CHARACTERIZATION OF HYDROTHERMAL LIQUEFACTION PRODUCTS OF FOOD

ZACHARY J BERQUIST
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Reviewed and approved* by the following:

Phillip Savage
Department Head, Chemical Engineering
Thesis Supervisor

Wayne Curtis
Professor of Chemical Engineering
Honors Advisor

* Signatures are on file in the Schreyer Honors College.
ABSTRACT

Three types of food, kale, potato, and tuna fish, were treated at hydrothermal liquefaction (HTL) conditions. Each individual food was reacted individually with water at temperatures of 275, 300, and 325 °C and holding times of 5, 15, and 30 minutes. Kale, potato, and tuna yielded bio-oil averages of 14.0%, 9.0%, and 27.8% by mass, respectively. The solid phase yields corresponded to 25.0%, 65%, and 2.0%, respectively. The average elemental composition of all the bio-oils was approximately 69% C, 8% H, 5% N, 1% S, and the balance oxygen amongst other species. The bio-oil and aqueous products for each food were analyzed via GC-MS, and NMR. The main products of the bio-oil phase were large carboxylic acids, as well as large heteroaromatic compounds.
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Chapter 1
Background

With the growing global population, problems are increased dramatically as resources are depleted faster. Providing clean water, food, and energy are among the major problems facing mankind today. A large quantity of resources are directed at growing food, and 70 billion pounds (~35% of total food production) of food waste is generated each year in the United States alone. The waste produced from food could be converted to useful products (water, fertilizer, liquid fuels) in a process referred to as hydrothermal liquefaction (HTL). HTL is a process where biomass is heated with water at elevated temperatures and pressures. The temperature range is roughly 270 – 370 °C and the pressure ranges from 10 – 25 MPa.

The water acts as a medium for the organic molecules to react and form several classes of molecules. The main products from HTL are water insoluble bio-oils and solids, but some water-soluble compounds are formed. The composition of the bio-oil product is similar to that of petroleum oil, and it can be upgraded downstream to produce products similar to that of conventional gasoline or oil. The aqueous phase is filled with organic compounds not safe to consume, so additional processes are needed to purify the water for drinking. On the other hand, the aqueous phase could be recycled and used as a fertilizer or food source for agriculture. The compounds found in the aqueous phase are naturally more polar than the compounds found in the organic phase. Consequently, these compounds are mostly nitrogen, sulfur, and phosphorus containing compounds, which are all critical nutrients for plants. In order to separate the components, an organic solvent, such as dichloromethane (DCM), is used to dissolve the water.
insoluble components. The water soluble components are left behind in an aqueous phase produced from the water added and the naturally occurring water in the biomass (if the biomass is not dried). The third phase found is an organic solid phase that is not soluble in either the aqueous or the organic liquid phases.

The first of the major branches in food, carbohydrates consist of several different subgroups: cellulose, hemicellulose, and starch. Each one has different properties and produces different types of products. HTL converts cellulose to oligosaccharides and monosaccharides. Even further degradation, thermally or chemically, will result in a series of gaseous, liquid, and solid products. Next, hemicellulose, which is composed of mostly branched five and six carbon sugars, yields carboxylic acids, polyols, and lactones. All of these are excellent precursors to liquid fuels. Large carboxylic acids can be reacted further to produce diesel, while polyols offer an oxygenated hydrocarbon. However, the oxygenation of these compounds must be monitored because the more oxygenated, the lower the heating value. Finally, starch, a polymer of glucose, depolymerizes to glucose and hydroxymethylfurfural. Unfortunately, these compounds are not ideal for fuel production, but they also are polar and are expected to found in the aqueous phase of HTL products. Upstream production of ethanol uses glucose, but it in itself glucose is not a fuel source.

The next major classification of molecule found in food is proteins. Proteins are a polymer of amino acids. Naturally, under intense conditions, proteins degrade to their amino acids. However, the peptide bond in proteins is much stronger than the glycosidic bonds in carbohydrates. Consequently, low temperature HTL reactions will yield significant numbers of amino acids as product. At all temperatures though, proteins experience degradation via damination and decarboxylation. These two pathways result in hydrocarbons, amines,
aldehydes, and acids. Bio-oils are also a product of protein degradation. Nitrogen is not desired to be in fuel because when burned NO\textsubscript{x} molecules are formed attributing to pollution and acid rain. Nitrogen is still desired because organisms need nitrogen for growth. Nitrogen and other undesirable contaminants such as sulfur, phosphorus, and metals, can be recycled. Ammonia is one of the most easily digestible nitrogen sources, and a common product of HTL. By isolating these valuable resources, fertilizers or nutrient water-feeds can be used to grow the plants that produce the food.

