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DEMETALLATION OF ALGAL BIOCRUDE OIL PRODUCED VIA HYDROTHERMAL LIQUEFACTION

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ABSTRACT

We investigated the effects of temperature (350-450 °C), holding time (10-60 min), water loading (30-95% by volume), and biomass loading (5-15% by weight) on bio-oil yield and metal distribution in the bio-oil from hydrothermal liquefaction (HTL) of *Nannochloropsis* sp. Liquefaction produced a biocrude, along with gaseous, aqueous, and solid by-product fractions. The yields of biocrude depend greatly on both reaction time and temperature, with the maximum yield, 35.36±1.50%, occurring at 350°C and 60 minutes. Further, the highest yield with respect to water loading by volume was at 60% (35.27±2.12%) while the highest yield with respect to biomass loading by weight occurred at both 10% and 15% (32.13±1.72). All obtained biocrude phases were analyzed via ICP-OES to determine the effects of changing the HTL process variables on the concentrations of metals, namely iron and sodium. Iron exhibited the lowest concentrations at reaction conditions of 450 °C and 30 minutes (608.32 ppm), water loading of 30% by volume (991±69 ppm), and biomass loading of 10% by weight (1463.54±4.47 ppm). Sodium exhibited the lowest concentrations at reaction conditions of 350°C and 60 minutes (103±120 ppm), water loading of 95% by volume (569±296 ppm), and biomass loading of 15% (569±26 ppm). The data for iron concentrations was much more consistent than that of sodium. The quantitative results reported herein provide the basis for determining the distribution of deleterious metals in bio-oil.

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Chapter 1

Introduction

Globalization today has caused economies around the world to grow at a rapid pace. For example, large countries like India and China are racing towards nationwide, modern industrialization. With this economic growth, however, there is a corresponding increase in a country's appetite for energy. This worldwide increase in energy appetite is rather troubling since a large majority of the energy used is produced from traditional, polluting, and nonrenewable sources like fossil fuels – coal, petroleum, and natural gas – and their derivatives. In the United States, for instance, fossil fuel sources make up 80% of energy consumption according to the United States Energy Information Administration (EIA, 2015).

Because these traditional fuel sources have such a large impact on humans' "carbon footprint," there is a growing desire to find alternative fuel sources that can mitigate or even remove pollutants such as carbon dioxide from the source-to-use process. Biofuel derived from organic species like algae is one such source.

Biofuels are fuels produced from biomass, organic matter from plants and animals. This form of energy has been gaining ground for several years mainly due to its alleviation of greenhouse gas pollution, ability to be quickly replenished, increasing availability, and potential for more stable energy pricing. Note that there is no net increase in carbon dioxide – a harmful greenhouse gas – associated with algal biofuels because any amount of carbon dioxide produced while combusting the fuel in an engine is sequestered from the atmosphere during the plant's lifetime, rendering this source-to-use process carbon neutral. On the other hand, greenhouse gas emission is a serious consequence of the earth's current fossil fuel "addiction." In the last twenty years, three-quarters of man-made carbon dioxide emissions have been due to the burning of fossil fuels (EPA, 2017).

Specifically, algae is an excellent biomass feedstock from which to derive biofuel because it has a very high photosynthetic efficiency when compared to other potential options. This property of algae allows it to grow rapidly. Moreover, algae has a high lipid content that can approach up to 70%, which promotes favorable oil yields (Barreiro, 2013). From an agricultural standpoint, algae has a high ratio of biomass yield per acre of farmland and is usually farmed on low-value land or offshore where there is no agricultural competition between other species.

The overarching goal of biofuels is to assimilate as seamlessly as possible into a process similar to that of upgrading traditional petroleum since both fuels are directly combustible and using similar processes would limit the amount of new infrastructure required for biofuels, making the source even more attractive. However, one of the main stumbling blocks to this goal is that crude bio-oil, created through liquefying wet algal biomass in a supercritical water medium, has a much higher metal content than crude petroleum. Additionally, bio-oil contains an array of metals that are not as prominent in petroleum, such as iron, due to the biological origins of the bio-oil feedstock. The extra metals associated with crude bio-oil would accumulate during industrial distillation processes used in refining, affect bio-oil properties, poison industrial catalysts, promote corrosion, and expedite fouling. Ultimately, studying the metal content of algal biocrude is key to the commercialization and implementation of this renewable replacement for petroleum. Algal metals are different from those found in crude traditional oil but, to this day, no studies exist that examine metal removal during either the conversion or work up of biocrude.

Chapter 2

Background

Properties of High Temperature Water

In this study, high temperature water is used as the medium to convert biomass into biocrude oil and other byproducts contained in either gaseous or aqueous phases. High temperature water is defined as both water above 200 °C and water at supercritical conditions, at least 374 °C and at least 22.1 MPA. At these high-temperature conditions, the diffusivity of water increases while its viscosity and surface tension decrease, making for an excellent reaction medium. Additionally, the dielectric constant of water decreases from 78 at 25 °C and .1 MPa to 14.07 at 350 °C and 20 MPa. A dielectric constant of 14.07 is much more conducive to the dissolving of organics such as fatty acids, proteins, and lipids, which are abundant in algae (Peterson 2008).

