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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.

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.

Table 1
Biochemical content (wt%, dry-basis) of algae.

	Protein	Carbohydrate	Lipid	Ash
Nannochloropsis sp.	56	32	9	3
C. prototheocoides	11	29	53	7
Scenedesmus sp.	50	31	8	11

3. Results and discussion

The first part of this section presents the results from the characterization and HTL of *C. prototheocoides* and *Scenedesmus* sp. The second section explains the modification of the reaction model and the network previously reported by Valdez and Savage (2013) to accommodate information about the biomass biochemical content. The final section assesses the ability of the modified model to correlate the experimental HTL results for microalgae.

3.1. Biochemical content and yields of product fractions

Table 1 shows the biochemical and ash content of the two algae species for which new HTL experiments were performed. We measured the biochemical content of *Nannochloropsis* sp. and included the values in Table 1 since they will be used later in the modeling. The direct measurement of the lipids and ash, and the estimation of the protein content of *Nannochloropsis* sp. given in Table 1 were within 5 wt% of the values reported by the supplier. The *Scenedesmus* sp. is similar in composition to the *Nannochloropsis* sp. but it is a freshwater species whereas *Nannochloropsis* is a marine alga. The similar biochemical makeup of these two species provides a way to test whether marine and freshwater algae behave differently during HTL. The protein and lipid contents of *C. prototheocoides* differ from those of the other species by about 40%. This large difference provides an opportunity to model and understand the effect of biochemical content on the HTL product fractions.

Table 2 shows the yields of solids, aqueous-phase products, gases, and biocrude from HTL of *C. prototheocoides* and *Scenedesmus* sp. Similar data for HTL of *Nannochloropsis* were reported previously (Valdez et al., 2012). The effects of time and temperature on the product yields were very similar to those previously discussed for HTL of *Nannochloropsis* sp. (Valdez et al., 2012). One difference, however, is that at 250 °C the yield of solids from *C. prototheocoides* increases at longer reaction times (>20 min). At higher temperatures the solids usually appear as gray powders, but these solids were black and tar-like. It is possible that at these moderate temperatures the biomass was carbonized (Levine et al., 2012) or that more organic-solvent insoluble products were formed from the primary products, resulting in a higher solid yield than shown previously for *Nannochloropsis* sp.

The yield of biocrude from *C. prototheocoides* approaches 50 wt%, which is very close to the measured value of lipids in that alga. Although the *C. prototheocoides* was richer in lipids compared to *Nannochloropsis* sp. and *Scenedesmus* sp., the yield of biocrude never exceeded 50 wt%. The yield of biocrude from *Scenedesmus* sp. is nearly four times the initial mass of the lipid fraction in the biomass, which again demonstrates that the biocrude yield is not dependent on the lipid portion only.

3.2. Incorporating biochemical content into the reaction network and model

This section describes how we incorporated biochemical content into the earlier reaction network and kinetic model (Valdez and Savage, 2013), to extend its applicability to other alga. Fig. 1 displays the reaction network, including the rate constants for each pathway, for this general model for HTL. This network simply combines the separate light and heavy biocrude fractions in our earlier network (Valdez and Savage, 2013) into a single lump. This simplified network reduces the number of pathways and the number of parameters needed for the corresponding model.

Treating each of the pathways in Fig. 1 as first-order reactions leads to the batch-reactor mass balances in Eqs. (1)–(6) as the basis for the reaction model.

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

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

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

Table 2
Yields (wt%) of product fractions from HTL of *C. prototheocoides* and *Scenedesmus* sp.

