Effects of Processing Conditions on Biocrude Yields from Fast Hydrothermal Liquefaction of Microalgae

Julia L. Faeth^a, Phillip E. Savage^{a,b,*}

^a*Department of Chemical Engineering, University of Michigan, 2300 Hayward Street, 3074 H.H. Dow Building, Ann Arbor, Michigan 48109, United States*

^b*Department of Chemical Engineering, The Pennsylvania State University, 160 Fenske Lab, University Park, Pennsylvania 16802, United States*

Abstract

This study investigated the effects of algae species, reaction time, and reactor loading on the biocrude yield from fast hydrothermal liquefaction (HTL) of microalgae. Fast HTL reaction times were always less than 2 min and employed rapid heating and nonisothermal conditions. The highest biocrude yield obtained was 67 ± 5 wt % (dry basis). With all other process variables fixed, increasing the reaction time in a 600 °C sand bath by 15 sec increments led to a rapid increase in biocrude yield between 15 - 45 sec. At longer times, the biocrude yield decreased. Low reactor loadings generally gave higher biocrude yields than did higher loadings. The low reactor loadings may facilitate biocrude production by facilitating cell rupture and/or increasing the effective concentration of algal cells in the hot, compressed water in the reactor.

Keywords: Biofuel, Hydrothermal Liquefaction, Microalgae

*Corresponding author. Tel.: +1-814-867-5876; fax: +1-814-865-7846
Email address: psavage@psu.edu (Phillip E. Savage)

1. Introduction

CO₂ emissions from the combustion of liquid transportation fuels contribute to anthropogenic global climate change. Renewable fuels from biomass may reduce the net CO₂ emissions from a life cycle perspective, depending on factors such as the energy intensity of biomass cultivation, harvesting/collection, and conversion processes. Hydrothermal liquefaction (HTL) of microalgae is a biomass conversion process that could reduce life cycle CO₂ emissions compared to petroleum-derived fuels, especially when algae cultivation is coupled with a wastewater treatment plant (Fortier et al., 2014). HTL also has the advantage of avoiding the energy-intensive biomass drying steps that are required for many other biofuel production processes (Marcilla et al., 2013). Briefly, HTL accomplishes biocrude production by the decomposition of biomolecules in hot compressed water via the combined action of elevated temperature, elevated pressure, and hydrolytic attack. HTL of microalgae has been the focus of several reviews (Barreiro et al., 2013a; Chow et al., 2013; Marcilla et al., 2013; Tian et al., 2014).

A large majority of the algal HTL literature examines hydrothermal reactions at 300 - 350 °C with reaction times on the order of tens of minutes. Faeth et al. recently described a variation on the HTL process, termed fast HTL (Faeth et al., 2013), that requires just a short reaction time (up to about 2 min) and rapid heating rates (150 - 300 °C/min). This rapid heating facilitates the production of biocrude from microalgae with yields comparable to or higher than those from conventional isothermal HTL (Faeth et al., 2013). More recently, there have been investigations of fast HTL of macroalgae (Bach et al., 2014), HTL of microalgae for short residence times in a

continuous flow system (Jazrawi et al., 2013), and fast HTL of bacteria and yeast (Valdez et al., 2014). These studies demonstrated the robustness of this fast HTL approach but much about this promising HTL variation remains unknown. To fill some of these gaps, we explore herein fast HTL of four species of microalgae: *Nannochloropsis* sp., *Chorella vulgaris*, *Botryococcus braunii*, and *Neochloris oleoabundans* and the effects of different aspects of reactor loading and reaction time on fast HTL of *Nannochloropsis* sp.

2. Materials and Methods

Materials used in this work are identical to those described previously (Faeth et al., 2013) and were purchased and/or constructed in the same manner. Briefly, mini batch reactors were constructed from 316 stainless steel with an internal volume of 1.67 mL. Most data reported herein describe batch reactions using *Nannochloropsis* sp. from Reed Mariculture, Inc., although we also compare results from HTL of *Nannochloropsis* sp. to those from *Chorella vulgaris*, *Botryococcus braunii*, and *Neochloris oleoabundans* cultivated at the University of Dayton Research Institute (UDRI). Batch mini-reactors were loaded with algae and water (Please see Tables S1 - S5 in the Supporting Information for loading details) and sealed to 45 ft-lbs using a torque wrench. Sealed reactors, accompanied by an empty thermocouple-equipped dummy reactor, were submerged in a fluidized sand bath preheated to 600 °C for fast HTL, and 350 °C for isothermal HTL. The reaction time was defined to begin at the instant reactors were submerged and to end at the instant reactors were quenched in a cold water bath.

