Hydrothermal Liquefaction of Food Waste

A Major Qualifying Project Report:

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Acknowledgments

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Abstract

Our project addresses one of today's biggest challenges: the sustainable management of food waste. An effective use of food waste could be chemical conversion into biofuel through the hydrothermal liquefaction (HTL) process. The objective of our project is to study the effectiveness of red mud, and pure metal oxides derived from its composition as potential catalysts for HTL. These catalysts’ impact on the production of bio-oil will be compared to that of Ceria Zirconia in the hopes of finding a cheaper alternative.
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1.0 Introduction

One of the biggest challenges today is the sustainable management of food waste. According to the Food and Agriculture Organization of the United Nations, approximately one-third of food produced globally for human consumption is either lost or wasted (HLPE, 2014). In the United States, 40 percent of food goes uneaten and is then sent to a landfill, where it cannot be used to its full potential (Gunders, 2012). The food waste stream can be valorized in a number of ways. It can be made into animal feed, composted, burned, or converted to useful process chemicals. An effective use of food waste could be the chemical conversion into biofuel.

Biofuel production from biomass can be completed through two main technological processes, pyrolysis and hydrothermal processing, which are both forms of thermal decomposition. Pyrolysis takes place at higher temperatures and over shorter reaction times compared to hydrothermal processing. The main difference between the two is that pyrolysis reactions require a dry feed while hydrothermal processing utilizes a water based feed. Hydrothermal processing is advantageous for food waste as it naturally has a high water content and only requires the occasional addition of water. For pyrolysis, energy must be spent to dry the waste before processing.

Biofuel can be produced using a catalytically enhanced hydrothermal liquefaction and carbonization process. More specifically the major reactions desired are the ketonization of carboxylic acids and the alkylation of phenolic compounds. In previous works, commercial catalysts have been found to do primarily base chemistry. This was an unexpected result and has shown the need for further research into solid base catalysts and how they will affect the process. An example of a catalyst that was used is Ceria Zirconia (CeZrO\textsubscript{x}). CeZrO\textsubscript{x} is a heterogeneous catalyst, chosen because of the stability of the parent oxides and because it is known to catalyze condensation and coupling reactions. While CeZrO\textsubscript{x} improves the bio oil higher heating value of model aldehydes to water insoluble products, it must be used at least 25 times for it to be economically viable (Maag et al, 2018). This high cost has led to the search for a cheaper alternative with similar catalytic activity.

A potential option that could fulfill the criteria of being an effective and low cost catalyst is red mud. Red mud is a byproduct of the production of alumina and it is estimated that over 150 million tons are produced annually (Stanford, 2016). Red mud is an attractive potential catalyst because of its abundance, high surface area, sintering resistance, resistance to poisoning, beneficial
metal oxides, and low cost. The presence of metal oxides in red mud is especially appealing because they are strong bases and insoluble in water, which could achieve the base chemistry that occurred in the previous work.

The objective of this project is to study the effectiveness of red mud, and pure metal oxides derived from its composition as potential catalysts for HTL of food waste. These catalysts’ impact on the production of bio-oil will be compared to that of Ceria Zirconia in the hopes of finding a cheaper alternative. The results of the project will be compared to similar work done by Mainstream Engineering in collaboration with Worcester Polytechnic Institute.
2.0 Background

2.1 Food Waste

The term, "biomass" can be defined as the total mass of living or recently dead organic matters within a given environment. Carbon, hydrogen, nitrogen, sulfur, and oxygen are the major components of any biomass. Biomass refers to all forms of organic matter potentially recoverable from a variety of renewable sources. These renewable resources include dedicated energy crops, agricultural crops, animal wastes, crop wastes from agricultural activities, wood and municipal wastes, etc. (Olanrewaju, 2012). One of the largest contributors to unused biomass is food waste. From production to consumption, food is lost as waste. In the U.S. alone, it is estimated that more than 30 percent, at a cost of $161 billion, of edible food goes to waste. “Food loss and waste refers to the edible parts of plants and animals that are produced or harvested for human consumption but that are not ultimately consumed by people ”(Lipinski Et al. 2013). The waste and loss of food leads to significant environmental, social, and economic costs. Economically, food waste represents a lost investment that can reduce farmers’ income and increase consumers’ expenses. Environmentally, food waste contributes to the largest volume of material in U.S. landfills, accounting for 21% of the waste stream (United Nations, 2017). It can also produce unnecessary greenhouse gas emissions and inefficiently uses water and land, which in turn can lead to diminished natural ecosystems (Lipinski, Et al. 2013).

Despite these large inefficiencies, there are ways to potentially reduce the amount of food that goes to waste. Many of these strategies have to do with food redistribution and donating, increasing the shelf life of foods, and adjusting the use-by and sell-by dates to accurately reflect when the food has gone bad. There are also methods that focus on diverting the food waste into energy production. Converting a portion of the food waste to energy could free up large amounts of landfill space, while powering vehicles and heating homes, thus reducing humanities carbon footprint. This concept is called Waste-to-Energy, and it has become the one of the fastest growing segments of the world’s quickly diversifying energy sector (Moss & Sheer, 2013).
2.2 Biofuel Production Process

Biofuel production occurs when biomass is converted to a useful, high energy form. Biomass to biofuel conversion is important because biomass alone is not suitable for energy production. Wood is one of the most used biomasses, predominately used as an energy source in its natural form, but is not suitable in an industrial setting (Tekin, 2014). As a result, scientists continue to study chemical processes to develop biofuels by transforming biomass. Currently there are three developed methods; pyrolysis, combustion, and a group of hydrothermal processes, which include hydrothermal gasification, carbonization, and liquefaction (Tekin, 2014).