Temperature (°C)	Time (min)	*C. prototheocoides*				*Scenedesmus* sp.			
		Solids	Aqueous-phase products	Biocrude	Gas	Solids	Aqueous-phase products	Biocrude	Gas
Ambient	0	93	0.88	2.9	–*	89	2.78	8.2	–
250	20	8.6	64	27	–	13	57	29	0.58
	30	18	54	28	–	16	43	40	0.78
	60	13	64	23	–	16	49	31	3.3
	90	24	49	27	–	11	51	38	0.47
300	10	16	49	30	4.3	14	48	39	0.0063
	20	13	43	43	1.5	15	47	38	–
	40	7.4	47	46	–	13	47	41	–
	60	8.4	46	46	–	9.5	49	34	7.7
350	10	5.6 ± 0.6	47 ± 8	44 ± 7	4.1 ± 2.4	9.6 ± 2.8	48 ± 2	41 ± 4	1.9 ± 1.7
	20	5.0 ± 0.9	44 ± 2	48 ± 1	3.4 ± 0.1	10 ± 2	51 ± 5	35 ± 7	3.3 ± 0.5
	40	5.0 ± 0.8	45 ± 4	46 ± 3	4.0 ± 3.1	8.4 ± 1.7	53 ± 3	37 ± 6	1.9 ± 1.7
	60	3.9 ± 0.1	41 ± 10	45 ± 4	10 ± 9	11 ± 4	44 ± 13	42 ± 10	3.7 ± 1.0
400	10	4.1	49	44	3.1	6.1	52	34	8.4
	20	3.3	48	43	5.0	11	49	31	9.7
	30	4.1	56	35	5.0	6.3	62	30	0.92
	40	3.1	51	40	6.1	8.1	62	29	0.18

* Not measurable.

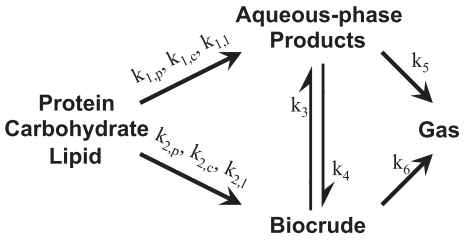

Fig. 1. HTL reaction network incorporating biochemical content.

$$\text{Aqueous-phase products}: \frac{dx_2}{dt} = -(k_4+k_5)x_2 + k_{1,p}x_{1,p} + k_{1,l}x_{1,l} + k_{1,c}x_{1,c} + k_3x_3 \quad (4)$$

$$\text{Biocrude}: \frac{dx_3}{dt} = -(k_3+k_6)x_3 + k_{2,p}x_{1,p} + k_{2,l}x_{1,l} + k_{2,c}x_{1,c} + k_4x_2 \quad (5)$$

$$\text{Gas}: \frac{dx_4}{dt} = k_5x_2 + k_6x_3 \quad (6)$$

The subscripts on each rate constant refer to specific reaction paths in Fig. 1, and the subscripts on each mass fraction, x_i, refer to specific lumped species (i.e., 1 is ash-free algae solids, 2 is aqueous-phase products, 3 is biocrude, 4 is gases, and p, l, and c represent protein, lipid, and carbohydrate, respectively). An implicit assumption here is that the protein, lipid, and carbohydrate fractions react independently and that they react with the same kinetics regardless of the algae species in which they reside.

The model calculates the weight fraction of proteins ($x_{1,p}$), lipids ($x_{1,l}$), and carbohydrates ($x_{1,c}$) in the ash-free solids as these materials are converted to biocrude, water-soluble products, and gases. The weight fraction of protein in the starting material ($x_{1,p}$) is the product of the total solids fraction (x_1) and the fraction of protein in the dry ash-free microalgae (x_p). As only the total solids content (x_1) of the HTL products was accessible experimentally, we used Eq. (7) to relate the calculated fractions of proteins, carbohydrates, and lipids to the total solids.

$$x_1 = x_{1,p} + x_{1,l} + x_{1,c} \quad (7)$$

This generalized model allows for the decomposition of the proteins, carbohydrates, and lipids in algal biomass to aqueous-phase products or biocrude at different rates. There are 6 rate constants ($k_{1,p}$, $k_{1,l}$, $k_{1,c}$, $k_{2,p}$, $k_{2,c}$, $k_{2,l}$), available to describe biomacromolecule decomposition during HTL.