Cooled reactors were opened and the products collected by pouring the

50 reactor contents into a glass centrifuge tube, rinsing the reactor with 9 mL
51 of dichloromethane, and collecting these rinsings in the same test tube. The
52 biocrude (organic phase), solid, and aqueous phase products were separated
53 with centrifugation and manual pipeting as described previously (Valdez
54 et al., 2012; Faeth et al., 2013; Roberts et al., 2013; Barreiro et al., 2013b).
55 Once separated, the biocrude products were dried under N₂. After drying,
56 the masses of the biocrude products were recorded. We report biocrude yields
57 as the mass of biocrude produced divided by the mass of dry algae loaded
58 into the reactor.

59 3. Results and Discussion

60 This section presents the effects of algae species, reaction time, and re-
61 actor loading on biocrude production from HTL of microalgae. The first
62 subsection includes four species of microalgae, but all subsequent subsections
63 focus on results from the HTL of *Nannochloropsis* sp.

64 3.1. Algae Species

65 Figure 1 depicts biocrude yields (in wt % on a dry basis) from fast (600
66 °C sand bath for 1 min) and isothermal (350 °C sand bath for 60 min) HTL of
67 four species of microalgae. The standard error from at least three replicates
68 of each reaction condition is represented by the error bars on this figure
69 and all others in this work, unless otherwise indicated. The biocrude yield
70 produced from isothermal HTL of *Nannochloropsis* sp. depicted in Figure
71 1 is taken from previous work (Faeth et al., 2013) and is based on a single
72 replicate.

73 For all species of microalgae examined in the present work, fast HTL pro-
74 duces biocrude yields comparable to those from isothermal HTL. Fast HTL
75 of *Botryococcus braunii* and *Nannochloropsis* sp. produced more biocrude
76 than did isothermal HTL. Along with the previous work investigating fast
77 HTL of bacteria and yeast (Valdez et al., 2014), these results are a testament
78 to the robustness of fast HTL as a biomass conversion process for microorgan-
79 isms. The differences in biocrude yields between different algae species likely
80 reflect the differences in biochemical composition (i.e., protein, lipid, carbo-
81 hydrate, ash) and/or cellular structure (i.e. cell wall strength, cell shape)
82 between species.

83 3.2. Reaction Time

84 To examine the effects of reaction time in greater detail, we conducted
85 fast HTL experiments with reaction times ranging from 0.25 - 2 min with
86 a sand-bath temperature of 600 °C, 15 wt % solids in slurry and 11 volume
87 % water loading (meaning that 11 % of the reactor volume is occupied by
88 water at room temperature). At these conditions, the biocrude yields increase
89 rapidly between 15 - 45 sec and decrease with further increases in reaction
90 time. The highest biocrude yield observed in this set of reactions is 55 wt
91 %. This biocrude yield is obtained after only 45 sec in the 600 °C sand bath.
92 At this reaction time, the empty, dummy reactor temperature was 188 °C,
93 which provided an estimate of the temperature in the HTL reactor.

94 The rapid increase in biocrude yield during this 30 sec interval might
95 be due to cell breakage occurring over this same interval. Cell breakage,
96 which could occur at different characteristic temperatures for different algal
97 species (Garcia Alba et al., 2012) and possibly be accelerated by rapid heat-

ing, would release triglycerides and other biomolecules that may contribute to high biocrude yields. Differences in thermal conductivity between the intracellular water and bulk water in the reactor may facilitate development of pressure differentials under rapid heating to induce cell rupture. Decreasing biocrude yields with increasing reaction time beyond 0.75 min is likely the result of hydrothermal degradation of cellular components to water-soluble and gaseous products, with the latter becoming more significant at temperatures exceeding the critical point of water (374 °C).

