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Methane fermentation of a mixture of seaweed and milk at a pilot-scale plant

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In this study, a pilot-scale plant was built to examine the practicality of producing biogas from seaweeds, widely available in Japan. *Laminaria* sp. and *Ulva* sp. seaweeds were mixed with other organic waste (milk) and used as fermentation materials. Though quantities and ratios of the materials were varied, the ratio of generated methane to input chemical oxygen demand (COD) was largely stable (0.2–0.3 m^3 methane/kg COD) and the organic acid concentration in the methane fermentation solution was low (<1200 ppm) during prolonged operation. These findings indicate that stable methane fermentation was achieved and that mixing with other organic material was effective in suppressing fluctuations in material amounts caused by the variable supply of seaweeds. Our results demonstrate the practical feasibility of biogas generation using seaweeds.

[**Key words:** Methane fermentation; Biogas; Seaweed; *Ulva* sp.; *Laminaria* sp.; Milk]

Renewable energy sources have been receiving increased attention in recent years as a result of the growing concern over global warming. Biomass is one such potential renewable energy source, and progress in its application is desirable. In this study, we examined the potential use of seaweed as a renewable biomass energy source. Although seaweed is an important component of Japanese cuisine, it has not previously been used as an energy source. Here we attempted to realize a system to generate power from seaweed biomass.

Japan is a nation surrounded by the sea. Recently, various problems caused by seaweeds have been recognized. Seaweeds of *Ulva* sp. grow in huge quantities and they pile up in the shallows. Such phenomena have been reported in many closed bay areas of Japan (1–3). These seaweeds spoil the view and release a stench because they soon begin to rot in place. Moreover, it is thought that they have a negative influence on the growth of shellfish near the shallows (4). Although seaweeds of *Ulva* sp. are commonly used in Japanese cuisine, the troublesome seaweeds are not of edible quality. Following complaints from those living near the sea, large amounts of such seaweeds have been collected and incinerated by some local governments. Similar phenomena, often referred to as a “green tide,” have been reported in other countries, such as France and Italy (5–10).

In Japan, seaweeds are cultivated and used as food, but recently, trials have begun to protect fisheries using seaweed cultivation to suppress ocean waves. Because seaweeds absorb nutrients from the sea, ocean remediation effects are also expected. Seaweeds of *Laminaria* sp. have been used for such trials. These trials appear to be somewhat effective; however, this application of seaweeds has given rise to a new problem, what to do with the periodically harvested seaweeds?

As a result, unwanted seaweed wastes are abundant, and effective use of them is desirable. Extracting energy from them is one such use, which could contribute to ocean remediation and help reduce greenhouse gas emissions. Because seaweeds contain much water (about 90%), fermentation techniques are more appropriate than practices such as gasification, which would consume much energy in the vaporization of water. Results of several laboratory-scale experiments on methane fermentation of seaweeds for energy production have been reported in the literatures (11–13). Habig and Ryther tested mesophilic fermentation of *Sargassum*, *Gracilaria*, and *Ulva* in a 2000-mL size fermentor (14). According to their results, *Ulva* was more digestible and produced more methane gas than *Gracilaria* or *Sargassum*. Hansson compared mesophilic and thermophilic fermentation using a green algae mixture of *Ulva*, *Cladophora*, and *Chaetomorpha* (15). Long-term (over 50 weeks) and continuous methane production was observed using a 2000-mL size fermentor. In the results, biogas production of mesophilic fermentation was slightly higher than thermophilic. Kerner et al. evaluated methane production from waste sludge of *Laminaria* and *Ascophyllum* after alginate extraction (16). Their experiments were carried out in bench scale (8000 mL) digesters at 35 °C. Methane production varied from 0.10 to 0.15 L/g-VS added during batch and from 0.07 to 0.28 L/g-VS added during semicontinuous fermentation.

In the present study, a pilot-scale plant was built for larger-scale practical processing of biogas from seaweeds (17). This plant contains a large methane fermentation tank (30 m^3). Seaweeds of *Ulva* sp. and *Laminaria* sp. were used as test materials. As described before, these seaweeds were treated as waste. Stable methane fermentation was observed in the case of *Laminaria* sp. as well as *Ulva* sp. in the plant. The methane gas yield was about 22 and 17 m^3/ton for *Laminaria* sp. and *Ulva* sp., respectively.

