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Catalytic upgrading of pretreated algal bio-oil over zeolite catalysts in supercritical water

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ABSTRACT

We report the catalytic hydrothermal upgrading of pretreated algal bio-oil. The reaction was performed at 400 °C for 240 min with the addition of 6 MPa H_2 and 10 wt.% zeolite catalyst in supercritical water (ρ_{H_2O} = 0.025 g/cm^3). Nine zeolites (Hβ, HZSM-5 (SiO_2/Al_2O_3 = 25:1), HZSM-5 (SiO_2/Al_2O_3 = 50:1), HZSM-5 (SiO_2/Al_2O_3 = 170:1), HY (5% Na_2O), HY (0.8% Na_2O), SAPO-11, MCM-41 (50% Si), and MCM-41 (100% Si) were screened to investigate their effects on the yields of the product fraction and the properties (e.g., elemental composition and heating value) of the upgraded bio-oil. The catalyst type affected the yields of the product fractions: SAPO-11 produced the lowest upgraded bio-oil yield of 42.4 wt.%, and MCM-41 provided the highest yield of 54.5 wt.%. Compared with non-catalytic upgrading reactions, all of the zeolites promoted the denitrogenation, deoxygenation, and desulfurization of the pretreated bio-oil due to the presence of acid sites. HY (5% Na_2O), HY (0.8% Na_2O), and HZSM-5 (SiO_2/Al_2O_3 = 25:1) showed the highest activity toward denitrogenation, deoxygenation, and desulfurization, respectively. The upgraded bio-oil mainly consisted of hydrocarbons, accounting for 80% in total and as high as 95.6% of the fraction below 400 °C.

1. Introduction

As one of the most important types of renewable biomass, microalgae have received increasing attention from both the academic community and industry due to their wide distribution, high photosynthetic efficiency, strong environmental adaptability, and short harvesting cycle. Therefore, microalgae utilization and conversion technology has become a new direction in the field of international renewable energy and a topic of interest for many researchers. To date, the utilization of microalgae has mainly focused on the production of biodiesel [1–4]. However, two major barriers are encountered during the large-scale production of biodiesel from microalgae using the traditional method: the screening and cultivation of algal species with high lipid contents and the required drying and extraction of the harvested algae to obtain the lipid. Therefore, many key technologies are required in addition to the initial investment, energy consumption, and low utilization rate of the raw materials. Thus, the research and development of new methods for the conversion of microalgae to liquid biofuels is a top priority.

Hydrothermal conditions are broadly defined as the use of a water-rich phase above 200 °C in conducting chemical reactions. Hydrothermal conditions are also known as subcritical water (<150–374 °C, 0.4–22.1 MPa) and supercritical water(SCW) (>374 °C, >22.1 MPa). Both types of water are non-toxic and environmentally friendly media with good mass transfer and heat transfer characteristics [5]. The properties of water, such as the density and dielectric constant, can be continuously controlled between gas-like and liquid-like values by varying the temperature and pressure. For example, at a pressure of 25 MPa, the dielectric constant decreases from approximately 78 at 25 °C to 27 at 250 °C and to 2 at 400 °C [5]. This decrease in dielectric constant increases the solubility of small organic compounds. Thus, the polarity of water and hence its ability to dissolve various solids, liquids, and gases that are otherwise insoluble or sparingly soluble can be significantly enhanced by transforming ordinary water into supercritical water. In addition, water at subcritical conditions can act as an acid or base catalyst, whereas supercritical water offers the unique possibility of shifting the dominant reaction mechanisms from free radical to ionic through manipulation of the water's density. However, many potential feedstocks, especially microalgae, have

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very high moisture contents. Therefore, hydrothermal processing of such biomass feedstocks is attractive from an energy perspective. The term "hydrothermal" used here refers to the processing of microalgae in water slurries at elevated temperature and pressure to facilitate the chemical conversion of the organic structures in the microalgae into useful fuels or chemicals. The process is meant to provide a means for treating wet biomass materials without drying and to access ionic reaction conditions by maintaining a liquid water processing medium.

Within the regime of hydrothermal processing, there are two main process groups: hydrothermal liquefaction and hydrothermal gasification. Hydrothermal liquefaction (also known as direct liquefaction), a traditional process, is accomplished at the lower end of the process temperature range (<370 °C) to obtain bio-oil. Hydrothermal gasification is accomplished at the upper end of the process temperature range (<370 °C) and can be considered an extension of the liquefaction mechanisms with subsequent decomposition of large molecules to smaller molecules and eventually to gas. In recent years, reports on the hydrothermal liquefaction of microalgae have increased significantly, and the vast majority has focused on the liquefaction behavior of different types of microalgae and the influence of experimental conditions on the components of the resulting bio-oil [6–9]. However, the bio-oil produced from the hydrothermal liquefaction of microalgae cannot be used directly due to its high viscosity and high N and S contents. Further treatment is required if a fungible transportation fuel is to be produced from this type of crude bio-oil. To date, the upgrading of crude bio-oil produced from the hydrothermal liquefaction of microalgae is rare. Duan and Savage [10] performed pioneering work on the upgrading of crude bio-oil derived from the hydrothermal liquefaction of microalgae in SCW. The SCW reaction medium alone appeared to allow for the complete desulfurization of the crude algal bio-oil, and the abundance of N and O in the treated bio-oils was considerably reduced. Subsequent studies [11,12] have demonstrated that the type of catalyst is the most influential factor affecting the fraction of N- and O-containing compounds and saturated hydrocarbons that remained in the upgraded bio-oil. Moreover, the presence of SCW could effectively reduce coke formation. Duan and coworkers [13–15] performed a series of studies on the upgrading of algal biocrude in SCW. Their results also suggest that the catalyst is a crucial factor significantly affecting the quality of the upgraded bio-oil and the cost of algal biofuel. Compared to expensive noble metal catalysts, inexpensive zeolite (HZSM-5) catalysts have also demonstrated good activities toward the denitrogenation, deoxygenation, and desulfurization of crude algal bio-oil. Furthermore, zeolites can facilitate cracking reactions that will convert the heavier components of the bio-crude into smaller fuel- range molecules [16–20]. Therefore, zeolites are considered potential catalysts for the large-scale production of algal biofuel.