2.2.1 Pyrolysis

The process of Pyrolysis starts with the complete drying of the biomass reactant. This step is crucial as the presence of water would raise the energy needed to heat the biomass. The dried biomass is then added to a reactor only filled with nitrogen or argon. The reactor is then heated to around 400-600° C. Initially, the reaction produces vapors and solids. Once the reaction is complete the product vapors are sent to be condensed. During the cooling process, heavy molecules shift to the liquid phase, while lighter gases do not change phase and are recovered as gas products. The light gases include H₂, CO, CH₄, C₂H₂, C₂H₄ (Zafar, 2009). The liquid product, also known as pyrolytic oil, is a tar like material produced from the decomposition of cellulose, hemicellulose, and lignin, the three main components of biomass. The liquid product is composed of different oxygenated hydrocarbons and water. The solid product is known as char and includes carbon, hydrogen, and oxygen (Tekin, 2014).

2.2.2 Hydrothermal Processes

Hydrothermal processing involves the heating and pressurization of biomass in the presence of water. One of the main benefits to this process compared to pyrolysis is that the biomass does not need to be dried before use. This removes a large quantity of energy needed to prepare the biomass. Hydrothermal processing can be broken down into three techniques, Hydrothermal Liquefaction (HTL), Hydrothermal Gasification (HTG), and Hydrothermal Carbonization (HTC).
HTL is performed at high pressured and supercritical water conditions. The biomass is converted to a liquid bio-oil that has a high-energy content (Kumar, 2010). The process is beneficial as it requires lower temperatures and in turn energy to perform. The reactions that occur during the process are dependent on the composition of the biomass. The main reactions that occur are depolymerization of the biomass, degradation of the monomers, and recombination of fragmented components.

Hydrothermal Gasification involves the thermochemical decomposition of biomass to a liquid, then to the gas phase. The reaction occurs above the critical water condition. As a result, this decomposition of biomass prevents the formation of bio-char, leading to higher gas yield. If the reaction occurs at supercritical conditions, the product gases are mostly hydrogen gas, or methane in the presence of a catalyst (Tekin, 2014). The main benefits of this process are high energy gases are produced which can be used in many application and there is limited production of bio-char.

The HTC process is the newest and cheapest of the three techniques. Biomass, in the presence of water, is heated, and pressurized at low temperatures for many hours. The temperature never exceeds 200°C, therefore its uses less energy and the water remains in subcritical form. The biomass for this process is carbohydrate rich and experiences three reactions during conversion. The carbohydrates are first dehydrated into 5-hydroxymethyl furfural, or furfurals. Next, the furfurals are polymerized into polyfurans, and are converted to carbon through intermolecular dehydration. Though the cost of this process is the lowest of the three, the technology is new, the reaction time table is long, and the carbon product has its own unique characteristics such as being more hydrophobic (Tekin, 2014).

2.3 Hydrothermal Liquefaction in depth

Hydrothermal liquefaction (HTL) is a useful technique in transforming biomass into liquid and solid fuels. HTL has a number of distinct advantages over other processes. HTL has the ability to handle a wide variety of feedstocks. This gives the process the distinct advantage of accepting a wet feedstock, perfect for biomass, which is often upwards of 70% water (Toor, 2011). The water in the hydrothermal liquefaction process acts as a solvent and a reactant. When water is heated close to its critical temperature in a pressurized system, it begins to behave as non-polar liquid and
dissociates much easier. (Kumar, 2010). The non-polar behavior of the liquid helps to solvate the organics in the biomass, and the H3O+ and OH− ions aid in the conversion of biomass molecules into more desirable compounds. Figure 1 shows the different temperature and pressure regions of water and which processes they are useful in.

![Figure 1 Effective reaction temperature zones](image)

The HTL process has been shown to produce bio-oils with energy densities between 35-37 MJ/kg and bio-char with a energy density around 28 MJ/kg which is similar to that of coal (Vardon, 2012). The hydrothermal liquefaction of biomass has been previously shown to produce more energy than it consumes (Gollakota, 2017). This means that the process could be run by burning part of the oil/char it produces and have a percentage left over. The percentage remaining can even be chemically upgraded to produce transportation fuels.

One downside to the HTL process is that a portion of the organic molecules dissolve into the aqueous phase and must be removed from the water before it may be discharged into the environment (Smith, 2014). The process also has been shown to be difficult to scale up. The vast majority of the research into HTL has been done in the laboratory setting in small scale reactors (Mosteiro-Romero, 2014). This means that the process conditions and costs are estimated but not implicitly known. The pressures and temperatures needed will greatly increase the cost of large scale equipment (Toor, 2011).

The major way that bio oil is produced is the reduction of oxygen composition from the biomass feed. Oxygen accounts for 40-60% of the dry weight of biomass (Peterson, 2008). This is
done by reducing the number of oxygen molecules bound to the organics and increasing the organic molecules size. The reduction of bound oxygen reduced the solubility of the organic compound by making it less polar and more hydrophobic. This reduction in oxygen increases the energy density of the resulting bio oil. Two major chemical reactions taking place are alkylation of phenolic compounds and the ketonization of carboxylic acids. Removing oxygen in these ways is ideal for the process as it either removes it as water, increasing the total carbon yield, or as carbon dioxide which increases the hydrogen carbon ratio of the final products (Peterson, 2008). Bio-oil products of the HTL process on average are less than 1% oxygen. The addition of catalyst have been shown to improve the percent conversion from the aqueous to oil phase.

