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Temperature effect on continuous gasification of microalgal biomass: theoretical yield of methanol production and its energy balance

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Abstract

A microalga, *Spirulina*, was partially oxidized at temperatures of 850°C, 950°C, and 1000°C, and the composition of produced gas was determined in order to evaluate the theoretical yield of methanol from the gas. The gas composition depended on the temperature, and the gasification at 1000°C gave the highest theoretical yield of 0.64 g methanol from 1 g of the biomass. Based on this yield, the total energy requirement for the whole process including the microalgal biomass production and conversion into methanol was obtained. Energy balance, which was defined as the ratio of the energy of methanol produced to the total required energy, was 1.1, which indicates that this process was plausible as an energy producing process. The greater part of the total required energy, almost four-fifth, was consumed with the microalgal biomass production, suggesting that more efficient production of microalgal biomass might greatly improve its energy balance.

Keywords: Microalgae; Biomass; Gasification; Methanol; Energy balance

1. Introduction

Significance of biomass fuels for CO_2 mitigation has been gradually recognized because of their renewable property, i.e. CO_2 is used in growth cycle of biomass feedstocks. From this point of view, the recovery of energy from biomass such as wood, energy plantation crops, and the residue of agricultural products are now being carried forward. Microalgal biomass has high productivity and could be cultivated on lands even unsuitable for agriculture or forestry. Though the microalgal biomass can be used as a solid fuel because of its high heating value of more than 4000 kcal/kg [1], we direct our attention to the conversion of it into methanol since methanol is one of liquid fuels which are easy to transport and is useful for other various purposes. In addition, its industrial producing method is well known. Many countries including Japan and United States [2] are taking great interest in methanol vehicles for practical use. Therefore, a demand for methanol will increase in the future. It is important to evaluate the energy balance in the methanol production process and to judge whether it pays or not as an energy producing process. Some reports relating to the energy balance through the gasification of the woody biomass have been presented [3], whereas that of microalgal biomass was not clarified.

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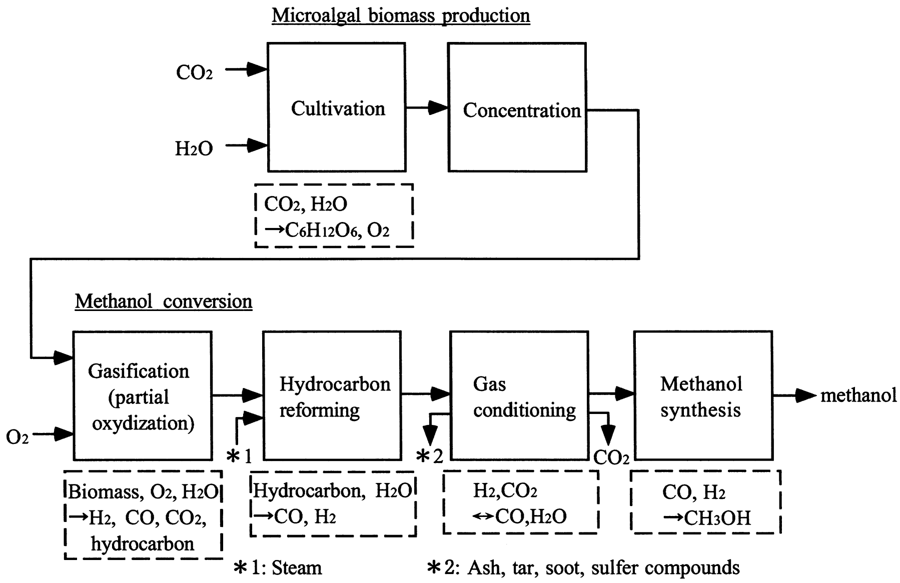

Fig. 1. Process of microalgal production and methanol conversion with gasification.

In this paper, the feasibility of methanol production from microalgal biomass was evaluated by the energy balance, i.e. the ratio of energy of methanol produced to total required energy in the whole process for methanol production. To calculate the energy balance, the methanol yield, which is able to be predicted from the composition of synthetic gas, is necessary to be known. At the temperature range 850–1000°C where the high methanol yield was expected [1], microalgal biomass was partially oxidized and the theoretical yield of methanol was calculated based on the obtained gas composition. In addition, the energy requirements in the methanol production process shown in Fig. 1 was calculated. Measures for improving the energy balance will be discussed.

