



Analysis of energy conversion characteristics in liquefaction of algae

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Abstract

The water environment and aquaculture in lakes have recently been influenced by the abnormal appearance of unpleasant water-bloom or eutrophication problems. It is the source reason of producing odors and being obstacles of water purification systems. Physical and chemical methods can remove algae from water and transform it to become algae sludge. Generally such algae sludge could be disposed as municipal wastes. However, algae and other biomass have become focal points as alternative energy resources, since they are renewable by fixation of CO₂ through photosynthesis from the atmosphere. This study applies a thermochemical liquefaction process to convert the biomass of algae into oil in the presence of water at high temperature (about 300–340 °C) and high pressure (about 20 MPa), with or without an alkali catalyst. Thermochemical liquefaction has the merit of not requiring a drying process for feedstock. The oil and energy yields were analyzed in a batch reactor with the 30 and 60 min holding times. The elemental composition was investigated in each product to clarify the energy conversion efficiency in the thermochemical liquefaction of algae. The maximum oil and energy yields were obtained at 33 and 40% on an organic basis. The mass balance of carbon and hydrogen was analyzed based on elemental composition. The following suitable operational conditions for thermochemical liquefaction of algae were suggested: reaction temperature of 340 °C, holding time of 30 min, and catalyst dosage of 5 wt.%.
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1. Introduction

Due to the high growth and urbanization rates in past decades, water quality degradation became a public-health threat. Eutrophication associated with nutrient content of wastewater and treatment plant effluents have become a serious problem for the water environment. Algal blooms as a result of abnormal algae growth have been found accelerated eutrophication in recent years, being the source reason of producing odor and being obstacles of water purification systems. The key point for preventing occurrence of algal blooms is to decrease the input load of nutrient material to water, and to remove the nutrients from water (Sugiura, 1994). The practical way to accomplish this is to extend the wastewater treatment system and to dredge sedimentary mud from lakes. Algae could be removed from water using physical and chemical methods such as flocculation, sedimentation, floatation, and filtration technologies. However, all of these methods produce a large amount of algae sludge. Dealing with these increasing amounts of algae sludge will be an issue point for improving the environment and preventing secondary pollution.

We know that the algae grow abnormally during eutrophication occurs in lakes by fixation of carbon dioxide in the atmosphere through photosynthesis, and is converted to algae biomass. Since algae has the ability to accumulate large amounts of storage lipids, the biomass of algae is an alternative source of energy, and the greatest feature of algae is that it is reproducible with photosynthesis (Dote et al., 1994). Therefore, it is important to use the renewable biomass as energy resources from the viewpoint of resources recycling. Biomass would make little or no net contribution to atmospheric greenhouse gases. Biomass-derived fuels would reduce greenhouse gas concentrations to the extent that they could replace fossil fuels now being used (Hasegawa, 2002).

Biomass energy conversion methods are divided into the biochemical methods (such as methane fermentation, alcoholic fermentation, etc.) and the thermochemical methods (such as direct combustion, heat decomposition, gasification, liquefaction, etc.). In these methods, thermochemical liquefaction is mainly aimed at obtaining low molecular weight liquid fuels yields from organic high molecular weight compounds by conversion of biomass in the liquid water at high temperature and high pressure in the presence of alkali catalyst without any reducing gas. The advantage of this process is not required feedstocks drying process (Appell et al., 1971). Since algae biomass usually has high moisture content, a drying process requires much heating energy due to the large latent heat of water vaporization. The process is attractive from the viewpoint of energy consumption and is a promising method for the biomass conversion. Thermochemical liquefaction could be an effective method for converting algal cells into oil or other types of energy.

Early work on the direct liquefaction was studied and expanded in the early 1970s by Appell et al.; the research demonstrated that cellulose material, all other carbohydrates, wood wastes, urban wastes, sewage sludge, agricultural wastes, etc., can be converted to oil with CO and H₂O for the H₂O–gas shift reaction, and Na₂CO₃ as a catalyst (Boocock et al., 1980; Dote et al., 1991; Minowa et al., 1994; Minowa et al., 1995; Murakami et al., 1990; Yokoyama and Suzuki, 1995). Yokoyama and his co-workers have developed a liquefaction process in hot compressed water around 300 °C and 10 MPa using sodium carbonate as the

catalyst, without any reducing gas such as H_2 and CO (Yokoyama et al., 1984). Also, several papers have been published on the liquefaction processes with different starting materials and conditions. However, a few studies on thermochemical liquefaction of algae have been conducted, and to the best of our knowledge, no extensive study on the energy analysis in the thermochemical liquefaction of algae has been reported.

