

## LIQUEFACTION OF HYDROCARBON-RICH MICROALGA

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### INTRODUCTION

A colonial green microalga, Botryococcus braunii, accumulates hydrocarbons(terpenoids) 30-70 % of its dry weight by fixing carbon dioxide in the atmosphere (1). Thus, the use of B. braunii could contribute to the reduction of the greenhouse effect if the hydrocarbons could be used as alternative liquid fuel. In laboratory, hydrocarbons of algal cells have been separated by extraction with organic solvent after freeze-drying and sonicating the algal cells. However, these procedures are not suitable for separation on a large scale because these are costly. Therefore, an effective method is expected for separating hydrocarbons as liquid fuel from harvested algal cells with high moisture content. We have proposed a new method for separating liquid fuel from algal cells of B. braunii by direct thermochemical liquefaction. The direct thermochemical liquefaction can convert wet biomass such as wood and sewage sludge to liquid fuel at around 300°C and 10 MPa using catalyst such as sodium carbonate (2,3). At the same time, the liquid oil can be easily separated (4). Therefore, it is expected that an amount of oil more than that of hydrocarbons in algal cells could be obtained because of the liquefaction of organic materials such as fiber, cellulose, and protein other than hydrocarbons in algal cells. In this paper, we discussed the applicability of the liquefaction of algal cells of B. braunii and the yield and properties of the liquid oil obtained by the liquefaction.

### EXPERIMENTAL

Botryococcus braunii Kutzing Berkeley strain was used for liquefaction. Culture conditions were as follows: continuous light at 3000 lx and 25°C in a modified Chu 13 medium (5). Algal cells were washed three times by filtration with a nylon sheet of 20 µm mesh. The properties of the algal cells are listed in Table 1. The algal cells contained 92 % of water. Hydrocarbons in algal cells were separated as follows: freeze-dried algal cells were sonicated with 50 ml of hexane for 30 min by a Sonicator 201M(Kubota, Japan). The suspension was filtered through No.2 filter paper(Toyo Roshi, Japan) and the hexane solution was evaporated at 30°C under vacuum conditions.

Liquefaction was performed in a 300ml autoclave made of stainless steel. The wet algal cells(about 30g) were charged in the autoclave. After purging the residual air with nitrogen, nitrogen was added to 2 MPa and then the autoclave was sealed. The reaction was started by heating the autoclave by an electric furnace. After heating the autoclave up to the required temperature(200 and 300°C), the temperature was maintained for 1 h, and then the autoclave was cooled.

The procedure for the separation of products is shown in Fig. 1. The oil obtained by liquefaction was defined as dichloromethane soluble(in this paper referred to as primary oil). Hydrocarbons in primary oil was extracted with hexane(10 ml-hexane/g-dichloromethane soluble x 5).

The analysis of elemental composition(carbon, hydrogen, and nitrogen) was made by a Perkin Elmer Elemental Analyzer(Model 240) and the content of

oxygen was calculated by difference. Heating value(MJ/kg) was calculated according to Dulong's formula,  $Q=0.3383C+1.442(H-O/8)$ , where C, H, and O are the weight percentage of carbon, hydrogen, and oxygen, respectively. Viscosity was measured by a viscometer(HAAKE, RV12) at 50°C.

#### RESULTS AND DISCUSSION

Properties of hexane soluble of the raw algal cells. The properties of the hexane soluble of the raw algal cells are shown in Table 2. The hexane soluble was obtained in the high yield of 58 % of its dry weigh, and had the good fluidity(56 cP) and the high heating value(49 MJ/kg).

Primary oil. The properties of primary oil are shown in Table 3. The yield of the primary oil obtained at 300°C were 52.9 % and that at 200°C was 56.5 %; these values were a little lower than the yield of the hexane soluble of the raw algal cells. This suggests that hydrocarbons of the raw algal cells were partly converted to dichloromethane insoluble materials such as char.

