Catalytic upgrading of pretreated algal oil with a two-component catalyst mixture in supercritical water

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ABSTRACT

Single-component catalysts present opportunities and challenges for upgrading crude algal bio-oil in supercritical water. Herein, we report the coordination of the action of two heterogeneous catalysts to upgrade pretreated algal oil to a hydrocarbon-rich fuel. The activities of several different catalyst mixtures for hydrothermal hydrodeoxygenation and hydrodenitrogenation of pretreated algal oil at 400 °C for 4 h were determined in a batch reactor. The yield of upgraded oil produced using each catalyst mixture ranged from a low of 63.2 wt.% in the Ru/C + Rh/γ-Al$_2$O$_3$-catalyzed reaction to a high of 77.2 wt.% in the Ru/C + Mo$_2$C-catalyzed reaction. Coke production was controlled in the presence of most of the two-component catalyst mixtures under these hydrothermal conditions. All the two-component mixtures exhibited excellent performance with respect to deoxygenation, denitrogenation, and, in particular, desulfurization. Ru/C + Mo$_2$C, Ru/C + Pt/γ-Al$_2$O$_3$, and Ru/C + Pt/C performed best with respect to deoxygenation, denitrogenation, and desulfurization and produced upgraded oils with O, N and S contents of 0.1, 1.8, and 0.065 wt.%, respectively. The upgraded oil produced with Ru/C + Mo$_2$C retained 89.7% of the heating value of the original pretreated oil and contained 98.5% of the material boiling below 450 °C. The upgraded oils consisted mainly of saturated hydrocarbons, which accounted for no less than 40% of the total peak area for the majority of the oils. Thus, we view the two-component catalyst mixture as a promising strategy for upgrading bio-oils derived from microalgae.

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1. Introduction

Algae are emerging as one of the most attractive feedstocks for the production of biofuels, a promising and environmentally friendly alternative to fossil fuels [1]. Algae typically contain significant amounts of moisture (i.e., up to 85 wt.%) after harvesting. Therefore, aqueous-phase processing (e.g., hydrothermal liquefaction (HTL)) of the biomass feedstock is attractive from an energy consumption perspective because it eliminates the need for a dewatering process [2]. HTL converts algae into an oily or tarry fluid (i.e., crude bio-oil) via reactions in and with liquid water at elevated temperatures (200–350 °C). This crude bio-oil has a calorific value that is twice as high as that of the algal biomass. Unfortunately, the crude bio-oil is typically too viscous to flow at room temperature and contains significant quantities of nitrogen, oxygen, and sulfur [3–5]; thus, it cannot be used directly as a transportation fuel. The nitrogen and sulfur in the crude bio-oil will generate SO$_x$ and NO$_x$ when burned, and therefore these heteroatoms must be removed as part of an upgrading process to produce fungible transportation fuel from this type of crude bio-oil.

Water above its critical point (i.e., 374 °C, 21.8 MPa) is known as supercritical water (SCW). SCW has reduced polarity and a low dielectric constant value, and therefore many weakly polar organics and light inorganic gases, such as H$_2$ and CO, are highly soluble in SCW. This improved solubility can also be beneficial for eliminating interphase transport limitations, allowing in situ extractions of coke precursors, providing longer time periods on stream for processing catalysts, and yielding higher diffusivities than liquids and higher heat transfers than gases [6]. Thus, SCW has great promise for biorefineries and the conversion of biomass to produce biofuels and bio-based chemicals [7,8]. For example, fatty acids can be converted to hydrocarbons in SCW [9]. Pyridine can be denitrogenated to n-butane and n-pentane in SCW [10]. Using SCW to upgrade crude bio-oil may lead to simpler biorefineries because the same reaction medium (i.e., water) can be employed in both the refining and generation processes. Furthermore, SCW alone (i.e., without a catalyst) could desulfurize the crude bio-oil to levels below the detection limit and could also effectively control coke formation [11,12]. SCW with added catalyst effects the same desirable changes as SCW alone but to a greater extent. Several different commercially available materials have been evaluated for upgrading algal crude bio-oil in SCW [4,11–15]. Of the catalysts examined, Ru/C and Raney-Ni have proven to be effective for the deoxygenation and denitrogenation of algal crude bio-oil, respectively [15]. Moreover, a mixture of these

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two catalysts exhibits higher performance with respect to deoxygenation and denitrogenation of algal crude bio-oil than either catalyst alone, implying that upgrading using catalyst mixtures containing two or more components could be a productive avenue for additional research on the upgrading of algal crude bio-oil in SCW. A fixed-bed reactor is typically superior to a batch reactor for enabling crude bio-oil hydrotreatment at a commercial scale. However, "char/coke" formation would likely be exacerbated in the presence of the greater heating rate compared to a fixed-bed reactor. Batch reactors create more stable molecules at hydrotreating temperatures, and the residence time may be more uniform in batch reactors than in flow reactors. Therefore, in the present study, we used a batch reactor instead of a fixed-bed reactor to perform the hydrotreatment experiments.

