A quantitative kinetic model for the fast and isothermal hydrothermal liquefaction of *Nannochloropsis* sp.

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Abstract

Hydrothermal liquefaction (HTL) is a technology for converting algal biomass into biocrude oil and high-value products. To elucidate the underlying kinetics for this process, we conducted isothermal and non-isothermal reactions over a broad range of holding times (10 s – 60 min), temperatures (100 – 400 °C), and average heating rates (110 – 350 °C min⁻¹). Biocrude reached high yields (≥ 37 wt %) within 2 min for heat-source set-point temperatures of 350 °C or higher. We developed a microalgal HTL kinetic model valid from 10 s – 60 min, including significantly shorter timescales (10 s – 10 min) than any previous model. The model predicts that up to 46 wt % biocrude yields are achievable at 400 °C and 1 min, reaffirming the utility of short holding times and “fast” HTL. We highlight potential trade-offs between maximizing biocrude quantity and facilitating aqueous phase recovery, which may improve biocrude quality.

Keywords: Hydrothermal liquefaction, microalgae, kinetic model, temperature profile

1. Introduction

Producing energy-dense fuels from biomass is a compelling strategy for reducing transportation-related CO₂ emissions because such fuels recycle carbon from the atmosphere via photosynthesis, rather than introduce ancient carbon from fossil resources. Moreover, microalgae have garnered considerable interest as biomass feedstocks because of their high photosynthetic efficiency, fast growth rate relative to terrestrial biomass, ability to be cultivated on non-arable land and thus avoiding competition with agriculture, and capability to convert solar energy into energy-dense compounds like lipids (Brennan and Owende, 2010). The energy required to convert algal biomass to biofuel precursors can exceed the heating value of the biomass if the processing necessitates drying prior to conversion. Hydrothermal liquefaction (HTL) is a process that uses high-temperature, high-pressure water to directly convert wet biomass to an energy-dense biocrude oil (Dote et al., 1994; Brown et al., 2010), obviating most of the

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energy penalties incurred by drying. Moreover, HTL also produces aqueous-phase and gaseous fractions as co-products.

Numerous studies have examined the effects of temperature and holding time on the product distribution created by isothermal HTL of microalgae (Jena et al., 2011; Garcia Alba et al., 2012; Valdez et al., 2012; Christensen et al., 2014). These studies all concluded that temperature has a much greater effect on product distribution than holding time; however the holding times employed were long (10 – 120 min) and reactions were generally quenched well after most algal solids had reacted to form products at temperatures relevant to HTL ($T \geq 250\text{ }^{\circ}\text{C}$).

Compared to prior work on isothermal HTL, far fewer studies have examined non-isothermal HTL with rapid heating (fast HTL). Faeth et al. (2013) used average heating rates of $170 - 350\text{ }^{\circ}\text{C min}^{-1}$ and obtained comparable or higher biocrude yields than from isothermal conditions but over much shorter timescales (1 – 5 min). The results suggest that microalgal HTL occurs on timescales much shorter than previously thought. Others have demonstrated similar results for fast HTL in batch reactors of corn stover (Zhang et al., 2008), bacteria and yeast (Valdez et al., 2014), and macroalgae (Bach et al., 2014), and for continuous HTL of microalgae ($200 - 990\text{ }^{\circ}\text{C min}^{-1}$) (Jazrawi et al., 2013; Biller et al., 2015). Moreover, very recently Cheng et al. (2016) developed a glass- and silicon-based chip to achieve even more rapid heating rates ($\sim 900\text{ }^{\circ}\text{C min}^{-1}$). They observed appreciable biocrude formation (38 % of maximum fluorescence intensity) at 1 min for at set-point temperature of $300\text{ }^{\circ}\text{C}$, further demonstrating the short timescales of algal HTL kinetics.

Despite this recent shift toward shorter holding times (1 – 5 min) (Faeth et al., 2013; Jazrawi et al., 2013; Biller et al., 2015; Cheng et al., 2016), the field currently lacks a comprehensive examination of HTL product fraction evolution with respect to time, temperature, and heating rate over timescales short enough to elucidate reaction kinetics. This gap in the literature presents an opportunity to explore these process variables in a more systematic manner. Additionally, few attempts have been made to quantitatively model microalgal HTL kinetics. There have been several attempts to model HTL product distribution at specific isothermal HTL conditions based on the biochemical composition of the microalgae (Biller and Ross, 2011; Teri et al., 2014; Leow et al., 2015), but none of those models attempt to predict kinetic behavior. Valdez and Savage (2013) developed a reaction network and posited the first kinetic model for the (isothermal) HTL of *Nannochloropsis* sp., a marine species of microalgae, encompassing a wide range of temperatures ($250 - 400\text{ }^{\circ}\text{C}$) and holding times (10 – 90 min). This model successfully correlated the yields of solid, biocrude, aqueous-phase, and gas products for the reaction conditions within the scope of the study. However, the data used to develop the model only included experiments with holding times of 10 min or longer, with no data at low solids conversion and little variation in product distribution by 20 min. This restriction on reaction times was imposed such that all reactions operated under predominantly isothermal conditions (reactor heat-up contributed to $\leq 50\text{ }\%$ of the holding time).

