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High yield bio-oil production by hydrothermal liquefaction of a hydrocarbon-rich microalgae and biocrude upgrading

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ABSTRACT

A green colonial microalgae *Botryococcus braunii* was hydrothermally processed under subcritical water conditions without the addition of catalysts, obtaining an oil yield as high as 68%. The higher heating value of liquefaction products is close to that of petroleum crude oil. The oil fraction from *Botryococcus braunii* liquefaction was specified for the first time, and the liquefaction mechanism was proposed. Due to the high lipid content of *Botryococcus braunii*, the liquefaction product distribution is quite distinct from other microalgae. The produced biocrudes contain ~9% oxygen, with oleic acid as the main source. Amides derived from oleic acid and proteins are the major nitrogenates in the biocrudes. The biocrude was processed using catalytic cracking and hydrotreating. Catalytic cracking mostly produces aromatics, while the majority of hydrotreating products are straight and branched hydrocarbons. The oxygen content in the catalytic cracking products was very low. The presence of amides in the hydrotreating feed changes the reaction pathway from hydrodecarboxylation to hydrodeoxygenation as a result of the competitive adsorption of amides on the active sites for hydrodecarboxylation. Both processes show satisfactory denitrogenation performance. Catalytic cracking displays superior ability than hydrotreating with regards to the removal of oxygen.

1. Introduction

Due to the depletion of fossil fuels and the upcoming energy crisis, alternative sources have been searched in order to meet the energy requirement. Biofuel, as a renewable energy source, has attracted the attention of the society. The first generation biofuels are mainly produced from food, which limits their wide application because of the competition with food supplies and agriculture land. The second generation biofuels, derived from non-food crops and non-edible components from food crops, agricultural and forestry wastes and municipal solid wastes, are economically infeasible to commercialize as a result of their low conversion rates [1,2]. Thus, focus has been spread to microalgae to produce the third generation biofuels.

Microalgae are a sustainable source of biomass. They can be grown at a massive scale on non-arable land, in fresh water and even in brackish/saline water [1]. These unicellular photosynthetic microorganisms grow rapidly and can be cultivated throughout the year [3]. Microalgae can be used to mitigate CO_2 at a rate of 1.83 kg CO_2 per kilogram dry algae [4], which to an extent reduces the global warming. In addition, microalgae are reported to have higher oil yields than other plant oil feedstock [5].

Various ways have been used to utilize microalgae to produce oils, including chemical conversion (esterification and transesterification), thermochemical conversion (gasification, liquefaction, pyrolysis and direct combustion) and biochemical conversion (anaerobic digestion, alcoholic fermentation and interesterification) [2]. Liquefaction is an attractive approach to convert biomass to biofuels. In this process, whole biomass is treated in its natural state [6]. By reacting with the highly active water under subcritical conditions, macromolecules in biomass are broken down into reactive fragments which then combine into oil molecules [7]. Although high pressures are observed in liquefaction processes [8], wet algal biomass can be directly used as the feed, which means no more drying is needed after the mechanical dewatering. Simulation results demonstrate that near 3 MJ energy could be saved producing 1 MJ biofuels by hydrothermal liquefaction, compared to the dry solvent extraction method in which about 2/3 of

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the energy is consumed by drying. Besides, the production line is shortened, which benefits the technology [9]. The produced biocrudes are thought to be suitable to upgrade in conventional crude oil refining units [10], which reduces the equipment capitals. Hydrothermal liquefaction is also advantageous because only a small amount of nitrogen in algae feedstock ends up in oil phase [5], which lowers the difficulty in post-processing. On the other hand, the inorganics including nitrogen contained in the aqueous phase, can be recycled as fertilizers [11].

