

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 CO₂ emission from the garbage disposal. H₂ produced from biomass (Bio-H₂) 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. H₂-CH₄ 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 H₂ 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 CH₄ 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

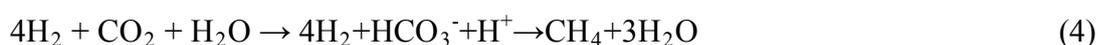
2.2. Methodology

2.2.1. H₂-CH₄ fermentation

The metabolism of H₂-CH₄ fermentation is as follows. Bacteria generate H₂ 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.



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.





When we develop high-efficient H₂-CH₄ 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.



Table 6 shows estimated calorific values of generated bio-H₂ and bio-CH₄. H₂-CH₄ fermentation is more efficient than Acidizing-CH₄ fermentation to recover energy.

Table 6 Calorific values of generated biogas on two pathways

	Calorie [kJ/ mol-glucose]
Acidizing – CH ₄ ferment.	2405
H ₂ ferment. - CH ₄ ferment.	2570

Representative bacteria of H₂ 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 H₂ 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 H₂.

2.2.2. Test equipment

The outline of test equipments in the laboratory is indicated in Fig.1. The volume of H₂ 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 H₂ fermentation is used as materials for CH₄ fermentation. CH₄ fermenter (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).

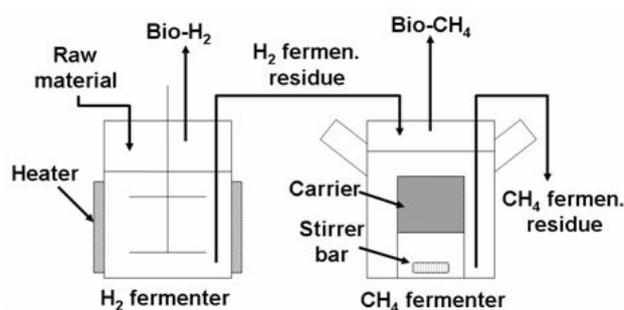


Fig. 1 Schematic diagram in the laboratory

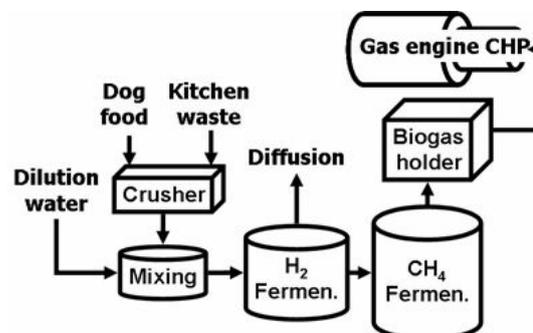


Fig. 2 Plant flow

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-H₂ 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 H₂ 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, H₂ fermentation became unstable. The determined feeding on weekday made the fluctuations of bio-H₂ in the all run time. In beginning of the week, bio-H₂ reduced and increased in weekend. The bands of fluctuation in the amount of bio-H₂ 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. H₂ 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 H₂ 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 H₂ fermentation.

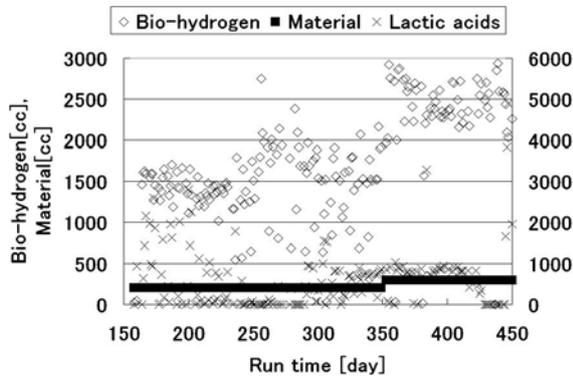


Fig.3 Generated bio-hydrogen

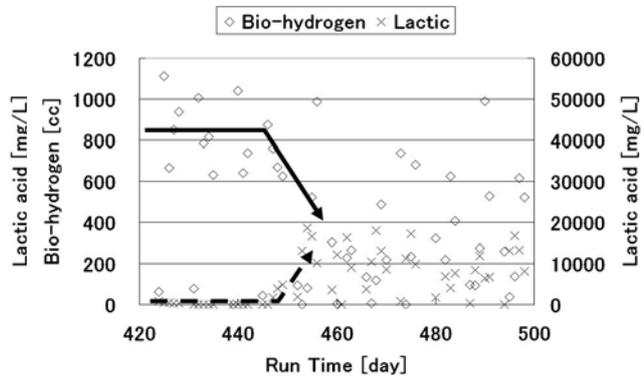


Fig.4 Increased lactic acid

Figure 7 shows the time variations of COD and VFA in the residue of H₂ fermentation. The residue of H₂ 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 CH₄ fermenter generated biogas including CH₄ of 60%. The energy recovery efficiency from biomass to bio-H₂ and bio-CH₄ 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.