It is essential that a microalgal HTL kinetic model incorporates data collected on the same timescale over which

reactions occur and that the actual temperature profile experienced inside the reactor is known if the heat-up time is comparable to the holding time. In this study, we sought to conduct the most thorough investigation of the coupled effects of time, temperature, and heating rate on HTL product yields to date. We then used this expansive database to develop a modified reaction network and quantitative kinetic model to calculate HTL product yields over a broad range of temperatures (200 – 400 °C), holding times (10 s – 60 min), and average heating rates (110 – 350 °C min⁻¹). This is the first kinetic model for fast HTL.

2. Materials and Methods

2.1. Experimental

A preservative-free slurry of 31 ± 1 wt % (s.d.) *Nannochloropsis* sp. and water was purchased from Reed Mariculture, who reported its composition to be 59 wt % proteins, 14 wt % lipids, and 20 wt % carbohydrates. The ash content was previously reported to be 6 wt % (Faeth et al., 2013). We constructed 1.67 mL batch reactors from a $3/8$ in. Swagelok® port connector and two caps, all of 316 stainless-steel construction. We loaded each reactor with enough algae slurry (0.309 – 0.589 g) and deionized water (0.353 – 0.673 g) to constitute a 15 wt % slurry of algae in water. We calculated reactor loadings such that reactor pressures would not exceed 400 bar at the final temperature. After loading, reactors were sealed to 45 ft-lbs. using a torque wrench.

Additional 1.50 mL proxy reactors for temperature measurements were constructed using a $3/8$ in. port connector, a cap, and a bored-through reducing union (reducing the internal diameter from $3/8$ in. to $1/8$ in.). An Omega Engineering, Inc. $1/8$ -in.-diameter 18-in.-long stainless-steel-clad K-type thermocouple was inserted into the $1/8$ -in. end of the reducing union such that the tip of the thermocouple resided in the middle of the reactor body when closed. We loaded each proxy reactor with enough deionized water to match approximately the total density in the HTL reactors. An Omega Engineering, Inc. UWBT-TC-UST-NA Datalogger recorded the temperature measured by the thermocouples in the proxy reactors every 0.1 s.

The loaded, sealed reactors were submerged in a Techne IFB-51 fluidized sand bath preheated to the specified set-point temperature. We define holding time as the time from the instant the reactor begins to heat up to the instant the reactor starts to cool down. At the end of the holding time, reactors were removed from the fluidized sand bath and quickly quenched in cold water. After about 3 min, the exterior of the reactors was dried with paper towels. For reactions with holding times less than 1 min, we placed proxy reactors in the sand bath simultaneously with the reaction vessels, and for all other reactions ($t > 1$ min) we used temperature profiles previously recorded at the same set-point temperature, averaged over at least two independent trials. Typically, reactors immersed at set-point temperatures of 200, 300, 400, 500, and 600 °C exhibited average heating rates of 110, 170, 230, 290, and 350 °C min⁻¹, respectively. These heating rates were calculated as linear averages over the time it took reactors to reach within 95 % of the maximum temperature change, typically about 95 s. For example, this threshold for a 300

°C set-point temperature would occur when the temperature is about 286 °C ($0.95 = (286 - 25)/(300 - 25)$).

Representative temperature profiles are listed in Table A.1 in Appendix A.

Within 2 h after quenching and drying, reactors were weighed, tapped forcefully on the benchtop three times, opened to release gases, and weighed again. We calculated the mass of gas evolved as the difference between these two reactor masses. Biocrude, aqueous-phase, and solid products were recovered according to the procedure described previously (Valdez et al., 2012). This procedure involves pouring the reactor contents into a glass conical centrifuge tube, rinsing the reactor with 9 mL of dichloromethane (> 95 % optima grade, Fisher Scientific) in small aliquots, and collecting these rinsings in the same glass tube. This tube was then mixed using a vortex mixer and centrifuged to facilitate phase separation.

Following centrifugation, the organic (dichloromethane-soluble) phase was manually collected using a pipette and transferred to a pre-weighed glass tube. The remaining aqueous phase and solid products were again mixed using a vortex mixer and centrifuged. The aqueous phase was transferred to a pre-weighed vial via pipette and the residual solids were left in the original glass tube. Tubes containing the dichloromethane-dissolved organics, remaining solids, and wet aqueous phase were each dried under nitrogen (99.998 %, Metro Welding Supply Corp.), using a Labconco® RapidVap® Vertex™ Dry Evaporator with a solid aluminum heating block at 35, 35, and 70 °C, respectively, and weighed until two consecutive cycles of drying and weighing produced tube masses varying by < 2 mg. The dried organic, solid, and aqueous phases are what we term the biocrude, solid, and aqueous-phase products, respectively. Furthermore, we define the volatiles fraction to be the compounds primarily dissolved in the aqueous phase but lost due to evaporation upon drying at 70 °C (Valdez et al., 2012). We also report the sum of the aqueous-phase and volatile product fractions, which is an estimate of the total material in the aqueous phase immediately post HTL (Jena et al., 2011). Product yields were calculated by dividing the mass of product collected by the initial mass of dry algae for a given reaction. The yield of volatiles was calculated by difference. In a few cases we observed gas yields that were higher than expected based on other data collected under similar reaction conditions. In these rare cases we used interpolation to estimate the gas yields. For some reactions conducted below 250 °C, the insolubility of unreacted algae in dichloromethane made it difficult to recover all of the material. In these cases we scaled the solid and aqueous-phase product yields to close the mass balance. Details about the procedure used for adjustment along with both the unadjusted and adjusted yields appear in Appendix A.