Biller and Ross reported that the lipids in biomass are easier to convert into bio-oil than proteins and carbohydrates [12]. Thermal gravimetric analysis of algal extracts indicated that most of volatiles (89%) are generated from lipids [13]. A colonial green microalga, *Botryococcus braunii* (*B. braunii*), is known to have a high lipid content which is up to 65% on a dry basis [14]. In addition, the relatively slow growth rate of *B. braunii* which is an obstruction of wide production of biofuels derivate from *B. braunii* has been improved [15]. However, very little research on *B. braunii* liquefaction has been conducted since *B. braunii* was first processed in 1993 [16]. In the publication, the authors produced a biocrude at a high yield without the participation of catalysts [16]. Another positive discovery was that the higher heating value of the biocrude (50 MJ/kg) exceeded that of crude oil. Sawayama et al. pointed out that converting *B. braunii* through hydrothermal liquefaction is energy feasible [17]. Additionally, unlike processing wood and sewage sludge, the effect of catalyst on the conversion of *B. braunii* to biofuels by liquefaction is insignificant [10]. In other words, the costs on catalysts can be saved in processing *B. braunii*.

Analysis of produced bio-oil is important. By knowing the composition of oil products, the exploration of reaction mechanism could be realized, and proper application could be figured out to make a full use of the biofuels. However, limited results have been published on the characterization of bio-oils originated from *B. braunii* [14]. Inoue et al. used silica gel column chromatography to separate the compounds in the biocrude produced from *B. braunii* liquefaction into three fractions: low molecular weight hydrocarbons (F1), botryococcenes (F2) and polar substances (F3) [18]. Due to the heating values, F1 and F2 can be further upgraded to obtain a transportation fuel, and F3 is suitable for a boiler fuel. In this work, the effect of temperature on the composition of biocrude produced from *B. braunii* by liquefaction was investigated. Conventional upgrading methods were used to process the biocrude. Mechanisms of liquefaction and upgrading processes were proposed.

2. Experimental

2.1. Hydrothermal liquefaction

The liquefaction experiments were carried out in an autoclave. 20 grams of frozen green algae *Botryococcus braunii* (NRC) was mixed with 4-fold of distilled water. The mixture was heated up to the target temperature (250, 280, 310 or 340 °C) at a heating rate of 4–5 °C/min. The reaction lasted for 15 min, with the stirring rate of 500 rpm.

The solid and liquid products of liquefaction were washed using hexane (98.5%, Sigma–Aldrich). The liquid mixture was collected by filtration. The organic phase was then separated followed by solvent evaporation, leaving the biocrudes. The yield of biocrudes was calculated using Eq. (1).

$$\text{Yield (wt\%)} = \frac{\text{Weight of biocrudes}}{\text{Weight of dry microalgae}} \times 100 \quad (1)$$

2.2. Upgrading of biocrudes

The biocrudes produced from liquefaction were processed using two ways: catalytic cracking and hydrotreating. Catalytic cracking was conducted in a fluidized catalytic cracking (FCC) reactor at two temperatures (450 °C and 500 °C) in China University of Petroleum with an industrial balanced FCC catalyst. The mass ratio of catalyst to oil was 8:1, and the residence time was about 12 s. The hydrotreating was performed at 360 °C and 1300 psi for 8 h using a self-synthesized unsupported CoMoS nano catalyst [19]. The catalyst-to-oil mass ratio was 1:150. A small amount of oil sample (ca. 2 mL) was taken at the 4th hour of reaction. Except for the information shown above, the detailed reaction system and operating condition information were listed in our previous publications: hydrothermal liquefaction reaction system [20], catalytic cracking reaction system [21,22], and hydrotreating reaction system [19,23].

2.3. Product analysis

The oil products from liquefaction and upgrading processes were subject to gas chromatography-mass spectrometry (GC–MS) system analysis using a gas chromatography-mass spectrometry (Shimadzu GCMS-QP5000) equipped with an HP-5 column (Agilent, 15 m × 0.25 mm × 0.25 μm). The peaks in the spectra were identified using an NIST library accompanying with the instrument. As different compounds have different response factors in GC–MS system [24,25], all GC–MS results shown in this work were recalculated based on the original testing peak areas and response factors according to the previous publication [26].