2. Experimental and analytical methods

A kind of microalgae, *Spirulina*, was used as a raw material for the gasification. Chemical composition was determined as follows. Carbon, hydrogen, and nitrogen were measured by CHN coder (Yanagimoto MT-5). Sulfur was measured using the burning capacity method according to JIS8813. Ash was measured by the heating ash method according to JIS8812. Moisture was measured by the heat dry method according to JIS8812. Oxygen was calculated as the difference between the amount of the *Spirulina* and the total amount of analyzed elements mentioned above. Heating value was measured as a low heating value by a nenken automatic calorimeter (Shimadzu CA-3) according to JIS8814.

Experimental apparatus for the gasification is shown in Fig. 2. The *Spirulina* was continuously supplied as a water-slurry into the reactor tube (silica grass: 30 mm$\phi\times$5200 mm) and partially oxidized under the presence of O_2. In order to repress the generation of tar and soot, microalgal content in the slurry was determined to 21% (dry-w/v) which achieved the ratio of H_2O (in the slurry)/C (in the microalgal cells) became 6 [1]. As a result of parameter survey the injection rates of microalga-water slurry and O_2 were determined at 0.25 g/min and 0.39 ml/min, respectively. Temperature of gasification was controlled in an electric furnace from 850°C to 1000°C. The composition of the gas was analyzed using a gas chromatograph (Shimadzu GC8A) equipped with TCD detector. Used columns were as follows: Molecular Sieve 5A 60/80 (GL Science) for N_2, O_2, H_2, and CO, Active Carbon 60/80 (GL Science) for CO_2 and CH_4, and Active Alumina 60/80 (GL Science) for C_2- and C_3-hydrocarbons.

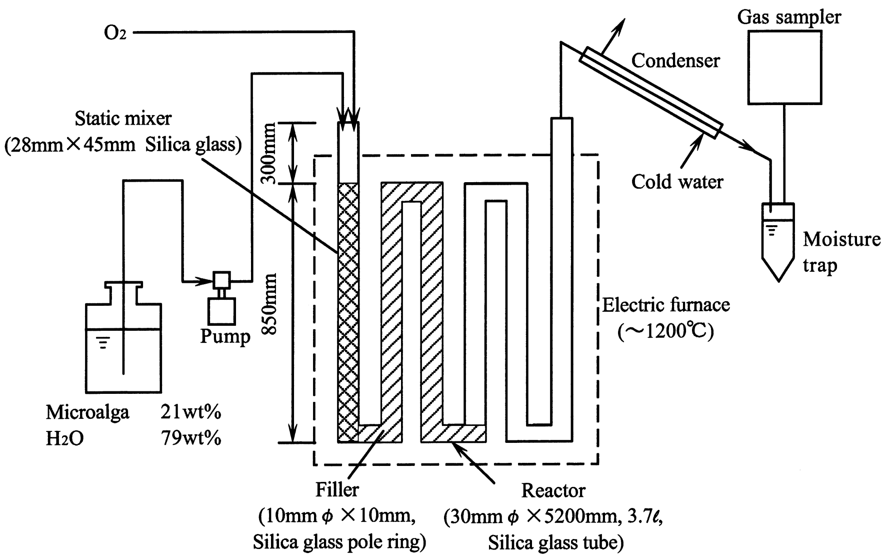

Fig. 2. Experimental apparatus for microalgal gasification.

Methanol was synthesized theoretically from CO, H_2, and hydrocarbons such as CH_4 and C_2H_4 in the gas by following reactions.

$$C_\alpha H_{2\beta} + \alpha H_2O \rightarrow \alpha CO + (\alpha + \beta)H_2 \quad (1)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (2)$$

In order to convert hydrocarbons into methanol, the reforming of hydrocarbons in the synthetic gas was carried out by a water-gas shift reaction [4] indicated as the formula (1). After that, to achieve the reaction indicated as the formula (2) completely, the ratio of H_2/CO was justified to ideal value of 2 [5] by the next step of gas shift (CO shift) reaction indicated as the formula (3).

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (3)$$

As a result, theoretical methanol yield (mol) was calculated by the following formula (4), where A, B, C, and D were the amounts of H_2, CO, CH_4, and C_2H_4 (mol) in a synthetic gas, respectively.

$$(A + B)/3 + C + 2D \quad (4)$$

To investigate the feasibility of the process as an energy producing one, the energy balance of the total process shown in Fig. 1 was clarified. To the calculation, many assumptions are made as follows. In the process of microalgal biomass production, its productivity dominates the scale of cultivation required for a production of certain amount of biomass. The productivity of microalgal biomass cultured outdoors depends on the kind of microalgae, the method and location of the cultivation. We assume the productivity of 30 g/m^2/day [6]. Raceway type ponds which are wide spread in commercial productions of microalgae are used for the cultivation [7]. CO_2 required for the cultivation are supplied by the direct injection of flue gas from a thermal power station. Before the gasification, the microalgal biomass is concentrated using settling ponds (0.1–2% (dry-w/v)) and centrifuges (2–21% (dry-w/v)).