The last major type of compound found in food is lipids. Fats are considered precursors to biodiesel which makes algae such a promising source of fuel. Algae are fast growing organisms that produce plenty of fats respective to their weight. As for food, fats are a significant portion of the mass/calories for relatively cheap foods and especially for fast food (e.g., french fries). Cooking oils, nuts, avocados, coconuts, etc. have high fatty acid compositions. Some of these are more expensive than others, but all find their way into food waste. Lipids at HT conditions degrade into fatty acids. Fatty acids can further degrade into a variety of products such as acetaldehyde, acrolein, and allyl alcohol. Since foods contain a mixture of lipids and fatty acids, all of these compounds should theoretically appear in the product of the HTL of food waste.

The laboratory work covered in this thesis was limited to HTL, but other hydrothermal techniques exist such as hydrothermal carbonization (HTC) and hydrothermal gasification (HTG). HTC reacts biomass at lower temperatures (sub-critical) though there are high temperature (up to 900 °C) HTC methods. On the other hand, HTG reacts biomass at extreme temperatures. The low end of HTG occurs from 300 - 500 °C, but this regime requires a catalyst. Temperatures above 500 °C can proceed without the need for a catalyst. HTC produces mainly a
carbonaceous material that mimics that of coal. HTC trials are the longest of the three ranging from 1-12 hours. This process tries to reproduce the formation of coal found in nature. HTG produces nearly all gases. Depending on the temperature range and catalyst, the major products are methane and hydrogen. The former is produced at lower temperatures and the latter at higher temperatures.

HTL is not nearly an ideal process at the moment. In order to use the bio-oils produced from HTL, several processing steps have to be implemented. The oil itself is not a viable energy source. Some of the major issues facing the HTL of biomass into fuel and other resources are the nitrogen content (heteroatoms in general), yield, demetallization, and operating costs. The first is one of the most challenging issues. If nitrogen and other heteroatoms like sulfur and phosphorus are left in the bio-oil, then not only are they burned and converted to pollutants, but also they can no longer be recycled into a fertilizer or other useful material. On the other hand, HTL does not require a dried feedstock since water is one of the vital reactants. However, in this work, significant water was added because the food could not be compressed enough to fit the necessary water. Without the added water, the reaction medium would contain no liquefied water. Since most of the mass of food is water, the mass fraction of the food that can eventually become bio-oil is minor (~5% or even less) compared to the whole mass reacted.

This paper aims to formulate an initial prognosis on the HTL of food waste for fuel production. Previous work has analyzed the products formed from HTL of specific types of macromolecules found in food. These include fatty acids, lignin, or other specific types of food. Recent work has begun to analyze the wide variety of foods and the effects the different composition of the foods (fats, protein, lignin, etc.) have on yields and composition of the product. Zastro et al. experimented with model food waste from a Thanksgiving dinner.
industrialized, the HTL of public organic waste would consist of a wide variety of foods, which Zastro et al. attempts to determine. However, the drawback of such a method is the individual effects of each food is not realized, which is critical to determining if certain organic waste should be excluded from the HTL of food waste. In addition, several factors weigh into the practicality of the process such as the ability to use all the products (bio-oil, aqueous phase, solid phase) as useful products to sell to industries. With a feedstock that is completely free, a carbon neutral fuel produced from food waste may become a legitimate fuel source.
Chapter 2

Experimental Procedure

Reacting

4.1 mL Swagelok® stainless steel reactor vessels were filled with one type of food and water. The tuna was Bumble Bee Seafoods® white chunk tuna, the kale was Glory Foods® Kale Greens, and the potato was Weis® canned diced potatoes. The amount of food added depended on the water content. The water content in the loaded reactor accounting for the food and water added(approximately 92% by mass), was held constant to reduce a possible variable. The food (ranging from 0.78 g – 1.0 g) was added was added after the water (ranging from 2.3 – 2.5 g). The reactors were then sealed using a torque wrench and a force of 45 lb. Each reaction condition was replicated thrice.

Figure 1. Swagelok® 4.1 mL Reactor
Techne Industrial Fluidized sand baths were used as the heat source for the reactions. The temperatures used for the reactions were 275, 300, and 325 °C. Once placed in the sand bath, the reactors were held for 5, 15, and 30 minutes. Once the reaction time commenced, the reactors were immediately cooled in an ice bath to return the contents to room temperature as quickly as possible. Once cooled, the reactors were allowed to dry for at least 4 hours in order for water to evaporate off the surface of the reactors.