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An important consideration when planning energy production from seaweed is the amount of seaweed collected because seaweed availability changes considerably with season and over time; further, large-scale seaweed storage is difficult for any length of time. It is not good for plant operations in economics. One solution is to mix other materials with seaweeds to level out fluctuations in supply. Such codigestion has been tried elsewhere; Cecchi et al. reported anaerobic codigestion of sewage sludge (18) and macroalgae using a 1-m^3 digester, and Madamwar et al. tested the anaerobic digestion of water hyacinth and cattle dung (19). They represented the biogas production from the mixture materials. We selected milk as other organic materials and evaluated methane fermentation of a mixture of seaweeds and milk. The reasons of selecting milk as the mixed material were as follows. (i) Unconsumed milk is also treated as waste and it is possible to obtain stable amount because it is discharged from dairy factories. (ii) Since milk is liquid, it is easy to be handled (storage and feeding) in the pilot-scale plant.

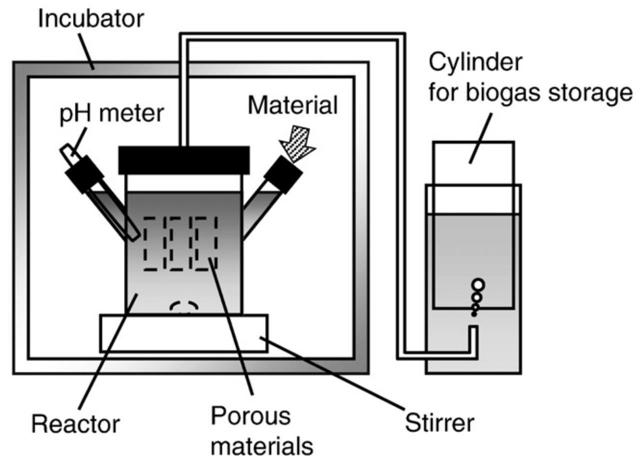

FIG. 1. Laboratory test apparatus.

MATERIALS AND METHODS

Materials Seaweeds *Ulva* sp. were collected in summer from the sea or the beach in mainly south area of Japan. Seaweeds *Laminaria* sp. were collected in spring from the sea in center area of Japan. On the beach, they were collected by hands. In the sea, they were collected on small ships and carried to land. They were packed in large containers and stored in a freezer (−20 °C) and thawed before use. Although the freezer was used to storage materials for long time in the tests, this way will not be used in a real plant because of consuming energy and cost. Because some collected materials contained large amounts of sand (especially collected on the beach), they were washed in fresh water before use. Milk used in the tests was mixed with seaweeds and introduced into the test apparatus. The milk was obtained in center area in Japan. Table 1 shows the characteristics of each test material. Because the seaweed composition was variable, the values presented are representative.

Laboratory tests Small-scale tests of methane fermentation were carried out in the laboratory, and the results were compared with the pilot-scale test results. The laboratory test apparatus, an anaerobic reactor (working volume: 1000 mL) made of glass, is shown in Fig. 1. At first, liquid from the pilot-scale plant (1000 mL) was put to the each reactor. The liquid was obtained from the methane fermentation tank in the pilot-scale plant before the tests in Table 3 started. The reactor was placed in an incubator and the inside temperature was maintained at 55 °C. Porous ceramic materials for fixing bacteria were placed inside the reactor. The volume of generated biogas was measured and stored in a cylinder placed in a water tank. The reactors were equipped with stirrers and pH was controlled within 7 to 7.5.

A mixture of seaweed materials (*Laminaria* sp. and *Ulva* sp.), milk, and diluting water was prepared for this test. Table 2 indicates the quantities used. The mixture was fed daily (semicontinuous) into the reactor after the prefermentation. In this prefermentation process, the mixture was maintained in an incubator at 35 °C within 3 days after adding the prefermentation liquid (1%) in the pilot-scale plant.

Pilot-scale test The pilot-scale plant consisted of four processing units: pretreatment, fermentation, biogas storage, and generation, as shown in Fig. 2. In the pretreatment stage, seaweed test materials were cut in a biaxial shredder after foreign objects, such as shells, were removed. Then, the seaweeds were cut further by using a cutter pump, to pieces only measuring several square millimeters, and diluted with water in a receiver tank. This mixture was then converted to a slurry state for ease of handling. Milk was stored in a storage tank and fed into a prefermentation tank as described below.