2.4 Previous Work Converting Food Waste

The hydrothermal liquefaction of food waste has been studied using many different catalysts. One particular study compared the effectiveness of a Sodium Carbonate (Na₂CO₃) catalyst to a Ceria Zirconia (CeZrOₓ) catalyst to convert food waste to bio oil. Na₂CO₃ is a homogeneous, alkali salt that has been reported to improve HTL carbon yield. That improvement is attributed to preventing the formation of post reaction carbon residue, or coke. The limitation of using a homogeneous catalyst is that it is expensive to recover and reuse the catalyst. Conversely, heterogeneous catalysts are reusable and have the potential to decrease costs and improve energy efficiency. CeZrOₓ was a heterogeneous catalyst chosen because of the liquid-phase hydrothermal stability of metal oxides, activity for promoting the desired reactions, and known to catalyze condensation and coupling reactions.

The study showed that using CeZrOₓ yielded a bio-oil with a high carbon content, decreased oxygen content, and increased heating value compared to the bio-oil produced using Na₂CO₃. In a single use the energy yield of CeZrOₓ is about two times that of the Na₂CO₃. While CeZrOₓ improves the bio oil higher heating value of model aldehydes to water insoluble products, due to cost it must be used at least 25 times for it to be economically viable. When compared to Na₂CO₃, CeZrOₓ is almost 30 times more expensive per gram. However, considering the 59% increase in energy yield and cost on the basis of energy yield and not feed processed, CeZrOₓ is more economical than Na₂CO₃. When CeZrOₓ is used 25 times compared to Na₂CO₃ only being reused twice, it is the better economic catalyst (Maag et al., 2018). Based on this result, less
expensive, water-stable oxide, heterogeneous catalysts should be explored since they might have the potential for energy and economically efficient conversion of food waste to energy.

2.5 Catalysts for Hydrothermal Liquefaction

Metal oxides are good catalysts for hydrothermal liquefaction for a number of reasons. Primarily they perform the same base chemistry observed during the ceria zirconia experiments. They are able to catalyze the dehydration and decarboxylation reactions that produce bio-oils. Metal oxides are insoluble in water even at supercritical water temperatures. They also have been shown to maintain they surface area and activity after long exposures to hydrothermal liquefaction conditions. This means that can be reused multiple times giving them a lower effective cost.

2.5.1 Red Mud

Red mud is a by product of the production of alumina from bauxite in the Bayer process. The Bayer process involves heating bauxite ore and sodium hydroxide in a pressure vessel to a temperature of 150 to 200°C. The resulting color of the red mud is attributed to the high concentration of iron. The red mud generated by this process is a highly alkaline waste material with a pH ranging from 10 to 12.5. (Shaoqing, Meili, Fang, & Zhihe, 2016) It is composed of aluminum oxide, iron oxide, silica, titanium oxides and hydroxides, shown in Table 1; however, these values can vary depending on the alumina refinery, the quality and nature of the bauxite ore and the extraction conditions.

<table>
<thead>
<tr>
<th>Major Component</th>
<th>Percentage Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>30-60%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10-20%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Trace-25%</td>
</tr>
<tr>
<td>CaO</td>
<td>2-8%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3-50%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2-10%</td>
</tr>
</tbody>
</table>

Table 1: Major components in Red Mud by weight percentage (Deelwal,Dharavath, & Kulshreshtha, 2014)
Currently there are about 80 active Bayer plants, 30 of which are in China, and 50 inactive plants, with a combined 3000 million tons of red mud (Stanford, 2016). Every year, approximately 90 million tons of red mud being produced and there is no plan to decrease this production. (Patel & Pal, 2015). The most common disposal method of the excess red mud of is by dumping it into secured large inland artificial ponds, shown in Figure 2. As a result of its hazardous corrosive nature this method poses a very serious threat to the environment. The red mud ponds cause the alkali to seep into the ground, resulting in trace amounts of heavy metals and radionuclides to infiltrate the water supply and produce alkaline airborne dust emissions (Patel & Pal, 2015). A wide variety of research has been done to determine how to properly dispose of or use the residue, however nothing has been determined to be economically viable and environmentally acceptable. Because of its abundance, low price, and beneficial metal oxides, scientists have explored the use of red mud as a catalyst.

Figure 2: Aerial View of Red Mud Ponds (Stanford, 2016)

Red mud offers a wide range of application for catalytic reactions like hydrogenation, hydroliquefaction, oxidation, however, in its natural form, the performance is low compared with
iron oxides and the available commercial catalysts, which show efficiency greater that 90% (Batra & Sushil, 2007). Red mud has been previously investigated as a catalyst for the hydro liquefaction of biomass however this was at higher temperatures (800° C), for the production of hydrogen from methane and coal (Klopries, Hodek, & Bandermann, 1990). It was found that red mud was not susceptible catalyst poisons like sulfur and did not lose its catalytic activity easily. Also because red mud is such an inexpensive catalyst, it does not need to be recovered like commercial catalysts. Modifications can be made to improve the performance of the red mud, like increase the surface area, increases the percentage of Fe₂O₃ and TiO₂ in the catalytically active phase and lower percentage of sintering agents like Na₂O and CaO. Activity can also be enhanced through physical and chemical treatments like acid activation, calcination, sulphidation, and reduction (Batra & Sushil, 2007). Its properties such as iron content in form of ferric oxide (Fe₂O₃), high surface area, sintering resistance, resistance to poisoning and low cost make it an attractive potential catalyst for converting food waste biomass into bio oil (Sushil & Batra, 2007).