High temperature water also has a dissociation constant (K_w) about one-thousand times larger than ambient water. H^+ and OH^- ions are more abundant in high temperature water so some acid or base dependent reactions occur in high temperature water without the need for catalysts.

Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is the process of obtaining low molecular weight crude oils from high molecular weight biomacromolecules in biomass. The conversion of biomass takes place in liquid water at very high temperatures, typically between 200-370 °C and pressures, typically between 10-20 MPa. Maintaining the proper temperature range is important since HTL reactions at temperatures approaching

500 °C usually require catalysts while reactions above 500 °C allow for homogenous gasification and thermolysis to occur, both of which greatly detract from the crude bio-oil yield.

The crude HTL bio-oil product is viscous. The oil contains combinations of straight and branched aliphatic compounds as well as aromatics and phenolic derivatives, carboxylic acids, esters, and nitrogenous rings. Bio-oil yields are typically expected to be around 25-60% of the original algae loading by weight, depending on the reaction conditions (Peterson, 2008). The crude oil obtained from the algae has a heating value between 35-45 MJ/kg, which is close to that obtained from crude petroleum oils, 42 MJ/kg (Peterson, 2008).

Similar to traditional fossil fuel sources, the composition of biomass varies. However, the building blocks of the fossil fuels, hydrocarbons, are much simpler than the macromolecules, carbohydrates, proteins, lipids, and lignin, that compose biomass. The reaction pathway for the breakdown of these macromolecules during the HTL reaction process is as follows (Valdez, 2012):

1. Depolymerization of macromolecules into monomers,
2. Decomposition of monomers by cleavage, dehydration, decarboxylation, and deamination,
3. Recombination of reaction fragments.

Another advantage of using HTL to make biofuels compared to processes such as fast pyrolysis is that there is no need to dry the algal feed stock since microalgae has a high moisture content and the high latent heat of water vaporization eliminates the drying step found in traditional thermochemical methods. Therefore, the HTL biofuel process is more energy efficient than traditional methods like pyrolysis.

Metals in Algae

Previous elemental analysis has revealed that, in addition to nitrogen and sulfur, many deleterious metals that must be dealt with in refining are also present in algae. The

list is rather extensive but contains all metals expected from living a species: sodium, iron, calcium, copper, potassium, magnesium, nickel, zinc, manganese, chromium, and aluminum (Ross, 2008). Note that the metal composition of algae varies depending on the supply in the plant's external (cultivating) environment, but in marine algae, which is the only feedstock considered here, iron and sodium and the most common. All of the listed metals have abundances ranging from a few parts per million up to a few thousand parts per million. For comparison, the most abundant and detrimental metals in traditional petroleum processing are simply nickel and vanadium (Jenifer, 2015).

In bio-oil processing, sodium, namely, forms low temperature melting compounds which form sticky ash that is deposited on surfaces inside reactors. Iron, on the other hand, affects industrial catalysts by increasing the amount of gas and coke obtained, decreasing yields, and can be corrosive in industrial processes. Fortunately, sodium can be removed rather simply with a desalter. However, iron removal is much more complicated since iron takes up several forms in algae (Caumette, 2009):

- Heme-ferrous containing porphyrins,
- Iron-sulfur clusters in many metalloproteins involved in metabolic pathways,
- Iron-contaning enzymes that assist with the assimilation of NO_3, respiration, and vitamin synthesis,
- Stored in plastid – known as ferritins.

Methods for Demetallation of Crude

To this day, no studies to remove metals from algal crude have been conducted. Petroleum processing might serve as a useful example since nickel and vanadium are generally present in porphyrins in crude oil and must be removed. The demetallation of crude petroleum is typically done in one of three main ways (Jenifer 2015):

- Physical – distillation, solvent extraction, filtration,
- Chemical – thermal processes such as visbreaking and coking,

- Catalytic hydroprocessing – porphyrins are hydrogenated to form a hydrogenated-metalloporphyrin intermediate that undergoes ring cleavage and deposit metals on catalyst surface.

Other emerging, nonconventional methods for crude dematallation are as follows (Jenifer 2015):

- Electrochemical – in petroleum processing, protonating agents enhance degradation of vanadium porphyrins,
- Microwave radiation – remove metals from crude treated with acid or alkali through agitating polar molecules and ions that oscillate due to an oscillating electric or magnetic field.

Fortunately, supercritical water, the medium for hydrothermal liquefaction, has been proven to positively contribute to demetallation, specifically for nickel removal from porphyrins (Mandal, 2011).

To date, there has not been a suitable and reproducible method for removing metals from algal crude oil. The objective of this experiment was to determine the influence of hydrothermal liquefaction process variables – temperature and holding time – on the metal content of the produced biocrude oil.

