Effect of temperature, water loading, and Ru/C catalyst on water-insoluble and water-soluble biocrude fractions from hydrothermal liquefaction of algae

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ABSTRACT: Hydrothermal liquefaction (HTL) converts algal biomass into a crude bio-oil (biocrude) and aqueous-phase products. The effect of temperature, water loading, and added H₂ and/or Ru/C catalyst on the properties of the biocrude that spontaneously separates from the aqueous phase post reaction and also the biocrude that is extractable from the aqueous phase by dichloromethane is explored herein. This report is the first to elucidate how the yields, compositions, heating values, and energy recoveries of the two biocrudes vary with the processing conditions above. Increasing temperature from 350 to 400 °C increased the yield of water-insoluble biocrude (38.1–42.5 wt%) and its hexane-soluble subfraction (63.7–85.6 wt%) while decreasing the yield of extractable, water-soluble biocrude (6.6–2.5 wt%). The Ru/C catalyst had the same effect. Reaction temperature and catalysts could be used to manipulate the proportions of water-soluble and water-insoluble biocrude from algae HTL and thereby manipulate biocrude quantity and quality.

Keywords: algae, hydrothermal liquefaction, biocrude, water loading, catalyst

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1. Introduction

Hydrothermal liquefaction (HTL) chemically converts high moisture biomass such as microalgae into energy-dense biocrude in hot compressed water (Valdez et al., 2011; López Barreiro et al., 2013; Tian et al., 2014). It obviates the need for energy inputs for drying the biomass that accompany traditional thermochemical conversion processes (e.g., pyrolysis). Four operationally defined product fractions (gases, aqueous phase, biocrude, and solids) emerge from HTL. The combined yield of gases and solids usually accounts for < 15wt% of the algae feed (dry basis). In bench-scale experiments, biocrude is often recovered from HTL products by addition of an organic solvent (e.g., dichloromethane (DCM)). That is, organic solvent is added to the entire product mixture to dissolve the biocrude, which tends to be a tarry material that can adhere to reactor walls. The solvent also extracts additional organic material from the aqueous phase. This solvent addition approach is convenient for recovering the low volume of product obtained from laboratory-scale, batch experiments. In large-scale, continuous production, however, addition of a solvent brings with it negative economic and environmental impacts (López Barreiro et al., 2015). The desire to better understand eventual solvent-free HTL operation has led to some recent studies that recovered as biocrude only that material that spontaneously separated from the aqueous phase post-reaction (López Barreiro et al., 2015; Elliott et al., 2013a and 2013b; Ramos-Tercero et al., 2015; Xu and Savage, 2014 and 2015).

Previous reports showed that the water-insoluble biocrude (which separates spontaneously from the aqueous phase post HTL) and the water-soluble biocrude (compounds extracted from the aqueous phase with an added organic solvent) possess significantly different elemental and functional group compositions (López Barreiro et al., 2015; Xu and Savage, 2014 and 2015). In comparison to the water-insoluble biocrude, the water-soluble biocrude is richer in heteroatoms and has less heating value (López Barreiro et al., 2015; Xu and Savage, 2014

and 2015). Clarifying how HTL operating parameters affect the quantity and quality of both water-insoluble biocrude, which is available without solvent addition, and water-soluble biocrude, would help advance HTL technological development. For example, a better understanding of how the amounts and compositions of the two biocrudes change with HTL process conditions can inform decisions regarding how best to upgrade the biocrudes and whether to recover the water-soluble material.

Ramos-Tercero et al. (2015) showed that recycling the aqueous phase from HTL back to the reactor led to higher yields of water-insoluble biocrude. This outcome was consistent with our earlier work (Xu and Savage, 2015) showing that increasing the HTL reaction time has the same effect. Presumably, the additional time in the reactor transforms organic molecules that had been water soluble into less polar molecules that partition into the biocrude phase post reaction. This present study expands upon previous work by identifying the influence of the HTL temperature, the reactor water loading, and use of a Ru/C catalyst. To the best of our knowledge, these variables are examined here for the first time. This information will be valuable in determining how best to optimize and operate an algae HTL system.