2.5.2 Metal Oxide Catalysts

2.5.2.1 Iron Oxide

Iron oxide is the largest component of red mud, giving it its characteristic red color. During the extraction of aluminum from bauxite ore the iron oxide matrix is disposed of as waste. Iron oxide has a number of useful characteristics for hydrothermal liquefaction. It is insoluble in water, has a very high surface area, is cheap and has a very low chance of sintering at the temperature of reaction. Iron oxide has been shown to produce oil based products from organic waste streams. Specifically it was used as the major catalysts for the production of acetone from livestock manure (Funai, 2011). The study found that iron oxide survived a high temperature reactor and water based feedstock for long periods of time with little loss of activity.

2.5.2.1 Calcium Oxide

Calcium Oxide (CaO) is metal oxide containing one calcium and one oxygen atom connected by a ionic bond. In its solid form is physical properties are a white odorless powder. CaO has been used and studied as catalyst in previous research, specifically the transesterification
of vegetable oils. It is known to be one of the best catalysts for biodiesel production due to its high activity, low cost, and large abundance.

2.5.2.2 Alumina

Alumina, also called Aluminum Oxide, is the product of the Bayer Process and the second most abundant component in red mud. In the Bayer Process Alumina is made when bauxite is crushed, mixed in a solution of sodium hydroxide, and seeded with crystals to precipitate aluminum hydroxide. The hydroxide is then heated in a kiln to drive off the water and produce several grades of powered alumina. One of the grades is activated alumina, which is a porous, granular substance that can be used as an adsorbent for removing water from gases and liquids and used as a substrate for catalysts. (Encyclopaedia Britannica, 2016). Aluminum Oxide catalysts are use in a variety of reactions. Its largest scale application is in the Claus Process. This process converts hydrogen sulfide waste gases into elemental sulfur in refineries. Factors such as purity, surface area, pore volume, and size distribution, and rate of deactivation influence the alumina catalyst performance and selectivity. It is also important to consider the crushing strength and resistance loss of quality of the catalyst pellets when assessing the quality of alumina. Investigators have also credited the effectiveness of the catalyst to the intrinsic acidity of the surface of activated alumina. (Hudson, Misra, Perrotta, Wefers, & Williams, 2000)
3.0 Experimental

3.1 Catalysts

Different solid base catalyst were used to determine their effect product phase distribution through hydrothermal liquefaction of food waste in batch experiments. These catalyst were selected based on cost, sustainability, and durability under hydrothermal liquefaction conditions. The catalyst that were chosen were red mud, Calcium Oxide (CaO), Alumina (Al₂O₃), and Iron (III) Oxide (Fe₂O₃). For comparison, three thermal runs were performed without using a catalyst. Each catalyst and control was ran at least three times to ensure the results were reproducible.

3.2 Food Waste Slurry Preparation

The food waste slurry was modeled after the slurry used by Mainstream Engineering. The feedstock was made up of common food items that include proteins, carbohydrates, fruits, vegetables, dairy, and fat. The food was mixed with DI water using a blender. The mixture was then stored in a jar between runs. For each run 100 grams of the mixture was combined with 5 grams of catalyst. The exact mixture is listed in Table 2 below.

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>Moisture Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Cheese</td>
<td>23.3</td>
</tr>
<tr>
<td>Canned Chicken</td>
<td>82.3</td>
</tr>
<tr>
<td>Instant Potatoes</td>
<td>19.2</td>
</tr>
<tr>
<td>Green Beans</td>
<td>415.5</td>
</tr>
<tr>
<td>White Rice</td>
<td>34.5</td>
</tr>
<tr>
<td>Apple Sauce</td>
<td>342.6</td>
</tr>
<tr>
<td>Butter</td>
<td>9.8</td>
</tr>
<tr>
<td>Water</td>
<td>41.5</td>
</tr>
<tr>
<td>Total</td>
<td>968.5</td>
</tr>
</tbody>
</table>

Table 2: Food Waste Slurry Components
3.3 Reactor Conditions

The hydrothermal liquefaction experiments were carried out in a 300 mL Parr stainless steel reactor rated at 3500 psi and 350 °C. The reactor was sealed with a teflon O-ring and two split ring closure clamps. The head of the reactor is equipped with a magnetic motor, pressure gage, thermocouple, pressurization valve, and emergency rupture disk. The temperature and the magnetic stirring motor were controlled by a Watlow temperature controller. The reactor was heated using an external heater. Simultaneously the magnetic stirrer was cooled by a VWO Scientific Products Water Circulator to ensure it did not overheat. The pressure of the reactor was monitored using a pressure gauge installed on the reactor head. The set up can be seen in figure 3.
The reactor was prepared by adding 100 grams of the food waste slurry and 5 grams of catalyst. The reactor was then sealed and connected to the stirring motor, temperature controller, and cooling water feeds. Prior to heating the slurry, the reactor’s headspace was purged with nitrogen and then brought to pressure. This process involved filing and then purging the reactor
with nitrogen three times, to insure that all the original air had been removed from the reactor. The reactor was then filled until the pressure gauge read 1100 psi. Once the reactor was pressurized the stirrer and external heater were turned on. Heating the reactor increased the pressure to the desired 3000 psi. If the pressure did not reach 3000 psi after heating the reactor, more nitrogen was added to achieve the desired pressure. Using the internal thermocouple, the final temperature of the food waste slurry was brought to 300°C and maintained for one hour to react. When the reaction was complete the heater was shut off and the reactor vessel was cooled using a water bath.

