



Modeling the effects of microalga biochemical content on the kinetics and biocrude yields from hydrothermal liquefaction



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HIGHLIGHTS

- Developed HTL kinetic model for production of biocrude from microalgae.
- Model uses biochemical composition of microalgae and HTL reaction conditions as inputs.
- Model predicted 70 reported biocrude yields from 12 studies to within ± 5 wt%.
- Model predicts microalgae richer in proteins and/or lipids give higher biocrude yields.

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ABSTRACT

A kinetic model for the hydrothermal liquefaction (HTL) of microalgae was developed and its performance in predicting biocrude yields was tested. Kinetic interactions between algal proteins, carbohydrates, and lipids were also included for the first time. These interactions provided a better fit of the data used to determine model parameters, but the kinetics model lacking interactions provided a better prediction of published biocrude yields. This model predicted 70 published biocrude yields to within ± 5 wt% given the biochemical composition of the alga and the HTL temperature and time as model inputs. Forty-two other published biocrude yields were predicted to within ± 10 wt%. The model accurately predicts that feedstocks richer in proteins or lipids give higher biocrude yields than those abundant in carbohydrates. This updated model better predicts the combined influences of HTL reaction conditions and algae biochemical composition on HTL biocrude yields than any other model currently available.

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1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical process that transforms wet biomass into a renewable fuel precursor known as biocrude-oil. HTL uses water at elevated temperatures (200–400 °C) and pressures (10–40 MPa) to decompose biomass and hydrolyze the constituent biomacromolecules into smaller organic compounds (López Barreiro et al., 2013a; Peterson et al., 2008). The HTL of biomass results in four operationally defined product fractions: a nutrient-rich aqueous-phase, an energy-dense biocrude oil, gas products composed primarily of CO₂, and residual solids.

Microalgae are attractive feedstocks for producing biocrude via HTL due to their high moisture content, fast growth rate, and capability of accumulating large quantities of lipids (Becker, 1994; López Barreiro et al., 2013a). Microalgae are single-cell organisms

composed primarily of proteins, carbohydrates, and lipids. The biochemical composition of microalgae varies amongst species and can be influenced by the environment in which they are cultivated. For instance, microalgae grown under stressed conditions, with restricted amounts of nitrogen-containing nutrients, can accumulate high (>50 wt%) quantities of lipids (Becker, 1994).

Previous HTL studies using microalgal species with different biochemical compositions or with model compounds (e.g., soy protein, corn starch, sunflower oil) demonstrated that the biochemical composition of HTL feedstocks influenced the yield of biocrude (Biller and Ross, 2011; Gai et al., 2015; López Barreiro et al., 2013b; Reddy et al., 2016; Teri et al., 2014; Valdez et al., 2014). For example, HTL of four biochemically distinct microorganisms (*Chlorella vulgaris*, *Nannochloropsis oculata*, *Porphyridium cruentum*, and *Spirulina*) under the same operating conditions (350 °C, 1 h) gave biocrude yields ranging from 21 to 36 wt% (Biller and Ross, 2011). Additionally, Teri et al. (2014) reported that biocrude yields from HTL of biomass model compounds were in the order of triglycerides \gg proteins > carbohydrates.

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The ability to use the biochemical composition of microalgae undergoing HTL to predict the yields of the resulting biocrude could be impactful in identifying microalgae species and processing conditions suitable for biocrude production. Valdez et al. (2014) correlated the effects of the biochemical compositions of three microalgae species (*Nannochloropsis* sp., *C. protothecoides*, and *Scenedesmus* sp.) on the yields of the four major HTL product fractions by developing a general kinetic model that accounted separately for the initial reactions of protein, carbohydrates, and lipids in the microalgae. Their reaction network, Fig. 1, shows microalgal proteins, carbohydrates, and lipids generating both aqueous-phase products and biocrude. Subsequently, the aqueous-phase products and biocrude can interconvert or further decompose into gas products. This model correlated the experimental data over a range of isothermal HTL temperatures (250–400 °C) and batch holding times (10–60 min). Very recently, Vo et al. (2016) used this same reaction network to correlate the yields of the product fractions from HTL of *Aurantiochytrium* sp. *KRS 101* at different isothermal HTL processing conditions.

A second approach for using feedstock biochemical compositions to predict biocrude yields is to assume that a fixed fraction of each biochemical component forms biocrude. These fractions serve as yield coefficients (A, B, C) and the biocrude yield can be estimated as the sum of the contributions expected from each biochemical component, as shown by Eq. (1), where the x_i are mass fractions relative to the initial mass of algae.

$$x_{BC, predicted} (wt\%) = Ax_{Proteins} (wt\%) + Bx_{Lipids} (wt\%) + Cx_{Carbohydrates} (wt\%) \quad (1)$$

These component additivity models offer the benefit of simplicity and they have seen success in predicting biocrude yields. The yield coefficients, however, generally apply only to one specific HTL temperature and, at best, a range of processing times from about 5–60 min (Billar and Ross, 2011; Li et al., 2017; Loew et al., 2015; Teri et al., 2014). New yield coefficients would need to be determined at every temperature of interest. Likewise new yield coefficients would need to be determined at every heating rate if nonisothermal conditions were used. Kinetic models with a fixed set of parameters, on the other hand, offer the capability of describing HTL under any conditions include nonisothermal, “fast” HTL with rapid heating (Hietala et al., 2016).

