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A general kinetic model for the hydrothermal liquefaction of microalgae

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HIGHLIGHTS

- Incorporation of algae biochemical content into a kinetic model for liquefaction.
- Model reveals that conversion rates differ for proteins, carbohydrates, and lipids.
- Experimental results for the liquefaction of *C. protothecoides* and *Scenedesmus* sp.

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ABSTRACT

We developed a general kinetic model for hydrothermal liquefaction (HTL) of microalgae. The model, which allows the protein, lipid, and carbohydrate fractions of the cell to react at different rates, successfully correlated experimental data for the hydrothermal liquefaction of *Chlorella protothecoides, Scenedesmus* sp., and *Nannochloropsis* sp. The model can faithfully account for the influence of time and temperature on the gravimetric yields of gas, solid, biocrude, and aqueous-phase products from isothermal HTL of a 15 wt% slurry. Examination of the rate constants shows that lipids and proteins are the major contributors to the biocrude, while other algal cell constituents contribute very little to the biocrude.

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1. Introduction

Hydrothermal liquefaction (HTL) is a high-temperature (>250 °C) and high-pressure (>4 MPa) process to convert wet biomass, including algae, into biocrude oil. The water present in the biomass slurry serves as both solvent and reactant to hydrolytically decompose the proteins, lipids, and carbohydrates in the algae cell. HTL circumvents the drying of the biomass, which is advantageous, because it reduces the energy investment required. The biocrude is an energy-dense oil (Dote et al., 1994; Minowa et al., 1995) that can be catalytically upgraded to a product that begins to resemble petroleum crude (Elliott et al., 2013).

Hydrothermal liquefaction of algal biomass has attracted increased attention in recent years, and process development work related to continuous operation and scale up has been reported (Elliott et al., 2013; Jazrawi et al., 2013). Process development, design, and optimization are facilitated by the availability of mathematical models that faithfully describe the process chemistry.

One approach for modeling process chemistry is to use molecularly explicit models, but such models require knowledge of the molecular composition of the feedstock. Indeed, understanding the composition provides a means for determining some of the numerous reactions that occur. Torri et al. (2011) used biocrude composition data to classify constituents as originating from the proteins, lipids, carbohydrates, or algaenans present in the alga feedstock, thus revealing some of the possible HTL reaction pathways. Changi et al. (2012) also identified some HTL reaction paths using different model compounds of algae. Detailed characterization of the molecular composition of the biocrude from the HTL of microalgae (Sudasinghe et al., 2014) is just underway. Moreover, initial results reveal that there are several thousand unique compounds present. The large number of compounds in the biocrude and their incomplete enumeration and quantification at present suggest that a molecular-level model for HTL of microalgae is not yet feasible. A simpler approach is in order.

We recently (Valdez and Savage, 2013) presented a reaction network and kinetic model, based on lumped product fractions (gas, solids, aqueous-phase products, light biocrude, heavy biocrude), to describe the HTL of the alga *Nannochloropsis* sp. This reaction network and HTL model provided reasonable estimation of yields of the solubility-based product fractions at different batch-holding times and reaction temperatures. This model worked well for one particular species (*Nannochloropsis* sp.) cultivated under the specific conditions used. In this article, we expand

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this species-specific model to move toward a more general lumped kinetics model for HTL of any algae species grown under any conditions.

There has been some prior work to this end, which guided the work reported herein. Lopez Barriero et al. (2013) reported how the variations in algal species and biochemical content can affect the yields of the product fractions. Biller and Ross (2011) presented a formula for estimating biocrude yield from HTL of algae at 350 °C for 60 min, based on the protein, lipid, and carbohydrate content of an algal feedstock. Their formula gave accurate predictions of biocrude yield for some microalgae while incorrectly predicting the yield for certain species of cyanobacteria. Nevertheless, they demonstrated that the concept of treating algae as a combination of protein, lipid, and carbohydrate could be useful for modeling. Regrettably, the formula applied to only a single reaction temperature/holding time combination, and it predicted the yield of biocrude only (no other products). To the best of our knowledge, no other attempts to create a model or formula capable of predicting the yields of the different product fractions for the HTL of any microalga have been reported.

Following Biller and Ross, we modified our previous HTL kinetic model (Valdez and Savage, 2013) to incorporate the biochemical content of the microalgae. Doing so permits the model to be used for other microalgae, regardless of species or growth conditions, simply by knowing the protein, lipid, carbohydrate, and ash content in the alga feedstock.

To generate data for parameter estimation for this generalized model for the HTL of microalgae, we hydrothermally treated *Chlorella protothecoides* and *Scenedesmus* sp. and measured the yields of solids, gases, aqueous-phase products, and total biocrude. We used the yields of the product fractions from both microalgae and previously reported results for the HTL of *Nannochloropsis* sp. (Valdez et al., 2012; Valdez and Savage, 2013) to determine the rate constants in the kinetic model.