We solved the set of differential equations above while simultaneously estimating the values of the rate constants (k_j) at a given temperature by minimizing the least square error between the experimental and calculated data points for each product fraction yield at each reaction time for each of the three algae species considered. We constrained the values of the rate constants from 0–0.35 min^{-1} to accommodate the fastest paths observed experimentally and to avoid excessive computational time. Valdez and Savage (2013) give more details about the parameter estimation.

3.3. Model correlation

Fig. 2 shows the correlation of the model to the experimental data from the HTL of each alga at 300 °C. A more complete assessment that includes all of the experimental data (Fig. 3) will be discussed next. This generalized model does a very good job of describing the temporal evolution of the product fraction yields from HTL of *Nannochloropsis* sp., *Scenedesmus* sp., and *C. prototheco-ides*. Thus, the modeling framework used herein appears to be capable of capturing differences in the HTL behavior of microalgae that arise due to differences in their biochemical content. Note that the yield of solids plotted in Figs. 2 and 3 are the yields reported in Table 2 minus the initial ash content of the algal biomass given in Table 1. If this difference was less than zero, we took the solids yield to be zero so that the value would retain physical meaning.

Table 3 shows the values of the rate constants calculated at each temperature. Inspection of the rate constants for the decomposition of carbohydrates reveals that their rate of producing aqueous-phase products is orders of magnitude faster than their rate of producing biocrude. Biller and Ross (2011) hypothesized the slow formation of biocrude from carbohydrates. This result from the model suggests that algae with a large amount of non-lipid and non-protein material would make a poor feedstock for HTL.

At 250 °C, the largest rate constant for biocrude production is for the conversion of protein to biocrude. At 350 and 400 °C, however, the rate constants for biocrude production from lipids exceed those for biocrude production from protein. This result suggests that HTL conditions sufficient for converting lipids to biocrude will also convert the protein fraction to biocrude and thereby produce a product with an undesirably high N/C ratio.

Fig. 3 shows a parity plot that compares model calculations to the experimental product yields obtained at all of the conditions investigated with all three algae species. Most of the data clustered on or near the parity diagonal, and the model shows a good

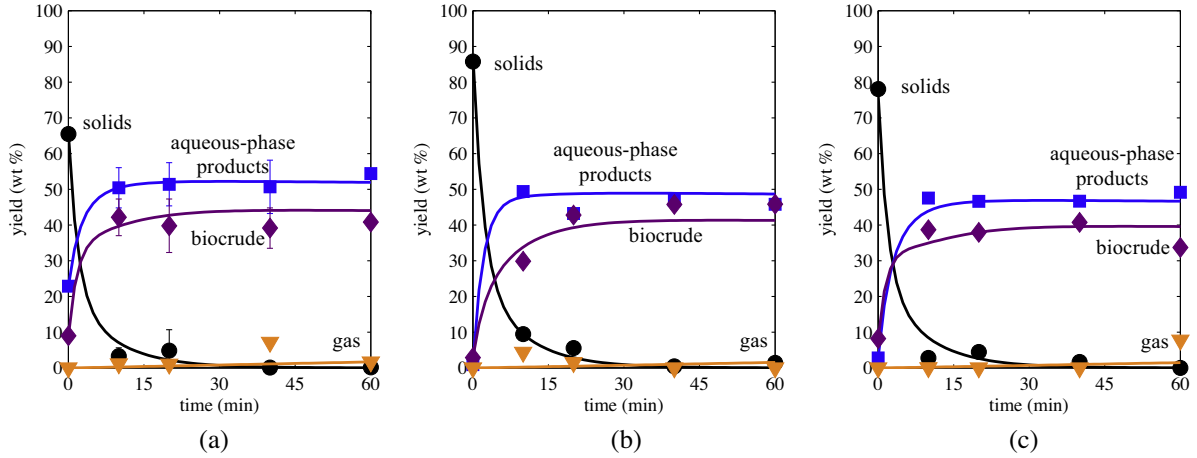

Fig. 2. Experimental (discrete points) and calculated (continuous curves) product fraction yields from HTL at 300 °C. (a) *Nannochloropsis* sp., (b) *C. prototheco-ides*, and (c) *Scenedesmus* sp.

