Effect of reaction time and algae loading on water-soluble and insoluble biocrude fractions from hydrothermal liquefaction of algae

Donghai Xu [a,b], Phillip E. Savage [b,c,*]

[a] Key Laboratory of Thermo-Fluid Science & Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi Province 710049, China
[b] Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States
[c] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, United States

ABSTRACT

Hydrothermal liquefaction (HTL) of algae produces a water-insoluble organic phase (biocrude) and an aqueous phase that also contains algae-derived organic compounds (water-soluble biocrude). We determined the influences of the HTL reaction time and algae loading (wt.% biomass in algae paste) on the yields and compositions of these two biocrudes. To the best of our knowledge this is the first detailed study of the water-soluble biocrude and how its yield and composition vary with processing conditions. Increasing the HTL reaction time from 10 to 60 min led to lower yields of water-soluble biocrude (from 6.4 to 3.6 wt.%) and higher yields of water-insoluble biocrude (from 38 to 41 wt.%). The total biocrude yield, however, was insensitive to the processing time. Longer HTL processing times also led to fewer and lighter GC-elutable compounds in the water-soluble biocrude. Increasing the algae loading from 8.6 to 18.7 wt.% led to higher yields of water-insoluble biocrude (from 29 to 44 wt.%) and lower yields of water-soluble biocrude (from 6.6 to 2.6 wt.%). The increase in the water-insoluble portion was much greater than the decrease in the water-soluble portion, so the total biocrude yield increased with loading. Increasing the wt.% of algae in the slurry placed in the reactors also produced biocrudes with greater heating value. HTL of algae paste with higher biomass content had the twin benefits of providing more total biocrude and a higher quality biocrude. Reaction time and algae loading can be used to manipulate the proportions of water-soluble biocrude and biocrude that spontaneously separate from the aqueous phase after HTL.

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1. Introduction

Hydrothermal liquefaction (HTL) converts wet organic material (e.g., biomass) into energy-dense biocrude via chemical reactions in and with hot compressed liquid water [1,2]. HTL is more appealing for processing wet feedstocks (e.g., algae) than are thermochemical conversion methods, such as gasification or pyrolysis, that require the biomass to be dried [3]. HTL of wet algal biomass produces an organic biocrude fraction, an aqueous fraction containing numerous polar organic compounds [4], a gas fraction, and a solid residue. The latter two product fractions generally appear in yields of just a few percent.

Two different approaches can be used to recover the biocrude from HTL. One approach is to allow the biocrude and aqueous phases to separate spontaneously due to their immiscibility and density difference (e.g., [5,6]). The second approach is to add an organic solvent, such as dichloromethane (DCM), to dissolve the biocrude, extract additional organic material from the aqueous phase, and facilitate biocrude recovery as a larger organic phase that separates from the co-existing aqueous and solid phases (e.g., [7]). The former approach has the advantage of being a simpler and "greener" process as no solvent extraction

step is needed and no organic solvent is required. The latter approach has the advantage of producing a modestly higher biocrude yield, since water-soluble material is extracted and recovered in the biocrude fraction. These water-soluble extractables tend to be richer in heteroatoms than the water-insoluble components of the biocrude [8], so this solvent extraction approach tends to produce a biocrude of lower quality (less heating value, more heteroatoms) than the former approach.

More generally, whether or not the water-soluble materials are extracted as biocrude affects aspects of the biorefinery apart from considerations of biocrude quantity and quality. If the DCM-soluble components are removed from the aqueous phase, then that aqueous phase will have a lower concentration of organic compounds. This lower loading could be beneficial if the aqueous phase is recycled directly to algae growth ponds. The reduced organic content would provide a less hospitable environment for growth of undesired invasive heterotrophic organisms in the algae pond. The lower concentration could be a disadvantage, however, if the biorefinery employed a process such as catalytic hydrothermal gasification to convert the dissolved aqueous-phase organic compounds into fuel gases (e.g., CH_4) to provide heat and power for the biorefinery [9]. Removing the DCM-soluble material from the aqueous phase would also hinder recovery of nitrogen and its recycling for algae growth, as more of the N atoms would be

removed from the aqueous phase and partitioned into the biocrude fraction.

The discussion above shows that the decision about whether to use an organic solvent for biocrude extraction or whether to rely solely on spontaneous phase separation of the HTL reactor effluent affects several aspects of biorefinery operation, economic viability, and environmental sustainability. To make this decision, one desires to know how solvent extraction affects the quantity and composition of the biocrude and the composition of the aqueous phase coproduct. To the best of our knowledge, our earlier preliminary work on this topic remains the only account in the archival scientific literature [8]. That account compared the biocrudes and aqueous phases from HTL at a single reaction condition and recovered by the two different approaches. The present study expands upon that work by determining the influence of the HTL conditions on the characteristics of the biocrude that spontaneously separates from the aqueous phase post-reaction and the biocrude that can be extracted from the aqueous phase using DCM. This information will be useful in deciding how best to design and operate an algal biorefinery that employs HTL.