**Extraction**

Using a wrench, the reactors were opened extremely carefully as to not allow too much product to escape as a result of high pressure gaseous products escaping and carrying the liquid (organic and/or aqueous) product out. Once opened, the products from the reactors were transferred into pre-weighed 15 mL plastic conical tubes. 9 mL of Omni Solv® HR-GC Grade dichloromethane was used to extract the remaining product with pipettes.
The conical tubes were then vortexed at 3000 rpm using a Fisher Scientific Digital Vortex Mixer (mo. 945415) and then centrifuged at 500 rcf using an Eppendorf® table top centrifuge (mo. 5810). The organic phase (dichloromethane phase) was then extracted using a pipette. This
phase was then transferred to a pre-weighed 15 mL glass evaporating tube and covered. The remaining two phases (solid and aqueous) were vortexed again at 3000 rpm and centrifuged at 1500 rcf. The aqueous phase was extracted using a pipette and was transferred to a pre-weighed 5 mL conical plastic tube and weighed after. All three tubes were stored for further analysis.

**Drying**

The 15 mL glass evaporating tubes were placed in a Labconco® RapidVap Vertex™ Evaporator for approximately 45 minutes. The tubes were removed as the samples became completely dry. Once dry, the tubes were weighed to determine the final weight. The solid phase was also dried by placing the tubes into a Thermo Scientific Lab Oven (mo. 658) for about 24 hours. The tubes were then weighed to determine the final mass.

**Analysis**

The elemental compositions of the biocrude phases were analyzed by Atlantic Microlabs, Inc. For the food stock samples, each specific food was dried in the lab oven until no loss in mass was detected (about 3 days).

The biocrude products (275°C, 15 min and 325°C, 15 min for each food) were analyzed using a Shimadzu® PQ2010 Ultra GC-MS. The dried biocrude was dissolved in approximately 5 mL of DCM. This solution was placed directly into the GC-MS testing vials. The initial column temperature was set at 60°C; the injection temperature was 250°C; the split ratio was 5; the
column inert gas flowrate was set to 0.82 mL/min. The sample was held at 60°C for one minute before increasing to 250°C at a rate of 10°C/min. The sample was held at 250°C for four minutes.

The biocrude products at the same conditions were analyzed using a Bruker® Spectrospin 400 UltraShield™ Nuclear Magnetic Resonance (NMR) machine. TopSpin® version 1.3 was used as the analysis program. Once the samples were inserted, the samples were locked. The ‘z1’ and ‘z2’ values were adjusted until the lock was maximized for each value. The samples were ran for 16 scans.
Chapter 3

Results

Observations

Each of the three foods responded differently to the HTL and these responses were noted at multiple points during the experimental procedure. First, some degree of bubbling occurs after the reactors are opened following the HTL. Tuna clearly produced the least amount of gaseous products because minimal if any bubbling occurred. As for kale, the bubbling was moderate. For potato, the bubbling was extreme. The reactors were mostly coated with liquid (mainly aqueous phase) upon opening. To measure the gaseous products, the mass of the reactors before and after opening are recorded to measure the amount of gas that left. However, in the case of potato and kale, the gaseous product yield is impossible to determine accurately because liquid from bubbling leaves the reactor and is removed entirely upon grabbing it, moving it, etc. Consequently, the gaseous product yields in this work are not reported.

The aqueous product phases also differed greatly. Because of the bubbling, potato and kale gave significantly lower and often impossible aqueous phase yields (negative percent yields) because of the lost liquid from the bubbling. In addition, the phases all looked different (Figures 3-5). The kale and tuna aqueous phases were both darker in nature, while the potato aqueous phase is nearly clear.
Figure 6. Example of 2 Solid Layers

Upon extraction, the three phases stored in the plastic centrifuge tubes formed three very distinct phases. However, potato formed two distinct solid phases (Figure 6). This indicates that two different, distinct solid products were formed from the HTL of potato. The lower phase is denser than DCM, while the higher phase is not.

