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Element and chemical compounds transfer in bio-crude from hydrothermal liquefaction of microalgae

Xiaohan Tang, Chao Zhang, Zeyu Li, Xiaoyi Yang *

School of Energy and Power Engineering, Energy and Environment International Centre, Beihang University, 37 Xueyuan Road, Haidian District, Beijing 100191, PR China

HIGHLIGHTS

- Fatty acid amide contents of bio-crude increased with temperature rising.
- Two types of N-heterocyclic compounds performed differently with temperature rising.
- High HTL temperature enhanced the heteroatom compounds in bio-crude.

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ABSTRACT

In this study, hydrothermal liquefaction (HTL) experiments of *Nannochloropsis* and *Spirulina* were carried out at different temperatures (220–300 °C) to explore the effects of temperature on bio-crude yield and properties. The optimal temperature for bio-crude yield was around 260–280 °C. Transfers of element and chemical compounds in bio-crude were discussed in detail to deduce the reaction mechanism. The hydrogen and carbon recoveries were consistent with the results of bio-crude yields at every temperature point. The relative percentage of fatty acid in bio-crude decreased and the amine and amide increased for both microalgae with temperature rising. The N-heterocyclic compounds in bio-crude increased with temperature rising for *Nannochloropsis*, while decreased when temperature increased from 220 °C to 280 °C for *Spirulina*. Bio-crude gained at higher temperature or from microalgae with high protein content may contain high heteroatom compounds.

1. Introduction

As a promising feedstock for the next generation biofuels, microalgae have advantages in growth rate and photosynthetic efficiencies (Chisti, 2007). Microalgae absorb large amount of carbon dioxide during the process of growth, which could be used for depurating flue gas (Zeng et al., 2011). Moreover, microalgae can be cultivated in marginal land and wastewater, which could avoid the competition with food supplies (Rawat et al., 2013).

Hydrothermal liquefaction (HTL) is a thermal chemical process carried out in subcritical water, which converts macromolecule polymers, such as protein, lipid and carbohydrate, to small molecules (Peterson et al., 2008; Toor et al., 2011). HTL can process protein and carbohydrate rather than lipids only, so microalgae with low lipid but fast growing rate can also be the available feedstock for HTL (Barreiro et al., 2013a). The character of water near its critical point (22 MPa, 374 °C) is different from that of water at room temperature, for example, the dielectric constant decreased, and the dissociation constant increased. So, hot-compressed water serves as solvent and catalyst, as well as reactant in the reaction of HTL (Barreiro et al., 2013a; Marcilla et al., 2013). The other advantage of using HTL to convert wet microalgae to biofuel is avoiding dewatering of microalgae, which could save lots of energy consumption (Marcilla et al., 2013; Yeh et al., 2013). The desired product of liquefaction is a liquid bio-crude or bio-oil, which is a promising renewable feedstock for co-refining in existing fossil-based refineries (Barreiro et al., 2013a). Besides, solid-residues, gas, and aqueous phases were also the products of hydrothermal liquefaction of microalgae.

There are a growing number of research about HTL of microalgae in recent years. The research focuses include the experiment conditions (Eboibi et al., 2014; Jena et al., 2011; Valdez et al., 2012), the strain selection (Barreiro et al., 2013), the kinetics model of reaction (Valdez and Savage, 2013; Valdez et al., 2014), and the mechanism of the process (Gai et al., 2015; Torri et al., 2012). Though many factors can affect the results of the HTL, temperature plays a crucial role in the whole process. The temperature referred in literatures varied from 200 to 400 °C (Eboibi et al., 2014; Jena et al., 2011; Toor et al., 2013; Valdez et al., 2012; Yu et al.,

* Corresponding author. Tel./fax: +86 01 82317346.
E-mail address: yangxiaoyi@buaa.edu.cn (X. Yang).

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2011a), and most of them were under the subcritical conditions (374 °C). Although the influence of reaction temperature on products yields has got many investigations, there are still some controversial viewpoints on the optimal temperature of HTL. Barreiro et al. (2013a) suggested that at subcritical conditions, an increase in reaction temperature appears to increase the bio-crude yield, and Jena et al. (2011) reported a maximum bio-crude yield (39.9%) was gained at 350 °C. However, in the research of Toor et al. (2013), the optimum temperature for maximum yield of bio-crude from *Spirulina* was at 220, 350, and 375 °C. It should be noted that higher reaction temperature means more energy input for the process, so making HTL of microalgae at relatively lower temperature available is meaningful.

