Algal Research 13 (2016) 53–68

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Effect of low temperature hydrothermal liquefaction on catalytic hydrodenitrogenation of algae biocrude and model macromolecules

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ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form 11 November 2015
Accepted 15 November 2015
Available online xxxx

Keywords:
Algae
Fuels
Heteroatoms
Hydrothermal liquefaction
Catalyst
Hydrodenitrogenation
Hydrodeoxygenation

ABSTRACT

Staged, low and high-temperature subcritical liquefaction were used to pretreat algae and generate a biocrude primarily characterized by free fatty acids and unsaturated hydrocarbons with reduced nitrogen heteroatom levels. Subsequently, catalytic hydrodenitrogenation and deoxygenation (HDN/HDO) was conducted using ruthenium (5% Ru/carbon) and cobalt molybdenum catalysts. Ru on carbon was the most effective HDO catalyst and generated the lowest level of nitrogen and heteroatoms in the resulting oil. A CoMo-S catalyst generated higher nitrogen and heteroatom levels, and resulted in a higher TAN value and lower heating value, probably due to the low sulfur levels in the biocrude. The highest quality oil was generated from a raceway strain using Ru/C and HTL pretreatment (225 °C, 15 min) with a repeated batch HDN/HDO step (3.24% N, 8.2% O, TAN of 12, 1.25% water, HHV 40 MJ/kg) and had a boiling point range of ~20% kerosene, ~30% distillate fuel oil, and ~50% gas oil. A 57% reduction in nitrogen content of the oil was realized when repeated HDN/HDO was coupled with HTL pretreatment using Ru/C (4.3 wt.%N), relative to 7.5%N for single stage HTL/HDO. Final yields for the highest quality oil generated via the coupled HTL/HDO process ranged from 15 to 22%. Recovery and reuse of the catalyst (Ru/C) resulted in a significant decline in activity potentially caused by coking and metals deposition.

1. Introduction

Algae have proven to be a viable biomass feedstock for conversion to fuel intermediates due to their high energy content and ability to grow autotrophically using carbon dioxide and sunlight. Hydrothermal liquefaction (HTL) of wet algae results in 29% higher bio-oil yield and 32% more energy recovery relative to other methods [1,2]. Past studies indicate that HTL bio-oil is more energy dense and shows higher thermal and oxidative stability than bio-oil produced from biomass pyrolysis [1,2]. HTL is performed using hot compressed water, since it is a highly reactive medium as it approaches its critical point (374 °C, 22.1 MPa) due to changes in properties such as acidity, solubility, density, dielectric constant and reactivity. The resultant bio-oil is a dark viscous liquid with an energy value 70–95% of that of petroleum fuel oil [3–5]. Under subcritical conditions, the hydrothermal liquefaction of algae yields multiple products from the hydrolysis/depolymerization of the algae macromolecules. These products include long-chain fatty acids (e.g., oleic acid), nitrogenated and oxygenated heterocyclics (e.g., pyrrolidine, phenol), and some long-chain hydrocarbons (e.g., pentadecane) [6]. Thus, HTL converts organic constituents of algae into a liquid bio-oil that in theory can be refined to diesel-like fuels via heteroatom removal mechanisms such as decarboxylation, decarbonylation, denitrogenation, and hydrodeoxygenation. The upgrading of HTL products such as amino acids, fatty acids, and carbohydrates has been investigated, yet there has been little research on catalytic conversion on mixtures of these molecules and the impact of nitrogen heteroatoms on catalytic upgrading [4,7–9].

However, due to the large amount of protein present in algae biomass, bio-oil or biocrude has a large abundance of nitrogen heterocyclic compounds, which can cause problems in catalytic upgrading. Nitrogen has been shown to poison and deactivate biocrude upgrading catalysts [10,11]. The nitrogenated compounds present in the bio-oil include nitrogen heterocyclics (pyridine, pyrrole, pyrrolidine, piperidine, and indole) and non-heterocyclics, such as, open-chain amines and amides (hexadecanenitrile, and hexadecanamides) [2,3,6,12,13]. Also, the presence of polypeptides and proteins leads to the high molecular weight compounds in the bio-oil in the range of 2000–10,000 g mol^{-1} [14]. These nitrogenated compounds can negatively affect catalytic activity and coupled with an abundance of oxygen in the biocrude, makes it unsuitable for co-processing with petroleum oil. Thus, it would be beneficial to create a biocrude low in nitrogen content and heteroatoms.