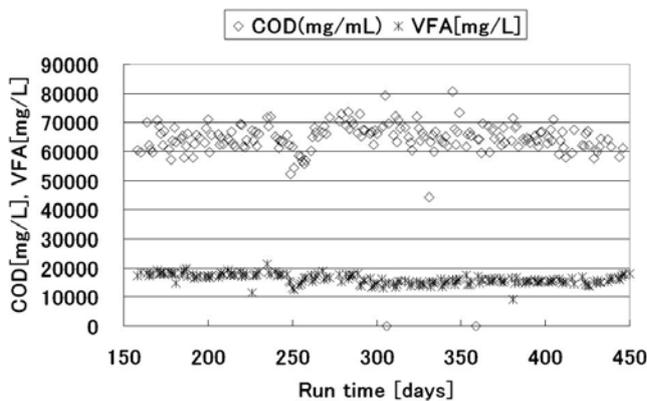


Fig. 5 COD-VFA in the residue of H₂ fermen.

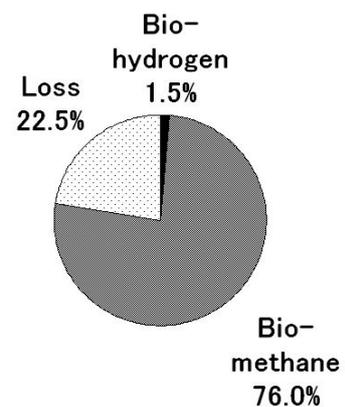


Fig. 6 Energy recovery in the laboratory

3.2. Pilot plant test

H₂-CH₄ 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 H₂ fermentation. The lactic acid density in the pilot plant test was higher than that in the

laboratory test. The increased lactic acid affected H₂ fermentation in the pilot plant compared with the results of the laboratory test. The concentration of lactic acid over 10000 mg/L prevents the generation of bio-H₂. In the pilot plant, the density of lactic acid was scarcely kept under 10000 mg/L.

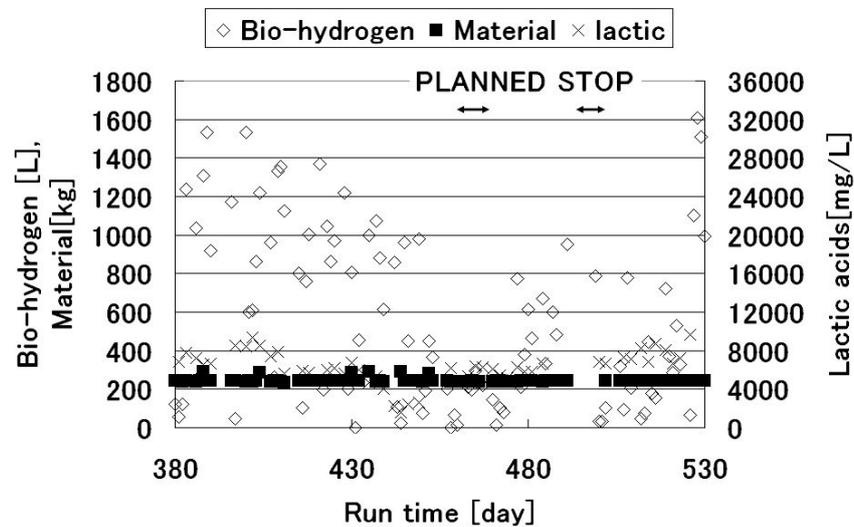


Fig. 7 Bio-hydrogen in the pilot plant

The residue of H₂ fermentation was sent into the CH₄ fermenter. The amount of bio-methane is indicated in Fig.8. Bio-CH₄ was stably produced during the operation period.