3.4 Analytical Technique

3.4.1 Retrieval and Analysis

Once the reactor had cooled, it was depressurized and the entire reactor was massed. Then contents were poured into a vacuum filtration system. The vacuum filtration system uses a Whatman 125 mmØ filter paper and a funnel connected to a vacuum to separate the aqueous phase of the mixture from the solid and oil phases. Before the filter paper was used, it was massed to determine how much of the contents of the vessel are lost on the filter paper. The flask with the aqueous phase was then massed and saved in vials for future analysis. The remaining solid and oil are massed again to determine how much oil remains in the solid mixture. The oil and solids left on the filter were then washed with acetone to dissolve and collect the oil. The process was repeated until the acetone slurry being produced was light brown in color. The filter, funnel, and solid were then massed again to determine the weight of the oil that was removed. The solids remaining on the filter paper were dried, weighed, and place in a vial for future analysis. The acetone was removed from the oil using a rotary evaporator heated within the range of 40 to 50°C. A flow diagram of the process is shown in Figure 4.
Figure 4: Experimental and Analytical Procedure
3.4.2 GCMS Analysis

The Gas Chromatography-Mass Spectrometry (GCMS) was used to identify the different substances in the aqueous phases. A sample was prepared by diluting the aqueous product with acetone. Three or four drops aqueous phase was added to the vial using a filter equipped syringe. The remaining volume is filled with solvent and then shaken to ensure a homogeneous solution. Then the vial is loaded into the Gas Chromatograph for analysis. The GC graphs of each catalyzed run were compared to the thermal runs and the differences were recorded. This was done for both the oil and aqueous phases to see the qualitative effect that the addition of that catalyst had on the process.

3.4.3 FT-IR Methodology

The oil samples were loaded into the Fourier Transform Infrared Spectroscopy machine to determine the vibrational frequency of a bond or collection of bonds in the samples. Before the sample could be recorded, the machine had to be purged with liquid Nitrogen. Once it was cooled the machine was run with no sample in it. The background spectrum was measured to create a baseline that was subtracted from the spectrum of the sample. While the background was recording the sample of oil was prepped. A drop of the oil was placed between two salt plates and secured in the stand. Then the holder was placed in the machine and the IR started recording the wavelengths. Each catalyst trial was run through the machine and analyzed. The analysis of these graphs is in a following section.

3.4.4 Decoking Methodology

To analyze our solid product we wanted to determine how much of it was catalyst and how much was produced coke. To do this we used the quartz tube furnace. We measured out three to four grams of our solid product and placed in our canoe crucibles taking the mass. We then placed it in the tube furnace for 24 hours to let the coke blow off slowly while the catalyst stayed in the crucible. After the coke was removed we massed the crucible again to gain the weight of the just
the catalyst. This gave us the ability to find the percent catalyst and percents coke in the solid phase.

![Figure 5: Scale and Decoked Catalyst](image)

### 3.4.5 Carbon, Hydrogen, Oxygen, and Nitrogen Content Analysis

The oil phase product was sent to MidWest Micro Lab for Carbon, Hydrogen, Oxygen, and Nitrogen analysis. This analysis will help determine the amount of organics in the oil phase and the values will be used to determine the higher heating values and the energy recovery for each catalyst reaction. The amount of organics, especially carbon, in the oil phase is important because it is expected to increase the oil’s energy density.

### 3.4.6 TOC Analysis

For further analysis, the aqueous samples were sent out to the Civil Engineering Department for Total Organic Content. Total organic content (TOC) is the measurement of the overall organic matter content in a sample. This is an important analysis because it will help determine the amount of organics that shifted from the oil phase to the aqueous phase. Ideally, there will be very little organics in the aqueous phase compared to the oil phase.
4.0 Results and Discussion

4.1 Red Mud Catalyst Analysis

A sample of the red mud that was used in our experiments was sent out to the Civil and Environmental Engineering Department for TXRF analysis to determine the exact composition. These results would validate the decision to try individual metal oxide catalysts that make up red mud to evaluate the effect they have in the hydrothermal liquefaction process. The results of the analysis are shown in Table 3.

<table>
<thead>
<tr>
<th>Metal Oxide Component</th>
<th>Mass Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>63.7</td>
</tr>
<tr>
<td>Alumina</td>
<td>15.2</td>
</tr>
<tr>
<td>Iron (III) Oxide</td>
<td>7.9</td>
</tr>
<tr>
<td>Potassium Oxide</td>
<td>4.1</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Phosphorus Oxide</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3: metal oxide components in red mud

The large amount of silica in the red mud sample could have a large effect in the chemistry in the HTL reaction. Our selection of metal oxide catalyst was based on research we had done on red mud. Our research showed that the composition of red mud is can vary depending on the alumina refinery, the quality and nature of the bauxite ore, and the extraction conditions. The research showed that red mud contained less silica than the experimental analysis showed. The catalyst we focused on were chosen based on our research. Literature stated that they were the top three compounds in the red mud however, our sample only contained a total on 23.6% of alumina, iron (III) oxide, and calcium oxide. This discrepancy between the literature and our analysis could have a large effect on the results.
4.2 Mass Balance