The catalytic processing units associated with petroleum refining have been tailored to low total acid number (TAN) and heteroatom levels in crude oil — typically, 0.3–6.6 mg of KOH/g or TAN, 2–8000 ppm nitrogen, and 0.4–4.5% sulfur [15–17]. Thus, given the high levels of free fatty acids and nitrogen in algae biocrude, fuel production or co-processing in a petroleum refinery requires heterogeneous catalytic hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN). Bai

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http://dx.doi.org/10.1016/j.algal.2015.11.009
2211-9264/

et al. [18] performed a catalytic screening study in which algae oil generated from the liquefaction of *Chlorella* (350 °C, 60 min) was subjected to a two-stage upgrading process — a high-temperature upgrading stage using hydrogen gas without catalyst (350 °C, 4 h) and supercritical upgrading stage using hydrogen gas with varying types of heterogeneous catalysts (400 °C, 4 h; 10 wt.%). Their work demonstrated that ruthenium on carbon (5 wt.%) and Raney nickel produced the best results. The two-stage process reduced the nitrogen content of the bio-oil from 8.0 to 2.0 wt.%. Duan and Savage [19] conducted a study on the effect of temperature (430 to 530 °C), time (2 to 6 h), and catalyst (Mo_2C, HZSM-5, or Pt/C) loading (5 to 20 wt.%) on algae bio-oil quality. This work indicated that high reaction temperatures (530 °C), long contact times (6 h) and high catalyst loading (10–20%) correlated with reduced nitrogen level (~5% to 1.5–2.5%N). The HDO temperature of 530 °C generated the lowest nitrogen content oil, yet higher amount of gas and coke phases.

This study was designed to determine if low temperature HTL (LT-HTL), followed by a higher temperature HTL, could be used to reduce nitrogen heteroatoms and then coupled with catalytic HDO/HDN to generate a refinery quality bio-oil. Performing a two-stage HTL process is a novel approach to minimize N and nitrogen heteroatoms in the HTL bio-oil. In theory it is possible to extract protein fractions from the biomass by a first stage low temperature HTL process, and separate the nitrogen rich aqueous fraction and then liquefy the remaining fractions to generate a bio-oil product via a second stage HTL step [20–22]. The nitrogen rich fraction in the aqueous phase from the pretreatment step can be recycled for algae cultivation, as indicated in recent studies [22–24]. Additional advantages of integrating nitrogen recovery with LT-HTL include a potential reduction in inhibitory compounds (e.g., phenolics, pyridines, carboxylic acids) and the resultant aqueous phase is sterile (contaminating microorganisms and viruses are eliminated). Moreover, LCA and process simulations of algae production indicate that scale-up of algae to liquid fuel processes is not sustainable without nitrogen and water recycling as part of an integrated design [25]. To the best of our knowledge the impact of nitrogen heteroatom reduction via a low temperature HTL step on catalytic HDO/HDN of algae bio-oil has not been studied.

2. Experimental methods

2.1. Materials

Freeze-dried *Spirulina platensis* was obtained from Earthrise Nutritionals LLC (Calipatria, CA), and *Nannochloropsis* sp. was obtained from Reed Mariculture ("Nanno 3600", strain CCMP525). A consortium of three algal strains (UGA Consortium, henceforth), namely *Chlorella sorokiniana*, *Chlorella minutissima*, and *Scenedesmus bijuga*, were grown and harvested for use in this study as well. Ruthenium (5 wt.% on carbon, 20 μm particle size, Ru/C) was obtained from Sigma-Aldrich (MO, USA). A cobalt oxide (3.4–4.5%) molybdenum oxide (11.5–14.5%) on alumina (Al_2O_3) catalyst (2.5 mm trilobe, CoMo) was obtained from Alfa Aesar (MS, USA). The CoMo/Al_2O_3 catalyst was reduced in the presence of flowing hydrogen (100%) at 400 °C in a tubular packed bed reactor (1 in. ID); 100 mL min^{-1} of hydrogen gas was passed over the catalyst for 2 h (CoMo-H_2). In addition, pre-sulfided CoMo/Al_2O_3 catalyst (2–7% CoS and 5–25% MoS, trilobe 2.5 mm, CoMo-S) was obtained from EureCat (EU). A mixed metal oxide catalyst (Red Mud) was obtained from Rio Tinto (Alcan, Canada). This catalyst was dried (105 °C), crushed, and sieved ($0.5 < dp < 2$, mm). The red mud particles were reduced in the presence of flowing hydrogen (100%) at 300 °C in a tubular packed bed reactor (1 in. ID); 90 mL min^{-1} of hydrogen gas was passed over the catalyst for 20 h (RRM).

