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Production of low-nitrogen bio-crude oils from microalgae pre-treated with pre-cooled NaOH/urea solution

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ABSTRACT

In this study, a novel two-stage hydrothermal liquefaction (HTL) process was employed to produce low-nitrogen bio-crude oils from microalgae, involving pre-treatment of the microalgae with a pre-cooled NaOH/urea solution or a dilute acid and HTL of the pre-treated algal feedstock at 250°C for 10–50 min. The results indicated that the pre-treatment with a pre-cooled NaOH/urea solution effectively removed carbohydrates and protein from the raw microalgae, leading to a decrease in carbohydrates and protein content by 12 wt% and 10 wt% (both absolute values), respectively, while retaining 70 wt% of the solid mass, corresponding to as high as 82% carbohydrates removal efficiency and 40% protein removal efficiency. The two-stage HTL process slightly increased the overall bio-crude oil yields relative to the conventional single-stage HTL process, and the bio-crude oils obtained from the two–stage HTL process have a better quality than those obtained from the single-stage HTL, in terms of lower nitrogen and oxygen levels and higher energy content.

1. Introduction

Due to the global shortage of fossil fuels and concerns about greenhouse gas (GHG) emissions, it has become important to develop economical and sustainable pathways for the production of bio-renewable liquid fuels. Recently, microalgae have been intensively investigated as a promising alternative source for bio-fuel production owing to their inherent advantages i.e., (i) high photosynthetic efficiency; (ii) high lipid productivity; (iii) ease of cultivation on marginal and non-arable land; (iv) potential recyclability of stationary emissions of carbon dioxide (CO_2); and (v) adaptability to seawater or waste water [1,2]. Various techniques (e.g., hydrothermal liquefaction and pyrolysis) have been employed to convert biomass into liquid bio-fuels. Compared to pyrolysis, hydrothermal liquefaction (HTL) is regarded as a more suitable method for feedstock with high moisture content since it requires no dewatering of the feedstock, thereby avoiding enthalpy energy loss [2]. In general, the yield and property of bio-crude oils obtained from HTL are dependent on the operating conditions, including reaction temperature, retention time, ratio of biomass to water, and catalyst [1–6]. Among them, reaction temperature has been commonly demonstrated to be the most important parameter for microalgae HTL. The appropriate reaction temperatures reported in the literature for maximizing bio-crude oil yield are in the range of 250–375°C [11]. Although a higher reaction temperature results in an increase in the oil yield, the nitrogen content in the bio-crude oil can be simultaneously increased. Yu et al. [7] observed that the nitrogen content in the bio-crude oil from *Chlorella* increased from 3.06 wt% to 7.46 wt% with reaction temperature rising from 200°C to 280°C with a constant residence time of 10 min. Garcia Alba et al. [3] investigated the effect of reaction temperature on the distribution of nitrogen in the bio-crude oil, and found that nitrogen tended to accumulate in the oil at higher temperatures. In addition, it should be noticed that a higher operational temperature is less energy efficient, thereby conducting microalgae HTL at a relatively lower temperature is a more economical option.

As is well known, microalgae-derived bio-crude oils commonly contain a high nitrogen content which could lead to undesirable NO_x emission in combustion. Therefore, further upgrading is necessary to improve bio-crude oil quality by reducing the heteroatom (e.g., nitrogen and sulfur) contents. Up to now, numerous upgrading strategies have been reported in the literature, such as supercritical fluid and hydroprocessing. Duan and Savage [8] processed the bio-crude oil from HTL of *Nannochloropsis sp.* in supercritical water (400°C) in the presence of Pt/C. Guo et al. [9] hydroprocessed bio-crude oils over bimetallic Ni-Cu/ZrO_2 catalyst to improve the algae bio-crude oils properties. Alternatively, a two-stage process

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could be employed to produce low-nitrogen bio-crude oils from microalgae. The two-stage process mainly consists of pre-treating raw microalgae at a low temperature (100°C–200°C), followed by a high-temperature liquefaction (250°C–375°C). For example, Jazrawi et al. [10] reported up to a 55 wt% nitrogen removal via HTL coupled with a mild acid pre-treatment (<200°C), when compared with the single-stage liquefaction.

In recent years, a biomass pre-treatment approach using a pre-cooled NaOH/urea solution was developed which showed a potential to disrupt cell wall and dissolve cellulose. In some previous studies, cellulose was found to be completely dissolved in a pre-cooled (−10 to −12 × °C) 7–8 wt% NaOH /11–12 wt% urea aqueous solution within 5 min at room temperature [12,13]. Compared to other conventional biomass pre-treatment methods (e.g., dilute acid), a NaOH/urea solution pre-treatment is more environmental friendly. The dilute acid pre-treatment could cause corrosion and generates "toxic" intermediates, leading to an increase in the downstream wastewater treatment cost [20]. In contrast, the process water produced from the pre-treatment with NaOH/urea solution can be recycled or used as a good catalyst for biomass hydrothermal liquefaction to improve the yield and quality of bio-crude oil products. For instance, NaOH has been commonly demonstrated to be an active catalyst for microalgae HTL [21]. Thus, the novel pre-treatment method with a pre-cooled NaOH/urea solution may provide a great potential to improve the HTL efficiency for microalgae. Microalgal cell walls are mainly composed of a complex assembly of cellulose and glycoprotein. Therefore, the pre-cooled NaOH/urea solution could be a possible pre-treatment approach for microalgal biomass.