Chapter 3

Research Objectives

The overall goal of this research is to determine the influence of hydrothermal liquefaction process variables on HTL-produced algal biocrude metal content. Specific objectives are:

1. Identify and quantify metals in the feedstock used for HTL.
2. Hydrothermally treat feedstock at different conditions.
    - Conduct HTL under isothermal and rapid heating reaction conditions in addition to varying the reaction temperature, holding times, and reactor loading.
3. Determine the metal content in the resultant product phases for each trial at each set of conditions and compare for analysis.
    - The metals of interest in this study are iron and sodium.

Chapter 4

Experimental Methods

Materials

Dried *Nannochloropsis* marine algae was provided by Sapphire Energy (**Figure 1**). The powder was used as received, but diluted as needed to achieve a slurry suitable for hydrothermal liquefaction. To contain the hydrothermal liquefaction process at severe conditions (temperatures greater than 250 °C and pressures greater than four MPa), ½ in. Swagelok port connectors, made of 316 stainless steel (.0028 in. wall thickness), were purchased (**Figure 2**). One end of the port connector was to remain permanently sealed at all times while the other was removed for reactor loading and unloading (extraction). Optima grade dichloromethane (>99.5%), purchased from Sigma Aldrich, was used in the extraction process to remove the crude product from the reactor following HTL. 99.998% pure N_2 was purchased from Praxair for use in product drying. Concentrated (>99%) ethylene glycol monobutyl ether (EGBE), also purchased from Sigma Aldrich, was used in the digestion of samples in preparation for ICP-OES analysis. 99.998% pure Argon was purchased from Praxair for the ICP-OES plasma. The ICP-OES machine was calibrated by diluting Oil Analysis Standard S-21+K (500ppm by weight) obtained from Conostan.

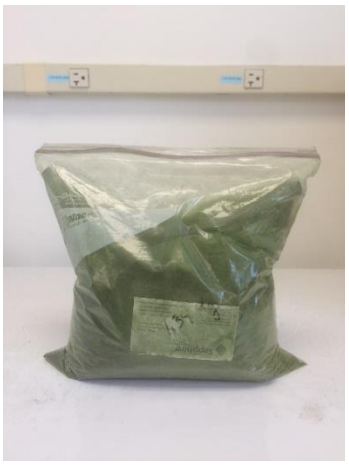

Figure 1 Dried Nannochloropsis Purchased from Sapphire Energy

Figure 2 Swagelock Port Connector Reactor. The permanent end of the reactor is located at the bottom of the image, with the removable end at the top.

Reactor Loading

For every trial, the port connector "reactor" was loaded with 15% algae by weight, with the rest comprising only deionized water. Due to varying the temperature and holding time at which each trial was conducted, the water portion of the reactor

loading varied from 30-95% water by volume as a result of changing densities. The reactor was weighed before and after loading to determine the total mass of the system inside the reactor. The reactor was then sealed, keeping ambient air in the reactor headspace, by securing the port connector in a bench-vise and fastening the cap with a torque wrench (45 ft-lbs).

Hydrothermal Liquefaction

Hydrothermal liquefaction occurred in an IFB-52 sand bath (**Figure 3**). The reaction was run in the sand bath at temperatures of 350, 400, 450, and 600 °C. A TC-8D temperature controller was used to maintain the reaction temperature within ± two °C of the set point. No agitator was present in the bath. At the lower temperatures of the range, longer holding times, on the order of one hour, were needed to ensure complete liquefaction and an isothermal environment. At the higher temperatures of the range, shorter holding times, on the order of 30 seconds, were needed to ensure complete liquefaction, without allowing enough time for significant gasification to occur. The reactors were removed from the sand bath, quenched in an ice bath for one minute, and allowed to equilibrate to room temperature for at least one hour (24 hours preferable) before being uncapped to analyze the products. The longer the reactor sets, the lower the risk of losing product through gas release (bubbling) during the uncapping process.

Figure 3 IFB-52 Sand Bath

The lid at the top of the reactor (white handle) was removed for placing reactors in the bath. The temperature was set using the green colored screen on the upper right hand side of the apparatus while the air=flow rate was set using the silver knob in the lower right hand corner.

Extraction

The reactors were uncapped with the same vise, torque wrench set up used for sealing. The reactors were then weighed before the contents were poured into a pre-weighed 10 mL conical glass test tube. The reactors were rinsed with nine mL of dichloromethane (DCM) to ensure that all of the reactor contents were collected. The dichloromethane was added to the reactor in small aliquots (< three mL). In previous works, Valdez, et al. found that polar solvents, such as DCM, typically increased bio-oil content and recovered more fatty acids, which increase the heating value of the oil (Valdez, 2011). At this point in the process the three phases of the HTL product, water soluble (aqueous), non-water soluble (organic or bio-oil), and solid, were not clearly visible (**Figure 4**).

Figure 4 The crude product immediately following extraction. The extract is very murky and further work-up must be done before the three phases of the extract become visible.