From the viewpoint of utilizing algae as an unused biomass resource, the thermochemical liquefaction process was applied in this study to convert algae into heavy oil at high temperature and high pressure. It is important to analyze the energy conversion efficiency by investigating the carbon and hydrogen mass balance. The objective of this study was to investigate the energy conversion characteristics, to clarify the yield of heavy oil and gas products by using a sodium carbonate catalyst, and to determine suitable reaction conditions for the energy conversion of algae.

2. Materials and methods

2.1. Algae preparation

The *Microcystis viridis* strain was isolated from Lake Kasumigaura, and cultivated in the laboratory of the National Institute of Environmental Studies. The cultivation of *M. viridis* was conducted as follows. First, a 10 l culture vessel containing 9 l of the medium was sterilized by autoclave (121 °C, 20 min). After the medium was cooled to room temperature (about 30 °C), and the *M. viridis* was inoculated; then, it was incubated at 30 °C under a photon flux density of 2000 lx in 12 h cycles. During the incubation, the disinfected air (passing through a 0.2 µm filter) was diffused at the bottom of the container at an aeration rate of 1.0 l/min. The incubation was continued for about 20 days and terminated in the latter period of logarithmic phase. The culture was then concentrated with a refrigerated centrifuge (Tomy Seiko, RS-20FIII), and the moisture content of obtained algae sludge was 95%. The obtained algae contained 46% carbon, 7.3% hydrogen, and 9.5% nitrogen.

2.2. Experimental apparatus

The experimental apparatus is illustrated in Fig. 1, which consists of an autoclave, an electrically heated furnace, a mixer and cooling circuit, a pressure holding circuit, etc. In a typical liquefaction process, algae biomass and the desired quantities of catalyst were charged in the autoclave. Nitrogen gas was used to purge the residual air in the autoclave, and pressure was raised to 3 MPa to avoid water vaporization. The reaction was then started to heat the autoclave using an electric furnace. The autoclave was heated up to the required temperature; the reaction temperature was maintained constant for the desired holding time. After the reaction was completed, the electric furnace was removed, and the autoclave was cooled down to room temperature.

The evolved gas was then removed from the autoclave reducing the pressure in the autoclave to atmospheric pressure. The autoclave was then opened, and the reaction mixture in the autoclave was removed from the autoclave for separation.

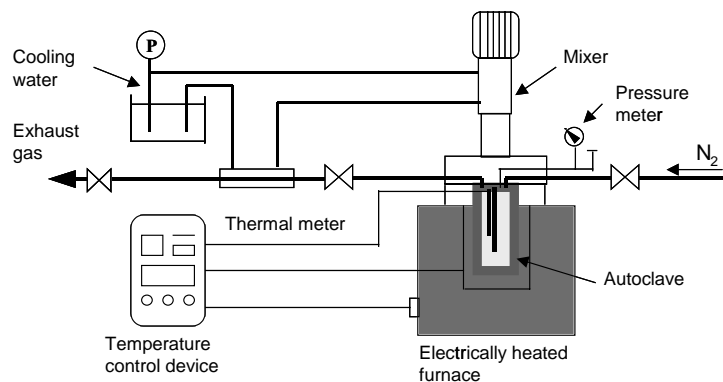


Fig. 1. The outline of experimental apparatus.

2.3. Reaction conditions

Algae biomass was liquefied into heavy oil through the thermochemical liquefaction process at high temperature and high pressure in the presence of an alkali catalyst without any reducing gas. The series experiments were conducted under the following various conditions: catalyst (Na_2CO_3) dosing rate of 0 and 5 wt.%; reaction temperature of 300 and 340 °C; and holding times of 30 and 60 min. The initial operational pressure was designed at 3 MPa and the maximum pressure of the autoclave was 10–20 MPa in order to decrease the water evaporation.

2.4. Separation and analysis

After the autoclave was cooled down to room temperature, the evolved gas was transferred to a sampling bag. The reaction mixture was then removed and dissolved by chloroform for separation. The separation procedure is illustrated in Fig. 2. The reaction mixture was extracted with chloroform to recover the oil by evaporating chloroform at 40 °C. The aqueous phase and insoluble mixture were separated by filtration. The chloroform insoluble fraction remaining on the filter paper was dried at 105 °C for 1 day to obtain a solid residue.