The elemental compositions of feed and bio-oil products were determined using a CHNS-932 elemental analyzer (Leco). The ash content of B. Braunii was measured using a muffle furnace and it is 0.7%. Based on the results of elemental analysis, the higher heating values (HHV) can be predicted using Boie's formula as shown in Eq. (2) [7]:

$$\text{HHV} = 0.3516 \times \text{C} + 1.16225 \times \text{H} - 0.1109 \times \text{O} + 0.0628 \times \text{N} \quad (2)$$

3. Results and discussion

3.1. Hydrothermal liquefaction of B. braunii

The wet *B. braunii* was hydrothermally processed in an autoclave. The oil yields at different temperatures are shown in Fig. 1. With the reaction temperature increasing from 250 °C to 310 °C, the oil yield increases by 27%. No more improvement on yield is observed when further increasing temperature to 340 °C. The oil

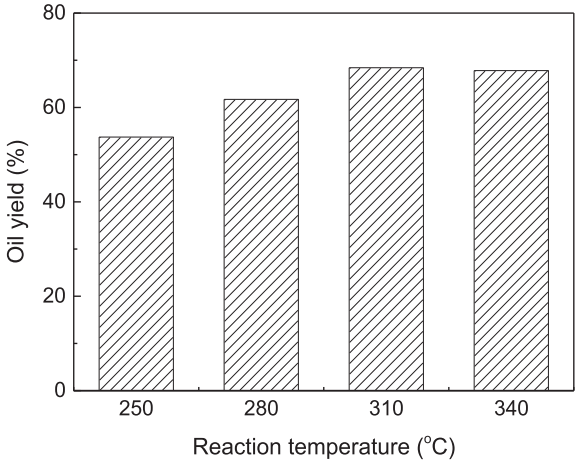


Fig. 1. Effect of temperature on biocrude yield.

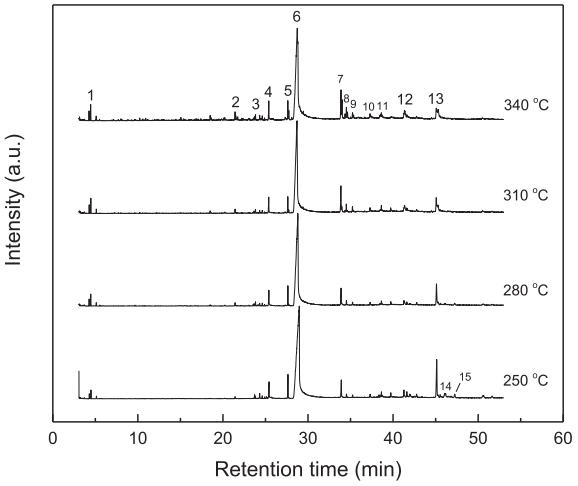


Fig. 2. MS chromatograms of biocrudes produced at various temperatures.

yields in this work are higher than those in the hydrothermal processing of other microalgae [10], which is due to the high lipid content in *B. braunii*. The yield trend is similar to those in the hydrothermal treatment of other algae biomass such as Desmodesmus sp. [7], Spirulina platensis [27] and Laminaria saccharina [28] in the same temperature range.

The biocrudes produced at different temperatures were analyzed using GC–MS. The MS spectra are shown in Fig. 2, with the major peaks listed in Table 1. With the increase of hydrothermal temperature, no significant change in the peak area of n-Hexadecanoic acid is observed. Higher liquefaction temperature results in less 9-Hexadecenoic acid, methyl ester, (Z)-; Oleic acid; and 1,30-Triacontanediol, as well as the compounds corresponding to peaks No. 14 and No. 15, while the contents of the other compounds increase with temperature. The tiny peaks appearing at the retention time <20 min for the high temperature samples represent mainly hydrocarbons, most of which are aromatics.

After analyzing the GC–MS spectra, the compounds in biocrudes can be classified into three groups: hydrocarbons (saturated and unsaturated), oxygenates (phenols, ketones, aldehydes, alcohols, ethers, acids and esters) and nitrogenates (indoles, pyridines, pyrazines, and amines). The contents of these group compounds are summarized in Table 1. The quantities of hydrocarbons and nitrogenates increase with temperature, especially when the operating temperature is approaching the critical temperature. On the other hand, the numbers for oxygenates are reduced at a higher temperature.