The conical tube, containing all three phases of product and any DCM used during extraction, was vortexed for 10 seconds at 3000 rpm and then centrifuged in an Eppendorf 5810 centrifuge at 800 relative centrifugal force (rcf) for three minutes. After centrifuging, the three product phases became visible. Because the density of DCM is greater than that of water, the organic phase laid underneath the aqueous phase with the solids acting as a partition in between the two (**Figure 5**).

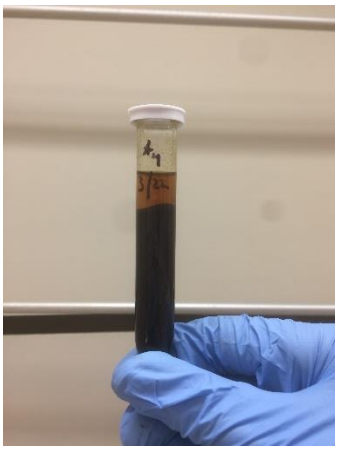

Figure 5 The crude product following vortexing and centrifugation.

Now, the three phases are clearly visible. The aqueous (light in color) phase lays on the top because it is less dense than the organic phase (dark in color) – due to using DCM as the extraction solvent – with the solid phase acting as a partition between the two.

The organic phase was transferred to a glass round-bottom test tube via a pipet. A syringe attached to a filter paper disc was used to ensure all solids were properly separated from the organic phase. The dichloromethane was removed from the organic phase by flowing N_2 over the organic phase tubes for approximately two hours via a RapidEvap (**Figure 6**). After about 90 minutes of evaporation, the samples were weighed every 15 minutes to check for consistency of mass, signaling the end of the drying process. Note that the evaporation conditions depend heavily on the solvent. This experiment used 40 °C and 30 psi for the DCM solvent. The DCM-soluble product that remained in the round-bottom tube following complete evaporation is classified as biocrude. The dried biocrude was then ready to be digested for ICP-OES analysis.

The aqueous and solid phases were collected but not processed in this experiment.

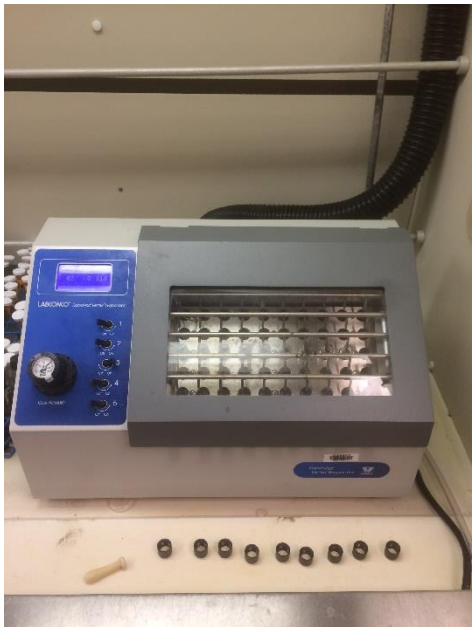

Figure 6 The RapidEvap device used for removing solvent from the biocrude.

The temperature of the evaporation process is set using the blue touchscreen in the upper left-hand corner. The pressure is set using the knob in the lower left-hand corner.

ICP-OES Analysis

The dried biocrude was dissolved in EGBE on a weight basis, between 50:1 and 80:1 EGBE to biocrude, in preparation for elemental analysis via ICP-OES (**Figure 7**). Before analyzing the sample, the argon line was connected to the nebulizer, and a blank solution, as well as several standards, were run to ensure the calibration of the machine and indicate expected values for wavelength emissions of each element of interest. The standards were created by diluting the purchased Conostan standard, originally at 500 ppm, to concentrations ranging from 1 to 30ppm in order to obtain a proper calibration curve. The metals examined via ICP-OES analysis include: sodium, iron, calcium, copper, potassium, magnesium, nickel, zinc, manganese, chromium, and aluminum. However, only data for iron and sodium will be analyzed for the purposes of this investigation.