2. Experimental section

2.1. Experimental procedures

We used the preservative-free *Nannochloropsis* sp. slurry, reactors, reagents, etc., that have been fully described in our previous report [8]. HTL experiments were carried out at 350 °C under two sets of conditions. One set explored HTL at four different batch holding times (10, 30, 45, and 60 min) and a fixed algae loading of 14.1 wt.%. The other set explored HTL at four different algae loadings (8.6, 11.4, 16.5, and 18.7 wt.%) at a fixed batch holding time of 20 min.

We loaded the reactor with known amounts of algae slurry and deionized water, sealed the reactor, and then placed it in a Techne Fluidized Sand Bath (Model SBL-2) maintained at 350 °C. When the desired reaction time was reached, we removed the reactor from the sand bath and quenched it in an ambient-temperature water bath. The reactor was equilibrated at room temperature for 1 h before collecting products.

We followed the procedure denoted as method 2 (M2) in our previous article [8] to collect, separate, and quantify the biocrude. Fig. 1 illustrates the main steps in the procedure. Briefly, we opened the reactor and directly collected the aqueous phase from the cool, equilibrated reactor by a pipette. We then added DCM to the reactor to dissolve and collect the water-insoluble biocrude (B) in the reactor as well as that adhering to the pipette. Note that the DCM did not come into contact with the aqueous phase co-product. DCM was added in these experiments for convenience and to ensure complete recovery of the water-insoluble biocrude. Its addition would likely be optional in a large-scale biorefinery where the biocrude–water separation could be done continuously and at higher temperatures. Evaporating the DCM by flowing N_2 in a drying apparatus (Vertex™ EVAPORATOR) led to isolation of the water-insoluble biocrude.

Centrifugation separated the aqueous phase that had been collected from any accompanying solids. We added DCM to the solid-free aqueous phase and mixed it thoroughly to extract the DCM-soluble, water-soluble material. These DCM-soluble and water-soluble compounds constitute the aqueous-phase contribution to the biocrude (B_A). The total mass of the biocrude (B_T) is the sum of the masses of the water-insoluble (B) and water-soluble (B_A) components. We further separated each biocrude into light (hexane-soluble) and heavy (hexane-insoluble) fractions as described previously [10].

2.2. Analysis methods

Biocrude samples were shipped to Atlantic Microlab, Inc., for elemental analysis. We identified components of the biocrudes by redissolving them in DCM and analyzing by GC–MS. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopic analysis (FTIR) of biocrudes were also conducted to characterize the biocrude. Detailed information about these instruments and procedures was reported previously [8].

The higher heating value (HHV) of biocrude was estimated by using the Dulong formula,

$$HHV\,(MJ/kg) = 0.338C + 1.428(H - O/8) + 0.095S \qquad (1)$$

where C, H, O, and S are the wt.% of each element in the biocrude.

Additionally, the biocrude yield, the fraction of total biocrude from the aqueous phase, the fraction of light biocrude, and the energy recovery in the biocrude were calculated as follows:

$$Biocrude\,yield = \frac{Mass\,of\,biocrude}{Mass\,of\,algae\,in\,reactor} \times 100\% \qquad (2)$$

$$Fraction\,of\,total\,biocrude\,from\,aqueous\,phase = \frac{B_A}{B + B_A} \times 100\% \qquad (3)$$

$$Fraction\,of\,light\,biocrude = \left(1 - \frac{Mass\,of\,measured\,B^H}{Mass\,of\,B}\right) \times 100\% \qquad (4)$$

Energy recovery of biocrude
$$= \frac{HHV\,of\,biocrude \times Mass\,of\,the\,biocrude}{HHV\,of\,initial\,dry\,algae \times Mass\,of\,the\,algae\,feedstock} \times 100\%. \qquad (5)$$

Three independent runs were carried out at the same conditions to determine the uncertainties in the experimental data. Results reported herein are average values and their uncertainties are the sample standard deviations.
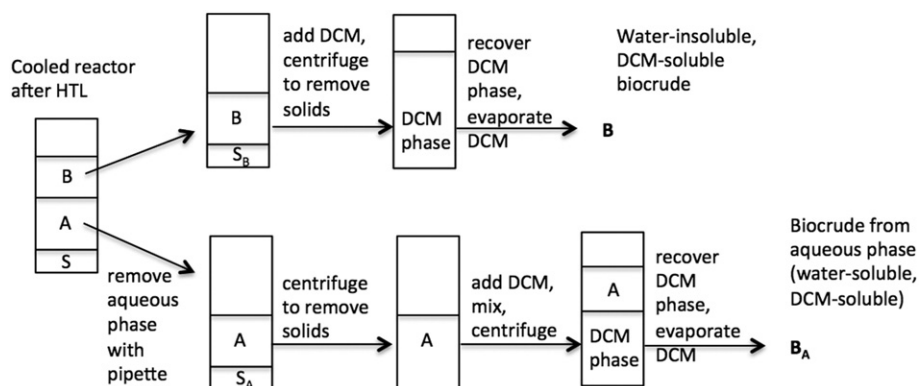

Fig. 1. Schematic diagram of product collection method. A = aqueous phase, B = biocrude, S = solids, and DCM = dichloromethane.