In the methanol conversion process from microalgal biomass, the plant scale is adopted to be 1000 t methanol/day. O_2 required for the gasification is supplied by a physical adsorption method (pressure swing adsorption). Hydrocarbon reforming is carried out under the presence of steam supplied by using waste heat. Ash, tar, soot and sulfur compounds in the synthetic gas are removed by a gas scrubber before the catalytic gas shift reaction. The ratio of H_2/CO is adjusted to favorite value, and sequentially, CO_2 in the gas is removed by a chemical absorption method where mono-ethanol-amine is used as an absorbent. Next to the CO_2 removal, methanol is synthesized by catalytic reaction. Methanol yield is assumed based on

Table 1
Assumptions for the calculation of energy requirements

Microalgal biomass production	
Cultivation	Raceway ponds (productivity=30 g/m^2/day) [6,7]
Concentration	Sedimentation (0.1–2% (dry-w/v)) and centrifuges (2–21% (dry-w/v))
Methanol conversion	
Gasification	Partial oxidization
O_2 supply	A physical adsorption method
Reforming	Steam was supplied using waste heat
Gas conditioning	
Gas shift	Catalysis
Ash etc. removal	Ash, tar, soot and sulfur compound were removed by a gas scrubber
CO_2 removal	A chemical absorption method
Methanol synthesis	Catalysis
	Methanol yield was calculated based on the experiments

Life of facilities were 20 years, and life of catalysts were 2 years. Annually, 3% of the energy for facility construction was required for maintenance.

the experiments. Life of facilities for biomass production and methanol conversion are assumed to be equal to 20 years, and 3% of the energy for facilities construction is required for their maintenance. Assumptions mentioned above were summarized in Table 1.

Energy for the construction of facilities including those for their maintenance and energy for their operation were calculated individually. Some kinds of energy unit such as electric power and calorific value were converted into the heavy oil mass, i.e. 1 kWh=0.245 kg of heavy oil, 10 000 kcal=1 kg of heavy oil.

3. Results and discussion

3.1. Gasification

Determined heating value of the *Spirulina* was 4050 kcal/kg, and its chemical composition was obtained to be as follows: carbon 41.0, hydrogen 6.4, oxygen 32.2, nitrogen 6.1, sulfur 0.4, ash 7.2, and moisture 6.7 (wt%). These values were comparable with other biomass such as woods and grass [8]. Gas composition obtained by the partial oxidization of the *Spirulina* at temperatures in the range 850–1000°C was listed in Table 2. This gas contained H_2, CO, CO_2, and CH_4 as the main constituents. Small amounts of C_2H_4, N_2, and O_2 were detected whereas hydrocarbons such as C_2H_6, C_3H_6, and C_3H_8 were not detected. As the temperature raised, the amount of H_2 increased whereas that of CO, CO_2, and CH_4 decreased. The carbon conversion ratio from carbon in the biomass to carbon in the gas increased from 93% at 850°C to nearly 100% at 1000°C, and the gas volume obtained from 1 g of biomass was consequently increased from 1.06 Nl at 850°C to 1.55 Nl at 1000°C. Theoretical methanol yield was listed in Table 2. It was the highest at 1000°C, and 0.64 g methanol would be obtained from 1 g of microalgal biomass. At 950°C, midpoint between 850°C and 1000°C, the theoretical yield was

Table 2
Effect of temperature on the gasification of microalgal biomass and theoretical methanol yield

Temperature (°C)	Produced gas volume (Nl/g biomass)	C in the gas/C in the biomass (%)	Gas composition (vol%)							Theoretical methanol yield (g/g biomass)
			H_2	CO	CO_2	CH_4	C_2H_4	N_2	O_2	
850	1.06	93.0	34.5	18.0	32.9	10.7	2.1	1.6	0.2	0.50
900	1.12	93.3	35.9	14.5	36.4	9.7	0.7	2.6	0.3	0.46
1000	1.55	103.0	48.2	9.8	31.1	9.1	0.1	1.5	0.2	0.64

the lowest and it was considered to be due to the excessive oxidization because the CO_2 content was found to be rather higher.

