



Research article

Upgrading of hydrothermal liquefaction biocrude from algae grown in municipal wastewater



Zhouhong Wang^a, Sushil Adhikari^{a,*}, Peter Valdez^b, Rajdeep Shakya^a, Cassidy Laird^c

^a Biosystems Engineering, Auburn University, Auburn, AL 36849, USA

^b Algae Systems, LLC, Daphne, AL 36526, USA

^c Biosystems Engineering, Clemson University, Clemson, SC 29634, USA

ARTICLE INFO

Article history:

Received 14 July 2015

Received in revised form 2 October 2015

Accepted 5 October 2015

Available online xxxx

Keywords:

Algae

Hydrothermal liquefaction

Hydrotreating

Isoparaffin

ABSTRACT

Algae biocrude was treated with hydrogen using metal catalysts supported on activated carbon for the production of biofuel. The biocrude was produced using hydrothermal liquefaction of microalgae (*Scenedesmus*-dominated polyculture) grown in municipal wastewater. Four metal catalysts (platinum, ruthenium, nickel and cobalt) were tested at 350 °C under the presence of high pressure hydrogen, and all the experiments were conducted at a weight hourly space velocity of 0.51 g/g_{cat}·h. Hydrotreating with all the catalysts increased higher heating value, while reducing viscosity and total acid number (TAN) of the biocrude. For example, biocrude upgraded using platinum catalyst increased the heating value from 45.9 to 47.0 MJ/kg and reduced the TAN from 11.56 to 0.1 mg KOH/g. In addition, the liquid produced was colorless. Furthermore, the use of ruthenium and platinum catalysts greatly enhanced the yield of hexadecane and octadecane in the hydrogen-treated liquids whereas heptadecane was less favored. Overall, hydrogen treatment of biocrude was effective in improving the quality of biocrude produced from algae grown in wastewater. The BET surface area was reduced for all the spent catalysts. An SEM-EDS analysis revealed that some liquid products and sulfur were deposited in the spent catalysts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Due to environmental concerns associated with the use of fossil fuels, national energy security and rural economy development, bio-based economy is attracting more interest around the globe. Microalgae, as a third-generation source of biofuel, has the advantage of high photosynthesis efficiency, high growth rate, high energy yields per unit area and is non-competitive to crop lands [1,2]. In addition, microalgae could produce lipids and high-value chemicals, which further increases its value [3–5]. Although the environmental impact of microalgae could be larger than certain terrestrial crops (e.g., corn, canola, and switchgrass) due to the excess use of water, the problem can be offset by utilizing flue gas (carbon dioxide) and wastewater from cities and municipalities to grow algae [2].

A number of thermochemical processes exist for the conversion of microalgae to biofuels. For example, pyrolysis of microalgae produces bio-oil yields ranging from 17.5% to 71% with the higher heating value (HHV) up to 41 MJ/kg [6–11]. However, conventional thermochemical conversion methods such as pyrolysis and gasification typically need dry feedstocks [12,13] for the production of liquid fuels or synthesis gas (or syngas). To avoid the need of drying energy, wet-conversion

methods like hydrothermal liquefaction (HTL) have become favorable for biomass that has high moisture content such as microalgae [14].

An HTL process uses high temperature and compressed water as reaction medium, reactant, and catalyst [15,16]. HTL of microalgae typically produces a dark mixture (biocrude) of phenol, hydrocarbons (alkanes, isoalkanes, aromatics), fatty acids, carbonyl-containing compounds and nitrogen-containing compounds along with a gas mixture of CO₂, H₂, CH₄ and lesser amounts of C₂H₄, C₂H₆ and some solid residues [17,18]. Although the HHV of HTL biocrude can be as high as 39 MJ/kg, its high oxygen, nitrogen and sulfur contents prevent it from being directly used as a liquid fuel [1,12,18–22]. Thus, further upgrading of this biocrude has become essential for the production of transportation fuel.

