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Short communication

Hydrothermal liquefaction of Cyanophyta: Evaluation of potential bio-crude oil production and component analysis

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ABSTRACT

This study investigated the effects of temperature (220–400 °C), reaction time (10–60 min), solid content (5–30%), and water density (0.11–0.58 g/ml) in hydrothermal liquefaction (HTL) of Cyanophyta for bio-crude. The maximum bio-crude yield of 39.54% was obtained at 370 °C, 10 wt.% solid concentration, and 50 min reaction time. Water density was not an important factor at the conditions studied. The biocrude contained phenols, benzene, alkanes, ketones, esters, aliphatic compounds and high content of N-containing heterocyclic compounds. High temperature (370 °C) favored formation of phenols, benzene, alkanes, fatty acids and PAHs, whereas relatively lower temperature condition (320 °C) favored producing alkenes and N-containing heterocyclic compounds.

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1. Introduction

The transformational technology from biomass to liquid fuel has attracted much attention in recent years. Bio-fuels and liquid petroleum fuels have similar energy densities, chemical structures and combustion performance. Algae-derived fuel is environmentally-friendly and capable of meeting the global demand for transport fuels [1].

Microalgae have many advantages such as a short cultivation cycle, hyperproductivity, and it can be grown on non-arable land. These features make it an attractive renewable bio-fuel source. Cyanophyta has 150 genera including 1500 species that are distributed in global waters [2]. The gradual industrialization, agriculturalizing and urbanization have caused water eutrophication, in which Cyanophyta can flourish and bloom. Cyanophyta blooms can damage the ecosystem, give off fetid odors and endanger human and animal health. In the past few years, Cyanophyta blooms frequently occur in many countries and regions such as Taihu lake in China [3], Lake Victoria in Africa [4], and southern waters in Belgium [5]. In 2013, the quantity of salvaged Cyanophyta from Taihu lake was about 1.45 million tons [5]. Proper and efficient handling is difficult due to its very high moisture content (>97%). Converting Cyanophyta into biofuel both prevents deterioration of water quality and releases its resource potential.

The typical approach for making bio-fuel from microalgae is through transesterification of lipids [6], which requires large quantities of energy for dewatering drying, and solvent extraction of the triglycerides from the dried biomass. In this process, the organic solvent is expensive [7]. By contrast, hydrothermal liquefaction (HTL) is considered to be a more promising technique for conversion of wet algal biomass at high temperature (>200 °C) and the pressure maintaining water in liquid phase [8]. "Wet" algal biomass can be directly converted to oil thus avoiding the energy penalty for dewatering and drying. Additionally, HTL is a promising process because of its ability to produce bio-crude from not just lipids, but also protein and carbohydrates, and it can also facilitate the recycle of nutrients required for algae growth [9]. Therefore HTL is suited for efficient resource utilization of Cyanophyta and other biomass with high moisture or low lipid content.

Previous investigations were performed on different algae strains, such as *Dunaliella tertiolecta* [10], *Nannochloropsis* sp. [7,9,11,12], *Spirulina platensis* [13–17], *Chlorella pyrenoidosa* [18,19], *Scenedesmus* [15], *Desmodesmus* sp. [20]. These studies have varied reaction times, temperatures, water densities, algae strains and loading concentrations in order to obtain optimum bio-crude yields and distribution of products. Most of these studies have shown that a temperature range of 250–370 °C results in the maximum oil yield, likely due to the higher ionic product of hot and compressed water. The higher ionic product catalyzes acid and base reactions by dissociated H^+ and OH^- from hot liquid water [21]. Zou et al. [22] showed that the maximum bio-crude yield of 25.8 wt.% can be obtained after HTL treatment of *Dunaliella* at 360 °C, 50 min batch holding time with Na_2CO_3. Zhou et al. [23] reported that, at 300 °C, 30 min reaction time, the maximum bio-crude yield of 23 wt.% was obtained by catalysis with Na_2CO_3. Brown et al. [7] studied HTL of *Nannochloropsis* sp. and found that a maximum bio-crude yield of 43 wt.% can be reached at 350 °C and batch holding time of 60 min. Yang et al. [24] found that HTL of *Microcystis viridis* produced the highest bio-crude yield at 33 wt.% which corresponds to an energy recovery of 40%.

Although previous investigations provided some valuable information about HTL on some limited algal species, very little research has

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addressed on HTL of natural Cyanophyta. To fill this gap, in this paper, wild-type Cyanophyta was used as feedstock. We mainly investigated the effects of reaction temperature, batch holding time, solid concentration and water density on the bio-crude yield. Besides, the chemical compositions of the resulting bio-crude were analyzed.

2. Experimental

2.1. Materials

The chemicals used in this investigation were dichloromethane (AR, Tianjin Hongyan chemical reagent factory, China), hexane (AR, Tianjin Fuchen chemical reagent factory, China), potassium sodium tartrate (AR, Tianjin Tianli chemical reagent factory, China), potassium iodide (AR, Tianjin Fuchen chemical reagent factory, China), mercury iodide (AR, Shanghai Shanpu chemical reagent factory, China), and ammonium chloride (AR, Tianjin Fuchen chemical reagent factory, China).

The wild-type Cyanophyta used in this investigation was obtained from Taihu lake in China (moisture content > 97%). It contains *Microcystis*, Basketballalgae, *Oscillatoria* sp., *Nostoc*, seaweed, and some mutant species and toxic substances caused by algal bloom, such as microcystins from *Microcystis*, anabaenins from *Anabaena flos-aquae*, and aphanizomenins from Aphanizomenon flos-aquae. For easy storage of feedstock and improving experimental repeatability, we dried the wet Cyanophyta at 80 °C for 72 h, then grinded it to obtain algae powder through a 100 mesh sieve.