The objective of the present work was to screen the activity of several different potential two-component catalyst mixtures for upgrading pretreated algal oil in SCW. This study is the first to examine the upgrading of pretreated algal oil in the presence of several potential two-component catalyst mixtures. A crude bio-oil produced from the HTL of Chlorella pyrenoidosa (C. pyrenoidosa) was selected and hydrothermally pretreated with added H_2 prior to use to reduce the content of nitrogen and sulfur, which are potential catalyst poisons during the upgrading process. The pretreated oil was then used as the feedstock in the two-component catalyst mixture screening study. The two-component catalyst mixture was prepared by mixing 5 wt.% Ru/C with 5% Pd/C, 5% Pt/C, 5% Pt/C (sulfide), 5% Pt/γ-Al$_2$O$_3$, 5% Rh/γ-Al$_2$O$_3$, CoMo/γ-Al$_2$O$_3$ (sulfide), MoS$_2$, Mo$_2$C, Raney-Ni, activated carbon, or alumina at a mass ratio of 1:1, respectively. All selected catalysts have been used individually to treat crude algal bio-oil in SCW [15], and most exhibited high performance with respect to the upgrading of pre-treated algal oil. Ru/C exhibited the best performance with respect to deoxygenation and produced an upgraded oil that contained the highest hydrocarbon content, the highest fraction of material boiling below 400 °C, and the highest heating value (45.1 MJ/kg) [15]. Therefore, Ru/C was chosen as the baseline catalyst in the present study. Some of the catalysts that we used lack long-term stability in hydrothermal environments because they are susceptible to sintering (e.g., Ni) or phase transitions (e.g., Al$_2$O$_3$). We did not exclude any catalysts from consideration because of these process-related issues. Rather, we chose to be inclusive of catalysts because our goal was to determine if these materials are effective in short-term liquefaction experiments. A material that lacks long-term stability but exhibits promising short-term effects can be further improved to develop different formulations that are both active and stable.

The effects of these catalyst mixtures on the product yields of the hydrothermal processing of pretreated oil and on the bulk properties (e.g., elemental composition and heating value) and molecular characteristics (e.g., molecular constituents and functional group allocation) of the upgraded oil were determined.

2. Experimental section

2.1. Materials

C. pyrenoidosa, a marine microalga with a lipid content of 19 wt.%, was used. It was cultured in a freshwater pond and obtained from

Shandong Binzhou Tianjian Biotechnology Co., Ltd. (North China). Proximate and ultimate analysis results of the algae are listed in Table 1. The inorganic composition of the microalgae was measured by X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF Spectrometer, and the results are provided in Table 1. The inorganic salts primarily comprised Na, Cl, and Ca, which may affect the product distribution during HTL of microalgae. Inorganic salts have often been reported to have positive effects on the HTL of microalgae [16,17]. Inorganic salts appear to improve liquefaction yields and decrease solid residues. Inorganic salts catalyze the hydrolysis of biomass macromolecules into smaller fragments, which are subsequently degraded into smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. These compounds further rearrange via condensation, cyclization, and polymerization to form the crude bio-oil.

All catalysts were of high purity and obtained from Sigma-Aldrich, except CoMo/γ-Al$_2$O$_3$ (3.4 wt.% Co, 9.5 wt.% Mo), which was obtained from Alfa Aesar. CoMo/γ-Al$_2$O$_3$ was received in a non-sulfided form, which was activated by subjecting it to a solvent mixture of 2 vol.% carbon disulfide and cyclohexane at 300 °C for 4 h. Table 2 provides detailed information on each catalyst. All catalysts were used as received. No catalyst was pre-reduced under H_2 prior to the upgrading experiment because the catalysts were exposed to an oxidizing hydrothermal environment when in use. Freshly deionized water was used in all experiments.

Two custom-made high-pressure and corrosion-resistant batch autoclaves were used to conduct the HTL, pretreatment, and upgrading experiments, enabling the recovery of both the liquid- and gas-phase products in a single run. The total internal volume of the reactors used for the HTL and upgrading were 164 and 58 mL, respectively. Prior to their use in experiments, the two reactors were loaded with water and seasoned at 400 °C for 4 h to remove any residual organic material from the reactors and to expose the fresh metal walls to SCW. The two reactors were heated using a molten salt bath consisting of potassium nitrate and sodium nitrate at a mass ratio of 5:4.

2.2. Procedure

2.2.1. Algal liquefaction

A total of 320 g of algal powder was liquefied in a 164-mL batch autoclave reactor in eight independent runs, producing approximately 128 g of crude algal bio-oil. The operating procedure was nearly identical to that reported previously [15]. In each run, 40 g of dry algal powder and 50 mL of freshly deionized water were loaded into the reactor, which was then sealed tightly. The reactions were conducted at 350 °C for 60 min. The pressure inside the reactor was maintained at 18 MPa. The crude algal bio-oil was extracted with dichloromethane. The dichloromethane in the extract was vaporized using a rotary evaporator to give the crude algal bio-oil. Further details on the extraction process are available in a previous publication [15].

2.2.2. Pretreatment

The crude algal bio-oil was hydrothermally pretreated in the 164-mL autoclave reactor. Thirty grams of the crude algal bio-oil and 16.4 mL of freshly deionized water were loaded into the reactor. The air inside the

Table 1
Proximate and ultimate analyses (wt.%, dry basis) of C. pyrenoidosa.

Proximate analysis					Ultimate analysis				
Volatile matter	Lipid	Fixed carbon	Ash	Moisture	C	H	N	S	O
81.2 ± 1.6	19.3 ± 0.4	16.4 ± 3	9.3 ± 0.2	10.4 ± 0.2	49.6 ± 1.0	7.0 ± 0.2	8.2 ± 0.2	0.5 ± 0.1	25.4 ± 0.5

Inorganic composition (wt.%, dry basis)

Na		Mg		Al		Si		P		Cl
1.17 ± 0.06		0.40 ± 0.02		0.17 ± 0.01		0.89 ± 0.04		0.51 ± 0.03		2.76 ± 0.14
K		Ca		Mn		Fe		Sr		Mo
0.43 ± 0.02		4.44 ± 0.22		0.08 ± 0.01		0.07 ± 0.01		0.21 ± 0.01		0.02 ± 0.00