Table 1

No.	Compound	Content (%)			
		250 °C	280 °C	310 °C	340 °C
1	Benzene, 1,3-dimethyl-	0.58	1.00	1.22	0.93
2	1-Heptadecene	0.17	0.28	0.34	0.52
3	2-Hexadecanol	0.16	0.38	0.33	0.81
4	n-Hexadecanoic acid	2.12	2.77	2.22	2.29
5	9-Hexadecenoic acid, methyl ester, (Z)-	2.29	2.35	1.75	1.53
6	Oleic acid	70.18	70.79	64.12	56.00
7	9-Octadecenamide, (Z)-	2.20	2.35	3.53	5.16
8	Octadecanamide	0.34	0.54	0.93	1.51
9	9-Octadecenamide, N,N-dimethyl-	0.25	0.42	0.67	0.59
10	9-Octadecenamide, N,N-diethyl-	0.29	0.30	0.59	0.93
11	9-Octadecenamide, n-butyl-	0.99	0.49	1.49	2.01
12	1,22-Docosanediol	1.05	1.03	2.19	2.70
13	1,30-Triacontanediol	6.42	4.46	3.64	1.64
14, 15	Not Identified	4.35	7.59	8.87	5.37
Total	Hydrocarbons	2.90	3.35	4.90	8.49
	Oxygenates	89.08	85.14	78.56	73.93
	Nitrogenates	3.67	3.92	7.67	12.21
	Not Identified	4.35	7.59	8.87	5.37

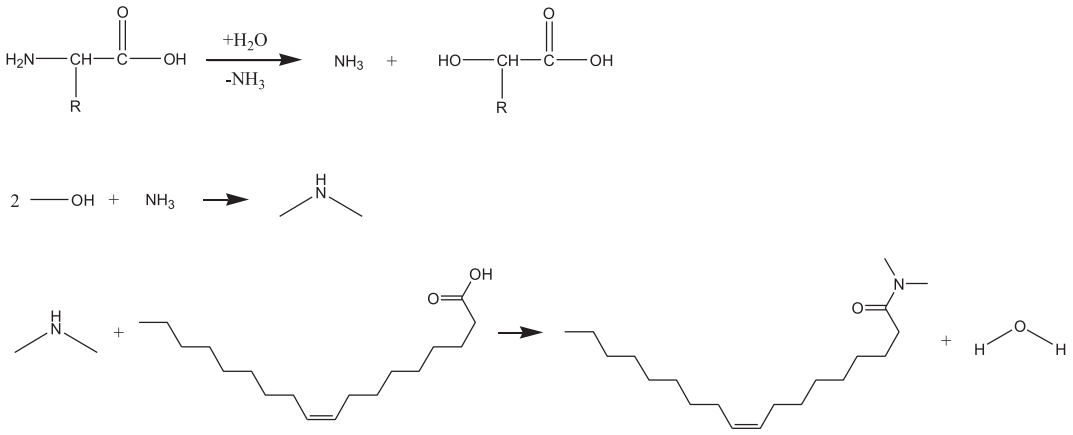
The high content of oxygenates, especially oleic acid, is likely due to the high lipid content in the feedstock. Under subcritical conditions, the hydrogen bonds between water molecules become weaker [11]. The dielectric constant of water is about 15–27 F/m, compared to 78.5 F/m under ambient conditions [29]. As a result, lipids which are insoluble in water at normal conditions have a good solubility in subcritical water. The solubility was reported to increase with temperature, and water and lipids even reached completely miscible for certain fatty acids [30,31]. Although the equilibrium of hydrolysis reactions is not influenced by the temperature [11], the high solubility of lipids in water at elevated temperatures facilitates the hydrolysis of triolein which is the main constituent of triacylglycerols in *B. braunii* [32], resulting in the large amount of oleic acid. Also, the generation of organic acids may come from protein decomposition [33].