2. Experimental section

2.1. Experimental procedures

A preservative-free *Nannochloropsis* sp. slurry, purchased from Reed Mariculture, Inc., had 32.5 ± 2.5 wt% of biomass content determined by drying three separate samples at 70 °C in an oven for 48 h. Its biochemical composition (dry basis) was 59 wt% crude proteins, 20 wt% carbohydrates, and 14 wt% lipid (Valdez et al., 2012). Its C, H, N and S contents were 52.6, 7.35, 8.58 and 0.57 wt%, respectively (Xu and Savage, 2014). The P, O, and ash contents were previously reported to be around 0.6, 28, and 3 wt%, respectively (Valdez et al., 2012). The reactors and reagents have been fully described in our previous report (Xu and Savage, 2014).

Most of the algae HTL experiments were conducted in 4.1 ml mini-batch reactors assembled from 1/2-in. 316 stainless steel Swagelok port connectors and caps. Reactions done with added H₂ or with gas analysis were done in such reactors also equipped with a length of stainless steel tubing and a high-pressure gas valve. Each reactor was loaded with carefully measured amounts of algae slurry and deionized water (and/or hydrogen, catalyst when desired), sealed, and then placed in a Techne Fluidized Sand Bath (Model SBL-2) preheated to the desired HTL temperature. When the desired holding time (20 min for all experiments reported herein) was reached, the reactor was removed from the sand bath and quenched in an ambient-temperature water bath. The reactor remained at room temperature for 1 h before product collection. The procedure denoted as Method 2 in our previous articles (Xu and Savage, 2014 and 2015) was used to separate, collect, and quantify biocrude. This method provided gas, aqueous phase, water-insoluble biocrude, and solid product fractions directly from the reactor. The water-soluble biocrude was collected through DCM extraction of the isolated aqueous phase. The water-insoluble biocrude was fractionated into light (hexane-soluble) and heavy (hexane-insoluble) subfractions. The separation procedures used here were identical to those reported previously (Xu and Savage, 2014).

HTL experiments were conducted at three sets of conditions. One set investigated the effect of temperature (320, 350, 370 and 400 °C) with a fixed algae loading of 11.4 wt% (0.8525 g algae slurry) and water loading at room temperature of 34.1 % of the reactor volume (1.3990 g deionized water). The temperatures selected correspond to those commonly used for algae HTL and temperature is an important HTL process variable (Tian et al., 2014). The second set determined the effect of water loading (reactors filled 19.5 %, 26.8 %, 34.1 % and 41.4 % with water at room temperature) on HTL at 350 °C with a fixed algae slurry loading of 0.8525 g. The third set determined the effect of adding H₂ (3 MPa) and/or Ru/C (10 wt% of dry algae loading)

on HTL at 350 °C with 11.4 wt% algae loading and 34.1 % water volume loading. The Ru/C catalyst (5 wt% Ru on carbon) was purchased from SigmaAldrich and used as received. The reactor pressures at 350 °C in all cases were around 16.5 MPa, and the reactor heat-up time was about 2–3 min.

2.2. Analysis methods

Atlantic Microlab, Inc., performed elemental analysis of the biocrudes and estimated the analysis errors as < 3% of the reported value. Gaseous products were identified and quantified by Agilent Technologies model 6890N gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), following the method reported previously (Brown et al., 2010). The cooled reactor was weighed post-reaction before and after venting the gas, and the difference in mass was the mass of the gases formed during HTL.

Product yields were calculated as the mass of a given product fraction divided by the mass of dry algae loaded into the reactor. The higher heating value (HHV) of biocrude was estimated from the Dulong formula (Duan and Savage, 2011),

$$\text{HHV (MJ/kg)} = 0.338C + 1.428(H - O/8) + 0.095S \quad (1)$$

where C, H, O, and S are the wt% composition of each element in the biocrude, and the O content was calculated by difference from the experimental C, H, N, and S values and reserving 1 wt% for other elements not analyzed.