The composition of the produced gas was determined by gas chromatography (Shimadzu, GC-8A). A thin-layer chromatograph (TLC-FID) was used for a preliminary separation of liquefied oil, and the four main fractions were classified as saturated compounds, aromatic compounds, resin, and asphalt (Goto et al., 1994; Maki and Sasaki, 1997). Furthermore, low molecular weight hydrocarbon compounds including saturated compounds and aromatic compounds were determined with a gas chromatograph mass spectrometer (GC-MS; Shimadzu GCMS-QP5050A) (Wang et al., 1994). The element composition of oil and residue were determined using a PE 2400 II CHNS/O analyzer (Perkin Elmer Japan Co. Ltd.). The heating value of oil was determined using a calorimeter (Shimadzu Auto-Calculation Bomb Calorimeter CA-4PJ). The concentration of organic carbon in the aqueous phase liquid was determined by a TOC analyzer (Shimadzu TOC-5000A).

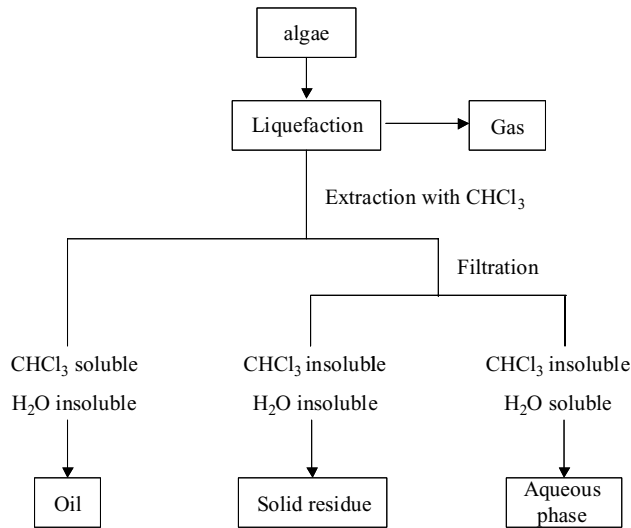


Fig. 2. Separation procedure of reaction products.

Oil and energy yields were proposed as two indicators for analyzing the energy conversion efficiency from algae with thermochemical liquefaction. The oil yield was defined as the ratio of the weight of oil products after liquefaction to the weight of organic matter in feedstock. The energy yield was defined as the ratio of the weight of C and H in oil products after liquefaction to the weight of C and H in feedstock.

3. Results and discussion

3.1. Oil production characteristics

3.1.1. Effect of reaction condition

The important factors in a thermochemical liquefaction process are temperature, holding time, and catalyst dosage. To investigate the influences of these factors on oil yield, we performed the thermochemical liquefaction of algae under different conditions of reaction temperature, holding time, and catalyst dosage. The results are presented in Figs. 3 and 4.

Fig. 3 illustrates the influence of reaction temperature and alkali catalyst (Na_2CO_3) dosage on oil yield at 30 min holding time. The oil yield at 340 °C exceeded that at 300 °C. Also, the oil yield increased with the addition of 5 wt.% alkali catalyst (Na_2CO_3). This indicates that reaction temperature and catalyst influence oil yield in thermochemical liquefaction; the higher the reaction temperature, the higher the oil yield. For the 60 min holding time, as illustrated in Fig. 4, the oil yield increased slightly with the increase of reaction temperature. The catalyst dosage had little effect on oil yield as demonstrated by comparing the reaction with and without catalyst addition. In Figs. 3 and 4, the average oil yield was less at 60 min holding time than that at 30 min. We believe that the thermochemical liquefaction of biomass

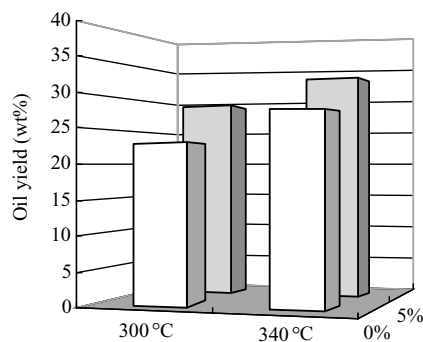


Fig. 3. Effect of reaction temperature and Na_2CO_3 dosage on oil yield with holding time of 30 min.

of algae was almost complete within 30 min, and further reaction would cause some oil to be decomposed, and cause decrease in the total oil yield. The maximum oil yield was 33% at the 30 min holding time, the reaction temperature of 340 °C, and the alkali catalyst dosage of 5 wt.%. We thus clarified that the catalyst addition had an obvious effect on the thermochemical liquefaction of algae.

