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Catalytic upgrading of bio-oil in hydrothermal liquefaction of algae major model components over liquid acids

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ABSTRACT

We selected acetic acid and sulfuric acid as liquid acid catalysts to investigate their performance on hydrothermal liquefaction (HTL) of algae major model components, including polysaccharides, proteins, lipids, and polysaccharides-proteins mixture. The aim of this study was to understand the catalytic effects of liquid acid catalysts as well as the formation process mechanisms and properties of the bio-oils from HTL of algae. We also used the two acids in HTL process of *Chlorella vulgaris* to estimate their catalytic performances in algae and compare this performance with the results from HTL of model components. Product distributions from different catalytic conditions were compared with blank results. Bio-oils were analyzed by elemental analysis, gas chromatography-mass spectrometry (GC–MS), and thermal gravimetric analysis (TGA). The results showed that the addition of acetic acid or sulfuric acid had no positive effect on the enhancement of bio-oil yield from HTL of individual algae major model components; however, the use of liquid acid catalysts could prevent the detrimental effect of interaction between polysaccharides and proteins on bio-oil yield. H/C ratios and higher heating values (HHVs) of bio-oils obtained from HTL of algae major model components increased significantly in the presence of acid catalysts. Sulfuric acid favored the oxygen removal process, and acetic acid reduced the nitrogen content in bio-oil from HTL of proteins. GC–MS results showed that bio-oil composition was greatly altered when adding acids. The light component proportion of catalytic upgraded bio-oils was significantly higher than that of bio-oils obtained with no catalyst. The results of HTL of *Chlorella vulgaris* with acid catalysts indicate that both acids favor to the hydrolysis of cellulose; therefore, the use of acid catalysts could accelerate the formation of bio-oil from cellular components. The difference between the HTL of algae major model components and real algae using acid catalysts was probably due to the complexity of algae structure.

1. Introduction

Algae are considered promising and environmentally friendly alternative feedstock for biofuel production [1,2]. Considering the high moisture content in algae, the hydrothermal liquefaction (HTL) process has been attracted much attention for algae conversion into bio-oil from an energy consumption perspective, as HTL eliminates the dewatering process. Generally, hydrothermal treatment of algae produces crude bio-oils with approximately 80% of the heating value of petroleum, and the crude bio-oils are richer in heteroatoms (N and O) [3]. As a consequence, extensive research has focused on applying various homogeneous and heterogeneous catalysts to HTL of algae aims to improve bio-oil yield and its quality [4]. Subcritical water is an excellent medium for homogeneous, fast, and efficient reactions. Homogeneous catalysts have received attention for liquefaction of algae because of their low cost and ability to partition into aqueous products without suffering from coking [5,6]. On the contrary, heterogeneous catalysts applied to the HTL process of algae could be easily coked or poisoned in the liquefaction system. Additionally, heterogeneous catalysts are difficult to separate from the residue after HTL. Therefore, the use of conventional homogeneous catalysts is still expected to be used in HTL of algae in the near future.

To date, the majority of catalytic HTL studies used homogenous acid or alkali catalysts, such as CH_3COOH, HCOOH, H_2SO_4, Na_2CO_3 and KOH [5,7,8]. The pH environment during liquefaction is crucial to the reactivity of biomass to break C—C or C—O bonds, and the pH is adjusted by introducing acid or alkali catalysts. Moreover, algae components, such as carbohydrates, will follow different reaction pathways under acidic or alkali environments depending on the ion product of water [9]. In addition to the influence of pH, acid or alkali catalysts can

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perform various catalytic effects on the HTL process based on their own chemical nature. For instance, the use of alkaline catalysts hinders the formation of char but favors to the formation of oil products from biomass feedstock with higher lignin content. For the three mineral acids (HCl, H_2SO_4 and H_3PO_4), it was found that the pH as well as the nature of acids, had great influence on the decomposition pathway. At lower pH, a rehydration of HMF to levulinic acid and formic acid was favored, whereas at higher pH, polymerization reactions were favored [10]. In some cases, the addition of a catalyst into the HTL process may not increase the bio-oil yield but could remarkably alter the product distribution. Ross et al. have found that the use of organic acids can improve the flow properties and lower the boiling point of the bio-oil [5]. Generally, acid catalysts were more favorable in HTL of algae, whereas alkali catalysts were more suitable in the conversion process of lignin or cellulose.

It is becoming more widely understood that optimal processing conditions of algae liquefaction vary with their biochemical content. Studies now are focusing on elucidating the chemistry of biomolecules in the complex reaction systems [11]. It is similar to the influence of catalysts on HTL of different algae species, which could also vary significantly causing by the catalyst selectivity. The varied catalytic role on HTL of algae leads to the necessity to investigate the specific catalytic effects on HTL of different algae components. Few studies have considered the specific catalytic behavior of acid catalysts on product distribution and properties from HTL of algae major model components. Watanabe et al. [12] found positive effects on oil formation from glucose with the use of an alkali catalyst, formic acid, and cobalt catalyst. Biller et al. [13] have tested the HTL process of a range of model biochemical components under the following conditions: 350 °C in water, 1 mol/L Na_2CO_3, and 1 mol/L formic acid. The results showed that Na_2CO_3 is favorable for algae with a high carbohydrate fraction, whereas algae with high protein and lipid content are most efficiently liquefied without these catalysts.