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

3. Results and discussion

This section shows how the yields and composition of water-insoluble and water-soluble biocrude are

affected by temperature, water loading, and catalyst. The solids yields and the gas yields were 5.1–9.0 wt% and 4.6–9.6 wt%, respectively. The main gas products were CO₂, H₂, CH₄, and C₂ light gases. This result is in accord with the gaseous compositions from algae HTL at different reaction conditions reported previously (Valdez et al., 2011). The mass balance in the experiments ranged from 91 to 96 wt%.

3.1. Biocrude yields

Fig. 1 displays biocrude yields from algae HTL at different temperatures. The total biocrude yields are consistent with previous values (40–50 wt%) for HTL of this biomass at 300–350 °C (Valdez et al., 2012). The yield of water-soluble biocrude declined from 6.6% to 2.5 wt% as temperature increased. Over this same temperature interval, the yield of water-insoluble biocrude increased so that the total biocrude yield was relatively stable at about 45 wt%. These trends are consistent with the increased conversion of water-soluble to water-insoluble biocrude with increasing temperature. That is, with increasing temperature, water-soluble, polar organic compounds could be more readily undergoing reactions to eliminate polar functional groups and thereby become water-insoluble biocrude molecules (Zou et al., 2010). The highest total biocrude yield was obtained at 320 °C probably due to lower production of gaseous products and non-extractable aqueous phase products at the lower temperature. Note, though, that the difference between this total biocrude yield and the others is about the same as the experimental uncertainty. Overall, temperature affected the yields of the individual biocrude fractions (water-soluble and water-insoluble) but not the total biocrude yield.

Fig. 1 also shows that higher temperature produces more hexane-soluble biocrude. This light biocrude fraction increased from 52.7 wt% to 85.6 wt% as temperature increased. These changes indicate the improvement of biocrude quality with increasing temperature because light biocrude is generally lower in heteroatoms and has a larger HHV (Xu and Savage, 2014 and 2015). Note that the water density at reaction

conditions in these HTL experiments dropped from 0.667 g/ml to 0.408 g/ml as temperature increased from 320 to 400 °C. Thus, the trends observed here that is attributed to temperature effects could also be due in part to any effect that water density might have.

Table 1 shows the effect of water loading on the biocrude yields. There were no consistent trends with respect to the effect of this variable on the yields of the various biocrudes. In many cases the differences in yield are comparable to the uncertainties.

Fig. 2 shows the influence of H₂ and Ru/C on biocrude yields. The only runs in Fig. 2 that show differences in yields of water-insoluble biocrude that exceed the uncertainties are those with added Ru/C vs. those without. The presence of Ru/C had the desirable effects of increasing the yield of water-insoluble biocrude, increasing the portion of that biocrude that is hexane-soluble (e.g., light biocrude), and decreasing the yield of water-soluble biocrude, which tends to contain more heteroatoms. The differences in these yields were such that Ru/C had no measureable effect on the total yield of biocrude (water-soluble plus water-insoluble components). The present results suggest that the role of Ru/C is mainly to promote the conversion of more algal material and water-soluble biocrude to water-insoluble biocrude.

In previous work, Ru/C increased the total biocrude yield (in the absence of H₂) from HTL of *Nannochloropsis* at 350 °C (Duan and Savage, 2011). This earlier work used *Nannochloropsis* that contained preservatives, whereas the present study used a specially ordered batch of *Nannochloropsis* that had no preservatives added. Unpublished work in our lab showed that HTL of the preservative-containing slurry that had been first washed in water several times produced biocrude yields measurably higher than those produced by HTL of the original preservative-containing slurry. It is possible that the carbon support in the previous catalytic HTL experiments served as an adsorbent for the preservatives (which inhibited biocrude production),

and that this in situ removal of the preservatives during HTL allowed the higher biocrude yield to be achieved.