According to Toor et al. [29], fatty acids have a relatively high thermal stability, and their degradation is suppressed by the hot compressed water. Thus, the amount of n-Hexadecanoic acid is almost unchanged. However, the content of oleic acid decreases from 70% at 250 °C to 56% at 340 °C. From Table 1, more amides are produced at higher temperatures. Jena et al. found a distinct amount of hexadecanoic acid and hexadecanamide in the liquefaction products from a microalga S. platensis [34]. However, no explanation regarding the formation of these components was provided by the authors.

Klingler et al. reported that ammonia was released by the deamination of proteins [33]. Amines would then be synthesized by reacting ammonia with lower alcohols [35]. The lower alcohol peaks are absent in GC–MS spectra, which is likely due to being cut with the solvent peak during MS signal collection, or these low boiling point alcohols being lost when evaporating hexane after biocrude extraction. The weakly basic amines would react with fatty acids, i.e., oleic acid, to produce amides through a condensation reaction. Under subcritical conditions, water plays a role of an organic solvent which suppresses the hydrolysis of amide bonds. Moreover, amide bonding is thermodynamic controlled; higher temperature favors the formation of amides [36], which explains the decrease of hydrothermally stable oleic acid and the increase of amides at elevated temperatures. A schematic of amide synthesis, taking 9-Octadecenamide, N,N-dimethyl- as an example, is shown in the picture below (Scheme 1).

The hydrocarbons in the liquefaction products may be produced through different pathways: (1) dehydration of alcohols, (2) decarboxylation of fatty acids, (3) feedstock hydrocarbons breaking down and recombination of the resultant radical fragments. All these reactions are favorable at higher temperatures in the studied temperature range [37–39], leading to larger hydrocarbon amount. A Fischer–Tropsch-type reaction could happen as well to produce hydrocarbons and oxygenates [40]. The small amount of naphthenes (not shown in Table 1) may come from the cyclobotryococcene which is abundant in the external hydrocarbons [32]. The aldehydes are mainly from the decomposition of carbohydrates and/or proteins [29]. The alcohols may be derived from the reduction of acids or a replacement reaction.

The biocrude produced at 310 °C was subject to elemental analysis, and the results are shown in Table 2. Compared to the feedstock *B. braunii*, the higher heating value of biocrude is increased by 1/3, with the value close to that of petroleum crude oil (42 MJ/kg [7]). In addition, the HHV of the biocrude is higher than those of liquefaction products originating from other microalgae [7]. The enhanced HHV mostly results from the significant reduc-



Scheme 1. Synthesizing 9-Octadecenamide, N,N-dimethyl-.

Table 2
Elemental composition of *B. braunii* and bio-oil products.

Sample name	C (wt%)	H (wt%)	N (wt%)	O* (wt%)	HHV (MJ/kg)
B. braunii	61.12	9.75	1.92	27.21	30.0
Biocrude @ 310 °C	78.22	12.19	0.91	8.56	40.8
Catalytic cracked oil @ 500 °C	89.07	10.86	0.17	–	44.0
Hydrotreated oil-8 h	82.32	13.28	0.29	4.11	44.2

* By difference.

tion of oxygen content. The removed oxygen could be in a form of CO_2 as a result of decarboxylation or H_2O due to dehydration [11].

3.2. Biocrude upgrading

Even though the oxygen content in bio-oils is reduced after hydrothermal treatment, it is still higher than that in conventional fuels [11]. The high oxygen content reduces the energy content of bio-oils. Also, the excess oxygen in biocrudes brings in disadvantages such as corrosive properties as well as low thermal stability [29]. As a result, further upgrading is necessary to remove oxygen from bio-oils and enhance the quality of bio-oils. Two conventional methods were used to eliminate the oxygen in bircrudes: catalytic cracking and hydrotreating.