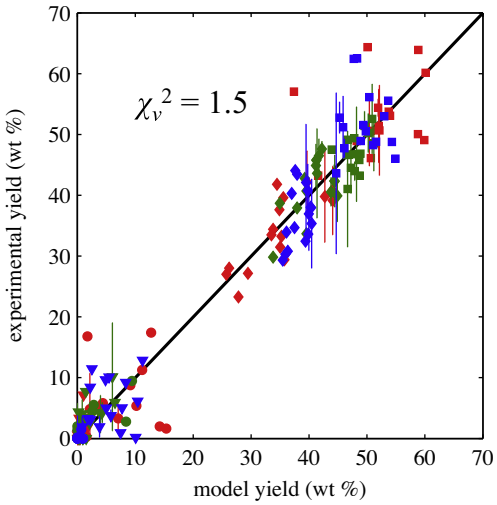

Fig. 3. Comparison of experimental and calculated product fraction yields (solids (●), aqueous-phase products (■), biocrude (♦), and gas (▼)) from the HTL of *Nannochloropsis* sp. (red), *C. prototheocoides* (green), and *Scenedesmus* sp. (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Optimized values of the rate constants at each temperature.

Path (Fig. 1)	Reaction	k (°C) [min^{-1}]			
		250	300	350	400
1,p	Protein → AP	0.095	0.20	0.28	0.33
1,l	Lipid → AP	0.15	0.35	0.35	0.35
1,c	Carb → AP	0.25	0.35	0.35	0.35
2,p	Protein → Biocrude	0.13	0.13	0.28	0.32
2,l	Lipid → Biocrude	0.031	0.11	0.33	0.35
2,c	Carb → Biocrude	0.00010	0.00010	0.0010	0.0032
3	Biocrude → AP	0.0044	0.14	0.30	0.35
4	AP → Biocrude	0.003	0.12	0.26	0.26
5	AP → Gas	0.00010	0.00040	0.0014	0.0014
6	Biocrude → Gas	0.00010	0.00020	0.00090	0.0053

correlation of the yields of the product fractions. Fig. 3 verifies that the model does not show any systematic bias toward any particular species of microalga or any particular product fractions, as the values corresponding to each microalga and each product fraction appear to be randomly distributed on both sides of the diagonal line.

We assessed the goodness of fit of the model based on the reduced chi-square (χ_v^2) statistic shown in Eq. (8). This statistic is the ratio of the weighted sum of the squared error between the experimental and calculated data and the number of degrees of freedom ($N - j$) where N is the total number of experimental data points and j is the number of parameters used to fit the data. The total number of data points (264) includes all experimental runs for *Nannochloropsis* sp., *C. prototheocoides*, and *Scenedesmus* sp. at all temperatures (T) and reaction times (t) investigated. For reaction conditions where the standard deviation (σ_i) was not determined experimentally, we estimated its value as the average of the standard deviation for the data generated at 350 °C for all algae, which is 3.1 wt%.

$$\chi_v^2 = \frac{1}{N-j}\sum_i^N \left(\frac{x_i^{expt}(T,t) - x_i^{calc}(T,t)}{\sigma_i(T,t)}\right)^2 \quad (8)$$

As shown in Fig. 3, the reduced chi-square statistic is 1.5, signifying that the model provides a good description of the experimental data.

4. Conclusions

The reaction network and kinetic model can correlate the effects of time and temperature on the yields of product fractions from HTL. The model treats microalgae as being composed of lipids, protein, and all else (largely carbohydrate), and it uses the same rate constant for conversion of each component regardless of the species. The key input data are the biochemical content and the HTL conditions. The values of the rate constants for conversion of lipids, protein, and carbohydrate suggest that algae that are richer in lipids or proteins will produce a higher biocrude yield than an alga that is carbohydrate-rich.

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