The fermentation stage was divided into prefermentation and methane fermentation to achieve higher fermentation efficiency. Seaweed slurry was treated with prefermentation (acid production) in the prefermentation tank (5 m^3) and then used as a substrate in methane fermentation. Liquid was stirred by a circulation pump equipped in a circulation line set outside of the tank. Temperatures were maintained in the range of 25 to 35 °C and pH was controlled within 5 to 7. Biogas containing methane was produced in the methane fermentation process. The temperature for methane fermentation was maintained at 55 °C. Inside the methane fermentation tank (30 m^3), porous ceramic materials, as in the laboratory tests, were used to immobilize the bacteria to minimize washout of bacteria. Sludge obtained from a methane fermentation plant of municipal food waste was used as a start-up inoculum for methane fermentation. The methane fermentation tank was also equipped with the circulation pump outside.

Because the biogas contained trace amounts of hydrogen sulfide, it was refined using a desulfurizing agent (ferric oxide). Purified biogas was stored in a gasholder (30 m^3) made of rubber. The residue from the methane fermentation was dehydrated and used as a fertilizer.

Biogas was employed as fuel for a cogeneration system that generated both electricity and heat. The present cogeneration system was powered by a gas engine generator. Heat (max. 22.7 kW) was recovered from the exhaust gas and cooling water from the engine casing. Biogas was mixed with city gas (natural gas) before being fed into the gas engine. The gas mixing system of the engine was of an improved type enabling it to handle biogas and city gas mixtures. The effects of using the mixed fuel were measured, and it was concluded that using the mixed fuel increased efficiency of electricity generation due to improving the condition of combustion. Electricity (max. 9.8 kW) generated by the gas engine was supplied to the electrical equipment of the plant. Heat discharged from the engine was used to heat the fermentation tanks.

Mixtures of *Laminaria* sp., *Ulva* sp., and milk were supplied daily (semicontinuous) under the conditions listed in Table 2. The quantity of milk supplied was fixed and that of seaweeds was varied to mimic the fluctuation pattern in seaweed yield or availability. Since the quantity of actual milk waste is quite stable, feeding amount of milk was fixed. The quantity of milk/the quantity of seaweeds was set to possible ratio in an actual plant assumed to be built in the future.

Analytical methods Biogas composition was measured using a thermal conductivity detector–gas chromatograph (TCD-GC; Shimadzu 8A-5). Organic acid concentrations in the fermentation solution were analyzed by a high-performance liquid chromatography (HPLC; Shimadzu 16S-5). The chemical oxygen demand (COD, using Cr) were measured by a COD meter (Central Kagaku HC-507). Biogas volume was measured using a gas flow meter (Shinagawa 8a-5) in the pilot-scale plant. The total solid (TS) was measured by a moisture analyzer equipped with halogen lamps for heating (A&D MX-50). The content of lipid was measured by the acid decomposition method (decomposition using HCl and extraction using ether). The Kjeldahl method was used for the measurement of the protein (Kjeldahl coefficient: 6.25). The ash

TABLE 1. Representative compositions of materials.

	Laminaria sp.	*Ulva* sp.	Milk
TS (wt.%)	11.0	11.0	12.0
Composition (wt.%, dry)			
Lipid	1.6	1.9	12.5
Protein	27.9	15.2	21.7
Carbohydrate	54.3	45.6	60.0
Ash	16.3	37.3	5.8
Elements (wt.%, dry)			
C	35.7	28.8	45.4
H	5.8	4.6	6.8
N	3.9	2.7	3.0

TABLE 2. Conditions of materials supplied in the laboratory tests.

No.	a	b	c	d
Amount of supply (g/day)				
Laminaria sp.	3.2	0	8.7	3.2
Ulva sp.	1.0	12.7	4.0	2.3
Milk	4.5	4.5	4.5	4.5
Dilution water	14.1	30.0	30.0	12.7
TS (wt.%)	4.4	4.1	4.1	5.1
HRT (d)	44	21	21	44

The values of amounts of supply are based on wet conditions. TS were calculated from the values described in Table 1.