3.2.1. Catalytic cracking

Catalytic cracking plays an important role in petroleum refining. In refineries, it processes crude oils into valuable products such as gasoline and diesel. In this work, two temperatures (450 °C and 500 °C) were used in processing the biocrude obtained from hydrothermal liquefaction of *B. braunii* at 310 °C. As the cracking temperature is increased only by 50 °C, liquid yield reduces from 75% to 65%, non-condensable gas increases from 3% to 9% and the liquefied gas increases by 5% from 8%. However, the coke amount is maintained similar, approximately 12.5%. The resultant oil products were analyzed using GC–MS, with the MS spectra shown in Fig. 3. The outcome of cracking is obvious. After cracking at 450 °C, the peaks of oxygenates and amides are barely visible. Elevating the process temperature to 500 °C leads to a further reduction of large molecules in the produced oil.

Hundreds of peaks were identified using the NIST database accompanying with the instrument, over half of which are aromatic compounds. The peaks having ≥1% of the total content of the identified compounds are listed in Table 3, and the summary contents of various groups of components are shown in Table 4. For the bio-oil processed at 450 °C, 84.8% of the total content of the identified compounds is due to hydrocarbons, 84.9% of which belongs to aromatic compounds. Compared to the feed, the contents of oxygenates and nitrogenates are reduced by 90.8% and 85.1%, respectively. When the operating temperature increases to 500 °C, over 90% of oil phase from hydrocarbons with the aromatics fraction of 92.8%, and less than 2% and 1% of oil phase are left for oxygenates and nitrogenates, respectively.

Due to the large amount of oleic acid in the feed, deoxygenation of the biocrude is basically cracking oleic acid. The cracking mechanism of oleic acid is believed to resemble that on an HZSM-5 catalyst [41]. It initiates with the hydride shift from the catalyst to the unsaturated bond in oleic acid followed by the cleavage of C–C bond at α and β positions. The hydrocarbon moiety is cracked into small fragments which can easily enter the pores of the catalyst and then are converted to important intermediates (mainly propenylbenzene and phenylbutene) through cyclization and

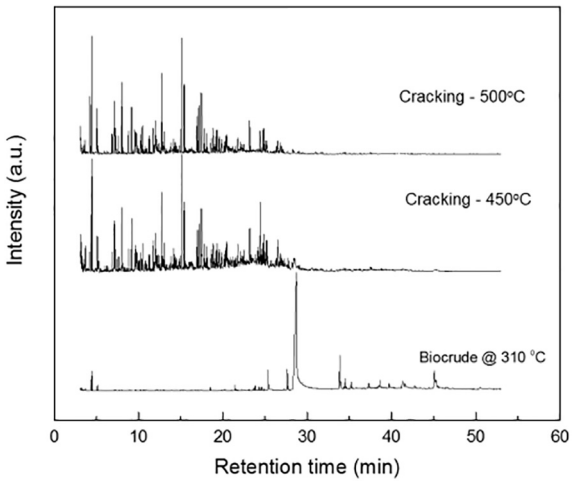


Fig. 3. MS chromatograms of catalytic cracked bio-oils.

Table 3
Identification of significant peaks in Fig. 3.

Retention time (min)	Compound name
4.265	Ethylbenzene
4.467	Benzene, 1,3-dimethyl-
5.053	Benzene, 1,2-dimethyl-
7.113	Benzene, 1-ethyl-3-methyl-
8.024	Benzene, 1,3,5-trimethyl-
9.162	Indane
10.443	Benzene, 1-ethyl-2,3-dimethyl-
11.985	1H-Indene, 2,3-dihydro-4-methyl-
12.774	Naphthalene
15.086	Naphthalene, 2-methyl-
15.412	Naphthalene, 1-methyl-
16.936	Naphthalene, 2-ethyl-
17.14	Naphthalene, 2,6-dimethyl-
17.414	Naphthalene, 1,5-dimethyl-
17.467	Naphthalene, 1,7-dimethyl-
20.381	1-Isopropenylnaphthalene
23.179	Phenanthrene
24.418	Benzene, dodecyl-
26.505	Naphthalene, 2-hexyl-

Table 4
Summary contents of the identified components in Fig. 3.