2. Methods

This section outlines the materials and experimental approaches used in this research. The first subsection describes the microalgae and the compositional analysis. The second subsection details the HTL procedures and the analysis of the product fractions.

2.1. Feedstock

We obtained *C. protothecoides* (UTEX #255) that was grown using the procedure described by Levine et al. (2012) to produce cells with high lipid content (>50 wt%). We concentrated the harvested algae to >15 wt% in an Eppendorf 5810 centrifuge. Dry *Scenedesmus* sp. microalgae was supplied by the Center for Advanced Energy Research at the University of Kentucky. We homogenized the dried *Scenedesmus* sp. by grinding it with a mortar and pestle until it could pass through an 850 micron mesh. We purchased a 35 wt% slurry of *Nannochloropsis* sp. in water from Reed Mariculture Inc.

We dried small aliquots of each alga, roughly 100 mg of solids, in pre-weighed aluminum boats, at 70 °C for 48 h to determine the water content of each feedstock. We sent dried samples of *C. protothecoides* and *Scenedesmus* sp. to Atlantic Microlab Inc. for measurement of nitrogen content.

Dried samples of the algae were pre-weighed in an aluminum boat and then placed in a Ney Vulcan 3-130 muffle furnace to remove all organic content. The furnace heated the samples from room temperature to 250 °C at a rate of 10 °C/min. After a 30 min holding period, the temperature of the furnace increased to 450 °C at a rate of 20 °C/min and remained at that temperature for 6 h. After the final holding period, we removed the aluminum boats from the furnace and cooled them to room temperature for at least 1 h in a desiccator before weighing them. The inorganic material remaining in the weigh boat is classified as ash.

We estimated the wt% protein of each alga by multiplying the nitrogen content (wt%) by 6.25 (Piorreck et al., 1984; Pistorius et al., 2009). We measured the lipid content of the microalgae using the procedure described by Valdez et al. (2014) to extract and transesterify the lipids and then analyze them via gas chromatography. The material remaining in the algae cell is primarily carbohydrates, but it also includes other material (e.g., chlorophyll). For the sake of convenience we refer to this remaining material, the mass fraction of which was calculated as the difference between unity and the sum of the mass fractions of the proteins, lipids, and ash, as carbohydrates, with the understanding that other materials also reside in this fraction.

2.2. Hydrothermal liquefaction

We hydrothermally treated 15 wt% slurries of *C. protothecoides* and *Scenedesmus* sp. at 250, 300, 350, and 400 °C for 10–90 min in stainless steel batch mini-reactors. Each reactor consisted of a ½″ Swagelok port connector with one end capped and the other fitted with a 1/8″ reducing union. We attached a High Pressure Equipment Company 15AF-2 valve to the reducing union via 8.5″ of 1/8″ OD stainless steel tubing. The volume of the reactor was roughly 4.1 mL. Depending on the desired reaction temperature, we loaded approximately 2.3–3.7 g of slurry. The loading was adjusted so that 95% of the reactor would be filled with liquid water for the HTL runs at subcritical temperatures. At 400 °C, the loading was adjusted so that the water density at these supercritical conditions would be approximately 0.5 g/mL.

To start the reaction, we submerged each reactor in a fluidized sandbath, pre-heated to the desired reaction temperature. The reactor was submerged for the desired batch-holding time and then quickly removed from the sandbath and quenched in room temperature water. After cooling the reactor for >30 min, we analyzed the gas products using the procedure described previously (Brown et al., 2010). We then opened the reactors, at the point between the union and the port connector nut, and poured the contents into a glass tube. We rinsed the reactor with a total of 9 mL of >95% dichloromethane (Fisher Scientific). We added 3 mL of solvent to the reactor, capped it, and agitated it vigorously on a vortexer for 10 min at 1000 rpm. After agitation, we added the rinse solvent to the glass tube and repeated the procedure twice more. Centrifugation separated the products into a solid phase and organic and aqueous liquid phases. We decanted the contents of the tube to recover organic- and aqueous-phase products. The dichloromethane-soluble products are classified as the biocrude. Flowing >95% pure nitrogen into the test tube for >6 h removed the dichloromethane from the biocrude. We weighed the remaining residue to calculate the biocrude yield. The dichloromethane- and water-insoluble residues that remained in the test tube after decanting were dried with flowing nitrogen for 6 h, weighed, and classified as the solids. Valdez et al. (2012) provide more specific details about the aforementioned procedure.

We report herein the yield of each product fraction; gas, solids, aqueous-phase products, and biocrude. Yield was calculated as the mass of the product fraction divided by the mass of algae (dry basis) loaded into the reactor. The yield of the aqueous-phase products was determined by difference, as previous results have shown that this assumption is reasonable (Valdez et al., 2012). To assess experimental variability, the runs at 350 °C were replicated three times and the reported uncertainty in the yield of each product fraction represents one standard deviation.

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