Overall, increasing temperature and adding Ru/C decreased the yield of water-soluble biocrude, as had increasing time and algae loading (Xu and Savage, 2015). This effect occurred presumably because some of the molecules initially formed from algae HTL contained polar groups and thus enjoyed solubility in water. Then, as the temperature increased or Ru/C was added, the compounds could more readily undergo deamination, decarboxylation, dehydration, oligomerization, addition, hydrogenation, etc. Some of the molecules were converted into water-insoluble biocrude or gaseous compounds. Others were converted into larger, less-polar molecules, which were consequently less soluble in water.

Figs. 1–2 and Table 1 also illustrate how the hexane-soluble fraction of the water-insoluble biocrude responded to changes in temperature, water loading and adding Ru/C and/or H₂. This metric is a proxy for biocrude quality, since the hexane-soluble compounds are less polar, lower boiling, and thus more desirable for fuel use than the heavier, more polar, hexane-insoluble compounds (Xu and Savage, 2015). Both the Ru/C catalyst and higher temperatures increased the hexane-soluble fraction of the biocrude. The catalyst and added thermal energy promoted reactions that led less biocrude to be water-soluble but more to be hexane-soluble. That is, the solubility of biocrude molecules in water was reduced but in hexane was increased. A similar trend was observed previously for algae HTL with increasing reaction time (Xu and Savage, 2015).

It is desirable to promote the yield of higher quality biocrude (e.g., hexane-solubles) and to reduce the yield of lower quality biocrudes (e.g., water-solubles). Increasing temperature and adding Ru/C represent two strategies that can be employed to this end.

3.2. Elemental compositions and higher heating values

This section discusses the effect of process variables on elemental compositions, HHVs, and energy

recoveries obtained at the different HTL conditions. These metrics are important for assessing the biocrude quality and the ability of the HTL process to recover the chemical energy originally resident in the algal biomass.

Table 2 displays elemental compositions and HHVs of the water-insoluble and water-soluble biocrudes produced at different temperatures. As temperature increased, the carbon content increased and the nitrogen content declined, but the H and S contents were relatively stable for the water-insoluble biocrude. There were no clear variations for the elemental compositions and HHVs of the water-soluble biocrude. Overall, one can conclude that higher temperature improves the quality of the water-insoluble biocrude. Table 2 shows that the highest temperature examined (400 °C) provided water-insoluble biocrude with the lowest heteroatom content. Recall that this condition also provided the highest fraction of that biocrude being hexane-soluble. The higher temperatures favor denitrogenation reactions to form ammonia and water-soluble nitrogenous compounds (Valdez et al., 2011 and 2012), which are partitioned into the aqueous phase after algae HTL.

The supporting information provides the elemental compositions and HHVs for the biocrudes produced at different water loadings and with added H₂ and Ru/C. None of these process variables had any clear and consistent effect on the elemental compositions. The HTL literature indicates, however, that Ru/C can reduce the sulfur (Duan and Savage, 2011) and nitrogen (Luo et al., 2015) content of biocrude if HTL is run for 60 min or longer. One observes no such effect in this study, most likely because the reaction time used here (20 min) is much shorter than those used in the studies above.

At all HTL conditions examined, the quality of the water-insoluble biocrude was always much better than that of the corresponding water-soluble biocrude in terms of a lower heteroatom content and larger HHV. As shown in Table 2 and the supporting information, the N and O contents in the water-soluble biocrudes were

more than twice those in the water-insoluble biocrude produced at the same conditions.

Table 3 delves further into this topic by providing the percentage of N and O heteroatoms in the total biocrude (water soluble plus water insoluble components) that comes from the water-soluble component. For each experimental run, the percentages of total biocrude N and O atoms resident in the water-soluble fraction are very similar to each other (e.g., 23.4 and 20.9% in Run 1), which is consistent with these water-soluble biocrude molecules containing both O and N atoms. Additionally, these N and O percentages are typically at least twice the value of the percentage of the total biocrude yield attributable to the water-soluble component (11.6% in Run 1). The heteroatom-containing compounds are mostly derived from proteins, carbohydrates, and lipids in the feedstock, via a series of depolymerization, decomposition, and addition reactions (Vardon et al., 2012; Toor et al., 2011).