3.1.2. Oil yield and energy yield

The quality of liquefied oil must be investigated when used as an energy source. Therefore, it is important to analyze both the oil yield and the energy recovery efficiency. As an indicator of energy recovery efficiency, energy yield was calculated for each reaction condition and presented in Table 1. For 30 min holding time, the energy yields with 5 wt.% catalyst dosage were 37.6% at 300 °C and 39.5% at 340 °C. These exceeded the values (29.4% at 300 °C and 27.6% at 340 °C) without a catalyst. The heating value of liquefied oil was determined as 28–31 kJ/g. For the 60 min holding time, the energy yield with 5 wt.% catalyst was less than that with the 30 min holding time. The heating value of liquefied oil was determined as 28–30 kJ/g. We believe that the heating value is relative to the elemental composition of oil, and the increase of C content could improve the heating value. The maximum energy

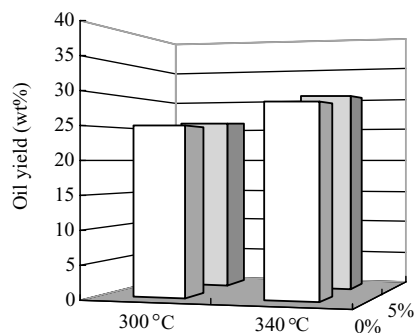


Fig. 4. Effect of reaction temperature and Na_2CO_3 dosage on oil yield with holding time of 60 min.

Table 1
Elemental compositions of bio-oils and energy yield from thermochemical liquefaction of algae

Holding time (min)	Na ₂ CO ₃ dosage (wt.%)	Reaction temperature (°C)	Elemental composition (%)					Energy yield (%)	Heating value (kJ/g)
			C	H	N	O	S		
30	0	300	61.3	7.9	7.5	21.5	1.9	29.4	30
	0	340	59.5	7.0	6.5	24.2	2.8	27.6	28
	5	300	62.2	8.0	7.5	19.9	2.4	37.6	31
	5	340	63.3	7.6	7.1	19.7	2.3	39.5	31
60	0	300	59.3	7.7	5.8	25.8	1.4	30.5	28
	0	340	58.5	6.9	6.2	26.1	2.3	31.6	27
	5	300	57.9	6.4	3.7	30.0	2.1	29.9	28
	5	340	61.3	8.0	6.2	22.3	2.3	37.8	30

yield of around 40% was obtained with the 30 min holding time, the reaction temperature of 340 °C, and the alkali catalyst dosage of 5 wt.%. The heating value of the obtained oil was 31 kJ/g, less than that of heavy oil (40 kJ/g). This suggests that the liquefied oil has the potential to be used as fuel and is a good energy resource.

3.1.3. Oil classification

Petroleum fuel is a mixture of various hydrocarbon compounds. Its main fraction has been categorized as saturated compounds, aromatic compounds, resin, and asphalt. Among these compounds, the saturated compounds fraction has been used as fuel in our daily life, i.e., for automobiles, heating devices, etc. Using TLC–FID analysis, which is a popular method for petroleum analysis, revealed that the liquefied oil consisted of four fractions: saturated compounds, aromatic compounds, resin, and asphalt. Furthermore, low molecular weight hydrocarbon compounds, which include saturated compounds and aromatic compounds, were detected by GC–MS. As indicated in Fig. 5, C17–C18 of *n*-alkane hydrocarbons and aromatic compounds are considered as main components of saturated compounds. Typical aromatic compounds of heavy oil (Nakamura et al., 2001) such as *n*-naphthalene and *n*-dibenzothiophene have also been found in liquefied oil. This means that the oil product obtained from the thermochemical liquefaction of algae can be classified as heavy oil.

