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Conversion efficiency and oil quality of low-lipid high-protein and high-lipid low-protein microalgae via hydrothermal liquefaction

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HIGHLIGHTS

- Hydrothermal liquefaction of a low-lipid and a high-lipid alga was studied.
- Optimized biocrude oil yields of high-lipid and low-lipid algae were 52% and 89%.
- High-lipid algae led to higher biocrude yield.
- Low-lipid algae led to a higher proportion of hydrocarbons in biocrude.
- Algae components impact oil yield and quality, but may not be in similar effects.

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ABSTRACT

Hydrothermal liquefaction (HTL) is a promising technology for converting algae into biocrude oil. Here, HTL of a low-lipid high-protein microalgae (*Nannochloropsis* sp.) and a high-lipid low-protein microalgae (*Chlorella* sp.) was studied. An orthogonal design was applied to investigate the effects of reaction temperature (220–300 °C), retention time (30–90 min), and total solid content (TS, 15–25% wt) of the feedstock. The highest biocrude yield for *Nannochloropsis* sp. was 55% at 260 °C, 60 min and 25% wt, and for *Chlorella* sp. was 82.9% at 220 °C, 90 min and 25% wt. The maximum higher heating values (HHV) of biocrude oil from both algae were ~37 MJ/kg. GC–MS revealed a various distribution of chemical compounds in biocrude. In particular, the highest hydrocarbons content was 29.8% and 17.9% for *Nannochloropsis* and *Chlorella* sp., respectively. This study suggests that algae composition greatly influences oil yield and quality, but may not be in similar effects.

1. Introduction

The discovery of petroleum has provided a strong driving force for the development of modern industrial society. However, the overuse of fossil fuel accelerated the fossil fuel crisis (Yakovlev et al., 2009), and brought about severe environmental pollution concerns. Harvesting renewable energy from biomass could reduce the dependency on fossil fuel as well as benefit the environment (Biller et al., 2011). Microalgae have unique advantages of being feedstocks for biofuels, such as high photosynthetic efficiency, non-arable land use, and tremendous environmental benefits through the capture of CO_2 and nutrients (Biller and Ross, 2011; Duan and Savage, 2011; Yu et al., 2011a; Zhou et al., 2010). Therefore, microalgae have attracted a growing interest as a promising feedstock for sustainable production of biofuels (Dote et al., 1994; Zhou et al., 2013).

Current algae-to-biodiesel technologies mainly focus on utilizing high-lipid algae (Miao et al., 2012). Wet biomass requires energy-intensive drying processes to remove excess moisture. In comparison, hydrothermal liquefaction (HTL) can directly convert wet biomass into a liquid biocrude oil with or without a catalyst (Ross et al., 2010; Yu et al., 2011a), carried out in a closed reactor at 200–350 °C and 5–15 MPa. HTL is regarded as one of the most promising methods for converting biomass into biofuels due to the non-requirement of drying feedstock and the efficient reaction medium (water) at high temperature and high pressure (Vardon et al., 2012; Zou et al., 2010). Biocrude oil production from microalgae through HTL has therefore received increasing attention (Duan and Savage, 2011).

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The conversion efficiency of microalgae HTL depends on various parameters including reaction temperature, retention time, the composition of feedstock and the catalyst. The chemical properties of biocrude oil are highly dependent on the feedstock composition including proteins, carbohydrates, and lipids (Yang et al., 2004). The algal components were converted into various compounds through HTL (Toor et al., 2011). Distinguished from the routine algae-to-biodiesel approach, which largely depending on lipid contents, HTL can convert not only lipids but also other organic components, such as proteins and carbohydrates into biocrude oil (Biller and Ross, 2011; Yu et al., 2011a). Biller and Ross (2011) reported that the biocrude oil yield was greatly dependent on algae species and contents. More lipids can be induced under nutrient-deficiency conditions, whereas more proteins can be produced under nutrient-rich conditions (Biller et al., 2011). One study reported that the quality and higher heating value (HHV) of the biocrude oil were directly influenced by algae composition (Ross et al., 2010), which indicated the biocrude oil contained 10–20% of oxygen and nitrogen, and the energy density of biocrude oil was usually in the range of 30–37 MJ/kg. Therefore, the challenge of algae HTL is to increase yield and improve the quality of biocrude oil at the same time (Chakraborty et al., 2012). Yu et al. (2011b) studied HTL of *Chlorella pyrenoidosa*, a common fast-growing low-lipid green microalgae and achieved a maximum oil yield of 39.4% with a HHV of 35.42 MJ/kg at 280 °C, 120 min (retention time) and 20% (TS). This work suggests that it is feasible to convert low-lipid algae into biocrude oil with compatible yield and quality, although further study is needed to probe the role of algal components on HTL. Zhou et al. (2013) recently investigated HTL of microalgae, combined with wastewater treatment, demonstrating that algal biomass can be converted into biocrude oil via HTL with a high oil yield (50%) by recycling the nutrients in the post-HTL wastewater.