Elemental Analysis

Since food is a feedstock that is naturally high in nitrogen and oxygen due to protein and carbohydrates, respectively, the biocrude composition is quite different from that of crude oil. Table 1 contains the elemental composition of the dried foods, as well as the average elemental composition of the bio-oil of each food.
Table 1. Compositions of Crude Oil and Biocrude

<table>
<thead>
<tr>
<th></th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>S(%)</th>
<th>O(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Oil</td>
<td>83-87</td>
<td>10-14</td>
<td>0.1-2</td>
<td>0.05-6</td>
<td>0.05-1.5</td>
</tr>
<tr>
<td>Kale Biocrude</td>
<td>71.15</td>
<td>8.76</td>
<td>5.19</td>
<td>1.08</td>
<td>13.82</td>
</tr>
<tr>
<td>Dried Kale</td>
<td>45.08</td>
<td>6.37</td>
<td>5.49</td>
<td>0.70</td>
<td>42.36</td>
</tr>
<tr>
<td>Tuna Biocrude</td>
<td>66.50</td>
<td>9.20</td>
<td>8.25</td>
<td>1.25</td>
<td>14.80</td>
</tr>
<tr>
<td>Dried Tuna</td>
<td>55.50</td>
<td>7.90</td>
<td>12.18</td>
<td>0.56</td>
<td>23.86</td>
</tr>
<tr>
<td>Potato Biocrude</td>
<td>70.68</td>
<td>7.24</td>
<td>2.00</td>
<td>0.16</td>
<td>19.92</td>
</tr>
<tr>
<td>Dried Potato</td>
<td>41.90</td>
<td>6.22</td>
<td>0.91</td>
<td>0.00</td>
<td>50.97</td>
</tr>
</tbody>
</table>

*In the elemental analysis, the oxygen content is taken as the balance

In addition, the effects of temperature and holding were analyzed for each of the foods. The elemental composition was determined. The dependences on holding time and temperature are shown below in Appendix A.

From the elemental analysis, the high heating value (HHV) of the biocrude can be determined from Equation 1.²

\[
HHV \left( \frac{MJ}{kg} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (1)
\]

The variables correspond to the dry weight percentages by mass of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash respectively. However, in the calculations used in this experiment, the ash is assumed approximately zero because oxygen is considered the balance. This will underestimate the HHV of the biocrude samples. Table 2 shows the average heating value of each food.

Table 2. High Heating Values of Biocrude Products

<table>
<thead>
<tr>
<th>Food</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Oil</td>
<td>42-44</td>
</tr>
<tr>
<td>Kale</td>
<td>33.8</td>
</tr>
<tr>
<td>Potato</td>
<td>31.1</td>
</tr>
<tr>
<td>Tuna Fish</td>
<td>32.5</td>
</tr>
</tbody>
</table>
The molar ratios of hydrogen to carbon, nitrogen to carbon, sulfur to carbon, and oxygen to carbon were plotted for each food. The temperatures experimented at were 275, 300, and 325°C and the holding times were 5, 15, and 30 minutes. Figures 7-18 display this data.

![Figure 7. Kale Molar Ratio of Hydrogen to Carbon](image)

![Figure 8. Kale Molar Ratio of Nitrogen to Carbon](image)
Figure 9. Kale Molar Ratio of Sulfur to Carbon

Figure 10. Kale Molar Ratio of Oxygen to Carbon
Figure 11. Potato Molar Ratio of Hydrogen to Carbon

Figure 12. Molar Ratio of Nitrogen to Carbon for Potato
Figure 13. Potato Molar Ratio of Sulfur to Carbon

Figure 14. Potato Molar Ratio of Oxygen to Carbon
Figure 15. Tuna Molar Ratio of Hydrogen to Carbon

Figure 16. Tuna Molar Ratio of Nitrogen to Carbon
In addition to the molar ratios, the heating values for each trial were also plotted for each food (Figures 19-21).
Figure 19. Effects of Temperature and Holding Time on Kale HHV

Figure 20. Effects of Temperature and Holding Time on Potato HHV
Yield Results

The four main products formed in the HTL of biomass are the biocrude, aqueous, solid, and gaseous products. As stated earlier, the gaseous product yields are not reported in this paper. In addition, the aqueous phase yields were also unreliable as the extreme bubbling from the gaseous products caused the less viscous water to escape along with the gas. Table 3 reports the average yields for the biocrude and solid phases.

**Table 3. Average Yields of Each Food**

<table>
<thead>
<tr>
<th>Food</th>
<th>Biocrude (%)</th>
<th>Solid (%)</th>
<th>Aqueous &amp; Gaseous (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>9.0</td>
<td>60.5</td>
<td>30.5</td>
</tr>
<tr>
<td>Tuna</td>
<td>27.8</td>
<td>1.9</td>
<td>70.3</td>
</tr>
<tr>
<td>Kale</td>
<td>14.0</td>
<td>25.0</td>
<td>61.0</td>
</tr>
</tbody>
</table>
Figures 7-13 detail the effects of temperature and holding time on the yields of biocrude and solid products. Only temperatures of 275 and 325°C were replicated three times to ensure accuracy.
Figure 24. Tuna Bio-oil Yield Dependencies

Figure 25. Kale Solid Yield Dependencies
GC-MS Data

Extensive analysis was performed on the aqueous and biocrude phases to determine the type of compounds found in the products. Six samples were analyzed. Each of the three foods
were analyzed twice, both at 15 minute holding times. The holding temperatures were 275°C for one sample and 325°C for the other. The only exception is potato, which was held for 30 min in this analysis.

