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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).

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

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]:

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

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

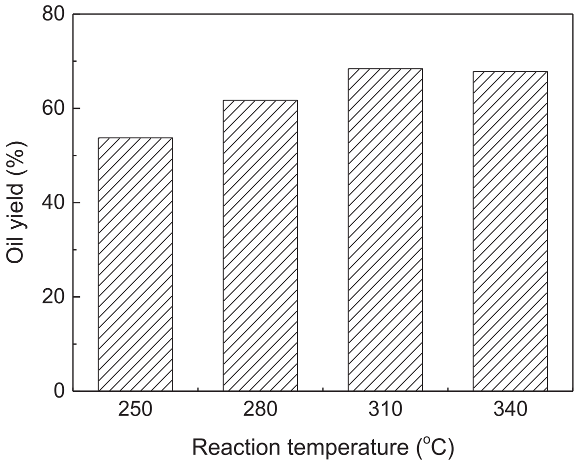

Fig. 1. Effect of temperature on biocrude yield.

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