Given the success of algae HTL kinetics models in fitting experimental data and the potential for such models to predict yields of all HTL product fractions at any arbitrary time and temperature combination, a kinetics model was expanded and investigated. Herein, the experimental data of Valdez et al. (2014) and Vo et al. (2016) were used to determine Arrhenius parameters for the reaction pathways in Fig. 1 that best fit this combined data set. Then these optimized Arrhenius parameters were used to predict published biocrude yields for HTL of various microalgae. This work tests for the first time the predictive ability of the general kinetic model first proposed by Valdez et al. This model then served as the foundation for exploring whether improved performance can be obtained by including kinetic interactions between

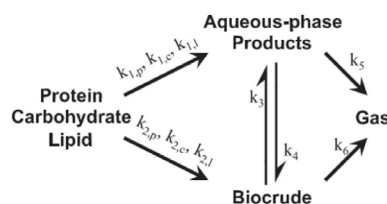


Fig. 1. Reaction network for HTL of microalgae with explicit consideration of biochemical content (Valdez et al., 2014).

the biochemical components of the biomass feedstocks. The abilities of this improved kinetics model, both with and without interaction terms, and the original models (Valdez et al., 2014; Vo et al., 2016) to predict published biocrude yields were compared. Finally, the present improved HTL kinetics model was used to predict the HTL conditions that give the highest biocrude yields for microalgae with different biochemical compositions.

2. Parameter estimation for isothermal HTL kinetics model

Experimental product fraction yields (Valdez et al., 2014; Vo et al., 2016) from isothermal HTL at different times (10–90 min) and temperatures (250–400 °C) were used to determine optimal values for the Arrhenius parameters in the kinetic model. These studies used 15 wt% and 14 wt% biomass slurries, respectively, and dichloromethane served as the solvent for recovering biocrude. The studies provide HTL data for four species of microalgae (*Aurantiochytrium* sp. *KRS101*, *C. protothecoides*, *Nannochloropsis* sp., and *Scenedesmus* sp.) with the biochemical compositions (dry weight basis) given in Table 1.

The model comprises first-order rate laws for each pathway coupled with the batch reactor design equation for each component, as shown by Eqs. (2)–(8). First-order rate laws were used due to their success in describing HTL of microalgae in previous studies (Valdez et al., 2014; Valdez and Savage, 2013; Vo et al., 2016). The mass fractions of the microalgal biochemical components and the product fractions are represented by x_i and the rate constants for each reaction pathway by k_i . The mass fraction of algal solids, x_s , is the sum of the mass fractions of protein, lipids, and carbs.

$$\frac{dx_{Protein}}{dt} = -(k_{1,p} + k_{2,p})x_{Protein} \quad (2)$$

$$\frac{dx_{Carbs}}{dt} = -(k_{1,c} + k_{2,c})x_{Carbs} \quad (3)$$

$$\frac{dx_{Lipids}}{dt} = -(k_{1,l} + k_{2,l})x_{Lipids} \quad (4)$$

$$\frac{dx_{AP}}{dt} = -(k_4 + k_5)x_{AP} + k_{1,p}x_{Protein} + k_{1,l}x_{Lipids} + k_{1,c}x_{Carbs} + k_3x_{BC} \quad (5)$$

$$\frac{dx_{BC}}{dt} = -(k_3 + k_6)x_{BC} + k_{2,p}x_{Protein} + k_{2,l}x_{Lipids} + k_{2,c}x_{Carbs} + k_4x_{AP} \quad (6)$$

$$\frac{dx_{Gas}}{dt} = k_5x_{AP} + k_6x_{BC} \quad (7)$$

$$x_s = x_{Protein} + x_{Lipids} + x_{Carbs} \quad (8)$$

Mathematica 11.1 was used to solve the system of ordinary differential equations and simultaneously determine optimal values for the apparent Arrhenius pre-exponential factors, A_i , and apparent activation energies, E_i for each rate constant by minimizing the sum of squared residuals (SS_{res}) (Eq. (9)). The NonLinearModelFit function was used to estimate directly the model

Table 1
Biochemical compositions (wt%, dry-basis) of microalgal species used for correlating kinetic model.

Microalgae	Protein	Carbohydrate	Lipid
<i>Aurantiochytrium</i> sp. <i>KRS101</i> Vo et al. (2016)	30	5.8	57.5
<i>C. protothecoides</i> Valdez et al. (2014)	11	29	53
<i>Nannochloropsis</i> sp. Valdez et al. (2014)	56	21	9
<i>Scenedesmus</i> sp. Valdez et al. (2014)	50	31	8

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