The Ru/C catalyst was selected due to its high activity for hydrodenitrogenation and deoxygenation activity of algal oil relative to a range of other catalysts [18]. CoMo metal catalyst was used given its reported HDO activity and hydrogenation of fast pyrolysis oil, vegetable oils, and free fatty acids [26,27] (Parapati et al., 2014; Harnos et al., 2012) and for bi-metallic catalyst HDO activity in the presence of sulfur for algal oil [28] (Guo et al., 2015). It has been reported in the literature that CoMo sulfidation via sulfur in the feed can activate the material (i.e., form CoMo-S) leading to HDO activity, although the activity is lower than if pre-sulfided catalyst is used [29] (Viljava et al., 2000). Thus, it was of interest to determine if sulfur in algal HTL feedstock would activate the catalyst and thus eliminate the need to supplement the feed with a source of sulfur. Red mud and iron catalysts have been demonstrated to hydrotreat vacuum residue [30], hydrocrack algae [31], and deoxygenate fatty acids [32]. We anticipated the lower activity due to the presence of other minerals in red mud, but were interested to determine if its activity was high enough to consider using it as pretreatment step (partial reduction in nitrogen and some cracking of triglycerides) before co-processing. Also, it has been reported that red mud self-activates for hydrogenation activity, via thermal cracking, release of sulfur, and sulfidation [30] (Nguyen-Huy et al., 2012).

2.2. Algae growth

A consortium of three algal strains (UGA Consortium, henceforth), namely *C. sorokiniana*, *C. minutissima*, and *S. bijuga*, were grown and harvested at The University of Georgia (USA). A monoculture inocula of the constituent strains were first grown in 20 L carboys under controlled conditions in a growth chamber at 25 ± 1 °C for 12 h with alternating light–dark cycles; the light intensity was 100 μmol m^{-2} s^{-1} 1 with continuous air bubbling. The final consortium was prepared by mixing equal proportions (v/v) of each individual strain and then using it as inoculum at 10% v/v for outdoor cultivation in raceway ponds under green house facilities at an algae bioenergy lab at the University of Georgia (UGA). The raceway ponds are constructed of HDPE plastic and are 1.32 m wide, 2.18 m long, and 0.61 m deep with a working volume of approximately 500 L at 0.17 m water depth. Standard algae growth medium BG 11 was used in fresh water for cultivation [33] Supplemental CO_2 was derived from a commercial 10% CO_2 storage cylinder and used as a carbon source and for pH control. The UGA designed carbonation column [33] was used for CO_2 mass transfer. Once the cell density in raceways reached 500 mg/L, the biomass was harvested using a continuous centrifuge and dried at 55 °C until constant weight was observed after multiple weighing. The dried biomass was packed in zip-lock bags and stored at 4 °C until further use. Subsequently, the dried microalgae was ground to a fine powder using a heavy-duty laboratory knife mill (Retsch SM 2000, Germany) with a screen size of 0.5 mm. The knife mills cutting blade rotor (1690 rpm, 60 Hz) was powered by a 1.5 kW electric motor.

Algal biomass, solid residues, HTL bio-oil, and HDO samples were analyzed for elementals C, H, N, S, and O (ultimate analysis) using a Flash 2000 organic elemental analyzer (Thermo Scientific) following methods outlined in ASTM D 5291. The analyzer was calibrated using BBOT or 2,5-Bis (5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (C—72.59%, H—6.06%, N—6.54%, O—7.42%, and S—7.43%) as the standard material. Atomic ratio and empirical formula of raw feedstock and the biocrudes were derived from the elemental results. Higher heating values (HHV) of solid and biocrude samples were measured using an isoperibol bomb calorimeter Model 1351 (Parr Instruments Co., Moline, Illinois) following ASTM D 5865 and D 4809 standard methods.

Carbohydrate content of the algal biomass was measured using the DuBois method [34] (DuBois et al., 1956), protein content was estimated by multiplying the elemental N content by a factor of 4.58 [35], and lipid content was measured by gravimetric method using an ANKOMXT10 automated extraction system (ANKOM Technology, Macedon, NY) where hexane was used as the extraction solvent. The