Algal Research 26 (2017) 131–134

Contents lists available at ScienceDirect

Algal Research

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

Influence of process conditions and interventions on metals content in biocrude from hydrothermal liquefaction of microalgae

Jimeng Jiang, Phillip E. Savage*

Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, United States.

ARTICLE INFO

Keywords:
Microalgae
Catalyst
Biocrude
Hydrothermal liquefaction
Metal
Demetallation

ABSTRACT

We determined how different reaction conditions influence the metals contents in biocrude oil and other product fractions from hydrothermal liquefaction (HTL) of microalgae. We then assessed the effect of using different solvents for biocrude recovery and adding catalysts on the metal content in the biocrude. The Fe content was lower and the Na content higher in biocrude produced at higher temperature (400 vs 350 °C) and longer holding time (60 vs 3 min). The Fe and Na contents were reduced over 50% and 95%, respectively, by use of methyl tert-butyl ether (MTBE) rather than dichloromethane as the organic solvent for biocrude recovery and they were reduced over 98% via additional application of a supported Ni catalyst during HTL. This work demonstrates that the hydrothermal treatment conditions influence the metal content in biocrude and that judicious selection of solvent and catalyst can lead to significant reduction in the metal content in biocrude.

1. Introduction

Hydrothermal liquefaction (HTL) has emerged as a preferred method for converting microalgae into a crude bio-oil. HTL uses hot, compressed water to break down the algae biomolecules. The biocrude is a potential petroleum replacement [15], but there remain several barriers. One such barrier is the presence of high concentrations of metals in the crude bio-oil.

Several reports provide the metal content of algae HTL biocrude for a specific set of HTL conditions [8,12]. Fe and Na are the most abundant metals. While sodium can be largely removed by a desalter in the refinery, iron is more difficult to remove. In a petroleum refinery, iron could deposit on and deactivate catalysts, thereby reducing yields of liquid products [13]. Anastasakis and Ross [2] focused on the distribution of Ca, Mg, Na, and K in different product fractions. Most of the potassium and sodium was in the aqueous phase, while most of the calcium and magnesium was in the solid residue.

Iron supplied from the culture media is mostly in the form of dissolved chelated complexes, primarily bound to ethylenediaminetetraacetic acid (EDTA). These compounds are much more stable than inorganic iron salts, and are able to serve as trace metal buffers [3]. Iron could also be present in harvested microalgae slurry as a result of flocculation processes employed. Iron in microalgae can be present in the form of heme, a ferrous-containing porphyrin, or Fe-sulfur clusters in a variety of metalloproteins that are involved in different metabolic pathways [10]. Some microalgae contain ferritins for Fe storage that are located in plastids. Jarvis et al. [7] characterized post HTL algal biocrude and identified numerous iron-containing porphyrins.

To date, there have been no reports on how the HTL processing conditions influence the metal content in the biocrude. That the conditions might have an influence is suggested by prior work where supercritical water (SCW) treatment has been shown to remove metals, such as nickel from porphyrin structures, even in the absence of catalyst and added hydrogen [9]. Additionally, there have been no reports on the metal content in algae biocrude produced via fast HTL [5], an emerging and more rapid approach for converting microalgae to biocrude.

Of course, manipulating HTL processing conditions may not alone be sufficient to produce biocrude that can be processed via existing refinery technology. The literature on both petroleum demetallation and on algae treatment provides some guidance, however, regarding process options and interventions that might be profitably explored to reduce metal content in biocrude even further. The most abundant metals in petroleum crude oil, nickel and vanadium, are also generally present in the form of porphyrins [1]. Physical methods (e.g., distillation, solvent extraction), chemical methods (e.g., visbreaking, delayed coking), and catalytic methods (e.g., hydroprocessing) can be applied for demetallation [1].

Wang et al. [17] showed that catalytic hydrotreatment of HTL algae biocrude (separated from the HTL mixture with isoparaffin) led to the accumulation of Fe on the carbon-supported metal (Pt, Ru, Ni, Co) catalysts. The goal of this study was not metal removal, however, so this

* Corresponding author.
E-mail address: psavage@psu.edu (P.E. Savage).

http://dx.doi.org/10.1016/j.algal.2017.07.012
Received 9 March 2017; Received in revised form 10 July 2017; Accepted 11 July 2017

result was largely mentioned in passing and noted simply as an observation. Wang et al. [16] showed that washing algal biomass with water and extracting oils from algae with different organic solvents can have a very large impact on the metal content in the algal oil.

Using this previous literature as a guide, we explore herein the influence of different hydrothermal processing conditions, different solvents for biocrude recovery, and different heterogeneous catalysts on the metal content in biocrude produced from HTL of microalgae.

2. Experimental methods

2.1. Chemicals and materials

Nannochloropsis sp. algae was provided by Sapphire Energy Inc., as a dried powder with 17.6 wt% ash content. Preservative-free algae paste (Nanno 3600) was purchased from Reed Mariculture Inc., and it had a 5.9 wt% ash content. Both feedstocks were used as received. Dichloromethane (DCM), methyl tert-butyl ether (MTBE), 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK), and ethylene glycol butyl ether (EGBE) were obtained from Sigma-Aldrich with over 99% purity. γ-Alumina and activated charcoal were obtained from Sigma-Aldrich as powders and used as received. Cobalt molybdenum oxide supported on alumina (3.4–4.5% cobalt oxide, 11.5–14.5% molybdenum oxide) was purchased from Alfa Aesar and ground into powder before use. Nickel on silica-alumina (66 ± 5% nickel) and aluminum silicate were purchased as powders from Alfa Aesar and used as received. A standard for quantifying metals (S-21 + K oil) and Elemental Blank Oil was purchased from Conostan Division, Continental Oil Company. The standard comprises 22 elements (at 500 ppm each), which include all the metals in algal biocrude. 1000 μg/mL iron and sodium standards in 2% HCl were purchased from High-Purity Standards.