Gasification seemed to be completed at higher temperatures of around 1000°C with the theoretical yield of methanol of 0.64 g/g biomass. Some reports suggest 0.45 t [1] and 0.5 t [9] of methanol are yielded theoretically from 1t of woody biomass by optimizing the gasification condition. In practical, 0.283 t of methanol is yielded [10]. Our theoretical yield from microalgal biomass was high enough compared with the above cases of woody biomass. It is also reported that the practical yield which is lower than the theoretical one will be owing to the incomplete gasification as a result of insufficient pulverization of the materials [11]. On the contrary, microalgal biomass did not need pulverization due to small and uniform particles that made the complete gasification possible with the resultant high methanol yield.

3.2. Energy balance

Energy requirements for 1 t of microalgal biomass production and methanol conversion from the same amount of microalgal biomass were obtained based on the assumptions in Table 1. Methanol yield was supposed as 0.64 g methanol/g biomass based on the calculation. Results were shown in Table 3. In the process of the biomass production, 53.9 kg of heavy oil was required for the facility construction and 171 kg for its operation. Methanol conversion required 1.1 and 56.6 kg of heavy oil for the facility construction and its operation, respectively. Total process required 282.6 kg of heavy oil as the result of summation of 224.9 kg for the biomass production and 57.7 kg for the methanol conversion. The produced energy, on the other hand, was 312 kg of heavy oil which was corresponded to 3.12 Gcal obtainable from 0.64 t of methanol. The ratio of produced energy to required energy was 1.1 which indicated that the energy balance was positive, i.e. this process was ineffective for an energy production.

The total process from microalgal cultivation to methanol synthesis is shown in Table 3. The major part of the required energy, about 80%, was occupied in the process of microalgal biomass production. In this process, microalgal cultivation was a major contributor of about 80% in the energy requirement, which led us to an idea that the energy balance would be improved by using microalgae which was produced in natural environment without an artificial cultivation. One of the candidates might be microalgae such as *Anabaena* or *Microcystis* bloomed in lakes and ponds where nutrients such as nitrogen and phosphate

Table 3
Energy requirements for a microalgal biomass production and methanol conversion through its gasification

	Energy (kg)[a]			Distribution (%)
	Facility construction	Operation	Total	
Microalgal biomass production				
Cultivation	32.6	146.0	178.6	63.2 (79.4)
Concentration	0.6	25.0	25.6	9.1 (11.4)
Maintenance	20.7	0.0	20.7	7.3 (9.2)
Subtotal	53.9	171.0	224.9	79.6 (100.0)
Methanol conversion				
Gasification, reforming	0.1	9.1	9.2	3.3 (16.0)
O_2 supply for gasification	0.3	10.3	10.6	3.7 (18.3)
Gas conditioning	0.2	31.5	31.7	11.2 (54.9)
Methanol synthesis	0.1	5.7	5.8	2.0 (10.0)
Maintenance	0.4	0.0	0.4	0.0 (0.8)
Subtotal	1.1	56.6	57.7	20.4 (100.0)
Total	55.0	227.6	282.6	100.0

[a]Energy is expressed as petroleum equivalent.

were enriched by water pollution. If such microalgae can be used as a raw material, the energy requirement for the biomass production would be reduced almost only to harvest, concentration, and transportation. If no further energy were required in this process, the ratio of produced energy to required one would exceed three times. This meant that the methanol production would be improved into an excellent energy producing process by selecting an appropriate method for biomass production which would consume smaller amount of energy.

Turning to the process of methanol conversion, the major contributor was the gas conditioning process including gas shift, removal of ash, tar, soot, and sulfur compounds, and removal of CO_2. This gas conditioning process occupied about 55% of the energy requirement in the methanol conversion process. Therefore, (1) conditioning of gasification which enables the ideal gas composition ($H_2/CO=2$) and the reduction of CO_2, tar, and soot, and (2) selection of biomass which would enable the reduction of ash and sulfur compounds, would be effective for energy saving to improve the energy balance. More investigations including efficiency improvement by using catalysts [12] in continuous gasification would be required to determine the technical viability of energy production from microalgae through their gasification as one of the measures for a global warming.

In conclusion, the almost complete gasification of a microalga, *Spirulina*, could be accomplished at a temperature around 1000°C, and the process which consisted of microalgae biomass production and methanol conversion was estimated to be plausible for an energy producing process.

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