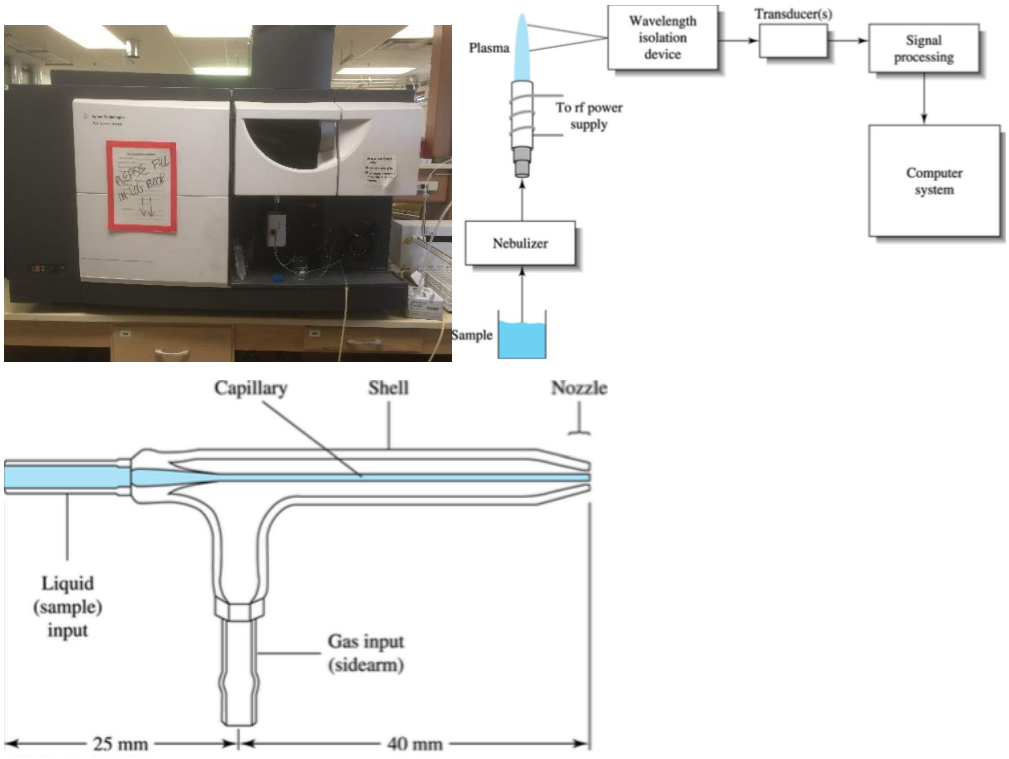

Figure 7 ICP-OES machine, Sample Nebulizer Specifications, and a General Diagram Outline.

ICP-OES machines used in the experiment (top left) alongside a detailed diagram showing how the sample is nebulized (bottom) and a general diagram outlining the steps of the analysis process. (top right). The nebulizer system

is hidden by the small white box located near the beaker on the experimental machine. The burner is located behind the black quarter-circle adjacent to the silver oven handle.

ICP-OES was determined to be the best method to observe the effects of varying HTL process variables on metal content in the biocrude because the nature of this research required a broad sweep in examining many different elements. ICP-OES typically operates at temperatures between 600-1000 K, which is hot enough to excite most elements such that they emit detectable light. The temperature is also hot enough to prevent the formation of most interferences, break down oxides, and eliminate most molecular spectral interferences that can be derived from a complex biological system like algal biomass. Also, similar systems like ICP-MS can be adversely affected by organic material contained in the plasma.

Chapter 5

Results and Discussion

Effects of Temperature and Holding Time on Bio-oil Yield

The effects of both holding time and temperature on bio-oil yield are shown in **Table 1**. Note that, based on the averages, the first four trials all have yields within about 10% of each other, with significant drop-off occurring in the last trial. The yields for this data, and all subsequent data, are calculated using the following formula.

$$Yield\ (wt\ \%) = \frac{Mass\ of\ Product\ Fraction}{Mass\ of\ Ash\ Free\ Algae} * 100\%$$

Table 1 The effects of both time and temperature on bio-oil yield. The loading of these trials was 15% algae by weight and 95% water by volume

Temperature (°C)	Holding Time (min)	Bio-oil Yield (%)			Average
350	10	25.05	38.51	35.05	32.87 ± 6.99
350	30	29.80	32.35	31.23	31.12 ± 1.28
350	60	35.69	33.72	36.66	35.36 ± 1.50
400	30	32.65	30.24	33.49	32.13 ± 1.68
450	30	17.62	15.95	17.56	17.04 ± 0.95

At milder temperatures, those closer to 350 °C, the formation of bio-oil is favored because the temperature is hot enough to convert the loaded algae powder to oil, but not hot enough to cause significant gasification or ashing, the formation of solids, to occur. Both of these phenomena greatly detract from the amount of bio-oil collected during extraction. Conversely, harsher temperatures, those around 450 °C and above, are beyond the threshold allowing the occurrence of gasification and ashing as evidenced in the considerably lower yield observed in the last trials. Further, temperatures below 250 °C are not sufficient for full bio-oil conversion as loaded solid biomass may go unreacted at these temperatures, detracting from calculated yields. For this reason, data below 250

°C was not considered for the purposes of this paper. Peterson et al. reported that liquefaction typically occurs in range of 250-400 °C, when hydrolysis becomes favorable, while gasification occurs in the range of 400-700 °C (Peterson, 2008). The data contained in table 1 is consistent with these findings.

Holding times also play a role in the yield of bio-oil, but go hand-in-hand with temperature. For instance, lower temperatures tend to require longer holding times in order to ensure full conversion of the loaded algae powder while higher temperatures tend to require shorter holding times to prevent gasification and ashing of the desirable bio-oil product. When conducting hydrothermal liquefaction, one must be wary of the tradeoff between these two process variables in order to find an optimum at which the maximum bio-oil yield is produced. For example, Garcia Alba et al., albeit using a freshwater algae strain and a loading of only 8% by weight, saw a maximum conversion of 49.4% running the reaction for only 5 minutes, but at a temperature of 375 °C (Garcia Alba, 2011). In this experiment, the optimum reaction conditions were found to be a temperature of 350 °C and a holding time of 60 minutes.