Catalytic hydrotreatment is a promising method to convert biocrude into fungible or “drop-in” fuel utilizing heterogeneous catalysts such as ruthenium, cobalt, nickel and molybdenum on different supports [23–26]. Hydrothermal liquefaction and in-situ upgrading have also been performed using catalysts such as nickel, ruthenium, platinum, and activated carbon, in which researchers have reported reduced elements (O, N and S) and viscosity, increased gasification efficiency, increased H/C ratio and alkanes production [1,27–35]. A number of HTL biocrude upgrading studies were performed in a supercritical water environment [28–30,32], while a handful studies [36–39] used hydrocarbon solvent (e.g. dodecane) in upgrading model compounds (e.g.

* Corresponding author.

E-mail address: sushil.adhikari@auburn.edu (S. Adhikari).

stearic acid). One of the challenges with HTL biocrude is extraction of organic phase from the reactor, and its handling because of high viscosity. The addition of solvent makes easier to extract organic phase of biocrude and handling during upgrading. In a commercial scale, upgraded fuel can be used as solvent instead of isoparaffin as used in this study. In addition, the complexity of biocrude can potentially lead to different reactions than model compounds so the study was conducted to upgraded biocrude in the presence of solvent, which has never been done before. It is expected that this study will fill the gap in the field of HTL biocrude upgrading in an environment of hydrocarbon solvent using heterogeneous catalysts for the production of transportation fuel, while upgrading of HTL biocrude using typical refinery process is still an important topic for bench-scale investigation.

2. Materials and methods

2.1. Hydrothermal liquefaction of algae for biocrude

Hydrothermal liquefaction of algae was performed at Algae Systems, LLC (Daphne, Alabama, USA) using their proprietary process, and was shipped to Auburn University (Auburn, Alabama, USA) for upgrading work. The microalgae was grown in a closed photobioreactor floating in Mobile Bay (Daphne, Alabama, USA). The photobioreactor was made of two plastic sheets welded together to make a closed container, and it was roughly 2 m wide and 21 m long (approximately 8000 L in volume). The photobioreactor was filled with primary effluent from a municipal wastewater treatment plant in Daphne, Alabama and 800 L of inoculum of *Scenedesmus* sp. After a growth period of at least four days, the algae was harvested from the photobioreactor and was concentrated to a slurry with 4.5 wt.% solids content. Biocrude was produced by hydrothermally processing the concentrated slurry at 300 °C in a pilot-scale continuous-flow reactor with a 2.1 gpm (gallon per minute) flowrate. The residence time of the reagent stream at the reaction temperature was approximately 6 min. After the reaction, the biocrude was extracted from the other HTL products using isoparaffin (Soltrol® 125 Chevron Phillips, a transparent mixture of C₉–C₁₁ isoalkanes and on-road diesel). The HTL biocrude in isoparaffin had dark green/brown color inherited from the algae HTL liquid, and had 13 wt.% of biocrude in the mixture.

2.2. Catalyst preparation

Four catalysts (Pt, Ru, Ni and Co) were tested in this study, and their loading for all the catalysts was 5 wt.% on activated carbon support. Platinum (product No. 205931) and ruthenium (product No. 206,180) supported on activated carbon were purchased from Sigma-Aldrich (St. Louis, Missouri) and used as received. Nickel and cobalt catalysts were prepared by impregnating their 2.5% nitrate solutions on activated carbon powder (Supelco, product No. 31616, purchased from Sigma-Aldrich). The amounts of nickel and cobalt nitrate solutions impregnated were adjusted to ~5 wt.% of activated carbon on metal basis. The slurry (metal nitrate and activated carbon) was shaken on a shake-bed overnight (50 °C, 180 RPM) and moved to an oven for drying. The slurry was dried at 72 °C for 24 h to remove excessive water from the catalysts and then increased to 105 °C for 24 h to completely dry them. The dried catalysts were stored in a desiccator until they were used. The catalysts were used without any prior calcination as done in another published document [40]. Direct calcination and reduction of catalysts were performed right before the experiments.