3.3. Energy recovery

Energy recovery is a key indicator of the effectiveness of an HTL process in capturing the chemical energy in the biomass in the biocrude that is produced. Since the biocrude heating values varied little with the process conditions, the energy recoveries largely tracked with the biocrude yields. Conditions that gave higher biocrude yields also gave higher energy recoveries. The energy recovery in the water-insoluble biocrude component ranged from 57–67% (average value of 62%) of the heating value of the biomass loaded into the reactor. The energy recovery from the water-soluble, extractable biocrude component ranged from 3.1–8.0% (average value of 5.9%) of that in the original biomass. Therefore, the biocrudes that spontaneously separated from the aqueous phase post-HTL contained about 62% of the chemical energy in the original algal biomass. The biocrudes extracted from the aqueous phase contained roughly another 6% of the chemical energy in the biomass. By performing the DCM extraction of the aqueous phase, this water-soluble material can be

recovered as biocrude and potentially refined into liquid fuels. These two average energy recoveries, as well as the total energy recoveries given in Table 3, have good agreement with previous research on energy recoveries in the different biocrudes from algae HTL at different times and algae loadings (Xu and Savage, 2015). The yields of water-insoluble biocrude and energy recoveries at various conditions in Table 3 are also in good accord with results from a related study (Ramos-Tercero et al., 2015). The increase in the total biocrude yield and the energy recovery, due to the extraction of water-soluble biocrude, comes at the expense of higher N and O content and a lower HHV.

The results presented and discussed herein suggest that selection of HTL process options and process variables can be used to affect tradeoffs between biocrude yield and quality. For example, bypassing the opportunity to extract biocrude from the aqueous phase products formed from HTL at 350 °C (Run 2) will result in loss of nearly 15% of the total biocrude and 12% of the energy recovery available (Table 3). For a high-volume process such as fuel production, losses of this magnitude have an enormous effect on process economics for a commercial-scale facility. At the same time, these losses are countered by the biocrude containing only 70% of the N and 73% of the O it would contain had the aqueous phase extractables been included. That is, one would obtain less biocrude, but it would require less upgrading to be used as a fuel. Additionally, operating at 400 °C (Run 4), which requires a greater process energy input than operating at 350 °C, would more than halve the biocrude mass loss and energy recovery loss accompanying solvent-free recovery of biocrude from an HTL process. Here, one would be trading energy inputs for more biocrude. Though the present study sheds the first light onto the effects of temperature and water loading and Ru/C catalysts on the biocrude fractions from HTL, it clearly points to the need for additional work to understand fully all of the tradeoffs involved in optimizing the operation of an algae HTL process.

4. Conclusions

Higher temperatures promote and Ru/C catalyzes the hydrothermal reactions that render organic compounds less polar. These reactions likely include elimination of heteroatom-containing functional groups and addition reactions. The results also revealed a heretofore unreported effect of catalysts during HTL. Adding Ru/C reduced the yield of water-soluble biocrude and increased the yield of water-insoluble biocrude, while having no effect on the total biocrude yield. Had the two biocrude components not been separated and studied individually, the unchanging yield of total biocrude could have been mistakenly interpreted as the absence of any HTL catalyst activity.

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Figure captions

Fig. 1. Biocrude yields (wt%) from algae HTL at different temperatures (34.1 vol% water loading, 11.4 wt% algae loading, 20 min).

Fig. 2. Biocrude yields (wt%) from algae HTL with different additives (350 °C, 20 min, 11.4 wt% algae loading, 34.1 vol% water loading).

Table captions

Table 1 Biocrude yields (wt%) from algae HTL at 350 °C and 20 min with 0.8525 g algae loading and different water loadings (20 min).

Table 2 Elemental compositions and heating values of biocrudes obtained from HTL at different temperatures (34.1 vol% water loading, 11.4 wt% algae loading, 20 min).