The trends shown in **Table 1** are well documented in other research. For instance, Hietala et al., using an algal loading mass of 15%, found that biocrude yields tend to increase as a function of temperature and time, but may reach a maximum value around reaction conditions of 400 °C and seven minutes. Hietala also found that for isothermal hydrothermal liquefaction little variation occurs in yields for reactions run near 350 °C (Hietala, 2016) no matter the holding time. These findings are consistent with the data collected in this experiment. Moreover, both Brown et al. (Brown, 2010) and Duan et al. (Duan, 2011), both of whom used the same water loading as in this experiment although with a slightly different strain of algae, reported that reactions with conditions of 350 °C and 60 minutes recorded yields of close to 30% using dichloromethane as the extraction solvent, as was done in this experiment. In order to increase yields to nearly 43%, Brown chose to use three, 15 mL, aliquots of DCM during the extraction process. This experiment used only one, 9 mL, aliquot. Nonetheless, the data from Brown and Duan further validate the experimentally obtained data.

Effects of Reactor Loading on Bio-oil Yield

The effects of algae loading by weight on bio-oil yield is shown in **Table 2**.

Table 2 Effects of Algae Loading on Bio-oil Yield. The reaction conditions for thesis trials were 400'C and 30 minutes.

Algae Loading (wt %)	Bio-oil Yield (%)			Average
5	29.04	29.40	27.21	28.55 ± 1.17
10	33.65	32.55	30.20	32.13 ± 1.76
15	32.65	30.24	33.49	32.13 ± 1.68

As expected, the more biomass loaded into the reactor, the higher the return of oil following the extraction process. The plateau seen in the averages of loadings at 10% and 15% is most likely coincidental since Valdez et al. concluded that for the same reaction conditions, as the biomass loading by weight increased from 5% to 35%, the corresponding bio-oil yield rose from 36% to 46% (for 350 °C and 60 minutes) (Valdez, 2011). More data points should be found in order to confirm or refute if the experimental data is supported by earlier work.

The effects of water loading by volume are shown in **Table 3**.

Table 3 Effects on Water Loading on Bio-oil Yield. The reaction conditions for these trials were 400'C and 30 minutes.

Water Loading (vol %)	Bio-oil Yield (%)			Average
30	37.00	27.59	29.60	31.40 ± 4.96
60	34.00	37.72	34.08	35.27 ± 2.12
95	32.65	30.24	33.49	32.13 ± 1.68

Here, a clear optimum is observed; at water loadings of 60% by volume the biomass yield is, on average, higher than the other trials. This may be because at lower volume loadings, 30%, there is not enough of a reaction medium present to ensure complete liquefaction of the biomass while at higher volume loadings, 95%, the amount of water produces a very large aqueous phase which can envelop molecules typically found in the organic – bio-oil – phase. However, results from Faeth et al. may show some inconsistencies with the data gathered in this experiment. The data from Faeth clearly shows that, if the biomass loading is held constant, as the water loading increases,

the bio-oil yield will decrease (Faeth, 2016). More data needs to be gathered in order to confirm whether or not Faeth's trend is applicable since a different strain of *Nannochloropsis* was used in this experiment.

Effects of Temperature and Holding Time on Sodium and Iron Concentrations

The effects of both holding time and temperature on the concentration of sodium in the bio-oil phase can be found in **Table 4** while the same for iron can be found in **Table 5**. Note that for the trials conducted at 450 °C not enough bio-oil was produced to be processed in the ICP-OES so the three samples had to be combined into one for proper analysis, resulting in only one data point. For all trials, a significant degree of inconsistency was observed for sodium concentrations at the same conditions. The inconsistency is not due to any form of experimental error but occurs at every trial. Iron concentrations, however, remained largely consistent from trial to trial.

Table 4 The effects of both time and temperature on sodium concentration. The loading of these trials was 15% algae by weight and 95% water by volume.

Temperature (°C)	Holding Time (min)	Na Concentration (ppm)			Average
350	10	1005.48	357.41	79.53	481 ± 475
350	30	110.92	84.95	278.22	158 ± 105
350	60	240.22	50.46	19.45	103 ± 120
400	30	338.89	463.90	902.96	569 ± 296
450	30		1103.42		1103

Table 5 The effects of both time and temperature on iron concentration. The loading of these trials was 15% algae by weight and 95% water by volume.