Batch mini-reactors with 4.1 mL internal volume were fashioned from 1/2-inch stainless steel Swagelok tube fittings (a port connector and two caps).

2.2. HTL procedure

We loaded the reactors such that each contained a 15 wt% solids (balance water) algae slurry. The total water loading was such that it would occupy 95% of the reactor volume at 350 °C (for reactions done at that set point) or provide a pressure of 40 MPa at 400 °C (for reactions done with higher set point temperatures). We loaded the heterogeneous catalysts and supports in the amounts required to achieve 25 wt% loading relative to the biomass on a dry ash-free basis. We used this high loading here simply to determine whether the methods chosen are effective. Future work will examine the effect of catalyst loadings. One reactor loaded with just deionized water also contained a thermocouple. This unit served as a proxy reactor and enabled recording of the reactor temperature.

We placed the loaded reactors in a fluidized sand bath (model IFB-51 from Techne) equipped with a temperature controller. The sand bath was preheated to the desired set point temperature. Fig. 1 shows the reactor temperature profiles for the sand bath set point temperatures used in this study. After conducting the reaction for the allotted time, we removed the reactors from the sand bath and quenched the reactions by placing them in an ice-water bath for 5 min. The reactors were then held at room temperature for at least 60 min before opening.

We poured the entirety of the reactor contents into a glass conical tube. We added one of the organic solvents (DCM, MTBE, MIBK) chosen for biocrude recovery in small aliquots to rinse the inner reactor wall as well as the cap, until all the contents were recovered. These solvent washes were typically added to the material in the conical tube, but for two runs they were instead placed in a different tube so that the organic solvent and aqueous phase products never came into contact. The reactor contents and organic solvent applied added up to around 10 mL in the conical tube. The multiphase mixture was then separated via

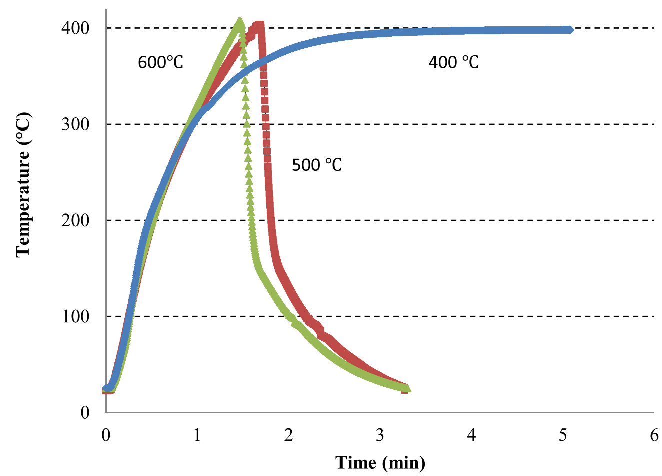

Fig. 1. Reactor temperature profiles at different sand bath set point temperatures for fast HTL (Runs 3–5 in Table 2).

centrifugation. A glass pipet was then used to recover the organic phase. We were careful not to collect any of the aqueous or solid phases with the pipet. This approach did leave behind a very small amount of the organic layer. We flowed N_2 over the separated organic phase to evaporate the solvent and isolate the biocrude. The conditions used for evaporation of DCM, MIBK, and MTBE were 38 °C, 100 °C, and 55 °C, respectively, for 2 h. The rest of the product work-up procedure was the same as that described previously [14].

The gravimetric yield of algal biocrude was calculated as the mass of biocrude divided by the dry, ash-free mass of the algal biomass loaded into the reactor. Atlantic Microlab, Inc. (Norcross, GA) determined the C, H, and N composition of the biocrude. We calculated the O composition by difference. The higher heating value (HHV) was calculated by using Dulong's formula [4] where C, H, and O represent the weight percentage of each element.

$$\mathrm{HHV\ (MJ/kg)} = 0.338C + 1.428\,(H - O/8)$$

2.3. Metal analysis

The metals in algal biocrude were analyzed by using Inductively Coupled Plasma Optical Emission Spectrometry (Agilent, ICP-OES 715). Biocrude oil samples were dissolved in EGBE on a 1:50 to 1:80 weight basis. A blank solution created by adding a given volume of element blank oil so as to match the solution viscosity to that of the samples was analyzed as a control. The metals content in the algal biomass and selected aqueous phase product samples were determined with ICP by staff at an on-campus lab.

3. Results and discussion

3.1. Metal concentration in algae biomass and HTL products

Table 1 shows that Na, K, P, S, Mg, and Fe were the most abundant in both algal biomass samples, with all of these elements being present at at least 1000 ppm. For the Sapphire algae, Ca was also present in excess of 1000 ppm. Na and Fe were the two most abundant metals in the biocrude from HTL at 350 °C and 60 min of both algal biomass samples. All other elements in Table 1 were below 300 ppm. Since Na and Fe were the most abundant metals in the biocrude, we focus solely on those elements for the balance of this report.

3.2. Effect of HTL conditions on Na and Fe content in biocrude

Table 2 (Runs 1–5) summarizes the effect of HTL temperature and