### Table 4. Major Compounds Found in Kale Bio-oil (275°C, 15 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecanoic Acid (Palmitic acid)</td>
<td><img src="image1" alt="Structure" /></td>
<td>7.2</td>
</tr>
<tr>
<td>Nonacosanone</td>
<td><img src="image2" alt="Structure" /></td>
<td>6.2</td>
</tr>
<tr>
<td>Nonacosane</td>
<td><img src="image3" alt="Structure" /></td>
<td>5.8</td>
</tr>
<tr>
<td>1,3-bis(1,1-dimethyl)-benzene</td>
<td><img src="image4" alt="Structure" /></td>
<td>2.9</td>
</tr>
</tbody>
</table>

### Table 5. Major Compounds Found in Kale Bio-oil (325°C, 15 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecanoic Acid</td>
<td><img src="image5" alt="Structure" /></td>
<td>4.5</td>
</tr>
<tr>
<td>1,3-bis(1,1-dimethyl)-benzene</td>
<td><img src="image6" alt="Structure" /></td>
<td>4.4</td>
</tr>
<tr>
<td>Nonacosane</td>
<td><img src="image7" alt="Structure" /></td>
<td>4.3</td>
</tr>
<tr>
<td>2,4-bis(1,1-dimethylethyl)-phenol</td>
<td><img src="image8" alt="Structure" /></td>
<td>3.3</td>
</tr>
</tbody>
</table>
Table 6. Major Compounds Found in Potato Bio-oil (275, 30 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-cyclopentanedione, 3-methyl</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>13.5</td>
</tr>
<tr>
<td>2-cyclopenten-1-one</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>7.24</td>
</tr>
<tr>
<td>5-methyl-2-furancarboxaldehyde</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>4.94</td>
</tr>
<tr>
<td>1-(2-furanyl)-ethanone</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>4.75</td>
</tr>
</tbody>
</table>

Table 7. Major Compounds Found in Potato Bio-oil (325C, 15 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecanoic Acid</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>6.4</td>
</tr>
<tr>
<td>1,3(1,1-methylethyl)-benzene</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>3.8</td>
</tr>
<tr>
<td>2,4-bis(1,1-dimethylethyl-hydrophenol)</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>3.2</td>
</tr>
<tr>
<td>Octadecanoic Acid</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>2.9</td>
</tr>
</tbody>
</table>
Table 8. Major Compounds Found in Tuna Bio-oil (275°C, 15 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecanoic Acid (Palmitic Acid)</td>
<td><img src="image1" alt="Structure" /></td>
<td>6.4</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td><img src="image2" alt="Structure" /></td>
<td>4.4</td>
</tr>
<tr>
<td>Hexadecanamide (Palmitamide)</td>
<td><img src="image3" alt="Structure" /></td>
<td>3.1</td>
</tr>
<tr>
<td>9-octadecenamide</td>
<td><img src="image4" alt="Structure" /></td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 9. Major Compounds Found in Tuna Bio-oil (325°C, 15 min)

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Area (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecanoic Acid (Palmitic Acid)</td>
<td><img src="image5" alt="Structure" /></td>
<td>2.7</td>
</tr>
<tr>
<td>1-methyl-9H-pyrido[3,4-b]indole</td>
<td><img src="image6" alt="Structure" /></td>
<td>1.7</td>
</tr>
<tr>
<td>1,2-diethyl-cyclohexane</td>
<td><img src="image7" alt="Structure" /></td>
<td>1.3</td>
</tr>
<tr>
<td>2,4-bis(1,1-dimethylethyl)-phenol</td>
<td><img src="image8" alt="Structure" /></td>
<td>1.3</td>
</tr>
<tr>
<td>4-ethyl-phenol</td>
<td><img src="image9" alt="Structure" /></td>
<td>1.2</td>
</tr>
</tbody>
</table>
Chapter 4
Discussion