Temperature (°C)	Holding Time (min)	Fe Concentration (ppm)			Average
350	10	2689.15	2516.76	2563.36	2590 ± 89
350	30	2091.47	2002.04	2037.99	2040 ± 45
350	60	1303.95	1272.45	1370.50	1320 ± 50
400	30	1300.29	1519.96	1627.43	1480 ± 167
450	30		608.32		608.32

The data in **Table 4** makes formulating distinct trends difficult. Large inconsistencies in sodium concentration are prevalent from trial to trial. In the algal system, sodium exists as the Na^+ ion so one would expect conditions that favor the formation of the aqueous phase (or less bio-oil), which is capable of dissolving the ions, to reduce the sodium concentration in the bio-oil phase. However, the data is not conclusive. Only a very weak correlation is able to be seen between these two pieces of data. The inconsistency in the sodium concentrations may result from an unequal distribution of the metal in the original dried biomass. If the dried biomass was shipped as a mixture of algae from different marine locations, each scoop of powder used in reactor loading could potentially contain a different sodium distribution depending on its growth environment – water temperature, salinity, and sunlight exposure.

Conversely, in table five, there is a rather blatant trend in the concentration of iron. As the reaction conditions became harsher, through either increasing the temperature and/or the holding time, less iron was seen in the bio-oil phase. This may be due to iron existing largely within complex biological structures such as heme porphyrins, heterocyclic rings with the iron in the center. More severe reaction conditions may favor the breakdown of these porphyrins, releasing the iron and allowing it to move between the three phases. Although most of the iron tends to stay in the bio-oil, the remaining fraction most likely aggregates in the solid phase.

The most important takeaway from these two tables is that there seems to be an optimum set of reaction conditions, 350 °C and 60 minutes, that minimize the concentrations of both sodium and iron. Recall that these conditions also maximized bio-oil yield.

Effects of Reactor Loading on Sodium and Iron Concentrations

The effects of algae loading by weight percent and water loading by volume percent on the concentration of sodium present in the bio-oil phase are shown in **Table 6** and **Table 7**, respectively. In a similar way to the 450 °C trials, not enough bio-oil was collected at 5% loading to analyze each trial so the three were combined into one. Additionally, only two trials were able to be analyzed from 30% and 60% water loading by volume.

Table 6 Effects of Algae Loading on Sodium Concentration. The reaction conditions for these trials were 400'C and 30 minutes.

Algae Loading (wt %)	Sodium Concentration (ppm)			Average
5		745.14		745.14
10	639.30	524.28	301.28	488 ± 172
15	338.89	463.90	902.96	569 ± 26

Table 7 Effects of Water Loading on Sodium Concentration. The reaction conditions for theses trials were 400'C and 30 minutes.

Water Loading (vol %)	Sodium Concentration (ppm)			Average
30	866.69	5706.22		3290 ± 3420
60	700.62	1007.23		854 ± 217
95	338.89	463.90	902.96	569 ± 296

Trends in **Table 6** are hard to formulate due to the inconsistency of the sodium data, especially if there are variations in the original algae powder. However, **Table 7**, seems to show a clear trend, as the water loading increases, the sodium concentration in bio-oil decreases. Since sodium exists as Na^+ in the algae, this conclusion is logical in that providing more water for the reaction allows a larger medium for these ions to dissolve and to "wash away" from the bio-oil.

Over 90% of sodium dissolves in the aqueous phase during hydrothermal liquefaction, based on a simple mass balance, despite the apparently large concentrations in the bio-oil phase shown in the data. The large sodium concentrations are a function of using marine algae as the feedstock.

The effects of algae loading by weight percent and water loading by volume percent on the concentration of iron present in the bio-oil phase are shown in **Table 8** and **Table 9**, respectively. Just as the sodium trials, only one data point was able to be taken for the 5% algae loading by weight and only two were able to be taken from 30% and 60% water loading by volume.

Table 8 Effects of Algae Loading on Iron Concentration. The reaction conditions for these trials were 400'C and 30 minutes.

Algae Loading (wt %)	Iron Concentration (ppm)			Average
5		1653.05		1653.05
10	1446.04	1534.95	1409.63	1460 ± 64
15	1300.29	1519.96	1627.43	1480 ± 167

Table 9 Effects of Water Loading on Iron Concentration. The reaction conditions for theses trials were 400'C and 30 minutes.

Water Loading (vol %)	Iron Concentration (ppm)			Average
30	1039.44	941.68		991 ± 69
60	1028.27	1383.54		1210 ± 251
95	1300.29	1519.96	1627.43	1480 ± 167

Similar to sodium, trends between algae loading by weight and iron concentration are difficult to determine. Nevertheless, the trend exhibited between water loading by volume and iron concentration is just the opposite than that of sodium. As the water loading increases, the iron concentration in the bio-oil phase also increases. Since the iron exists inside hydrocarbon-based, nonpolar porphyrins within the algae, this conclusion is logical in that providing more water for the reaction causes these hydrophobic molecules to congregate in the bio-oil phase if they have not turned into ash as part of the solid phase.