In the present study, a three-stage hydrothermal processing was applied to (a) liquefy dry microalgal biomass to generate crude algal bio-oil, (b) hydro-pretreat the crude algal bio-oil to obtain pretreated bio-oil, and (c) upgrade the pretreated bio-oil to produce upgraded bio-oil. We primarily focused on the third upgrading step, utilizing hydrogen as well, to render a bio-crude with lower N and S contents that is a more suitable feedstock for further refinery upgrading.

The purpose of this study was to screen the activity of nine different potential zeolite catalysts (Hβ, HZSM-5 ($SiO_2/Al_2O_3 = 25:1$), HZSM-5 ($SiO_2/Al_2O_3 = 50:1$), HZSM-5 ($SiO_2/Al_2O_3 = 170:1$), HY (5% Na_2O), HY (0.8% Na_2O), MCM-41 (50% Si), MCM-41 (100% Si), and SAPO-11) for the hydrothermal upgrading of pretreated algal bio-oil. Some of the zeolites used lack long-term stability in a hydrothermal environment, but we did not disqualify any of the catalysts from consideration because of this process-related issue. Rather, we chose to be inclusive of the catalysts because our goal was to determine whether these materials would be effective in short-term upgrading experiments. If a material that lacks long-term stability exhibits promising short-term effects, then additional work can be performed to develop different formulations that are both active and stable. A biocrude produced from the hydrothermal liquefaction of *Chlorella p.* was selected and hydrothermally pretreated with added hydrogen to reduce the contents of N and S, which are potential poisons of the catalyst during processing. The pretreated bio-oil was then used as the feedstock for the zeolite catalyst screening study. The effects of these catalysts on the product yields, bulk properties (e.g., elemental composition and heating value), and molecular characteristics (e.g., molecular constituents and functional group allocation) of the upgraded bio-oil were determined.

2. Experimental

2.1. Materials

Chlorella p. powder was purchased from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (Binzhou, Shandong province, North China). Its proximate and ultimate analysis, along with other properties, is available in a previous publication [15]. All nine zeolite catalysts, including HZSM-5 (SiO_2/Al_2O_3 mass ratios of 25:1, 50:1, and 170:1), MCM-41 (100% Si, 50% Si), Hβ, SAPO-11, and HY (0.8% Na_2O, 5% Na_2O), were provided by Tianjin University, Tianjin, China. All other chemicals were obtained in high purity from Sigma–Aldrich.

Two custom-made, high-pressure, corrosion-resistant batch reactors were used to carry out the hydrothermal liquefaction, pretreatment, and upgrading experiments. The total internal volume of the reactors used for the hydrothermal liquefaction and upgrading was 1000 and 58 mL, respectively. Prior to their use in the experiments, the reactors were loaded with water and seasoned at 400 °C for 4 h to remove any residual organic material and expose the fresh metal walls to SCW water.

2.2. Procedures

2.2.1. Hydrothermal liquefaction

Aliquots of 150 g of algae powder and 400 mL of deionized water were loaded into the 1000 mL reactor. The reactor was heated by an electric jacket with a heating power of 2.5 kW. The mechanical agitator was set at 1000 rpm. The reaction time was the time required for the temperature inside the reactor to reach 350 °C. The highest pressure achieved inside the reactor was 15 MPa. A temperature of 350 °C was selected because it resulted in the highest yield of crude bio-oil from the hydrothermal liquefaction of microalgae [9]. After 60 min, the power was switched off, and the reactor was cooled by the cooling coil contained within. After the reactor had cooled, it was depressurized and opened. Dichloromethane was added to extract the oil fraction and separate it from the aqueous phase. The separated aqueous phase can then be reused as the subsequent reaction medium for the pretreatment of crude algal bio-oil. Next, the extract was filtered, and the dichloromethane in the extract was evaporated using a rotary evaporator. The remaining material was the algal biocrude.

2.2.2. Pretreatment

Biocrude hydrothermal pretreatment was carried out in the 58 mL batch reactor, which is unmixed. Aliquots of 10 g of the algal biocrude and 6 mL of freshly deionized water were loaded into the reactor. The air inside the reactor was displaced by purging the reactor headspace with hydrogen for approximately 15 min. The