Elemental Analysis

The main purpose of HTL of biomass is to provide a clean and renewable fuel source. Several factors affect the effectiveness of the fuel including impurities (S, N, metals, etc.) and the energy density. The bio-oils produced from the HTL of food are lower in energy compared to crude oil, and the nitrogen content is significantly higher in the bio-oil due to the existence of proteins in the feed stock.¹⁴ Significant upgrading techniques are required before bio-oils produced from food waste (or algae) are of high enough quality. The type of food also determines affects the amount of impurities. Tuna, having the highest protein content, also contained the highest levels of nitrogen in its bio-oil by a factor of over two for the next highest, kale. Sulfur was the only other impurity measured in the bio-oil. For all food, its levels were on the lower end of the crude oil range. Finally, the heating values were roughly the same, with kale producing the highest energy density, and potato producing the lowest energy density (Table 2). Oxygen severely reduces the energy density of a fuel, and the potato bio-oil contained the highest level of oxygen. Starch, which is a highly oxygenated polymer with a molecular formula of \((C_6H_{12}O_5)_n\), accounts for a majority of potato’s biomass. As for kale, there is a more balanced ratio of carbs, fats, and proteins. These foods contain a wide variety of organic compounds such as different amino acid ratios, carbohydrates, and fats. The impact of these types of molecules on the heating value cannot be explicitly determined from the work done in this paper.
The dependencies on holding time and temperature also produced interesting results (Figures 7-18). Some of the trends seen in the composition and heating values can easily be attributed to the similarities in the foods initial composition. Kale’s dry mass consists of mostly carbs and protein, tuna’s consists of mostly protein and fats, and potato’s consists of almost all carbs. Therefore, trends are seen between kale and potato, and kale and tuna. No trends were explicitly seen between potato and tuna, which is expected; tuna contains no carbs at all. Despite the macromolecular similarities, the complexity of the molecular composition of the foods results in data that varies in consistency. Some of the results recorded values that were so low, the trends or data can be viewed as unreliable, but also unnecessary. For example, the sulfur content for all three foods was below 0.2% on a molar basis. With a percentage this low, the accuracy of the measurements is unreliable because Atlantic Microlabs, Inc claims an accuracy of ±0.3% on all of their reported mass percentages. Regardless, the sulfur content for all the foods was so low that there should be no concern on reducing the already incredibly low sulfur content by means of changing the holding time/temperature.

For the high heating value (Figures 19-21), both kale and tuna experienced identical trends. The heating value decreases as the holding temperature increases from 275°C to 300°C, but only for a 5 minute holding time does the heating value continue to decrease. As for potato, the heating value generally increased with increased holding time and temperature. The effects of proteins and fats may have dominated the trends seen in kale and tuna. The trends seen in tuna and kale reflect the trends seen in experiments with microalgae. For algae, fast HTL (holding times under 5 minutes) yield the highest energy densities. Microalgae is a heavily researched organism because its ability to transform into fuel. It should come as no surprise that kale reflects the trends of microalgae because both are plants. Tuna also contains mostly carbs
and fats (on a dry weight basis), so it is not surprising kale and tuna share trends. For potatoes, or carb-based foods in general, the reaction kinetics have not been studied, but these trends are expected to differ.

Yield Data

Determining the amount of bio-oil recovered from reacting food waste is an integral part of deciding whether food to fuel via HTL is a legitimate process. In the experiments, tuna yielded a significant bio-oil yield compared to kale and potato, with potato posting the lowest bio-oil yield. Potato however, reported the highest solid yield, with tuna yielding the least. These trends are significant because it explains the types of products that HTL of foods produce depending on the composition of macromolecules. For potato, the starches and other carbohydrates form a majority of the solid phase products. This is confirmed because tuna yielded the least amount of solids, while kale produced between the two. Meanwhile, the amount of bio-oil produced from biomass may be directly associated with protein and fat content. With potato, little bio-oil was produced indicating that carbohydrates may not be ideal for bio-oil production. The bio-oil produced from potato was also the least energy dense.

As stated previously, kale and tuna experienced similar trends in the elemental analysis. The compositions of the main components changed in a similar manner. However, the bio-oil yields experienced the exact opposite trends (Figures 22 & 24). In addition, the effect of holding time on yield showed no identical trends either. Strangely for potato, the most delicate experimental conditions (5 min and 275°C) yielded the most bio-oil (Figure 23), but when the holding times increased to 15 and 30 minutes, the bio-oil yield was the lowest of six trials.
Algae has produced equally interesting and inconsistent results.\textsuperscript{11} Although the work by Luo et al. is more consistent, the trends are not perfectly consistent. An example is that the biocrude yield generally increases, but decreases between 10 and 30 minute holding times. Results like this that prove that the kinetics of the HTL reactions are extremely complicated. One of the most challenging issues in the field of HTL is figuring out the kinetics of the reaction. Determining how and why certain compounds form different products is crucial for optimizing the HTL process. The overall proposed mechanism of HTL products is shown in Figure 28.