For each hydrothermal liquefaction run the mass of the food slurry and catalyst were recorded before and the mass of each product was recorded after the reaction shown in Table x. The values before each reaction were consistent, as all trials used 100.00 g of food and 5±0.015 grams catalyst. Post reaction the values were different based on the catalyst used. The data shows that the red mud produced the highest amount of oil and the lowest amount of aqueous product. Iron oxide produced the most water phase product and the least oil and coke. When the solid product was decoked, we found that iron oxide and alumina both retained all of the catalyst, while red mud and calcium oxide lost 20-30% though the reaction. The loss of catalyst is consistent with the ICP-MS analysis performed on the aqueous phase.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Thermal</th>
<th>Red Mud</th>
<th>Calcium Oxide</th>
<th>Iron Oxide</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food</td>
<td>100.00</td>
<td>100.00</td>
<td>105.01</td>
<td>105.01</td>
<td>105.01</td>
</tr>
<tr>
<td>Catalyst</td>
<td>N/A</td>
<td>5.0138</td>
<td>4.9899</td>
<td>5.0039</td>
<td>5.0064</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>105.00</td>
<td>104.98</td>
<td>105.00</td>
<td>105.00</td>
</tr>
<tr>
<td>Food</td>
<td>78.5</td>
<td>76.0</td>
<td>79.5</td>
<td>85.5</td>
<td>77.0</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.08</td>
<td>4.34</td>
<td>3.77</td>
<td>5.09</td>
<td>5.23</td>
</tr>
<tr>
<td>Coke</td>
<td>2.92</td>
<td>3.15</td>
<td>5.72</td>
<td>2.90</td>
<td>2.76</td>
</tr>
<tr>
<td>Total</td>
<td>88.0</td>
<td>96.0</td>
<td>99.50</td>
<td>99.5</td>
<td>95.5</td>
</tr>
</tbody>
</table>

Table 4: Mass Balance before and after reaction

The amount of catalyst that leached into the aqueous phase was determined by ICP-MS analysis. Table 5 shows the weight percentages of aluminum, calcium, iron, and cerium that leached into the aqueous phase. Leaching can be problematic on extended use as the catalyst is losing quality with every use. The large amount of calcium that leached into the aqueous phase is consistent with the loss of catalyst after the HTL process. In a previous study, the ceria zirconia catalyst was studied and found approximately 0.2% Ce leached into the aqueous phase. These
results are similar to the leaching of the alumina and the aluminum in the red mud. The alumina recovered 5 grams of its original catalyst after the decoking. The low leaching percentages for the aluminum, iron, and cerium are positives for the catalysts, however when compared against each other the iron oxide is the superior catalyst. Minimal leaching into the aqueous phase shows that the catalyst is stable under HTL conditions. The iron oxide is a much less expensive catalyst compared to the cerium zirconia. Although the low leaching percentage of the ceria zirconia means that it could be reused multiple times, the low cost of the iron oxide means that reusability of the catalyst becomes less important.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Leached Al [wt%]</th>
<th>Leached Ca [wt%]</th>
<th>Leached Fe [wt%]</th>
<th>Leached Ce [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Oxide</td>
<td>0.0</td>
<td>0.0</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>0.0</td>
<td>13.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Red mud</td>
<td>0.3</td>
<td>23.1</td>
<td>3.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Alumina</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ceria Zirconia</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 5: Weight percent of each element leached into the aqueous product from the original catalyst

The oil yield, shown in Table 6 was calculated by divided the amount of oil produced by the weight of the food waste slurry without the weight of the water. We found a 14% increase in oil yield on average when using a catalyst. When comparing bio-oil yield from HTL reactions, using the CeZrO\(_x\) has a 54% oil yield, while using red mud catalyst has 73.4% and using alumina catalyst has 65.3% oil yield.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Oil Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>45.3</td>
</tr>
<tr>
<td>Red Mud</td>
<td>73.4</td>
</tr>
<tr>
<td>Ceria Zirconia</td>
<td>52.0</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>50.65</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>45.3</td>
</tr>
<tr>
<td>Alumina</td>
<td>65.3</td>
</tr>
</tbody>
</table>

Table 6: Oil Yields
4.3 Hydrothermal Liquefaction Product Results

The oil, liquid, and solid products were analyzed to determine the effectiveness of the catalyst. The oil samples were sent to a MidWest Micro Lab for CHON analysis. The majority of samples showed an increased carbon content in the oil phase. The amount of carbon in the oil is valuable as a precursor to transportation fuels. Improving the carbon yield of the oil phase is expected to increase the oil’s energy density. The alumina catalyst was the only one to have a decreased carbon content when compared to the original food waste. The CHON content of the original food waste slurry was determined by Mainstream Engineering. Table 8 shows the elemental content when using each catalyst.

Using the CHON analysis results, we were able to calculate the higher heating value and the energy recovery. Higher heating value (HHV) refers to the heat released from the combustion of a fuel with the original generated water in a condensed state. The HHV was calculated using Equation 1 from Demirbas (1997). The HHV and the energy recovery results are shown in Table 7.

\[
HHV [MJ/kg] = 33.5[C] + 142.3[H] - 15.4[O] - 14.5[N]
\]

Equation 1: Higher Heating Value Equation

Calculating energy recovery is a useful way of determining how effectively the energy in the feedstock is being converted into the oil phase product. One compares the oil yield and its HHV to the HHV of the feedstock using Equation 2.

\[
\left( \frac{HHV_{oil} \times Yield_{oil}}{HHV_{Feed}} \right) \times 100
\]