Algae contain macromolecular polysaccharides, proteins and lipids. Therefore, examining the catalytic HTL process of polysaccharides, proteins and lipids individually could provide new insights into the catalytic HTL mechanism of algae. In this work, we selected crude polysaccharides and proteins which were extracted from algae and hydrolysis product of lipids (mixtures of fatty acids and glycerol), as the algae major model components for HTL with liquid acid catalysts (acetic acid or sulfuric acid). The effect of acetic acid or sulfuric acid on bio-oil production from HTL of polysaccharides-proteins mixture was also discussed. By evaluating the formation pathways and characteristics of bio-oils under different catalytic control, the results could provide a fundamental basis for catalyst screening in the HTL of algae.

2. Materials and methods

2.1. Materials

We purchased crude polysaccharides and proteins extracted directly from algae and *Chlorella vulgaris* from Shanxi Pioneer Biotech Co., Ltd. The feedstock was milled to obtain a fine powder by passing through 40-mesh. The powder was dried at 100 °C for 24 h prior to use. Oleic acid and glycerol were mixed in a molar ratio of 1:3 representing a model lipid material. All chemicals and reagents were analytical grade.

2.2. Apparatus and experimental procedure

The liquefaction process was performed in a stainless steel autoclave, equipped with an electrically heated furnace, a magnetic stirrer and a temperature controller. In a typical run, the autoclave was charged with 10 g polysaccharides, protein powder, and oleic acid-glycerol mixtures or *Chlorella vulgaris* with 100 mL of sulfuric acid (0.01 mol/L) or acetic acid (0.1 mol/L). The autoclave was sealed, and the reaction was started by heating the autoclave after purging with nitrogen for 5 min. The reaction time was taken from the point at which the reactor reached a set temperature (220, 260, or 300 °C), and maintained for 20 min. The pressure was approximately 1.4 MPa, 3.6 MPa and 8.5 MPa when reaches 220, 260 and 300 °C. After the process, autoclave was cooled down to room temperature. Following liquefaction, the gas products were collected in a gas sampling bag and analyzed by gas chromatography (GC). Then, liquid products were separated by a series of filtration and extraction procedures (Fig. 1). 30 mL of dichloromethane was added before the filtration to extract oil compounds, and another 30 mL of dichloromethane and 30 mL of water was used to wash the solid residue. Dichloromethane (CH_2Cl_2) was added to the filtrate after filtering out the residue and the two phases were separated. The CH_2Cl_2 phase was evaporated at 40 °C under reduced pressure to remove the solvent, and the remaining liquid product was defined as bio-oil. The aqueous phase was vacuum evaporated at 65 °C to remove water and the residue was defined as water-soluble organics (WSOs). The residue was dried at 105 °C for 12 h and then weighed. Each experiment was conducted in duplicate. Average values were reported. Product yield was calculated by the following equations:

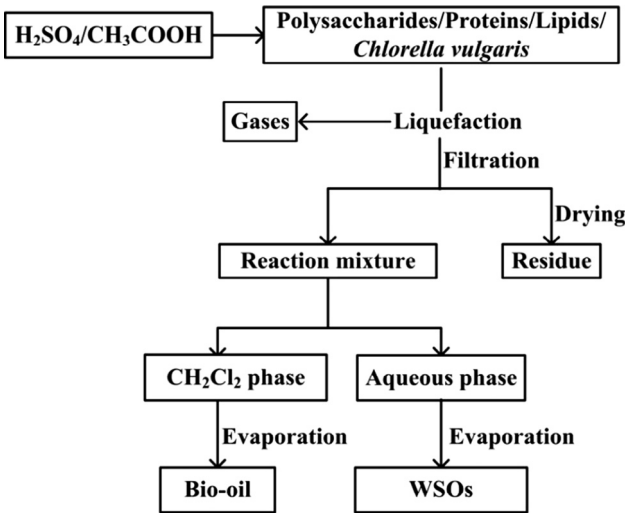

Fig. 1. Scheme of HTL procedure and product separation.

$$\text{Bio-oil yield (wt\%)} = W_{bio-oil}/W_{feed} \times 100\% \quad (1)$$

$$\text{Residue yield (wt\%)} = W_{residue}/W_{feed} \times 100\% \quad (2)$$

$$\text{WSOs yield (wt\%)} = W_{WSOs}/W_{feed} \times 100\% \quad (3)$$

$$\text{Gas yield (wt\%)} = 100\% - \text{bio-oil yield (wt\%)} - \text{residue yield (wt\%)} - \text{WSO syield (wt\%)} \quad (4)$$

2.3. Analysis of bio-oil

Elemental compositions of bio-oils were analyzed by using a CHNO elemental analyzer Flash 2000. HHV of bio-oils was calculated by Dulong formula [14].

GC–MS analysis of bio-oils were carried out using an Agilent 7890A/5975C (Santa Clara, CA, US) with a HP-5 column (30 m × 250 μm × 0.25 μm). The carrier gas was helium with a flow rate of 1.0 mL/min. 1 mL of CH_3OH solution of the sample (0.1–0.2 g/mL) was injected into the column. The injector was set at splitless mode with an inlet temperature of 280 °C. The GC–MS oven temperature was held at 40 °C for 1 min and then risen to 300 °C with a heating rate of 5 °C/min. Compounds were identified by means of the National Institute of Standards and Technology (NIST) library of mass spectra.

Thermal gravimetric analysis (TGA) of bio-oils was performed in nitrogen atmosphere. Samples were purged to a constant weight at