3. Results and Discussion

This section reports the product yields from HTL of *Nannochloropsis* sp. at temperatures of 100 – 400 °C, holding times of 10 s – 60 min, and average heating rates of 110 – 350 °C min⁻¹. Following the experimental results, we propose a reaction network and kinetic model.

3.1. Product fraction yields

Figure 1 depicts the yields of product fraction i (x_i) from HTL of *Nannochloropsis* sp. The black lines on the plots represent typical reactor temperature profiles resulting from set-point temperatures of 200, 300, 400, and 500 °C. Each individual point represents a single HTL reaction shaded to show the product fraction yield and plotted at the holding time and final reactor temperature reached. Table A.2 in Appendix A lists the exact product yields used in Figure 1.

Figure 1a depicts solid yields. To the best of our knowledge, this is the first study to capture the shift from low conversion (< 30 %) at short holding times ($t < 1$ min) and low temperatures ($T < 250$ °C) to high conversion (~100 %) at typical isothermal HTL conditions ($t > 20$ min, $T > 300$ °C). As expected, solid yields are highest at short holding times and low temperatures (bottom left) and lowest at long holding times and high temperatures (top right). Solid yields decrease monotonically with increasing reaction severity throughout the entire range of HTL reaction conditions examined until a lower bound (on the order of the ash content) is reached. At a set-point temperature of 300 °C, for example, this lower bound is observed for $t > 3$ min, and this time decreases with increasing temperature. At $t > 3$ min, and $T = 200$ °C, solid product yields decrease with increasing holding times, though complete conversion is not observed within the range of reaction times examined at this temperature. Above 200 °C, solids yields decrease dramatically with increasing temperature; moreover, solids conversion at 200 °C is remarkably slower than at 250 °C, compared to other 50 °C increments (e.g. 250 °C compared to 300 °C). This may indicate that hydrolysis of algal biomolecules becomes much more kinetically favorable in the range of 200 – 250 °C, which is consistent with temperatures reported in the literature (Sasaki et al., 2000; Rogalinski et al., 2008; Garcia Alba et al., 2012).

Figure 1b displays biocrude yields. The trends in biocrude yield were of comparable magnitude and opposite to those of solid yields, with yields generally increasing as a function of temperature and time. At short holding times, a maximum yield was reached at around 300 – 400 °C and 3 – 7 min. At longer times characteristic of isothermal HTL, this maximum yield shifts to a lower range of 250 – 350 °C, with little variation in yields after 5 min. This temperature range for maximizing biocrude yield and these trends are in agreement with myriad studies for isothermal HTL (Biller and Ross, 2012; Valdez et al., 2012; Eboibi et al., 2014; Christensen et al., 2014; Sudasinghe et al., 2015). At 400 °C, biocrude yields show a slight, yet non-negligible decrease with increasing reaction time. Decreasing biocrude yields with increasing time at temperatures above 350 °C has also been observed previously (Jena et al., 2011; Valdez et al., 2012).

Figure 1c shows that gas yields generally increase with increasing temperature and time. Although the trend at long reaction times is consistent with previous studies (Jena et al., 2011; Garcia Alba et al., 2012; Valdez et al., 2012; Christensen et al., 2014), the gas yields in the present work are higher than those reported previously for *Nannochloropsis* sp. (Valdez et al., 2012) but on the same magnitude as those for other microalgae (Jena et al., 2011;

Garcia Alba et al., 2012). This difference in observed gas product yields may be a consequence of measurement technique. In this study, we measured the mass of gas evolved shortly after the reaction by the difference in mass of vented and unvented reactors, however Valdez et al. (2012) employed reactors equipped with gas valves to measure gas by GC analysis. We took care to ensure that the mass of gas evolved was measured within 2 h after reactions were quenched to limit the extent that carbon dioxide, the principal component of the gas phase (Brown et al., 2010; Jena et al., 2011; Garcia Alba et al., 2012), dissolves in the aqueous phase. The dissolution kinetics of carbon dioxide from the gas phase into the aqueous phase are fast, with a forward rate constant of $1 \times 10^{10} \text{ s}^{-1}$ (Stumm and Morgan, 1996). However, diffusion of dissolved carbon dioxide in water is slow, with a diffusion coefficient of $\mathcal{D} = 2.233 \times 10^{-9} \text{ m}^2/\text{s}$ (Cadogan et al., 2014). Our analysis shows that < 25 % of the carbon dioxide would have dissolved in the aqueous phase within 2 h of time between quenching a reaction and gas measurement. Moreover, we agitated the reactors by forcefully tapping them on the benchtop three times before opening to further liberate carbon dioxide back into the gas phase. See Appendix A for an extensive analysis of this phenomenon.