Chapter 6

Conclusion

This work serves to quantify directly the concentration of metals in the bio-oil formed by hydrothermal liquefaction of microalgae run at varying conditions. Doing so gave insight into the distribution of deleterious metals in bio-oil and how these metals are processed during HTL. As the reaction conditions became more severe, less iron was seen in the bio-oil phase due to iron existing as heme porphyrins in the biomass. Harsh reaction conditions favor the breakdown of these porphyrins since they have a high thermal stability. Although most of the iron tends to stay in the bio-oil, the remaining fraction aggregates in the solid phase. Original hypotheses expected that conditions favoring the formation of the aqueous phase, which is capable of dissolving sodium ions, would reduce the sodium concentration in the bio-oil phase. However, the data obtained was largely inconclusive. This work also examined effects of reactor loading on the concentrations. Unfortunately, trends between algae loading by weight and both iron and sodium concentrations were difficult to determine. Nevertheless, as the water loading increased, the iron concentration in the bio-oil phase clearly increased since the porphyrins containing the iron inside the algae are nonpolar. Providing more water for the reaction caused these hydrophobic molecules to congregate in the bio-oil phase if they had not turned into ash as part of the solid phase. Conversely, as the water loading increased, the sodium concentration in bio-oil decreased since providing more water for the reaction allows a larger medium for sodium ions to dissolve and to “wash away” from the bio-oil.

With the experimental protocol used herein, the effects of HTL process variables on bio-oil yield, which have been well-documented in previous works, were also examined. Data for the effects of reaction temperature and holding time are consistent with that of Peterson et al. in that at temperatures around 350 °C the formation of bio-oil is favored while gasification and ashing are limited, increasing yields (Peterson, 2008).

Lower temperatures required longer holding times while higher temperatures required shorter holding times in order maximize bio-oil yield as is consistent with the findings of Garcia Alba et al. (Garcia Alba, 2011). As expected, the more biomass loaded into the reactor, the higher the return of oil following the extraction process, which is confirmed by Valdez et al. (Valdez, 2011). However, data for the effects of water loading on yield were inconsistent with previous findings. Faeth et al. reported that, if the biomass loading is held constant, as the water loading increases, the bio-oil yield will decrease (Faeth, 2016), which is somewhat opposite of what was observed. Note that for a given solvent and given microalgae strain, the yield of bio-oil that is recovered can depend on the specific lot of algae used and the specific conditions, such as the solvent, used to recover the crude bio-oil.

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Honors chemical engineering student with particular field experience in process engineering for a world-leading industrial-gas company. Technical skills gained through developing two research initiatives and captaining Penn State's Lunar Lion team. Pursuing a technical, full-time role that requires solving complex problems.

EDUCATION

The Pennsylvania State University | University Park, PA **Graduating May 2017**

- **Schreyer Honors College**: Bachelor of Science in Chemical Engineering

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ENGINEERING EXPERIENCE

Air Products and Chemicals, Inc. | *Plant Process Engineering Intern* | Houston, TX **Summer 2016**

- Managed project to determine real-time heat exchanger fouling across 50+ plants, increasing plant efficiency up to 10%.
- Engaged in daily collaboration with dozens of plant engineers and operators along the Gulf Coast in troubleshooting plant process, equipment, and environmental issues for 19 sites.

Air Products and Chemicals, Inc. | *Process Technologies Intern* | Trexlertown, PA **Summer 2015**

- Streamlined process calculations by developing a handful of excel tools for important process variables such as catalyst bed fluidization, fuel pressure, and fluid flow across control valves.
- Ensured two newly renovated sites passed safety requirements through modeling plant shut-down logic.
- Created approximately 100 plant-wiring folders for start-up engineers and contractors during construction of a project.
- Analyzed trends in equipment designs, fuel compositions, and differential pressures for 50+ plants.

Penn State Lunar Lion |*Captain of Test Project Development* | University Park, PA **Fall 2013 – Fall 2014**

- Chaired weekly meetings and oversaw a group of 12 students that prepared and tested the spacecraft's propulsion system for use in competition.
- Edited and approved physical changes made to the spacecraft regarding its landing and movement on the moon.

RESEARCH

Biofuel from Algae and Food Waste | University Park, PA **Fall 2015 – Present**

- Proved the feasibility of using hydrothermal liquefaction of biomass to create a crude oil that allows nutrients from the biomass to be recovered in a byproduct; currently exploring product demetallization.

Particle Behavior Simulation | University Park, PA **Spring 2015**

- Coded a thermodynamics-based, mathematical simulation to model particle association and dissociation in solution to better understand molecular tendencies.

LEADERSHIP

Omega Chi Epsilon Engineering Honor Society | University Park, PA **Fall 2015 – Present**

- Lead weekly, hour-long tutoring sessions for students or small groups seeking help with courses in the chemical engineering curriculum.
- Organize monthly Lunch-and-Learn events with faculty and industry representatives for 45-55 members.

Schreyer Consulting Group | University Park, PA **Spring 2015 – Present**

- Participate in monthly networking opportunities with Penn State Schreyer alumni working in the consulting field.
- Practice case study interviewing 2-3 times per semester.

Soles 4 Souls Shoe Drive | State College, PA **Spring 2014**

- Organized and executed a weeklong shoe-drive to benefit those in need, collecting over 100 pairs of shoes.