Type of products	Contents (%)	
	Cracking-450 °C	Cracking-500 °C
Hydrocarbons	84.83	90.83
Oxygenates	7.20	1.39
Nitrogenates	1.14	0.63

aromatization reactions. Aromatics (benzene derivatives and naphthalene derivatives) can be synthesized from these intermediates via cracking and alkyl rearrangement reactions. The acid moiety of oleic acid is converted by means of decarboxylation and decarbonylation. The resultant hydrocarbon is cracked to short-chain alkenes which undergo oligomerization, cyclization and aromatization to generate aromatics. Considering the structural similarity, the cracking pathway of amides is reasonably assumed to resemble that of oleic acid, except for the replacement of decarboxylation/decarbonylation by deamidation. As a byproduct of cracking process, H_2 enters gaseous phase, lowering the H/C ratio of oil product. The bio-oil processed by catalytic cracking at 500 °C contains less than 1% oxygen (see Table 2), which meets the criteria of conventional fuels [11].

3.2.2. Hydrotreating

Hydrotreating is another important unit operation in petroleum refining. The biocrude obtained at 310 °C was hytrotreated using a CoMoS nano catalyst under high-pressure hydrogen atmosphere. The liquid biocrude was hydrotreated for 8 h and the liquid yield was 90%. Liquid samples were taken at 4 h and 8 h of the reaction and were analyzed by GC–MS which spectra were shown in Fig. 4. Compared to the feed, the peaks corresponding to fatty acids and amides in the spectra of hydrotreated oils shrink significantly. New peaks appear in the MS chromatogram of 4 h sample. As the reaction proceeds, the contents of fatty acids and amides become more, and more peaks arise in the spectrum of final product. The peak information is listed in Table 5.

Like the catalytic cracked oils, hydrocarbons are the main products in hydrotreated oils, with the amount of over 75% in the 8 h oil on an area basis (seen in Table 5). Further analysis of GC–MS results indicates that near 95% of them are straight and branched hydrocarbons. From Table 5, octadecane has the most significant peak with the contents of 12.46% and 14.67%, respectively, at 4 h and 8 h reaction, whereas the contents of heptadecane which has

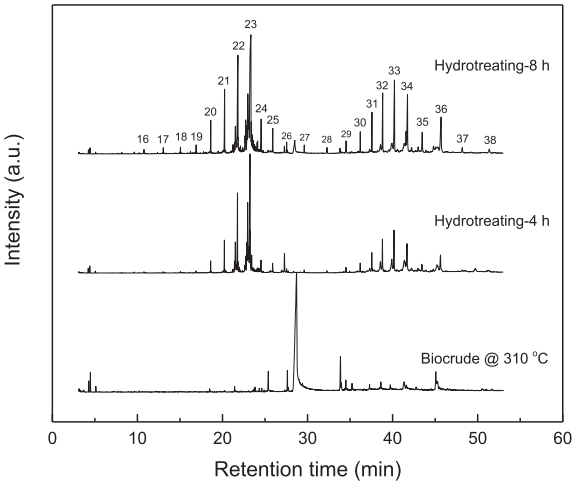


Fig. 4. MS chromatograms of hydrotreated bio-oils.

the second significant peak are much smaller. Research indicated that octadecane and heptadecane are the final products of hydrodeoxygenation and hydrodecarboxylation of oleic acid, respectively [19,42]. Thus, hydrodeoxygenation is the dominate reaction in hydrotreating the bio-oil from *B. braunii* liquefaction. This finding is distinguished from Zhang's results obtained from hydrotreating a waste cooking oil using the same catalyst, where the hydrodecarboxylation reaction predominated [19]. The reason could be due to the different composition of feed oils. Zhang et al. proposed that the hydrodeoxygenation of oleic acid occurred on the unsaturated sites of the CoMoS catalyst, whereas hydrodecarboxylation took place on the sulfur-saturated sites [19]. According to the results of Kwak et al., the Brønsted acid sites on a CoMoS/Al_2O_3 catalyst can be completely consumed by nitrogen containing compounds [43]. Therefore, the sulfur-saturated sites on CoMoS catalyst which provide Brønsted acidity [44,45] are accessible to

Table 5
Hydrotreating products distribution.