Figure 1d depicts aqueous-phase product yields. At every set-point temperature except 200 °C, aqueous-phase product yields increase initially to a maximum value at moderate reaction severity, then decrease at high reaction severity. At short times, they reach a maximum at about 320 – 380 °C and 45 s – 2 min. We postulate that rapid heating ($175 - 375 \text{ °C min}^{-1}$) could be facilitating protein and amino acid recovery in the aqueous phase. Garcia-Moscoso et al. (2015) developed a similar, yet more rapid process they refer to as flash hydrolysis (240 – 320 °C, 6 – 12 s) with essentially instantaneous heating achieved by mixing pre-heated, pressurized water with algal slurry in a continuous reaction system. These conditions allowed peptides and arginine, among other protein-derived co-products, to be readily recovered while simultaneously preserving the lipid content of the algal solids. Rapidly heating reaction mixtures to elevated temperatures seems to favor protein-derived product recovery in the aqueous-phase while also apparently minimizing cross-reactions between lipids and protein (Garcia-Moscoso et al., 2015).

At longer times and isothermal conditions, aqueous-phase product yields monotonically decrease with increasing temperature and reaction time (for set-point temperatures above 200 °C only), reaching a minimum at 400 °C and 40 min and a maximum at 200 °C and 40 min. These trends are consistent with those reported previously for yields of aqueous-phase products (Jena et al., 2011; Garcia Alba et al., 2012; Valdez et al., 2012; Christensen et al., 2014). Moreover, a number of recent studies have explored low-temperature (125 – 225 °C) pre-treatment steps, usually as a means of reducing the nitrogen content of the algal solids thereby improving the quality of the resulting biocrude oil produced from a subsequent HTL reaction (Miao et al., 2012; Costanzo et al., 2015; Jazrawi et al., 2015) or transesterification reaction (Levine et al., 2013; Lu et al., 2015) while simultaneously producing a nutrient-enriched aqueous phase. In terms of the solid and aqueous-phase product yields, our results at 200 °C are consistent with the findings of those studies. Moreover, Costanzo et al. (2015) and Jazrawi et al. (2015) showed that reactions responsible for nitrogen recovery in the aqueous phase are acid catalyzed with rates that increase with reaction

severity.

Figure 1e illustrates the volatile product yields. Volatile yields are essentially zero for $T < 250$ °C, and very low at short holding times ($t < 2$ min). At high reaction severity, volatile yields increase substantially, especially at $T \geq 350$ °C and $t \geq 2$ min. These values for volatile yields and the aforementioned trends are consistent with those reported by Valdez et al. (2012) and Christensen et al. (2014) (through the difference between their mass recovery and unity in the latter case). Moreover, these trends are nearly equal and opposite of those for aqueous-phase products, suggesting that aqueous-phase components are degrading to form smaller, more volatile compounds in this region. The aqueous phase was dried at 70 °C, and it is likely that some of these compounds become volatile in the range of $25 < T < 70$ °C. Increases in volatile yields also occur simultaneously with small decreases in biocrude at high reaction temperature ($T \geq 300$ °C) and long reaction times ($t \geq 40$ min). These concurrent phenomena suggest that aqueous-phase product degradation is the primary reaction pathway to produce volatiles, but that some degradation of biocrude at elevated temperatures and long reaction times cannot be ruled out.

Given the results in Figures 1d and 1e, along with previous studies indicating that volatile products are produced primarily from aqueous-phase products (Valdez et al., 2012), we also plot aqueous-phase product and volatile yields combined in Figure 1f. The trends for the combined volatile and aqueous-phase products match those of just the aqueous-phase products in Figure 1d at low reaction severity and those of the volatiles in Figure 1e at high reaction severity. Some experiments at extended holding time ($t \geq 20$ min) show decreased volatile and aqueous-phase product yields and increased gas yields, suggesting that gasification of aqueous-phase products occurs at those conditions. We expect these values to show more variability than the other products because, like volatile yields, these values were calculated by difference rather than by direct measurement.

3.2. Kinetic model development

We sought to derive a reaction network and develop a corresponding kinetic model that accurately describes the behavior of microalgal HTL over the entire range of reaction conditions employed. We began with the kinetic model and associated reaction network developed by Valdez and Savage (2013), which was corroborated both by isothermal algal HTL reactions (Valdez et al., 2012) and additional isothermal reactions of the individual product fractions (solid, biocrude, and aqueous-phase products) (Valdez and Savage, 2013). Using their model to predict the results discussed in Section 3.1 resulted in the parity plots shown in Figure A.1. This model reasonably calculates biocrude yields from HTL at the conditions employed in that study (Fig. A.1b), although the aqueous-phase and volatile product yields were over-calculated and gas yields were under-calculated, likely due to the differences in gas quantification discussed in Section 3.1. However, the model breaks down ($\sigma = 17$ wt %) at holding times shorter than 10 min (Fig. A.1a), clearly demonstrating the need for a model that describes fast HTL.