3.3. Reactor Loading

There are three ways to systematically vary the contents of the mini batch reactor during fast HTL. One way is to use a fixed amount of water in each reactor, but vary the amount of algae. A second way is to load different amounts of algae slurry with a fixed solids content (e.g., 15 wt %). The third way is to use a fixed amount of dry algal biomass in each reactor but vary the amount of water added. This section examines each of these methods.

These variations in reactor loading will be reported and discussed in terms of two key variables: the percentage of the reactor volume occupied at room temperature by the water loaded into the reactor (hereafter referred to as volume % water) and the solids content (wt %) in the algae slurry present in the reactor at $t = 0$. These two variables control the “effective concentration” of algae solids in hot compressed water at a given reaction temperature. As the reactor is heated, some of the liquid water must vaporize to maintain the saturation pressure, which leaves less water in the liquid phase. The lower the water loading, the higher the relative amount of water that must vaporize.

123 We define the effective concentration (wt %) of algae as the mass of dry
124 algae in the reactor divided by the mass of algae plus the mass of liquid water
125 in the reactor at a given temperature. The mass of liquid water in the reactor
126 at a given temperature was calculated using mass balances and the steam
127 tables (Haar et al., 1984). Figure 2 depicts how the effective concentration
128 at 266 °C varies with the vol % water loading and solids content (wt %).
129 The numbers superimposed on Figure 2 represent the biocrude yields from
130 HTL reactions encompassing all three variations on reactor loading described
131 previously. The 266 °C temperature represents the temperature a dummy
132 reactor typically reaches after 1 min in a 600 °C sand bath, based on the
133 average of all temperature profiles collected in this study.

134 At high vol % water loading and high solids content, the algae concen-
135 tration at reaction conditions is nearly the same as the initial wt % loading.
136 At low water loadings, however, the effective concentration can depart sig-
137 nificantly from the initial wt % loading. For example, an initial loading of
138 25 wt % slurry that provides enough water to fill just 10 % of the reactor
139 at room temperature will have an effective concentration of about 30 wt %
140 when the reactor reaches 266 °C.

141 3.3.1. Fixed Water Loading

142 Figure 3 illustrates how biocrude yields from fast HTL (600 °C for 1 min)
143 of algae change with respect to the algal solids content (wt %) when a fixed
144 amount of water (either 11 or 30 vol %), was added to each reactor. The
145 mass of algae added to each reactor was adjusted to obtain the desired wt %
146 of dry algae solids content.

147 At 11 vol % water in Figure 3, biocrude yields decrease from 67 wt % to

148 43 wt % as the solids content of the algal slurry increases from 5 to 25 wt %
149 solids. The highest biocrude yield with 30 vol % water is also observed after
150 fast HTL of a reaction mixture containing 5 wt % algae solids. However, fast
151 HTL reactions with 30 vol % water resulted in all biocrude yields being within
152 5 wt % of the maximum biocrude yield for all solids contents examined. This
153 difference in biocrude production between high and low water loadings could
154 possibly be explained by changes in effective concentration.

155 3.3.2. *Fixed Solids Content*

156 To manipulate the vol % water in the reactor and maintain fixed solids
157 content, the mass of both algae and water were varied. As the vol % water
158 increases, the biocrude yields decrease slightly. As indicated in Figure 2, the
159 effective concentration of algal biomass in the reactor at reaction conditions
160 increases as mass loadings (and vol % water) decrease. Effective concentra-
161 tions for the reaction conditions with fixed solids content increase from 15.4
162 to 18.8 wt % as the vol % water decreases from 60 % to 10 %. If the re-
163 actions of algal biomass to produce biocrude are greater than zero-order, an
164 increase in the effective concentration of the reactant(s) in the liquid phase
165 would increase the rate of biocrude production. It is also possible that cell
166 breakage is facilitated by the low loading reaction environments, as discussed
167 previously.

168 3.3.3. *Fixed Biomass Loading*

169 For a constant biomass loading, as the water loading decreases, the effec-
170 tive concentration increases. Based on experiments with a constant biomass
171 loading, biocrude yields generally increase as the effective concentration in-

172 creases. This observation further supports the idea that the effective con-
173 centration of algal biomass in the reaction mixture has an effect on biocrude
174 production.