To the best of our knowledge, the pre-treatment method using pre-cooled NaOH/urea solution has not been demonstrated for microalgae. Therefore, in this present study, the feasibility of using pre-cooled NaOH/urea solution for microalgae conversion was investigated. The effects of the pre-treatment on the yield and quality of microalgal bio-crude oil products were further investigated by HTL of raw and pre-treated microalgae at 250°C for 10–50 min.

2. Materials and methods

2.1. Materials

Food-grade powder *C. vulgaris* was purchased from a health-food store (Pure Bulk, Inc., Roseburg, USA). The obtained microalgae sample has a moisture and ash content of 4.3 wt%. and 7.1 wt%, respectively. The ultimate analyses on a dry basis are as follows: 51.5 wt% carbon, 7.7 wt% hydrogen, 9.8 wt% nitrogen, 0.5 wt% sulfur, and 23.4 wt% oxygen (calculated by %O = 100% − %C − %H − %N − %S − %Ash). The major chemical components of *C. vulgaris* are lipid, protein, and carbohydrates with 13.0 wt%, 61.3 wt%, and 16.1 wt%, respectively. Reagent grade dichloromethane (DCM) was purchased from Caledon Laboratories Ltd (Georgetown, Canada). The sodium hydroxide and urea used in the pre-treatment tests were obtained from Sigma-Aldrich (Oakville, Canada).

2.2. Pre-treatment studies

2.2.1. Pre-cooled NaOH/urea solution method

Microalgae pre-treatment studies with pre-cooled NaOH/urea solution were performed using a procedure modified from that reported by Cai and Zhang [19], as briefly described below. An amount of 35 g of NaOH/urea solution was prepared by mixing NaOH, urea, and distilled water (7:12:81 by weight) and stored in a freezer (−5 to −10°C) overnight. An aliquot of 7.0 g of *C. vulgaris* was thoroughly mixed with the de-frozen NaOH/urea solution for 5 min at room temperature. The mixture was then neutralized with 1.0 M HCl solution, followed by centrifugation. After that, the solid fraction was separated from the aqueous phase by vacuum filtration, and directly used as the feedstock for HTL experiments.

2.2.2. Dilute acid method

An amount of 7.0 g of dry microalgae and 35 mL of 2% (v/v) sulfuric acid were mixed thoroughly and placed in an oil bath at 120°C for 20 min with constant agitation at 60 rpm. The mixture was thereafter cooled to room temperature and then neutralized with 1.0 M NaOH solution. The solid fraction was separated via centrifugation, and subsequently filtrated to recover the solid fraction, which was directly used for HTL studies.

2.3. Hydrothermal liquefaction process

A 100 mL bench-top autoclave reactor equipped with a magnetic drive stirrer, was used for the HTL tests (Parr 4590, Illinois, USA). In a single-stage HTL run, 7.0 g of crude biomass with 35 mL of distilled water were loaded into the reactor. In a two-stage HTL experimental run, the pre-treated microalgae slurry sample as described earlier was mixed with additional distilled water to make a total of 42 g in the reactor. The reactor was sealed and flushed with nitrogen for 3 times to remove residual air inside the reactor. Afterwards, the reactor was heated from room temperature to the pre-set temperature of 250°C at a heating rate of 5°C/min for ~45 min. This temperature was maintained for 10 min, 30 min, and 50 min. Throughout the reaction process, the pressure was monitored by a pressure gauge attached to the reactor head. The final pressure was ~45 bar at 250°C. At the end of the reaction, the reactor was rapidly quenched to room temperature using a water bath to stop the reaction. After the pre-set residence time elapsed, the reactor was immediately quenched in a water bath to stop further reactions. After the system cooled to room temperature, the gaseous products were released via the fume hood (in this work gas samples were not collected and analyzed, as our preliminary tests showed that the total yield of gases at 250°C was negligibly low, less than 5 wt% and CO_2 was the main gas species formed in the process). The reactor contents were then completely rinsed into a beaker using DCM. This reaction mixture was then filtered, and the filter residue was further washed with DCM. The residue was then dried for 12 h at 105°C to obtain a dry solid residue fraction. The two-phase mixture was transferred to a separation funnel to isolate the aqueous phase (upper layer) from the bio-crude oil phase (lower layer). The bio-crude oil phase was transferred to a pre-weighed 500 mL Erlenmeyer flask to remove DCM by rotary evaporation at 45°C under reduced pressure and to obtain bio-crude oil product. Liquefaction yields are expressed in wt% and were calculated as follows:

$$Bio\text{–}crude\ oil\ yield = \frac{Mass_{Bio-crude\ oil}}{Mass_{dry\ microalgae}} \times 100\% \quad (1)$$

$$Solid\ residue\ (SR)\ yield = \frac{Mass_{solid\ residue}}{Mass_{dry\ microalgae}} \times 100\% \quad (2)$$

$$Aqueous\ phase\ \&\ Gas\ yield = 100\% - Bio\text{–}crude\ oil\ yield - Solid\ residue\ yield \quad (3)$$

All HTL experiments were performed in triplicate and the repeatability of liquefaction yields was typically ±5 wt%. The bio-crude oil recovery and extraction procedure is shown in Fig. 1.