In general, the results discussed in Section 3.1 support the reaction network developed by Valdez and Savage (2013). The exception is that our results do not immediately suggest that a biocrude to gas pathway exists. Given that small

but appreciable gas formation occurs at low reaction severity conditions, where no biocrude is present, we instead employ a direct solids to gas pathway instead of biocrude to gas. Moreover we add an aqueous-product to volatile pathway to describe that transition shown in Figures 1d and 1e. Figure 2 presents this modified reaction network with pathways that lead to biocrude (B), aqueous-phase product (A), gas (G), and volatile (V) formation from algal solids (S). We assume each reaction pathway in Figure 2 to be psuedo-first-order and follow Arrhenius kinetics:

$$k_{ij}(t) = A_{ij} \exp\left(\frac{-E_{ij}}{RT(t)}\right) \quad (1)$$

Here, $k_{ij}(t)$ is the rate constant for the reaction pathway from reactant i to product fraction j , A_{ij} is the pre-exponential factor, E_{ij} is the activation energy, R is the gas constant, and $T(t)$ is the temperature, which is time-dependent during the non-isothermal part of each experiment. Applying Equation 1 and the batch reactor design equation to the reaction network in Figure 2 yields the following system of first-order ordinary differential equations for the temporal evolution of the product fraction yields, x_i :

$$\frac{dx_S^*}{dt} = -(k_{SB} + k_{SA} + k_{SG})x_S^* \quad (2)$$

$$\frac{dx_B}{dt} = k_{SB}x_S^* + k_{AB}x_A^* - k_{BA}x_B \quad (3)$$

$$\frac{dx_G}{dt} = k_{SG}x_S^* + k_{AG}x_A^* \quad (4)$$

$$\frac{dx_A^*}{dt} = k_{SA}x_S^* + k_{BA}x_B - (k_{AB} + k_{AG} + k_{AV})x_A^* \quad (5)$$

$$\frac{dx_V}{dt} = k_{AV}x_A^* \quad (6)$$

Given that solids and aqueous-phase product yields approach steady nonzero values at the highest reaction severities explored herein, we also employed the following change of variables:

$$x_S = x_S^\infty + x_S^* \quad (7)$$

$$x_A = x_A^\infty + x_A^* \quad (8)$$

x_S and x_A are measured directly (Figure 1a and 1d, respectively) and we calculated $x_S^\infty = 4 \pm 1$ wt % and $x_A^\infty = 12 \pm 4$ wt % based on the average values of x_S and x_A for all experiments above 300 °C with holding times longer than 8 min. x_S^∞ represents the average amount of unreacted (primarily ash) and repolymerized solids remaining at high reaction severity, and our reported value is consistent with reported solid yields in the literature for HTL of *Desmodesmus* sp. (Garcia Alba et al., 2012), *Nannochloropsis* sp. (Valdez et al., 2012), *Phaeodactylum tricornutum* (Christensen et al., 2014), and *Spirulina platensis* (Jena et al., 2011) at these conditions. x_A^∞ represents the average amount of aqueous-phase compounds remaining at high reaction severity, and our reported value is consistent with reported aqueous-phase product yields for *Desmodesmus* sp. (Garcia Alba et al., 2012) at these conditions (also dried at 70 °C). Incorporating x_S^∞ and x_A^∞ in the model ensured that it would always calculate reasonable yields for those product fractions.

We performed three control experiments, following the same procedure outlined in Section 2 at room temperature (25 °C) and a holding time of 60 min, to determine the initial condition for the model to be $x_{S,0} = 84 \pm 2$ wt % ($x_{S,0}^* = 80 \pm 3$ wt %), $x_{A,0} = 15 \pm 2$ wt % ($x_{A,0}^* = 3 \pm 4$ wt %), $x_{B,0} = 1 \pm 0$ wt %, $x_{G,0} = 0$ wt %, and $x_{V,0} = 0$ wt %. Using the temperature profiles and product yield data from each experiment, we calculated values for all kinetic parameters by simultaneously solving the system of first-order, ordinary differential equations in MATLAB® with the function `ode23s`. We then used `lsqnonlin` to minimize the objective function, which consisted of a 45 (experiment) by 5 (product) matrix of differences between the observed and calculated weight fractions. Confidence intervals for parameters were calculated using the function `nlparci`.

3.3. Kinetic model results

Table 1 displays the Arrhenius parameters for the chemical reaction pathways, with confidence intervals representing the standard deviation. These parameters are valid on the temperature, holding-time, and average-heating-rate ranges of 100 – 400 °C, 10 s – 60 min, and 110 – 350 °C min⁻¹, respectively.

The activation energies for the solids conversion pathways ($S \rightarrow B$, $S \rightarrow A$, and $S \rightarrow G$) are comparable to those reported for the hydrolysis of various compounds in high-temperature water, including proteins to amino acids (46 – 191 kJ mol⁻¹) and acylglycerides to free fatty acids (50 – 105 kJ mol⁻¹) (Changi et al., 2015). The values are lower than those reported for carbohydrate conversion, including cellulose, starch, and mono- and disaccharides (92 – 164 kJ mol⁻¹) (Changi et al., 2015), perhaps because carbohydrates constituted just 20 wt % of the initial biomass. Moreover, carbohydrate conversion has been demonstrated to be slower than the conversion of proteins and lipids (Biller and Ross, 2011; Teri et al., 2014). The activation energies in Table 1 for gas formation pathways ($S \rightarrow G$ and $A \rightarrow G$) are comparable to those reported by Guan et al. (2012) for hydrothermal gasification of algae, when the reported rate constants for individual gaseous species are lumped together (Valdez and Savage, 2013). In general, our model features pre-exponential factors and activation energies higher than those reported by Valdez and Savage (2013). This translates to calculated values for k_{SB} and k_{SA} that are about an order of magnitude higher than those calculated using the Valdez and Savage (2013) model.

