



Catalytic hydrotreatment of crude algal bio-oil in supercritical water

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ABSTRACT

We report herein on the catalytic hydrotreatment of crude bio-oil, produced from the hydrothermal liquefaction of a microalga (*Nannochloropsis* sp.) over palladium on carbon (5% Pd/C) in supercritical water (SCW) at 400 °C and 3.4 MPa high-pressure H₂. Influences of wide ranges of reaction time (varied from 1 to 8 h) and catalyst loading (varied from 5 to 80 wt%) on treated oil composition and yield, gas products composition and yield, and hydrogen consumption were explored. The C, H and energy recoveries were determined. The results demonstrated that longer reaction times and higher catalyst loadings did not favor the treated oil yield due to the increasing amount of gas and coke products formation but did lead to treated bio-oil with higher higher-heating-value (HHV) (41–44 MJ/kg) than that of the crude feed. Highest HHV of treated oil (~44 MJ/kg) was obtained after 4 h using an 80 wt% intake of catalyst on crude bio-oil. The product oil produced at longer reaction times and higher catalyst loadings, which was a freely flowing liquid as opposed to being the viscous, sticky, tar-like crude bio-oil material, was higher in H and lower in O and N than the crude feed, and it was essentially free of sulfur (below detection limits). Typical H/C and O/C molar ratios ranges for the bio-oils treated at different reaction times and catalyst loadings were 1.65–1.79 and 0.028–0.067, respectively. The main gas-phase products were unreacted H₂, CH₄, CO₂, C₂H₆, C₃H₈ and C₄H₁₀. Overall, many of the properties of the treated oil obtained from catalytic hydrotreatment in SCW in the presence of Pd/C are very similar to those of hydrocarbon fuels derived from fossil fuel resources.

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1. Introduction

Global energy crisis and environmental concerns have motivated more researchers to think about alternatives for fossil derived liquid transportation fuels. Biomass, as a promising alternative due to its high abundance, renewability and carbon neutral, is being paid more attention worldwide. Bio-oil derived from the direct hydrothermal liquefaction of wet biomass, which has lower oxygen content and higher higher-heating-values (HHV) than that of from fast pyrolysis, shows much promise as feedstock avoids the large energy penalty associated with vaporizing the moisture content [1,2]. Of the different biomass candidate for hydrothermal liquefaction, microalgae are very promising feedstock for alternative energy generation because of their higher photosynthetic efficiency, faster growth rate, and higher area-specific yield relative to terrestrial biomass. Moreover, microalgae farming for bio-oil production provide a solution to the food versus fuel debate [3–5]. However, crude algal bio-oils derived from the noncatalytic or catalytic hydrothermal liquefaction of microalgae [7,8] still contain

heteroatoms (O, N, S) which are much higher than the minimum requirement of ASTM [6] and thus further chemical or physical upgrading is needed. Up to now, numerous upgrading strategies that improve crude bio-oil quality and reduce oxygen, nitrogen and sulfur content were reported in the literature, including hydrotreatment (e.g., hydrodeoxygenation, hydrodenitrogenation and hydrodesulfuration), and hydrocracking [9,10]. Of these proposed crude bio-oil upgrading strategies, catalytic hydrotreatment is a promising one which involves the treatment of crude bio-oil with hydrogen in the presence of a heterogeneous catalyst. The main advantage of this technology is that it requires infrastructure which is widely available in all existing petroleum refinery units. However, this upgrading process usually requires high partial pressure hydrogen (up to ~30 MPa) to enhance the intrinsic H₂ solubility in the liquid phase. H₂ solubility in the liquid phase is inversely proportional to temperature, overcoming this solubility limitation at high temperatures often required for hydrotreatment process. One important development in solving this gas solubility problem in liquid phase at higher temperatures is the use of supercritical fluids. With employing supercritical fluids, the H₂ solubility limitation can be potentially improved or eliminated by bringing the feedstock and hydrogen into a single phase. Another advantage of using supercritical fluids is that small tuning in pressure or

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temperature can achieve an optimal combination of liquidlike densities yet gaslike transport properties so that to extract and transport the coke precursors from the catalyst pores to effectively suppress the coke formation and thus extending the life time of catalyst [11].

Since crude algal bio-oil produced from hydrothermal liquefaction will be formed in an aqueous environment, and it may be advantageous from a process engineering perspective to do oil hydrotreatment in that same environment (water). In addition, water is “green”, safe to handle, inexpensive, and environmentally compatible. The critical temperature of water (374 °C) is within the range of temperatures encountered in many oil refinery operations. Furthermore, the tunable properties (e.g., density and polarity properties) of SCW in the critical region have a dramatic impact on the reaction selectivity. Therefore, crude bio-oil hydrotreatment in near- or supercritical water (SCW) may be a path toward crude bio-oil upgrading. There have been previous studies of heavy hydrocarbon treatment in SCW [12–15]. Most of these previous studies, however, usually involved uncatalyzed treatment.