![Figure 28. Simplified Reaction Pathway](image)

**Figure 28. Simplified Reaction Pathway**

**Figure 28** is a simplified pathway for the types of products formed HTL. The relative rates of the reactions depends on the reaction conditions. In general, the biomass starts out as solid product or heavy bio oils due to the large macromolecules in food. As HTL occurs, the solid products can be broken down and converted into any of the other three product types. With this logic, the solid product yields should decrease with holding time and temperature. However, this is not the case. It occurs sometimes and not others. For example, the solids yield decreased with increasing holding times, but the potato solids product increased with increased holding
times. This implies that the reaction pathway for foods is clearly more complicated than Figure 10 implies. Once gaseous products are formed, it would be uncommon for the products to reform and become solid or aqueous products again. Gaseous product formation is an essentially irreversible process. On the other hand, the formation and reactivity of bio-oil products is a more unique and complicated pathway. Typically, multi-step reactions are thought of as A -> B -> C pathways. In HTL, the most sought after product, bio-oil, experiences unique trends that would indicate that each reaction pathway involving solid, aqueous, and bio-oil products is reversible. This can be seen as bio-oil yield for tuna increases and then decreases as the holding time is increased at a constant temperature of 275 °C. In this scenario, the formation of bio-oil products becomes more prominent as during the 5-15 minute frame, but then the bio-oil product in the reactor is converted to aqueous products in the 15-30 minute frame. The lower bio-oil yield could be the result of increased gaseous products, which are inherently permanent products as discussed earlier.

**Analysis**

The most interesting result from the GC-MS chromatograms is that the most popular compound was palmitic acid (hexadecanoic acid). This compound is the most commonly found fatty acid in animals, plants, and microorganisms. Despite that some foods contained lower levels of fats compared to others, all of the bio-oils contained significant amounts of this compound. Long fatty acids in general were commonly found in the GC-MS results. This bodes well for the production of transportation fuels. The most frequently occurring compounds contain no heteroatoms besides oxygen. As mentioned earlier in this thesis, fuels that contain
oxygen only experience decreased heating values and no other downsides. Besides the bio-oil produced from tuna at 275°C, no other compounds were seen that contained nitrogen. In the elemental analysis, nitrogen consisted of about 10% of the mass. This indicates that the largest and most common compounds contain no nitrogen. Therefore, the smaller compounds in the bio-oil must contain the nitrogen. These compounds were unable to be analyzed. However, proteins degrade rapidly in HTL. The nitrogen might exist as nonpolar amino acids. These findings show that the separation and removal of the heteroatoms could be done with distillation. The smaller compounds, which most likely contain nitrogen, could be boiled off leaving the heavy hydrocarbons and acids behind. Distillation is already widely used in the petroleum industry. The bio-oils produced from HTL could be inserted directly into the separation techniques already implemented by the oil industry.

The NMR results confirm the findings of the GC-MS. The peaks in the NMR spectra confirm that saturated alkanes compose a significant part of the samples. Each of the spectra contains a sharp peak around a shift of 1 ppm. In addition, some of the samples show signs of aromatics. Some of the peaks are more distinct than other ones. Regardless, multiple spectra contain peak around the 7.5 ppm shift range indicating the existence of aromatic molecules. According to the GC-MS results, the major compounds found are saturated hydrocarbons and aromatics. Each of the samples contains a series of smaller peaks to the left of the major saturated hydrocarbon peak. These peaks could be the result of ketones, double bonded carbons, or possibly amines. Since amino acids are expected to exist in the bio-oil (just at small concentrations), some of the peaks in that area most certainly are attributed to their existence. Interestingly enough, no peaks were found for carboxylic acid groups. Some of the major compounds found from the GC-MS were carboxylic acids. In addition, amino acids contain a
carboxylic acid group. This could mean that the amino acids formed from the degradation of proteins may react further and produce derivatives of amino acids. The amine groups on the amino acids could react with the carboxylic acid groups and form gases such as CO\textsubscript{2} and H\textsubscript{2}. These gases are known products of HTL\textsuperscript{17}. Overall, the GC-MS results are confirmed by the NMR results.