3.2. Gas production characteristics

The produced gas consisted mainly of methane and carbon dioxide. As shown in Table 2, the concentrations of components in the produced gas were higher indicating that algae were changed by gasification under the conditions of high temperature and high pressure. From the composition of produced gas, the high concentration of carbon dioxide suggested a previous deoxidization reaction. Since the methane volume at the reaction temperature of 340 °C exceeded that at 300 °C, as indicated in Table 2, we believe that the liquefaction temperature promoted the methanation reaction. In this experiment, slight amounts of hydrogen and carbon monoxide gas were detected. We believe that during the thermochemical liquefaction, the high molecular weight organic matter was initially degraded into low

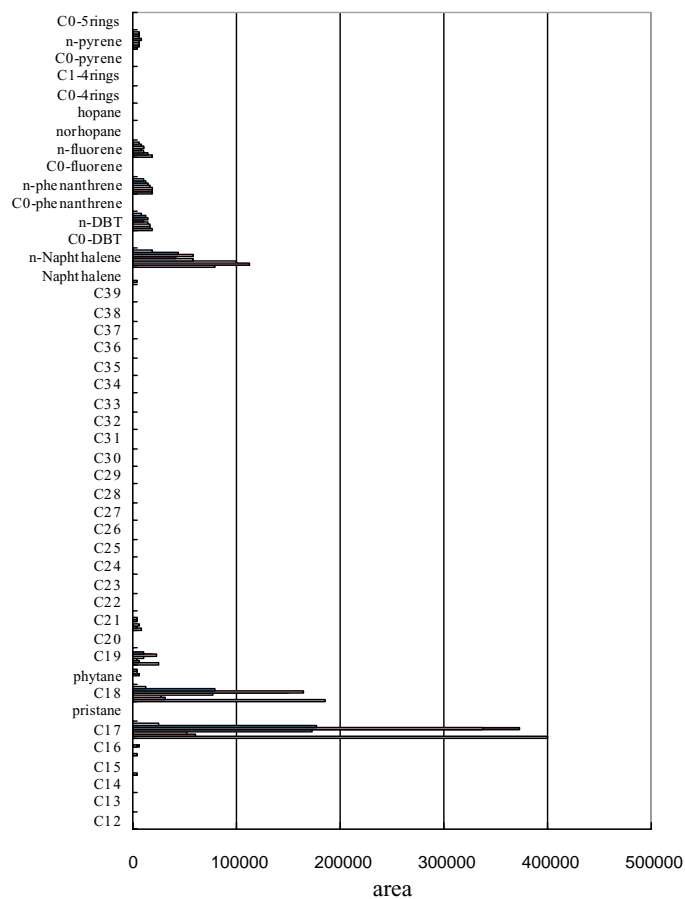


Fig. 5. GC–MS profile of composition of liquified oil.

Table 2

Production of methane and carbon dioxide in the thermochemical liquefaction of algae

Holding time (min)	Na ₂ CO ₃ dosage (wt.%)	Reaction temperature (°C)	Gas volume (l)	Concentration (ppm)	
				CH ₄	CP ₂
30	0	300	1.1	56	625
	0	340	1.1	376	1250
	5	300	1.4	31	625
	5	340	1.5	227	1300
60	0	300	1.7	65	250
	0	340	1.5	352	1300
	5	300	1.5	74	750
	5	340	1.8	283	650

weight molecular water-soluble products through hydrolysis reaction in the presence of a catalyst, and some water-soluble products were gasified to methane, hydrogen, and carbon dioxide; while the remaining water-soluble products could be polymerized to oil. With a higher reaction temperature, the amount of methane increased due to promotion of methanation. As shown in Table 2, the heating value of methane gas obtained from liquefaction of algae at 340 °C was 6.6–10.1 kJ/kg of organic matter in feedstock. This suggests that one part of organic matter in algae could be converted to methane gas, and the produced gas has the potential to be used as fuel after removal of carbon dioxide.

3.3. Features of residual solids

Solid yield calculations were applied to analyze the residual solid from thermochemical liquefaction of algae. The solid yield is defined as the ratio of the organic matter weight in residual solid after liquefaction to the organic matter weight in feedstock. Table 3 indicates that the solid yield for the series experiment was low and less than 5%. However, without the addition of sodium carbonate catalyst and 60 min holding time, the obtained solid yield was 4.5%. When sodium carbonate catalyst was added, the solid yield decreased with increasing the reaction temperature, and decomposition was promoted by sodium carbonate addition. Therefore, a catalyst is recommended for the thermochemical liquefaction of algae. From the elemental composition analysis of residual solid, energy yield could be calculated through the C and H content in residual solid and the feedstock. The energy yield of residual solids ranged from 0.8 to 5.2%, as indicated in Table 3.