No.	Compound	Contents (%)	
		Hydrotreating-4 h	Hydrotreating-8 h
16	Undecane	0.1	0.17
17	Dodecane	0.06	0.16
18	Tridecane	0.1	0.2
19	Tetradecane	0.09	0.24
20	Pentadecane	0.5	0.95
21	Hexadecane	1.48	2.41
22	Heptadecane	4.85	6.64
23	Octadecane	12.46	14.67
24	Nonacosane	0.57	1.01
25	Eicosane	0.49	0.87
26	Heneicosane	0.28	0.51
27	Docosane	0.19	0.59
28	Tricosane	0.2	0.34
29	Tetracosane	0.41	0.61
30	Pentacosane	0.57	0.81
31	Hexacosane	1.13	1.59
32	Heptacosane	2.72	3.09
33	Octacosane	3.97	5.02
34	Nonacosane	3.57	4.27
35	Triacontane	1.21	1.6
36	Hentriacontane	2.9	3.89
37	Dotriacontane	0.76	0.41
38	Tetratriacontane	0.32	0.45
Total	Hydrocarbons	69.24	75.36
	Oxygenates	14.58	9.78
	Nitrogenates	0.58	0.78

the nitrogen containing compounds in the feed. Compared to waste cooking oil which contains only carbon, hydrogen and oxygen [46], 0.91 wt% nitrogen is present in the biocrude produced from *B. braunii* liquefaction. In other words, amides play an adverse role in oleic acid hydrodecarboxylation by competitively adsorbing on the sulfur-saturated sites of the catalyst, resembling the poisoning influence of nitrogen containing compounds on desulfurization catalysts [43].

Hexadecane and pentadecane, similar to octadecane and heptadecane, result from hydrodeoxygenation and hydrodecarboxylation of hexadecanoic acid, respectively. Likewise, the amount of even carbon number hydrocarbon is larger than that of the odd carbon number counterpart. The n-paraffins with carbon numbers lower than 15 are due to hydrocracking, and those with carbon numbers larger than 18 are a result of polymerization [19].

As the hydrotreating duration prolongs, the quantity of hydrocarbons increases, while that of oxygenates decreases. In spite of the reduced oxygenates, the amount of oxygen in the final product is quite high (see Table 2), which limits the direct application of this hydrotreated bio-oil as a petroleum alternative. The high oxygen content explains why the hydrotreated oil has a higher H/C ratio than the catalytic cracked oil but a similar higher heating value to the latter. Although the area of nitrogenates is reduced compared to that in feed spectrum, it shows insignificant change from the 4 h sample to the 8 h sample, which confirms the negative effect of nitrogen containing compounds. Employing a catalyst which can quickly process nitrogen containing compounds may accelerate the oxygen removal from biocrudes.

4. Conclusions

A microalga rich in hydrocarbons, *Botryococcus braunii*, was processed by hydrothermal liquefaction in the temperature range from 250 °C to 340 °C. More hydrocarbons were produced at higher temperatures. Likewise, higher temperature favored the synthesis of amides. Oleic acid, as the main constitute of oxygenates, displayed a decreased amount with temperature, which is due to the conversion to other components such as amides. The oil products from catalytic cracking and hydrotreating had almost the same higher heating values. The deoxygenation mechanism of biocrude in an FCC reactor resembled that on an HZSM-5 catalyst, with aromatics as the main products. Unlike the case of waste cooking oil, the removal of oxygen in biocrudes through hydrotreating was dominated by hydrodeoxygenation pathway, which is due to the competitive adsorption as well as the poisonous effect of the co-existing amides in the feed. Alkanes were produced in the hydrotreating process. Considering the hydrogen consumption and the quantity of final product (higher oxygen content) of hydrotreating process, catalytic cracking is a better opinion for upgrading biocrudes from hydrothermal liquefaction of *B. braunii*. The trace amount of oxygen in the catalytic converted products allows these bio-oils as a suitable petroleum blending.

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