175 3.3.4. All Reactor Loading Variables

176 Figure 2 depicts the biocrude yields with respect to both vol % water and
177 algal slurry solids content for all reactor loading experiments discussed above.
178 Generally, biocrude yields increase with increasing effective concentration for
179 a given slurry solids content (this also corresponds to a decrease in vol %
180 water). For a given vol % water, the correlation between biocrude yields
181 and effective concentration is less clear. Further research may be required
182 to elucidate more completely how and why the effects of reactor loading
183 influence biocrude yields.

184 3.4. Summary of Results

185 Fast HTL produced biocrude from four different species of microalgae
186 with yields comparable to those available from isothermal HTL, further il-
187 lustrating that fast HTL is a robust process. The processes that produce
188 biocrude from microalgal biomass are very fast. The highest biocrude yields
189 from non-isothermal HTL of a 15 wt % algal slurry with 11 vol % water
190 were obtained at times between 0.75 - 1.0 min (using a 600 °C sand-bath
191 set-point temperature). Such rapid conversion might arise from cell break-
192 age that occurs at characteristic temperatures, possibly accelerated by high
193 heating rates and thermal conductivity differences between intra- and extra-
194 cellular material which could induce pressure differentials across cell walls.

195 Different aspects of reactor loading affect biocrude yields. Fast HTL of

196 mixtures with low solid contents can produce high biocrude yields when the
197 total mass in the reactor is low. Specifically, we observed the highest biocrude
198 yield of 67 wt % after HTL of a 5 wt % algal slurry, 11 vol % water in a 1
199 min in a 600 °C sand bath. In contrast, variation in algae solids content in
200 reactions with high total mass loadings (high vol % water) does not appear
201 to have a clear impact on biocrude production via fast HTL. This observed
202 increase in yield with low water loading and low solids content could be due,
203 at least in part, to an increase in the effective concentration of algae cells in
204 the liquid phase of the reaction, relative to an otherwise identical reaction
205 with high total mass loading.

206 Manipulation of reactor loading by fixing the solids wt % content and ad-
207 justing the total mass of the reaction mixture revealed a decrease in biocrude
208 yields with increasing mass. Further, biocrude yields decreased as the mass
209 of water increased for fast HTL reactions with a fixed amount of dry algae
210 biomass. Both of these trends reinforce the idea that increased effective con-
211 centration of algae in the liquid phase during rapid heating may facilitate
212 biocrude production. Additionally, the volume % water has a greater effect
213 on biocrude yields than does the wt % of dry algae solids present in the
214 slurry.

215 4. Conclusions

216 This study provides the most detailed examination to date of how fast
217 HTL processing conditions (including biomass feedstock, reaction time, and
218 reactor loading) affect biocrude yield. The results discussed in this work
219 suggest that physical phenomena, in addition to chemical reactions, may

220 contribute to the improved biocrude yields obtained via fast HTL under
221 certain operating conditions, and that further research in this area is needed
222 to better understand and model the fast HTL process.

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232 6. Supplementary Information

233 The Supporting Information provides details regarding the algae and wa-
234 ter loadings for all experiments. Table S1 contains the loadings for the data
235 presented in Figure 1, Table S2 contains the loadings for the reaction time
236 experiments (not depicted in a figure), Table S3 contains the loadings for
237 Figure 3 (also depicted in Figure 2), Table S4 contains the loadings for the
238 fixed solids content experiments (depicted in Figure 2, along with other ex-
239 periments), and Table S5 contains the loadings for fixed biomass loading
240 experiments (depicted in Figure 2, along with other experiments).

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Figure 1: Biocrude Yields from Fast (600 °C sand bath, 1 min, 30 vol % water loading) and Isothermal (350 °C sand bath, 60 min, 55 vol % water loading) HTL of Different Algae Species, 15 wt % solids in slurry

Figure 2: Biocrude yields (wt % dry basis, in text) from fast HTL at different reactor loadings at different vol % water and slurry solid contents. Sand-bath temperature = 600 °C, 1 min

Figure 3: Biocrude yields from fast HTL (sand-bath temperature = 600 °C, 1 min) with different slurry solid contents at low (11 vol %) and high (30 vol %) water loading