**Final Notes**

The purpose of this experiment is to determine the practicality using food waste as a feedstock for fuel production. The HTL of algae is a much more commonly researched process because it uses a feedstock that can be harvested and grown as needed. Microalgae is also naturally better suited to be a feedstock for fuel production due to its high lipid content. Although, the benefit of food waste as a feedstock is that it is free. The experiment in this work aimed to research three different types of foods reacted by themselves with water. In reality, an industrial scale HTL facility would use a vast combination of food wastes. The products found in the HTL of mixed foods is an interesting concept. The mix of macromolecules would certainly influence the reaction pathways observed in this work. Future work should include further analysis on the reaction kinetics, and what types of products are formed under various reaction conditions. Experiments should also be done on ‘mimic’ food waste, where the feedstocks in the reactions are predetermined mixtures of different types of foods. The reaction kinetics, yields, and product types should also be classified and compared to that of the individual results.
The experimental conditions in this work prevented reliable yield data for the aqueous and gaseous products. Future work could involve using pressure valves in the reactors to obtain reliable gas and aqueous yields.
Chapter 5

Conclusion

Kale, tuna fish, and potato were all reacted at HTL conditions and all reported significant bio-oil yields. Kale and tuna, which contain higher amounts of fat and protein per dry weight, reported much higher bio-oil yields compared to potato. Potato on the other hand, produced solid yields much higher than that of kale or tuna, most likely due to its high starch content. Each compound contained long hydrocarbons and aromatics as the major products in the bio-oils according to the GC-MS results. The NMR spectra confirmed the compounds found. This thesis has found that reacting food at HTL conditions yields a bio-oil that upon refining could provide a legitimate fuel source.
Appendix A

GC-MS Data

Figure 29. GC-MS Chromatogram for Kale (275°C, 15 min)
Figure 30. GC-MS Chromatogram for Kale (325C, 15 min)
Figure 31. GC-MS Chromatogram for Potato (275°C, 30 min)
Figure 32. GC-MS Chromatogram for Potato (325C, 15 min)
Figure 33. GC-MS Chromatogram for Tuna (275C, 15 min)
Figure 34. GC-MS Chromatogram for Tuna (325C, 15 min)
Appendix B

NMR Data

Figure 35. NMR Spectrum for Kale Bio-oil (275°C, 15 min)
Figure 36. NMR Spectrum for Kale Bio-oil (325°C, 15 min)
Figure 37. NMR Spectrum for Potato (275C, 15 min)
Figure 38. NMR Spectrum for Potato (325°C, 15 min)
Figure 39. NMR Spectrum for Tuna (275C, 15 min)
Figure 40. NMR Spectrum for Tuna (325C, 15 min)


Academic Vita of Zachary Berquist  
zjb5037@psu.edu

Education
The Pennsylvania State University (University Park, PA)  
*College of Engineering*  
*Schreyer Honors College*  
**Intent to Graduate:** May 2016  
**Expected Degree:** B.S. Chemical Engineering  
**Expected Minor:** Economics  

Relevant Courses:
- Thermodynamics  
- Technical Communication  
- Chemical Reaction Engineering  
- Fuel Sciences  
- Chemical Engineering Laboratory  
- Chemical Engineering Technologies

Work Experience

**Air Liquide** (Morrisville, PA)  
*Intern*  
- Experienced chemical processes such as distillation, separations, and scrubbing  
- Designed and installed a level indicator/transmitter system  
- Operated and troubleshooted multiple processes  
May 2015 - Jul 2015

**Academic Excellence Center** (University Park, PA)  
*Chemistry Tutor*  
- Educated students in introductory chemistry courses  
- Also tutored mathematics and physics when needed  
Jan 2014 - Present

**Franco’s Trattoria** (McMurray, PA)  
*Server*  
- Waited on up to 6 tables at once  
- Maintained cleanliness and restocked restaurant  
May 2014 - Jan 2015

Leadership/Activities

**Dr. Philip Savage’s Algal Research Lab** (University Park, PA)  
*Undergraduate Assistant*  
- Performed research in High Temperature Water (HTW) treatment of algae  
- Investigated possible pathways and mechanisms for HTW treatment  
- Ordered equipment and participated in publishing articles  
Aug 2014 - Present

**Hospitality THON Committee** (University Park, PA)  
*Cadet*  
- Led meetings, organized events, and communicated information for 22 students  
- Set up and worked multiple fundraisers over course of the school year  
- Helped raise over $13 million for the Penn State IFC/Panhellenic Dance Marathon  
Sept 2014 - Present

**IM Sports Participant** (University Park, PA)  
- Squash, flag football, golf, racquetball, basketball  
  (champion)  
Sept 2012 - Present

Achievements

**The President’s Freshman Award**  
- 4.0 GPA first semester  
- Dean’s List  
  7/7 Semesters  
Fall 2012