The heating value of the primary oil obtained at 300°C was 47.5 MJ/kg and that at 200°C was 42.0 MJ/kg; these values were equivalent to petroleum oil. Especially, the heating value of the primary oil obtained at 300°C was much higher than that of the oil obtained by liquefaction of other biomass. The viscosity of the primary oil obtained at 300°C was as low(94 cP) as that of the hexane soluble of the raw algal cells. However, the viscosity of the primary oil obtained at 200°C was too high to measure it; the primary oil was like a rubber. Therefore, the primary oil obtained at 300°C could be used as fuel oil.

The oxygen content of the primary oil obtained at 300°C was a little higher than that of the hexane soluble of the raw algal cells. However, it was much lower than that of the oil obtained by liquefaction of other biomass.

Hexane soluble. The properties of the hexane soluble of primary oil are shown in Table 4. The yield of the hexane soluble of the primary oil obtained at 300°C was 44 % and that at 200°C was 39 % on a dry algal cells basis. This meant that the primary oil obtained at 300°C contained 83% of hexane soluble and that at 200°C contained 69 % of hexane soluble. The elemental composition of the three hexane solubles was almost equal. The hexane solubles of the primary oil obtained at 300 and 200°C had good fluidity as well as the hexane soluble of the raw algal cells. In spite of thermal treatment at high temperature, the same properties of the hexane soluble of primary oil as that of the hexane soluble of the raw algal cells.

In summary, The direct thermochemical liquefaction could provide an effective method for separating liquid fuel from the hydrocarbon-rich microalga, *B. braunii*. Although the yield of primary oil was a little lower than that of the hexane soluble of the raw algal cells, the yield of primary oil might be possibly improved by use of suitable catalyst such as sodium carbonate. The bench-scale plant to continuously liquefy sewage sludge run successfully (6); thus, it might be possible to liquefy the algal cells on a large scale.

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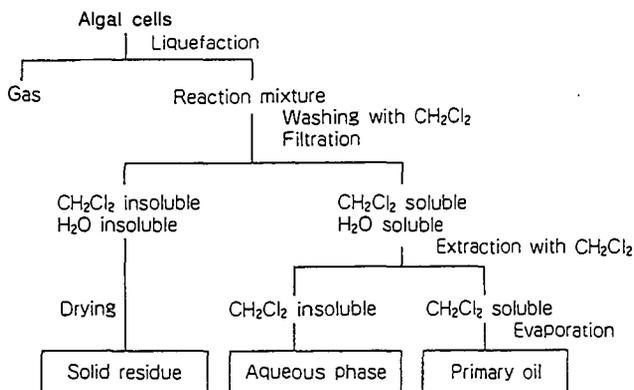


Fig.1 Procedure for the separation of primary oil

Table 1 Properties of microalga used for liquefaction

Moisture content	Dry solid	Ash	Organics
(%)	(%)	(%) <sup>1)</sup>	(%) <sup>1)</sup>
92.0	8.0	2	98
Elemental analysis (%) <sup>1)</sup>			
C	H	N	O
68.7	10.9	1.3	19.1

1) On a dry algal cells basis

Table 2 Properties of the hexane soluble of raw algal cells

Yield (%) <sup>1)</sup>	Heating Value (MJ/kg)	Viscosity (cP, @50°C)	Elemental analysis(%)			
			C	H	N	O
58	49.4	56	84.6	14.5	0.1	0.9

1) On a dry algal cells basis

Table 3 Properties of primary oil

Temp. (°C)	Yield (%) <sup>1)</sup>	Heating Value (MJ/kg)	Viscosity (cP, @50°C)	Elemental analysis(%)			
				C	H	N	O
300	52.9	47.5	94	83.3	13.7	0.4	2.6
200	56.5	42.0	-	78.6	11.9	0.0	9.5

1) On a dry algal cells basis

Table 4 Properties of the hexane soluble of primary oil

Temp. (°C)	Yield (%) <sup>1)</sup>	Heating Value (MJ/kg)	Viscosity (cP, @50°C)	Elemental analysis(%)			
				C	H	N	O
300	44	49.2	77	84.5	14.3	0.1	1.1
200	39	50.3	170	83.5	15.3	0.1	1.1

1) On a dry algal cells basis