Figure 3a shows the instantaneous selectivity, $S_{Sj} = k_{Sj}/k_{S,T}$, of solids conversion reactions $S \rightarrow j$, where $j = A, B, G$, with respect to temperature. Here $k_{S,T} = k_{SA} + k_{SB} + k_{SG}$ is the total rate constant for disappearance of solids. The selectivities of solids to aqueous-phase products and biocrude decrease and increase monotonically, respectively, with increasing reaction temperature, with the rate of biocrude formation from solids exceeding that of aqueous-phase product formation at around 275 °C. This trend suggests that rapidly heating the reaction mixture to 275 °C or higher would maximize biocrude production from algal solids.

Figure 3b depicts the instantaneous selectivity, $S_{Aj} = k_{Aj}/k_{A,T}$, of aqueous-phase product conversion reactions $A \rightarrow j$, where $j = B, G, V$, with respect to temperature. Here $k_{A,T} = k_{AB} + k_{AG} + k_{AV}$ is the total rate constant of

disappearance of aqueous-phase products. The selectivity of aqueous-phase products to biocrude follows that of aqueous-phase products to gas closely throughout the entire range of temperatures plotted, although biocrude is slightly favored below 170 °C, and gas is slightly favored for 170 – 270 °C. The selectivity of volatile product formation, S_{AV} , increases substantially with reaction temperature, rendering volatiles the favored product fraction above 270 °C.

Figure 4 depicts observed product fraction yields and model solutions calculated using representative temperature profiles for each set-point temperature. Several data also show standard deviations obtained from replicate reactions (dotted lines); these experimental uncertainties are comparable to those reported by Valdez and Savage (2013) and Faeth et al. (2013). Figures 4d and 4e show that the model correlates the data very well at set-point temperatures of 350 and 400 °C, respectively. The model solutions at 250 and 300 °C (Fig. 4b and 4c, respectively) are generally good, with the exception of an over-prediction of aqueous-phase product yields at intermediate holding times. Model calculations for solid, biocrude, and gas yields remain well correlated in this region, however. The model exhibits the lowest accuracy in Figure 4a for a set-point temperature of 200 °C. Here, the model under-predicts solid yields (over-predicts conversion) and correspondingly over-predicts aqueous-phase product, biocrude, and gas yields.

One possible explanation for the reduced accuracy in Fig. 4a and 4b is that the non-homogeneity of the algal slurry causes the reaction mixture to deviate from pseudo-first-order and/or Arrhenius kinetics behavior, with the cell walls potentially imposing an energy threshold for liberating the intracellular components of the algae. Garcia Alba et al. (2012) examined SEM images of the solids product fraction before and after conducting hydrothermal liquefaction of *Desmodesmus* sp. at temperatures in the range of 200 – 275 °C. They found that there were significant morphological differences in the solids fraction in this region, with major degradation observed between 225 and 250 °C (Garcia Alba et al., 2012). The reduced model accuracy at $T_{sp} \leq 250$ °C and the results presented by Garcia Alba et al. (2012) demonstrate that further studies of hydrothermal conversion at low temperatures of microalgae with different types of cell walls may be required to improve model accuracy in that region. In general, however, the quality of the agreement between observed and calculated product yields at $T_{sp} \geq 300$ °C demonstrates the utility of the present kinetic parameters and reaction network at calculating yields for both non-isothermal and isothermal HTL conditions.

Figure A.2 shows residual plots for each product fraction. The model over-calculates solid yields (Fig. A.2a) at moderate reaction severity; above 280 °C the residuals are significantly smaller. The residual plots highlight that, at low to moderate reaction severity ($T < 280$ °C, $20 \text{ s} < t < 3 \text{ min}$), the model tends to deviate from observed product fraction yields by a larger magnitude than at moderate to high reaction severity, with the exception of volatile yields. This observation reaffirms a need for future studies to further elucidate reaction kinetics in this low-to-moderate severity region.

Figure 5 depicts parity plots of the observed and calculated biocrude yields, for several previous studies (Biller and Ross, 2011; Valdez et al., 2012; Faeth et al., 2013; López Barreiro et al., 2013; Leow et al., 2015). The specific data

points that were selected appear in Table A.3 in Appendix A. We chose data within the scope of our model limits, including experiments conducted at 400 °C or lower for microalgae of the genus *Nannochloropsis*. Moreover, due to limited availability of temperature profile information, we assumed an isothermal temperature for data from the López Barreiro et al. (2013), Biller and Ross (2011), and Leow et al. (2015) studies and assumed temperature profiles typical for this study for data from the Faeth et al. (2013) and Valdez et al. (2012) studies. The standard deviation was 5 wt %, which is comparable to the experimental uncertainties shown in Figure 4 and demonstrated in studies with a similar experimental procedure (Valdez and Savage, 2013; Faeth et al., 2013). Figure 5 demonstrates that the model can be successfully applied for biocrude prediction to microalgae within the *Nannochloropsis* genus and of a similar biochemical composition over a broad range of reaction conditions. Comparison of model-predicted yields to literature data for other products is much less meaningful, due to differences in experimental procedures. See Appendix A for further explanation on model validation for other product fractions.

3.4. Calculated yields

With the establishment of a kinetic model that can describe algal HTL as a function of temperature and time, irrespective of heating rate, we now use it to improve our understanding of the kinetics that govern this process. Figure 6 depicts density plots of product fraction yields as functions of temperature and time for isothermal HTL. Dashed lines correspond to the maximum aqueous-phase product (x_A^{max}) and biocrude (x_B^{max}) yields achievable as a function of isothermal HTL temperature.

