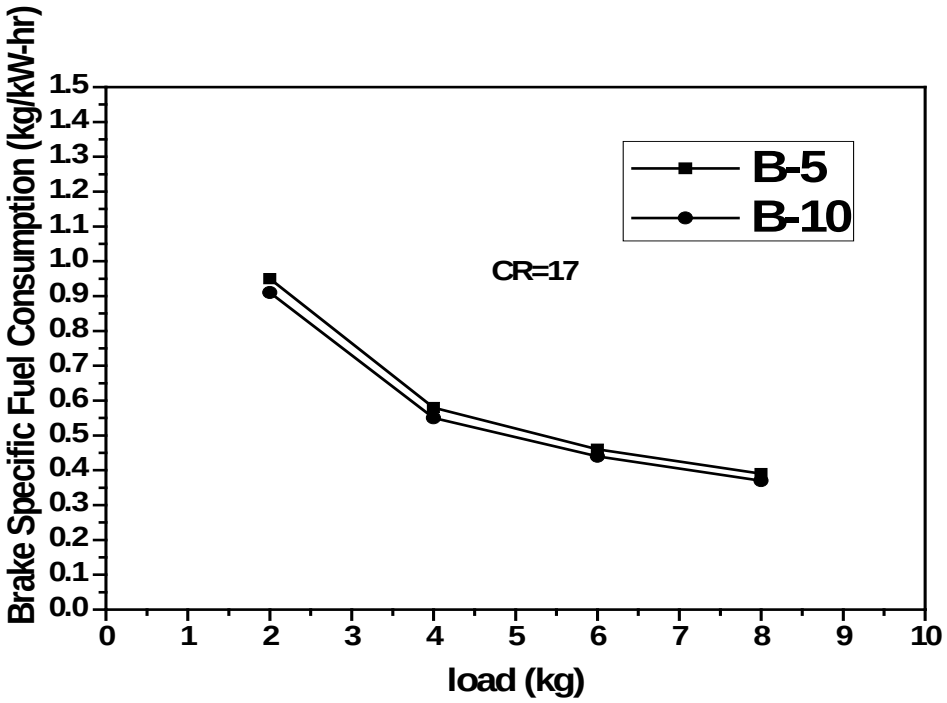


*Fig. 5. Variation of Brake Specific Fuel Consumption with different loads at CR of 17 for B-05 & B-10*

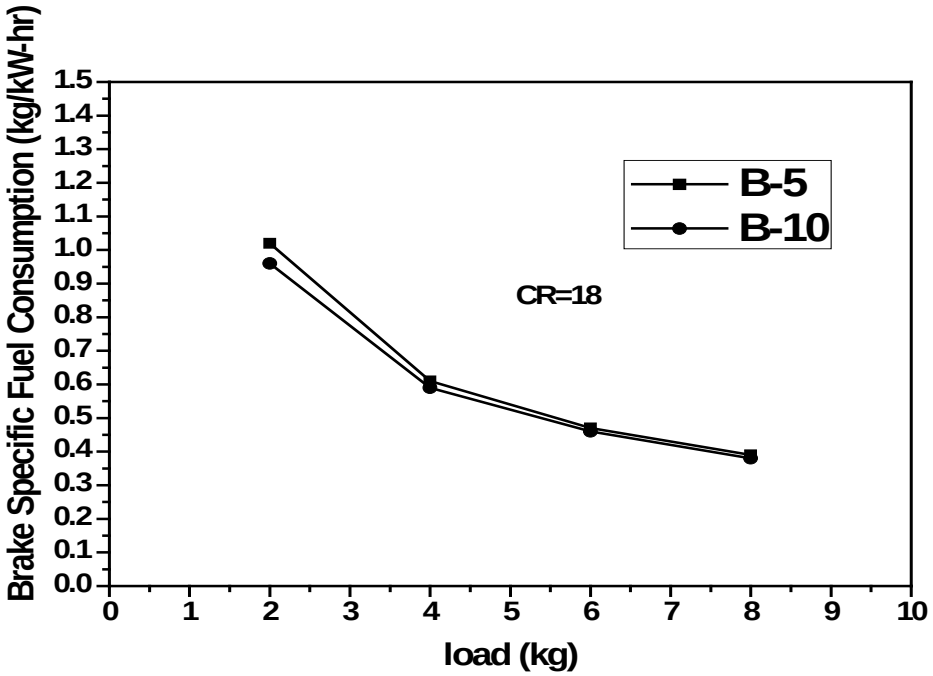


*Fig. 6. Variation of BSFC with different loads at compression ratio 18 for B-05 & B-10*

## 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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