There were also some studies about the influence of reaction temperature on the properties of bio-crude. Gai et al. (2014) investigated the effects of operating conditions on bio-crude yield and quality, found that a higher carbon recovery of bio-crude oils could be obtained at high temperatures and a lower nitrogen recovery of bio-crude oils could be obtained at low temperatures. Yu et al. (2011b) investigated the influence of reaction temperature on the distributions of carbon and nitrogen in the products from HTL, found that both carbon and nitrogen tended to preferentially accumulate in the bio-crude as temperature and retention time increased. Garcia Alba et al. (2012) observed that the nitrogen content in bio-crude was remarkably increased with temperature rising from 175 to 275 °C, and thereafter, maintained constant at around 6 wt.%. Yoo et al. (2015) suggested the HTL at low temperature produces a high quality bio-crude due to the low concentration of asphaltene and heteroatoms. In order to find out the transfer principle of element and understand the reaction mechanism of HTL for microalgae, some other researchers have analyzed the chemical compounds of bio-crude and tried to deduce the reaction pathway of HTL for microalgae. Torri et al. (2012) reported that the generation of cyclic dipeptides and amino acids side chains, carbohydrates derivatives and products from the cross reaction of protein and carbohydrates was due to the breakdown of protein and cellulose at higher temperature (300–375 °C). Gai et al. (2015) analyzed the chemical composition and functional groups for the bio-crude oil obtained from HTL of two low-lipid content microalgae, found that the bio-crude oil with a higher percentage of aliphatic functional groups was obtained at higher reaction temperatures (280–320 °C). Though many works have been carried out, the HTL reaction mechanism is still unclear and the effect of element transfer on bio-crude quality had not got enough investigated.

In order to get detailed understanding of element and chemical compounds transfer and the possible reaction mechanism in HTL, two different microalgae *Nannochloropsis* (*Nan.*) and *Spirulina.* (*Spi.*) were selected to investigate the HTL performance at relatively low temperature (220–300 °C) in this study. The generation and conversion of nitrogen containing compounds in the process of HTL of microalgae were carefully analyzed because the quality of bio-crude is highly related to the nitrogen compounds content. Furthermore, the effects of difference in biochemical component of *Nannochloropsis* and *Spirulina* on the performance of HTL were also analyzed to investigate the reaction mechanism of HTL process.

2. Methods

2.1. Materials

Nannochloropsis and *Spirulina* were selected to run HTL experiments in this study.

Nannochloropsis was verified as a desirable feedstock for biofuel because of the best combination of both high lipid content and fast biomass productivity (Rodolfi et al., 2009). *Spirulina* is a kind of cyanobacteria that has been used as food and nutrition for many years due to the very high protein content and other valuable nutrients (Spolaore et al., 2006), which made it largely cultivated around the world. *Spirulina* was also largely used as feedstock in bio-energy field (Aikawa et al., 2013; Jena et al., 2011) in recent years, in spite of the high nitrogen content. *Spirulina* was provided by Shandong Binzhou Tianjian Biotechnology Co., Ltd. (Shandong, China). *Nannochloropsis* was provided by Shandong Yantai HaiRong biology technology co., Ltd. (Shandong, China). The feedstock was used as received.

2.2. Analysis of feedstock

The moisture content of the microalgae was determined by weight difference after drying the samples at 105 °C for 24 h. The ash content of the microalgae was measured gravimetrically after heating the samples at 250 °C for 30 min and then holding at 575 °C for 3 h. The C, H, and N contents of microalgae were measured by an elemental analyzer (EA3000, Euro Vector Co. Ltd., Italy). The S content was measured by an automatic sulfur detector (5E-8S/AII, Changsha Kaiyuan instrument Co. Ltd., China). The O content was calculated by subtraction of the N, C, H, and S contents from the total measured weight. The higher heating value (HHV) was calculated according to Dulong's function. The biochemical composition of the microalgae was analyzed by Dalian Institute of Chemical Physics (DICP), Chinese Academy Sciences. The carbohydrate content was analyzed by the sulfuric acid–anthrone method. The protein content was determined based on the BCA method. The lipid was determined as fatty acid methyl esters by *in situ* transesterification (Feng et al., 2011). Duplicate or triplicate was conducted for each experiment and the characteristics of *Nannochloropsis* and *Spirulina* were presented in Table 1.

2.3. HTL experiments

HTL experiments were performed in a 500 ml autoclave batch reactor made of stainless steel. In each experimental run, 10 g of dry microalgae were mixed with 90 ml of distilled water. The sample was added into the reactor as slurry. Nitrogen was introduced to purge the residual air in the autoclave for about 3 min and kept 0.1 MPa gauge pressure in reactor. The experiments were performed at 220, 240, 260, 280, and 300 °C for 60 min, respectively. It took about 50–70 min to reach the reaction temperature. After each test, the autoclave was rapidly cooled down to room temperature by using compressed air.

After the reactor was cooled down, the pressures and temperatures were recorded. The gas products were sampled through a control valve into gas sampling bags. The reaction mixture was collected carefully, and the reactor was rinsed with dichloromethane

Table 1
Ultimate, proximate and biochemical analytical results of microalgae.

	Nannochloropsis	*Spirulina*
Moisture (%)	3.1 ± 0.06	7.8 ± 0.26
Ash (%)	8.9 ± 0.32	8.2 ± 0.01
N (%)	6.29 ± 0.09	10.21 ± 0.04
C (%)	49.27 ± 0.93	45.61 ± 0.32
H (%)	7.27 ± 0.12	6.66 ± 0.04
S (%)	0.83 ± 0.01	0.79 ± 0.04
O[a] (%)	36.34	36.74
HHV (MJ/kg)	20.5	18.4
Protein (%)	36.4 ± 4.6	48.5 ± 2.1
Lipid (%)	19.05 ± 0.13	5.89 ± 0.11
Carbohydrate (%)	12.4 ± 0.9	10.8 ± 0.8

[a] Calculated by difference.