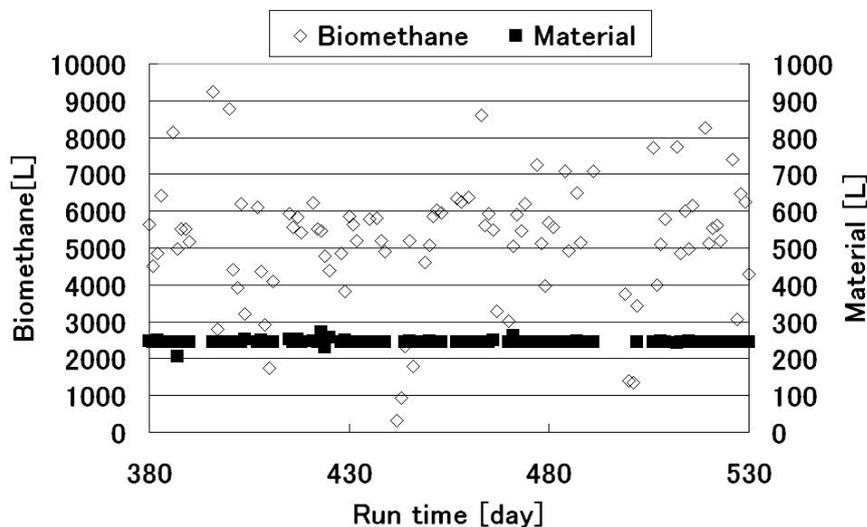


Fig. 8 Bio-methane in the pilot plant

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. In the same plant, another test was carried out, in which the oxidization was pretreated instead of the H₂ 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.

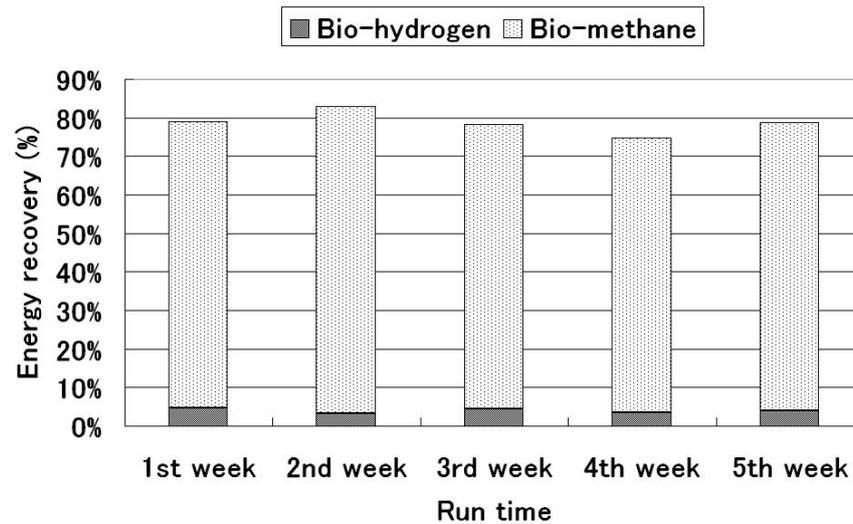


Fig. 9 Energy recovery

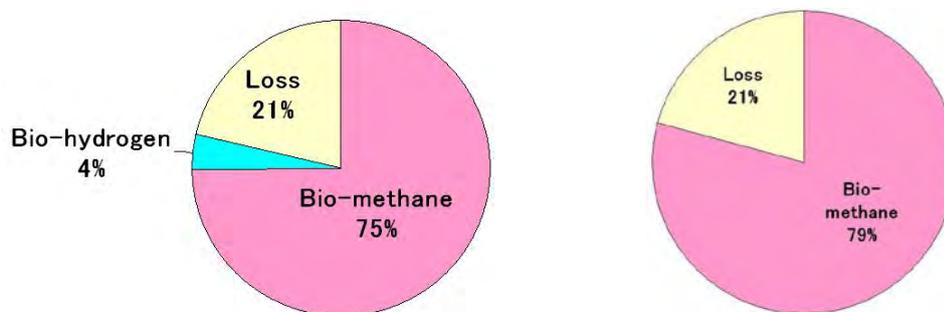


Fig. 10 Comparison of recovery efficiency
(Left: H₂-CH₄ fermentation, Right: Acidizing - CH₄ fermentation)

4. Conclusions

OF-1 is determined to generate H₂ in the environment which is high temperature and acidic. The stable operation in the H₂ - CH₄ fermentation system was developed. Though metabolites generated by H₂ fermentation harm the H₂ 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 H₂ fermentation was found to be good substrates for CH₄ fermentation. The energy recovery efficiency in H₂ - CH₄ fermentation was about 80 %. The efficiency value was equivalent to that of the acidizing - CH₄ fermentation.

Future plan is aimed for increasing bio-H₂ 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.

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