Figure 6a illustrates the change in the calculated solids yields, x_S^{calc} , over time for different temperatures. At short times ($t < 30$ s) and low temperature ($T < 250$ °C), little solids conversion occurs. Beyond this region, solids react readily with increasing temperature and time, and complete solids conversion can be achieved for all temperatures examined. The curve for the maximum aqueous-phase product yield, x_A^{max} , coincides with the region where the solids completely disappear (i.e., $x_S^{calc} \approx x_S^{\infty}$), which seems reasonable if the algal solids are the main producers of aqueous-phase products. Moreover, the curve for the maximum biocrude yield, x_B^{max} , always occurs well beyond the point of solids depletion, indicating that secondary reactions contribute significantly to biocrude production.

Figure 6b shows the calculated biocrude yields. Biocrude formation increases substantially with reaction temperature at short times, coinciding with the corresponding decrease in solids (Fig. 6a). Biocrude yields as high as 46 wt % are achievable after 1 min at 400 °C. Once solids completely disappear, the biocrude yield is much less sensitive to reaction severity. This trend of little variation also holds over a fairly wide region of temperature and times, but shifts downward with increasing reaction time, from a range of 325 – 400 °C at 1 min to a range of 225 – 350 °C at 60 min, for example. In general, the biocrude yield increases with reaction severity, but the existence of maxima indicates that it does decrease at elevated temperatures ($T > 350$ °C) and long reaction times ($t > 20$ min). At times of 10 – 60 min, these maximum yields occur between 300 – 350 °C. This range of temperatures is in excellent agreement with numerous previous studies conducted under isothermal conditions for various microalgae, including

375 °C for *Desmodesmus* sp. (Garcia Alba et al., 2012), 300 – 350 °C for *Nannochloropsis* sp. (Brown et al., 2010; Valdez et al., 2012), 350 °C for *Phaeodactylum tricornutum* (Christensen et al., 2014), and 350 °C for *Spirulina platensis* (Jena et al., 2011). The maximum biocrude yield ranged only from 45 – 46 wt % regardless of temperature ($T \geq 300$ °C). This modest variation is within the uncertainty in the data, and it indicates that HTL is a very robust process in that it can achieve nearly the same maximum biocrude yields over a very wide range of temperatures and times. This robustness may provide opportunities to select HTL conditions that provide high biocrude yields and also optimize some other desired outcome (e.g. biocrude quality, nitrogen recovery in the aqueous phase, etc.).

Figure 6c displays gas yields, x_G^{calc} , calculated over time for several temperature profiles. Gas yields are fairly low at low reaction severity, but increase with increasing temperature and time beyond the point of solids depletion (Fig. 6a). At longer reaction times ($t > 30$ min), gas formation is favored at moderate temperatures (250 – 350 °C). The global maximum calculated gas yield of 20 wt % occurs at $T = 280$ °C and $t = 60$ min.

Figure 6d depicts the calculated yields of aqueous-phase products, x_A^{calc} . At low reaction severity, aqueous-phase product yields increase significantly with increasing temperature and time until solids are depleted and then decrease with further increases in reaction severity. Moreover, the maximum aqueous-phase product yield itself, x_A^{max} , decreases monotonically with increasing temperature, from a global maximum of 52 wt % at $T = 200$ °C and $t = 50$ min, to 35 wt % at $T = 400$ °C and $t = 10$ s. Notably, the temperature range that maximum aqueous-phase products are produced at long times is consistent with those reported in the literature, including 225 – 250 °C for *Desmodesmus* sp. (Garcia Alba et al., 2012), 250 °C for *Nannochloropsis* sp. (Valdez et al., 2012), and 200 °C for *Spirulina platensis* (Jena et al., 2011). Similar to x_A^{max} occurring at the point of solids depletion (Fig. 6a), the maximum biocrude yield, x_B^{max} , always occurs when the yield of aqueous-phase products reaches approximately 20 wt % or less.

Figure 6e shows x_V^{calc} , the calculated volatile yields. At short times, volatile formation only occurs at $T > 300$ °C, increasing rapidly in the range of 350 – 450 °C. At longer times, volatile yields become appreciable only at $T > 275$ °C. Similarly to gas yields, the volatiles yield increases monotonically with increasing reaction time, due to the irreversibility imposed by the reaction network in Figure 2. The global maximum is 44 wt % at $T = 400$ °C and $t = 60$ min, the most severe reaction condition shown. Volatiles are also the most favored product at elevated temperatures ($T > 350$ °C), given the high values of the Arrhenius parameters for the rate constant for the $A \rightarrow V$ reaction pathway. For completeness, we also show aqueous-phase and volatile product yields together in Figure 6f.

Examined together, the plots in Figure 6 illustrate that one can decouple effects of temperature and time on the HTL product distribution. Above 250 °C and 30 s, biocrude and aqueous-phase product yields increase dramatically with increasing reaction severity until solids are depleted. Aqueous-phase product yields reach a maximum at that region and decrease with increasing reaction severity while biocrude yields increase modestly and volatile yields become appreciable. At extreme reaction severities, biocrude yields begin to decrease modestly and volatile yields increase

substantially. Examination of longer reaction times in Figure 6 shows that temperature plays a larger role than time in determining product distribution; aqueous-phase products, biocrude and gas (collectively), and volatiles are favored below 225 °C, between 225 – 350 °C, and above 350 °C, respectively.