3.4. Characteristics of aqueous phase

The pH values of the aqueous phase, which were determined immediately after completion of the reaction, ranged from 7 to 8. Non-purgeable organic carbon (NPOC) has been applied to determine the organic concentration in the aqueous phase in order to avoid the influence of extraction solution. As shown in Table 4, NPOC in aqueous phase decreased at both holding times when no sodium carbonate catalyst was added and the reaction tem-

Table 3
Elemental composition and energy yield of residue solid from thermochemical liquefaction of algae

Holding time (min)	Na ₂ CO ₃ loading (wt.%)	Reaction temperature (°C)	Residue solid (%)	Elemental composition (%)				Energy yield (%)
				C	H	N	S	
30	0	300	1.9	44.7	4.5	5.2	1.1	2.3
	0	340	1.9	25.9	2.2	2.5	0.6	1.3
	5	300	3.4	21.4	2.0	2.2	0.7	2.0
	5	340	1.4	28.4	2.9	2.7	0.9	1.1
60	0	300	4.5	51.9	5.5	5.4	1.2	5.0
	0	340	4.5	53.6	5.8	5.2	1.3	5.2
	5	300	2.5	41.0	4.5	4.5	1.2	2.8
	5	340	1.0	28.3	2.5	2.9	1.2	0.8

Table 4
Properties of aqueous phase from thermochemical liquefaction of algae

Holding Time (min)	Na ₂ CO ₃ dosage (wt.%)	Reaction temperature (°C)	TOC (%)	TN (%)	NH ₄ -N (mg/l)	NO ₃ -N (mg/l)	NO ₂ -N (mg/l)	TP (mg/l)	PO ₄ -P (mg/l)
30	0	300	0.487	0.117	533	6.2	0.45	5.38	3
	0	340	0.416	0.116	609	2	0.35	4.4	3.25
	5	300	0.405	0.103	463	6.6	0.6	3.95	3.25
	5	340	0.478	0.109	550	3.1	0.9	3.05	2.45
60	0	300	0.494	0.116	550	4.7	0.55	4.68	3.05
	0	340	0.436	0.121	633	2.6	0.6	2.45	2.15
	5	300	0.439	0.117	574	3.5	0.75	3.58	3.45
	5	340	0.463	0.121	659	1.35	0.35	2.75	1.55

perature was raised. We believe that the high reaction temperature evaporated the volatile organic matter in the aqueous phase. However, NPOC in aqueous phase increased with addition of sodium carbonate catalyst and a raised reaction temperature. We proposed that the organic matter in feedstock shifted into the aqueous phase as non-volatile organic carbon due to promotion of sodium carbonate.

The nitrogen and phosphate contents in the aqueous phase were presented in Table 4, half of the total nitrogen was determined to be NH₃-N; little NO₃-N or NO₂-N was detected. The total nitrogen of various tests ranged from 998 to 1157 mg/l, and total phosphate ranged from 2.45 to 5.38 mg/l, suggesting that the further development of post-treatment for remaining waste liquid is needed.

3.5. Mass balance

An example of mass balance or elemental conversion ratio during the thermochemical liquefaction of algae was calculated from the carbon and hydrogen content in each product, as depicted in Fig. 6. Around 40% of carbon and 35% of hydrogen in feedstock were changed into oil, around 17% of carbon and 2% of hydrogen became gas as by-products, and also around 1.9% of carbon and 0.2% of hydrogen were contained in residual solids.

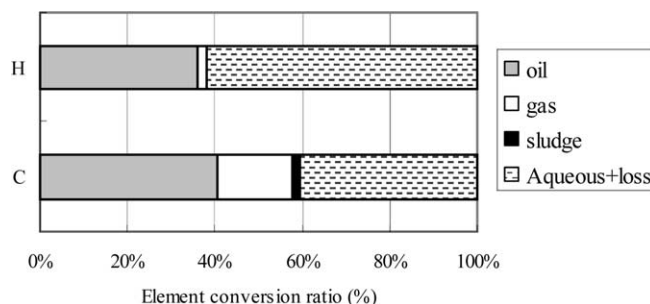


Fig. 6. The element conversion of carbon and hydrogen during the thermochemical liquefaction of algae.

We also estimated that around 40% of the carbon and 60% of the hydrogen remained in the aqueous phase or evaporated as light organic fractions during the process.

As mentioned above, NPOC has been applied to determine the organic concentration in the aqueous phase. Therefore, some organic matter loss is considered due to the vaporization of volatile materials in the aqueous phase during the pretreatment process.