2.3. HTL biocrude upgrading

Upgrading experiments were carried out in a 450 mL Parr reactor equipped with a glass liner, controllable stirrer and heating mantle. The actual reactor volume was 400 mL once the volume of liner and stirrer was subtracted. Ultrahigh purity grade hydrogen gas (99.999%) was

used for all the experiments in this study. In each experiment, 3.6 g of catalyst was reduced under 1000 psig of hydrogen for 1 h at 300 °C right before use. Once the reduction of the catalyst was complete, the reactor was carefully loaded with approximately 55 g (or 72 mL) of biocrude in isoparaffin and heated to 350 °C for 4 h. All the experiments were conducted at a weight hourly space velocity (WHSV) of 0.51 g_{oil}/g_{cat}·h, which was calculated according to Eq. (1). The temperature and pressure profiles during the hydrotreating/upgrading experiments can be found in the supplementary material (Fig. S1).

$$\text{WHSV} = \frac{13\% \times \text{Weight of biocrude in isoparaffin (g}_{\text{oil}})}{\text{Weight of catalyst (g}_{\text{cat}}) \cdot \text{Reaction time (h)}} \quad (1)$$

After the experiment, the reactor was cooled to ~5 °C using an ice-water mixture to stop any further reaction. Product gas from the reactor was collected when the reactor slowly went back to ~19 °C (room temperature). Mass of the reactor, liner, catalyst and product was recorded before and after each experiment. Reacted mixture remained on rotor and the cap of the reactor was wiped off with a paper towel and the amount of that oil was added into the final mass of the liquid. Pressure and corresponding temperature during the experiments were also recorded to determine hydrogen consumption.

Upgraded liquid mixed with catalyst was centrifuged (model Dynac 0101, Becton, Dickinson and Company, Franklin Lakes, New Jersey) at 2700 rpm for 10 min to separate catalyst from the liquid. The liquid was then filtered using a 0.2 μm syringe filter and used for all the analyses. The catalyst separated after centrifugation was washed with toluene (>200 mL), filtered and dried with air to determine the amount of catalyst left after the reaction. Toluene used for washing catalyst was removed using rotary evaporator, and the amount of liquid collected after washing catalyst was recorded. All experiments were performed in duplicates.

2.4. Analysis of products

2.4.1. Yield of products

Due to the complexity of the biocrude and product mixture, we use mass loss as an indication of material loss (or eliminated, e.g. by gasification) during the experiments. The mass loss after hydrogen treatment was calculated using Eq. (2).

$$\text{Weight loss\%} = \left(1 - \frac{W_f - W_{c+1}}{W_{ca} + W_l}\right) \times 100\% \quad (2)$$

where,

W_f	the mass of reactor vessel with product, catalyst, and glass liner.
W_{c+1}	the mass of reactor vessel and glass liner before the reaction.
W_{ca}	the mass of catalyst added for the reaction.
W_l	the mass of HTL solution added for the reaction.

Hydrogen consumption and pressure change were all calculated at a temperature of 20 °C. The data recorded were first adjusted to the condition of 20 °C using ideal gas law before calculation. The pressure change was calculated based on Eq. (3).

$$\text{Pressure change\%} = \frac{P_f - P_0}{P_0} \times 100\% \quad (3)$$

where,

P_f	is the final pressure adjusted to 20 °C by the ideal gas law.
P_0	is the initial pressure adjusted to 20 °C by the ideal gas law.

2.4.2. Liquid product

Liquid product after centrifugation was characterized for absorption (using UV-Vis), water content, viscosity, higher heating value (HHV),

Download English Version:

<https://daneshyari.com/en/article/6656705>

Download Persian Version:

<https://daneshyari.com/article/6656705>

[Daneshyari.com](https://daneshyari.com)