Examining Figure 6 also demonstrates an interplay between aqueous-phase products and biocrude. For a given reaction time, the maximum biocrude yield generally occurs at temperatures about 100 °C higher than the maximum aqueous-phase product yield. As previously discussed, the increase in biocrude yield observed between x_A^{max} and x_B^{max} can be entirely attributed to aqueous-phase products reacting to form dichloromethane-soluble products (biocrude) because solids are essentially depleted in that region (x_S^{calc} is of order x_S^∞). Aqueous-phase products are rich in nitrogen, and it has been demonstrated that nitrogen incorporation in the biocrude increases with reaction time and temperature in this range (Jena et al., 2011; Garcia Alba et al., 2012; Valdez et al., 2012; Faeth et al., 2013; Jazrawi et al., 2013; Cheng et al., 2016). Therefore, it seems plausible that this increase in biocrude yield with holding time is the result of nitrogen-containing aqueous-phase compounds reacting to become less polar or incorporating themselves with larger organic molecules through mechanisms like the Maillard reaction (Tian et al., 2014; Teri et al., 2014; Changi et al., 2015). We speculate that maximizing aqueous-phase product formation either through short reaction times and rapid heating or longer reaction times at lower temperatures (200 – 225 °C) may be desirable from a biocrude quality and energy input standpoint. Doing so may lower nitrogen incorporation into the biocrude (and maximize nitrogen recovery into the aqueous phase for recycling), reducing the burden of downstream catalytic hydrodenitrogenation reactions necessary for biocrude refinement (Tian et al., 2014).

4. Conclusions

We elucidated algal HTL kinetics through a comprehensive study of the coupled effects of temperature, reaction time, and heating rate on algal HTL product yields. We used these data to develop a reaction network and kinetic model valid over a broad range of holding times (10 s – 60 min), including much shorter timescales (10 s – 10 min) than previously established. Calculated yields correlate well with observed yields, and the model shows that biocrude yields as high as 46 wt % are achievable at 400 °C and 1 min. The model highlights potential trade-offs between biocrude quantity and quality.

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Pathway	$\log(A)$ [$\log(s^{-1})$]	E_a [kJ mol^{-1}]
$S \rightarrow B$	5.0 ± 0.6	74 ± 6
$S \rightarrow A$	4.0 ± 0.5	65 ± 6
$S \rightarrow G$	3.9 ± 0.7	68 ± 8
$B \rightarrow A$	3.8 ± 1.0	99 ± 19
$A \rightarrow B$	1.7 ± 0.5	59 ± 8
$A \rightarrow G$	2.3 ± 0.5	64 ± 7
$A \rightarrow V$	7.6 ± 1.5	119 ± 17

Table 1: Arrhenius parameters for reaction pathways in Figure 2.

(a) Solid

(b) Biocrude

(c) Gas

(d) Aqueous-phase products

(e) Volatile products

(f) Aqueous-phase and volatile products

Figure 1: Product fraction yields from the hydrothermal liquefaction of *Nannochloropsis* sp. plotted as functions of final reactor temperature and holding time. Solid lines represent typical temperature profiles based on sand-bath set-point temperatures of 200, 300, 400, and 500 °C.

Figure 2: Reaction network for the fast and isothermal hydrothermal liquefaction of *Nannochloropsis* sp. S, B, A, G, and V represent solids, biocrude, aqueous-phase products, gases, and volatiles, respectively.

Figure 3: (a) Instantaneous solids conversion selectivities, $S_{Sj} = k_{Sj}/k_{S,T}$, where $k_{S,T} = k_{SB} + k_{SA} + k_{SG}$, with respect to temperature. Dark gold, brown, and gray-blue lines correspond to aqueous-phase products (A), biocrude (B), and gas (G), respectively. (b) Instantaneous aqueous-phase product conversion selectivities, $S_{Aj} = k_{Aj}/k_{A,T}$, where $k_{A,T} = k_{AB} + k_{AG} + k_{AV}$, with respect to temperature. Brown, gray-blue, and dark magenta lines correspond to biocrude (B), gas (G), and volatiles (V), respectively.

Figure 4: Model solutions (solid lines) and experimentally observed yields (x_i) over time at different set-point temperatures (T_{sp}) for solids (green circles), aqueous-phase products (gold triangles), biocrude (brown squares), gas (pale blue pentagons), and volatiles (purple hexagons). Dotted lines show standard deviation for selected experiments.

Figure 5: Parity plot of observed vs. **calculated** biocrude yields for data reported by Faeth et al. (2013), López Barreiro et al. (2013), Valdez et al. (2012), Biller and Ross (2011), and Leow et al. (2015).

Figure 6: (a) Solid, (b) biocrude, (c) gas, (d) aqueous-phase, (e) volatile, and (f) aqueous-phase and volatile product yields calculated as functions of time, t , and isothermal temperature, T . Solid black lines correspond to the yield contours marked by numbered ticks on the bar legend. Dashed lines show the maximum aqueous-phase product (x_A^{max}) and biocrude (x_B^{max}) yields at each temperature.