Equation 2: Energy Recovery
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C Content [%]</th>
<th>H Content [%]</th>
<th>O Content [%]</th>
<th>N Content [%]</th>
<th>HHV [MJ/kg]</th>
<th>Energy Recovery [%]</th>
<th>HTL Water TOC [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food waste slurry</td>
<td>58.3</td>
<td>10.3</td>
<td>29.3</td>
<td>2.0</td>
<td>24.6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Thermal</td>
<td>72.5</td>
<td>10.0</td>
<td>13.8</td>
<td>3.7</td>
<td>35.8</td>
<td>66.1</td>
<td>24300</td>
</tr>
<tr>
<td>Ceria Zirconia</td>
<td>67.8</td>
<td>9.2</td>
<td>19.1</td>
<td>4.0</td>
<td>32.3</td>
<td>68.2</td>
<td>19800</td>
</tr>
<tr>
<td>Red Mud</td>
<td>68.4</td>
<td>8.5</td>
<td>19.4</td>
<td>3.82</td>
<td>31.4</td>
<td>93.7</td>
<td>16700</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>72.0</td>
<td>9.4</td>
<td>14.3</td>
<td>4.4</td>
<td>34.6</td>
<td>63.8</td>
<td>19500</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>72.1</td>
<td>8.6</td>
<td>14.2</td>
<td>5.0</td>
<td>33.5</td>
<td>69.0</td>
<td>25300</td>
</tr>
<tr>
<td>Alumina</td>
<td>45.35</td>
<td>9.1</td>
<td>44.36</td>
<td>1.2</td>
<td>21.2</td>
<td>56.3</td>
<td>18900</td>
</tr>
</tbody>
</table>

Table 8: Product analysis results table showing CHON content in oil phase, Higher Heating Values, Energy Recovery, and Total Organic Carbon in the Water phase

The initial HHV of the food waste slurry was calculated by Mainstream Engineering to be 24.6 MJ/kg. The Hydrothermal Liquefaction process does increase the HHV, however when comparing the effect of a catalyst the higher heating values are about the same. The thermal run, that used no catalyst, is only slightly more than the trials that used a catalyst.

Despite having a lower HHV, red mud performed the best in terms of energy recovery, oil yield, and had the most carbon content in the oil phase. Iron oxide has the highest HHV overall, however, the bio oil yield is one of the lowest. Compared to the Ceria Zirconia catalyst, the cheaper metal oxide catalysts are worth using. The HHVs are about the same or in some cases (iron oxide and calcium oxide) better. When comparing bio-oil yield the ceria zirconia has a 54% yield, while the red mud has 73.3% and the Alumina has 65%. Calcium oxide and red mud were over all the best catalysts. They both had high bio oil yields and had the two highest energy recoveries when compared to the others.

Total Organic Content (TOC) is the amount of carbon found in an organic compound. The TOC was determined for the water phase shown in Table 8. Organics in the water phase are not ideal because they cause a decreased oil yield and the costs to treat the wastewater must be considered. Red mud has the lowest TOC in the water phase, while calcium oxide had the highest TOC.
Using the information from the product analysis, we were able to determine the amount of organics in each phase to compare to the original organic content. Figure 8 shows the product distribution of each phase after the reactions using different catalysts.

Figure 8: Mass fraction of Organics in each product phase for each catalyst

The oil phase in each catalyst produced the most organics when compared to the other phases. The red mud catalyst showed the most shift in organic products from the water phase to the oil phase. The red mud oil product contained 73.4% of the total organics. The ceria zirconia and the iron oxide catalyst had similar organic content to the uncatalyzed results. The ceria zirconia and the iron oxide oil product contained 45.33% and 52.0% of the total organic content, respectively. They showed a significant loss of organics and a much smaller organic content in the oil phase. The largest loss of organic content was the iron oxide catalysts with a 25.1% loss.

4.4 IR Analysis

The oil product was also analyzed via infrared spectroscopy (IR). Infrared spectroscopy measures and records the vibrations of atoms within the sample. With this data we are able to determine the functional groups in our samples. Our samples graphed very similar functional groups across the different catalysts. We discovered that our samples showed both stretching and
bending C-H vibrations, as well as alkyne, nitrile, alkenes, C=O groups. The spectrum also shows O-H groups on each graph which we assumed to be from residual water in our oil phase. These functional groups show that our oil includes considerable amounts of carbon, hydrogen, oxygen, and nitrogen. These four elements are essential in calculating higher heating value (HHV) of our oil.

The IR Spectroscopy of the red mud oil confirmed the results of the elemental content analysis. The graph showed that there was a large amount of carbon in the oil. The elemental analysis determine that the oil is made up of 68.4 percent carbon. The sharp peaks at 1750 cm⁻¹, 1450 cm⁻¹, and 1350 cm⁻¹ indicate carbon-oxygen double bond, carbon-carbon double bond, and carbon-oxygen bond, respectively.

![Infrared Spectroscopy of Red Mud Oil](image)

Figure 9: Infrared Spectroscopy of Red Mud Oil

4.5 GCMS Analysis

We also analyzed the aqueous product with the gas chromatography mass spectrometry, or GCMS. By using the combination of gas chromatography and mass spectrometry we were able to identify different chemicals in our aqueous sample. Our samples, like IR, regardless of catalyst
showed to have similar compounds. Most samples we tested showed a pentanone group at a retention time of 12, Glycerin at a retention time of 20, and a pyridinol group at both 27 and 29.5 retention time. This shows that our aqueous product containing carbon, hydrogen, and oxygen compounds. These compounds are high-energy compounds that we want to be in the oil phase. This leads us to believe there is untapped energy in the aqueous phase we want to look further into harnessing in the future.
5.0 Conclusion

The hydrothermal liquefaction (HTL) is a promising technology capable of converting food waste into an oil, aqueous, and solid phase. We found a 14% increase in oil yield on average when using a catalyst. The catalyst that performed the best overall was the red mud. The red mud produced the most amount of oil compared to the other catalysts, a 93.7% energy recovery and the lowest total organic content (TOC). The higher heating value of the red mud was on the lower side compared to the others however; its other positives outweigh the others.