In our previous articles [16,17] on crude algal bio-oil upgrading and upgrading optimization studies in SCW, we treated a crude bio-oil derived from *Nannochloropsis* sp. in SCW to discover how the properties of the treated bio-oil depend on the experimental conditions. These results suggested that the SCW reaction medium alone seemingly provided complete desulfurization of the crude algal oil, and the abundance of N and O in the treated oils was considerably reduced, though some N and O still remained in the treated oils. Upgrading optimization study [17] further indicated that temperature was always the most influential for each of the oil properties examined. The lowest temperature examined (430 °C), regardless of other conditions, appeared to be the best for producing a treated oil with highest hydrogen content and energy density. However, the desirable properties of this treated oil are very close to that of obtained at 400 °C in our upgrading study [16], suggesting that higher temperature would not guarantee to give treated oil with higher hydrogen content and HHV. It is well known that higher temperatures would favor the condensation reactions between aromatics in the treated oil, which can lead to mesophase formation, and consequently coke. In addition, higher temperature will suffer from more energy input penalty. Therefore, from the considerations of carbon “efficiency” and energy conservation, 400 °C might be the more suitable temperature to be selected for further studies on the upgrading of crude algal oil. Of the remaining three factors investigated in the upgrading optimization study, catalyst loading had the greatest effect on the HHV and O/C ratio in the treated oil. Reaction time had the greatest effect on the H/C and N/C ratios. Thus, these two factors in achieving desirable effects on the product oil are very important and should be included in the control factors for the further upgrading studies.

In present study, crude algal bio-oil was hydrotreated in SCW at 400 °C with different reaction times and catalyst loadings. Effect of reaction time (varied from 1 to 8 h) and catalyst loading (varied from 5 to 80 wt%) on the treated oil elemental composition and yield, gas products composition and yield, and hydrogen consumption were examined, respectively. Obviously, catalyst loadings employed in this work sometimes are far greater than the loading typically used for the hydrotreatment reactions. However, our previous study [17] suggested that catalyst loading had the greatest effect on the HHV and O/C ratio in the treated oil. So, rather than refusing to do experiments within the typical catalyst loadings, we opted to increase the catalyst loading beyond the typical scales so as to see the possible highest HHV and lowest O/C ratio in the treated oil. It should be noted that higher catalyst loading is undesirable in view of the economic implication. However, if the catalyst can be recycled, large catalyst loading amount is not a problem. Previously, we used Pt/C as the upgrading catalyst and found

that it had desirable effects on the product oil. In comparison, in this study, we use Pd/C as the hydrotreatment catalyst instead of Pt/C, because previous study [18] suggested that Pd/C catalyst is more active than Pt/C on the deoxygenation of fatty acids.

2. Experimental

2.1. Materials

Microalga (*Nannochloropsis* sp.) paste was purchased from Reed Mariculture (*Nannochloropsis* 3600™). Our earlier articles gave its elemental and chemical composition along with other properties [7,8]. The Pd/C catalyst (5 wt% Pd, metal dispersion = 21%, specific surface area = 863 m²/g, micropore volume = 0.255 cm³/g, average particle size = 25 μm) was purchased from Sigma–Aldrich. Both the alga and the catalyst were used as received. Freshly deionized water, prepared in house, was used throughout the experiments. Helium, hydrogen, and argon were obtained from Cryogenic Gases. Gas standards for quantitative analysis were purchased from Air Liquide Specialty Gases. The 400 ml autoclave used for the production of crude bio-oil from the hydrothermal liquefaction of microalgae and the 316-stainless steel batch reactors used for the catalytic hydrotreatment were employed as described in our previous article [16].

2.2. Procedures

2.2.1. Liquefaction experiment

We generated about 12 g of crude bio-oil which resulted in a yield of 34% on the dry microalga base by liquefying 150 mL of the microalga paste in the autoclave reactor. The procedure was nearly identical to that reported previously [16]. In the present experiment, air instead of H₂ was charged to prevent the water from vaporizing during the reaction. The dichloromethane in the filtrate was vaporized by using high pressure (140 kPa) nitrogen at room temperature in a fume hood instead of by using a rotary evaporator at 30 °C under vacuum in the previous study [16]. It should be noted that the relative proportion of liquid products from the liquefaction of microalgae was dependent on the heating rate, however, variations in the heating rate did not significantly affect chemical composition of the liquid products [19].

2.2.2. Upgrading experiments

The catalytic hydrotreatment experiments were carried out in a stainless-steel batch mini reactor. The whole procedure was almost identical to our previous publication [16]. In the present study, 0.4 ml of freshly deionized water was added into the reactor. The air inside the reactor was displaced with helium by repeatedly applying vacuum (–86 kPa) and charging with 140 kPa He. The reactor was next pressurized to 140 kPa (gauge) with helium and then further charged with hydrogen to 3500 kPa. After the reaction, the reactor was cooled in a refrigerator for 30 min, it was then placed in ambient conditions for at least 15 h to allow the liquid–gas system to reach equilibrium prior to performing the gas-phase analysis. The dichloromethane in the separated filtrate was evaporated by using small-pressure (70 kPa) nitrogen at room temperature in fume hood.

The treated oil yield was calculated as its mass divided by the mass of crude bio-oil loaded into the reactor. After filtration, the filter paper together with the remained solid residue were dried at 110 °C for 12 h in an oven and then weighted. The solid weight was calculated by using the overall weight subtracted the weight of filter paper. The non-catalyst solid residue was defined as coke whose amount was evaluated by subtracting the weight of catalyst from the residue, and its yield was calculated as its mass divided by the mass of carbon loaded into the reactor. It should be noted that the

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