3.6. Applicability discussion

As mentioned previously, algae are not only the product of eutrophication in natural lakes but also can be used as an alternative source of energy. It is important to use the renewable biomass like algae as energy resources from the point of resources recycling. Thermochemical liquefaction as an energy conversion technology has been clarified that it is possible to be used as a measure for dealing with algae sludge.

Several kinds of energy conversion technologies can be applied to change biomass to energy such as biochemical methods or methane fermentation, alcoholic fermentation, thermochemical methods or direct combustion, heat decomposition, gasification, and liquefaction. Since the biomass has the characteristics of variety, abundant volume, and seasonal fluctuation, it is important to select a suitable process to treat the biomass. Several technologies have been developed and applied in the worldwide. For example, wood material and municipal garbage have been used for electricity generation by direct combustion (DOE, 1990); sugarcane and cone have been used as a fermentation feedstock in ethanol production (Goldenberg et al., 1993), and livestock feces and urine have been used in methane fermentation for bio-gas production (NEDO-GET-9815, 1999). Also, gasification generation and indirect liquefaction, in which liquid fuel can be polymerized through gasification are predicted to be in real use in future decades (Solantausta et al., 1997).

Thermochemical liquefaction is a special biomass conversion technology that is mainly aimed at obtaining low molecular weight liquid fuels yields from organic high molecular weight compounds in the high-temperature, high-pressure liquid water. Generally, it was considered uneconomically for high-pressure conversion compared with common pressure reaction from the point of design, maintenance, and costs. However, dry biomass with low moisture content or a drying process is necessary for common pressure conversion processes such as combustion electricity generation, gasification, and liquefaction. Biomass usually has high moisture content because it comes from natural living organisms such as plants and microorganisms. This type of wet-biomass is unsuitable for common pressure conversion without a drying process. Much heating energy will be consumed if wet-biomass is treated with a common pressure thermochemical conversion method. The total energy consumed in a high-pressure conversion process is less than that in common pressure conversion processes. Based on an estimation of the energy balance for a practical scale, the sludge liquefaction process was evaluated as a net energy producer (Itoh et al., 1992).

Since bio-energy is presently not competing with the chemical energy in cost estimation now, there are still a few applications of bio-energy and its conversion technology in the world. However, the bio-energy utilization reduces global CO₂ in the world. It is expected that such bio-energy will be applied in the near future through the development of various conversion technologies and combinations of biomass collection, suitable energy produc-

tion, transportation, and utilization technologies. A total system based on social, economic, and environmental points is needed.

4. Conclusion

Algae, a main products of eutrophication occurring in lakes, was liquefied in hot compressed water at different reaction temperatures and holding times with or without sodium carbonate as the catalyst. The energy conversion characteristics were investigated based on the product distribution and mass balance. The following findings were obtained:

1. A 33% maximum oil yield could be obtained from the thermochemical liquefaction of algae under the following conditions: 5 wt.% of sodium carbonate dosage, reaction temperature of 340 °C, and holding time of 30 min.
2. The elemental composition of liquefied oil composed of 62% of carbon, 8% of hydrogen, 8% of nitrogen, and 2% of sulfur. Its heating value was 31 kJ/g, and the liquefied oil has the potential to be used as a good energy resource.
3. The liquefied oil contained *n*-alkane of C17–C18 hydrocarbon as a main component of saturated compounds, so typical aromatic compounds of heavy oil, such as *n*-naphthalene and *n*-dibenzothiophene have been found in liquefied oil, and it is considered that the liquefied oil should be classified as heavy oil.
4. A high concentration of carbon dioxide was found in gas products due to deoxidization. Also, the methanation reaction was promoted by liquefaction temperature as the CH₄ product gas volume at a reaction temperature of 340 °C was significantly greater than that of 300 °C.
5. The total nitrogen in the aqueous phase ranged from 998 to 1157 mg/l, and half of the total nitrogen was detected as ammonia nitrogen. The total phosphate ranged from 2.47 to 5.38 mg/l suggesting that the further development of post-treatment of remaining waste liquid is needed.
6. The thermochemical liquefaction of algae could be conducted at high moisture content. The process has the merit that feedstock drying process is not required. It also has the benefit of the energy efficiency in the total process. It is possible to set up a sustainable eco-system with minimum load to the environment, and substance circulation and energy reuse. Further system development from algae collection to final utilization is needed.

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