In comparison with the ceria zirconia catalyst, the red mud and many component metal oxide catalysts are superior. The red mud had a similar HHV to the ceria zirconia, however in every other category it performed better. The higher oil yield in the red mud shows that the catalyst is more effective in shifting the organics to the oil phase. The successfulness of the catalysts coupled with the cheap price of it make it a better option than the ceria zirconia.

The oil product is valuable as a precursor to transportation fuels, however the loss of organics to the aqueous phase limits process economics. Organics in the aqueous phase are undesirable due to lower oil yields and costs associated with commercially wastewater treatment. Improving food waste HTL oil yields has been previously shown using a relatively expensive CeZrO\textsubscript{x} catalyst.

Catalyst recovery is an important aspect to consider when choosing an effective catalyst. The ceria zirconia catalyst has a very low leaching percentage however, the cost of the catalyst is much more than the metal oxide catalyst or the red mud. The alumina catalyst had the lowest leaching percentage proving it is stable under HTL conditions. The red mud lost 20-30% of its weigh during the HTL reaction, the loss was mostly caused by the leaching of calcium into the aqueous phase.

Our results from the constituent metal oxide runs showed success in certain analysis methods, but not in others. Concurrently, the red mud showed success across multiple methods of analysis. We think this may be as a result of the different metal oxide working together to promote the best results. For example, the alumina had a high oil yield, similar to that of the red mud, however, in the other categories it was not as successful. The high carbon content and HHV of both the iron oxide and calcium oxide catalyst on their own could contribute to the similar values.
in the red mud. To further investigate these results, we recommend that catalysts with varying weight percent of metal oxides are used.
6.0 Recommendations

For future studies into determining an effective catalyst for the conversion of food waste into biofuel, we recommend a continued investigation into the use of red mud. Our results showed that red mud was an effective catalyst. Our research has created an initial foundation for this catalyst but needs to be explored further to ensure the robustness of our findings. We recommend that future groups consider the gas phase when performing the organics content analysis. This could be done by weighing the reactor before the reaction and after the reaction before the pressure is released. Once the weight is determined, a gas would be chosen, mostly likely methane, that could be used to determine how much carbon is present in the gas. They could also capture gas, as the reactor is depressurized and send the gas to be analyzed.

Another recommendation for future work could be to test the durability and effectiveness of the catalyst by using it in repeated reactions. This would involve decoking the solid produce post reaction to recover the catalyst. One would test for reaction effectiveness over a period of reuses of the catalyst. Finding the reusability of the catalysts’ could help to determine the cost of the overall reaction or enable a possible Packed Bed Reactor in a scale up scenario.

We would also like to test the reaction settings to investigate the best possible situation to run the reaction. Investigating the heater ramp speed, the total reaction time, the cool down speed, and the possibility of adding process gases to the internal atmosphere would all help to optimize the process to reduce costs and improve yields. This would involve changing reaction heat up rate to ensure that no reaction occurs during the heat up period. We are also interesting reaction time. Our reactions all ran for a constant 1 hour, but we are interested to see if that is the optimal time for this process. Changing the reaction time could offer better oil yields or different oil compositions as well as improve process economics. The cooling speed, similar to the heating rate, can have effects on transient reactions, which could possibly affect oil yield and composition. The addition of process gases to the internal reactor atmosphere has been shown in literature to increase the heating value of oil recovered. Knowing this is should be investigated in the presence of the red mud catalyst. With enough research, the thermodynamic and mass transfer limitations of the system could be calculated and mathematical models can be generated. These models could help to guide future research into scale up.
Given the results from the red mud sample analysis, we recommend that future groups investigate silica as a potential catalyst. Our sample had a silica mass percent of 63.7% and this large amount could have had a substantial effect on the chemistry in the HTL reaction. Future groups should compare the silica results with the results from the red mud trials. The results from the analysis also showed that there was potassium oxide and phosphorus oxide in the sample. These compounds could also be investigated as potential catalysts.

Our research showed that the concentration of the compounds in red mud can vary depending on the alumina refinery, the quality and nature of the bauxite ore, and the extraction conditions. Because of this information, we recommend that future experiments vary on the concentration of the red mud compounds as potential catalysts. These models catalysts could be compared to the original red mud to see the effects a specific compound has on the HTL chemistry.
7.0 Works Cited


8.0 Appendix

8.1 IR Spectroscopy Graphs

Alumina Oil Phase IR

Uncatalyzed Oil Phase IR
Ceria Zirconia Oil Phase IR

Iron Oxide Oil Phase IR
Iron Oxide, Red Mud, and Calcined Red Mud Oil Phase IR comparison

Calcium Oxide Oil Phase IR
Red Mud Oil Phase IR
8.2 GCMS Graphs

Red Mud 1 Aqueous Phase

Red Mud 2 Aqueous Phase
Red Mud 3 Aqueous Phase

Uncatalyzed 1 Aqueous Phase
Uncatalyzed 2 Aqueous Phase

Uncatalyzed 3 Aqueous Phase
Iron oxide 2  Aqueous Phase

Iron oxide 1  Aqueous Phase
Iron oxide 3 Aqueous Phase

Ceria Zirconia 1 Aqueous Phase
Ceria Zirconia 2 Aqueous Phase

Ceria Zirconia 3 Aqueous Phase
Calcium Oxide 1 Aqueous Phase

Calcium Oxide 2 Aqueous Phase
Calcium Oxide 3 Aqueous Phase

Alumina 1 aqueous Phase
Alumina 2 Aqueous Phase