The purposes of this study were to: (1) compare the performance of HTL of two microalgae, *Nannochloropsis* sp. and *Chlorella* sp., with significantly different lipid and protein contents; (2) investigate how lipid and protein contents affect the yield and quality of biocrude oil; and (3) examine the influence of operational conditions (reaction temperature, retention time, and TS) on HTL of microalgae through a orthogonal design.

2. Methods

2.1. Materials

Two microalgae strains were provided by ENN Science & Technology Co., Ltd. (Langfang, China), i.e. *Nannochloropsis* sp. *(abbr.* B) with low-lipid high-protein content, and *Chlorella* sp. *(abbr.* Y) with high-lipid low-protein content. The samples were stored at 4 °C, and used within two months. Table 1 shows the proximate and ultimate analyses of the two microalgae samples including proteins, lipids, carbohydrates, ash and the moisture contents.

2.2. HTL apparatus and procedures

The HTL was performed in a 100 mL batch reactor (Model 4593, Parr Instrument Company, Moline, Illinois, USA). The reactor consisted of a stainless steel cylinder, a blender, and an aluminum block heater with a maximum operating temperature of 350 °C and a maximum pressure of 35 MPa.

The microalgae samples were stored at −20 °C in a freezer. The samples were transferred to a refrigerator at 4 °C overnight and thawed at 45 °C for 8 h prior to use. The samples were then mixed with deionized water (Water Purification Systems, Integral-3, Millipore, Germany) to obtain the desired TS. The feedstock was then loaded into the reactor. After the reactor was sealed, nitrogen (99.98%) was pumped into the reactor three times to purge the residual air and reach a set initial pressure inside the reactor prior to reaction. The set initial pressure was 0.6 MPa (Yu et al., 2011a), and the stirring speed was 380 rpm. The heating rate is approximately 5 °C min^{-1}. The reactor was then heated up to the designated reaction temperature. The retention time was defined as the elapse time starting from the reactor reached the reaction set temperature.

Operational parameters being investigated included reaction temperature, retention time and TS, in the ranges of 220–300 °C, 30–90 min and 15–25% wt, respectively. In this study, we chose the representative ranges of reaction temperature, retention time and TS based on not only the characteristics of algae in different contents of different lipids and proteins, but also recent literature focused on algal HTL, such as Yu et al. (2011a), Biller and Ross (2011), and Toor et al. (2013). An orthogonal design was developed using these three parameters.

All yields listed are the average values and standard errors of triplicate HTL experimental results. The liquefied fraction and biocrude oil yield were determined based on dry feedstock using Eqs. (1) and (2). The biocrude oil and the solid residue were dried to remove water in a vacuum drying chamber (DZF-6050, CIMO Medical Instruments Co., ShangHai, China) at −0.06 MPa, 55 °C for 8 h.

$$\text{Biocrude oil yield}\,(\%) = \frac{\text{Mass of raw oil}}{\text{Mass of dry matter of microalgae}} \times 100 \quad (1)$$

$$\text{Liquefied fraction}\,(\%) = \left(1 - \frac{\text{Mass of solid residue}}{\text{Mass dry matter of microalgae}}\right) \times 100 \quad (2)$$

Energy recovery was defined as the ratio of HHV of biocrude oil against that of the algal feekstock, which can be calculated using Eq. (3):

$$\text{Energy recovery of biocrude oil}\,(\%) = \frac{\text{HHV of biocrude oil} \times \text{mass of biocrude oil}}{\text{HHV of dry algae} \times \text{mass of dry algae}} \times 100 \quad (3)$$

Table 1
Physio-chemical characteristics of microalgae.

Algae species	Moisture (%)	Chemical composition based on total solid				
		Ash (%)	Crude Protein (%)	Crude lipid (%)	Crude fiber (%)	Non-fibrous carbohydrate* (%)
Nannochloropsis sp.(B)	71.6 ± 0.3	6.3 ± 0.04	52.4 ± 1.2	14.1 ± 0.3	5.3 ± 0.2	21.9 ± 0.3
Chlorella sp.(Y)	72.4 ± 1.1	4.9 ± 0.07	9.3 ± 0.5	59.9 ± 0.8	12.7 ± 0.3	13.2 ± 0.1

* Calculated by difference.