2.2. Experimental equipment and procedures

2.2.1. Hydrothermal reaction experiments

We used 316 stainless-steel mini batch reactors with an internal volume of 4.1 mL. The reactors constructed from a 1/2 in. Swagelok port connector, caps, and 1/2 to 1/8 in. reducing union were fitted with 9 in. of 1/8 o.d. stainless steel tubing and a high-pressure valve with grafoil packing. Prior to use in reactions, all the assembled reactors were loaded with 2 mL of deionized water and heated up to 500 °C for 30 min to expose the reactor walls to the HTL conditions.

After loading the algae powder and water into each reactor, we sealed the reactors and connected them to a vacuum pump. The reactor was vacuumed completely under a pressure of 1.5 psi to avoid the undesired effect from residual air on the reaction process. Before reactions, a Techne fluidized sand bath (SBS-4) with a Techne TC-8D temperature controller was preheated to the reaction temperature. The reaction started when we placed the reactors vertically into the sand bath, in which the reactors were heated up to the desired temperature within approximately 2 min. We stopped the timer immediately upon removing the reactors from the sand bath. Then the reactors were then immersed into a room temperature water bath and left for at least 40 min to quench the reaction.

2.2.2. Product separation

We opened the cooled reactors to recover the liquid fraction. The liquid products were transferred to a centrifuge tube by a pipette. The reactor was washed twice more with addition of dichloromethane to ensure that all the contents were collected and transferred. After that, the tube was centrifuged at 800 r/min for 20 min. We used a pipette to transfer the aqueous phase to a sample vial. The dichloromethane soluble phase was transferred to a round bottom flask, and the dichloromethane was then removed by a rotary evaporator under vacuum pressure of 48 kPa at 39 °C. The leftover material was the bio-crude obtained from HTL treatment. The solid phase was dried in an oven at 80 °C for 6 h to remove any residual solvent. We mixed the bio-crude with hexane. We refer to the hexane soluble portion as “light bio-crude” and the hexane insoluble fraction as “heavy bio-crude”.

2.2.3. Analytical methods

Identification of the key chemical compounds in the extracted light bio-crude was analyzed with a gas chromatograph (GC, Agilent 6890 N) equipped with a mass spectrometric detector (MS5973) and a HP-5MS nonpolar capillary column (30 m × 0.25 mm × 0.5 μm) using helium as the carrier gas. The injector temperature was 300 °C and 1 μL of light oil/hexane solution was injected. The oven was held at 80 °C for 2 min followed by temperature ramping to 290 °C at 6 °C·min^{-1} and then held for 10 min. A NIST mass spectral library was used to identify the compounds. We did not perform GC analysis of the heavy oil portion as previous work revealed that its components generally did not elute from the GC [12].

Fourier transform infrared spectroscopic analysis (FT-IR) was performed on a Nicolet Nexus 470 FT-IR spectrometer to determine the functional groups of the bio-crude (scan range: 400–4000 cm^{-1}). The elemental compositions (C, H, O and N) of the obtained bio-crude were determined by a Vario EL III elemental analyzer. The standard deviation for C, H, and N element is less than 0.1% and for O element is less than 0.2%.

NH_3 content in the aqueous phase was determined by Nessler's reagent colorimetric method. Quantitative analysis was done spectrophotometrically and a linear calibration was established by using standards of known ammonia concentrations. The total organic carbon (TOC) in the aqueous product was analyzed by a commercial TOC analyzer (Shanghai EURO TECH, ET1020A).

2.3. Data interpretation

In this investigation, bio-crude yield is calculated from Eq. (1) demonstrated as follows:

$$\text{Bio-oil yield} = \frac{m_2}{m_1} \times 100\% \quad (1)$$

where m_1 is mass of Cyanophyta feedstock (g); m_2 is formed bio-crude (g).

The higher heating value (HHV) of bio-crude derived from Cyanophyta HTL is calculated from Eq. (2) [25]:

$$\text{HHV}(\text{MJ}\cdot\text{kg}^{-1}) = 0.338\text{C} + 1.428(\text{H} - 0.125\text{O}) \quad (2)$$

where, C, H, and O represent weight percentages of carbon, hydrogen and oxygen, respectively. S content was not analyzed because of the instrumental limitation, so the HHV excludes heating value from sulfur oxidation.

3. Results and discussion

3.1. Feedstock composition

The elemental analysis results of the Cyanophyta feedstock are shown in Table 1. Before the test, the Cyanophyta powder was dried at 105 °C for 4 h. Protein, lipid and polysaccharide are the main chemical components in algal biomass [10]. So we mainly performed analysis on the contents of protein, lipid and carbohydrate in Cyanophyta feedstock: The protein content was analyzed by using the Kjeldahl method; the lipid content was analyzed by Soxhlet extraction method and petroleum ether used as a solvent; the Anthrone colorimetric method was adopted to determine the content of the carbohydrate. The testing results are shown in Table 2.

Table 1
Elemental analysis result of Taihu lake Cyanophyta.

C_d/wt.%	H_d/wt.%	O_d/wt.%	N_d/wt.%	P/wt.%	$S_{t,d}$/wt.%	Water/wt.%	Ash/wt.%
49.05	6.41	27.02	8.59	0.14	0.82	4.31	8.11

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