Table 3 Summary of biocrude characteristics from algae HTL at 20 min and different conditions.

Fig. 1. Biocrude yields (wt%) from algae HTL at different temperatures (34.1 vol% water loading, 11.4 wt% algae loading, 20 min).

Fig. 2. Biocrude yields (wt%) from algae HTL with different additives (350 °C, 20 min, 11.4 wt% algae loading, 34.1 vol% water loading).

Table 1

Biocrude yields (wt%) from algae HTL at 350 °C and 20 min with 0.8525 g algae loading and different water loadings (20 min).				
Water loading (vol%)	19.5	26.8	34.1	41.4
Algae loading (wt%)	15.5	13.1	11.4	10.0
Yield (wt%) of water-insoluble biocrude	37.4±2.4	43.2±2.1	38.1±1.8	39.3±2.5
Yield (wt%) of water-soluble biocrude	4.5±0.4	4.4±0.4	6.6±0.6	4.2±0.4
Total biocrude yield (wt%)	41.9±2.6	47.6±2.4	44.7±2.5	43.5±2.8
Hexane-soluble portion (wt%) in water-insoluble biocrude	61.2±4.3	71.2±5.2	63.7±5.3	71.5±6.1

Table 2

Table 2

Elemental compositions and heating values of biocrudes obtained from HTL at different temperatures (34.1 vol% water loading, 11.4 wt% algae loading, 20 min).

Temperature (°C)	Biocrude	Elements					HHV (MJ/kg)
		C	H	N	S	O	
		(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	
320	Water-insoluble	75.16	9.95	4.58	0.62	8.69	38.12
350	Water-insoluble	76.39	10.05	4.64	0.59	7.33	38.92
370	Water-insoluble	76.78	9.98	4.33	0.53	8.69	38.12
400	Water-insoluble	77.90	9.96	4.11	0.61	7.56	38.71
320	Water-soluble	61.61	8.53	10.65	0.74	17.47	29.96
350	Water-soluble	63.67	8.28	11.20	0.31	15.54	30.60
370	Water-soluble	61.15	8.42	10.36	0.56	18.51	29.44
400	Water-soluble	63.15	8.48	9.71	0.85	16.81	30.53

Table 3

Table 3

Summary of biocrude characteristics from algae HTL at 20 min and different conditions.

Run	HTL Condition	Biocrude yield		N content		O content		Energy recovery	
		Total	Water-sol	In total	Water-sol	In total	Water-sol	From total	Water-sol
		yield	uble % of	biocrude	uble % of	biocrude	uble % of	biocrude	uble % of
		(wt%)	total	(wt%)	total	(wt%)	total	(%)	total
1	320 °C, 34.1 vol%	47.3	11.6	5.29	23.4	9.71	20.9	70.7	9.3
2	350 °C, 34.1 vol%	44.7	14.8	5.61	29.5	8.54	26.9	67.6	11.9
3	370 °C, 34.1 vol%	44.8	10.3	4.95	21.5	9.70	19.6	67.1	8.1
4	400 °C, 34.1 vol%	45.0	5.6	4.42	12.2	8.07	11.6	69.3	4.5
5	350 °C, 19.5 vol%	41.9	10.7	5.43	22.0	8.68	22.2	63.6	8.5
6	350 °C, 26.8 vol%	47.6	9.2	5.22	18.8	8.81	18.2	72.3	7.4
7	350 °C, 41.4 vol%	43.5	9.7	4.76	20.9	8.21	20.0	67.1	7.6
8	350 °C, 34.1vol%, H ₂	42.1	12.8	5.94	23.7	9.06	25.0	63.1	10.2
9	350 °C, 34.1vol%, Ru/C	45.7	9.6	5.16	20.2	8.21	21.2	70.5	7.3
10	350 °C, 34.1vol%, H ₂ +Ru/C	43.5	8.3	4.95	18.1	7.95	17.7	68.2	6.3