Catalytic Hydrothermal Liquefaction of Food Waste

A Major Qualifying Project

Submitted to the Faculty of

Worcester Polytechnic Institute

in partial fulfillment of the requirements

for the Degree in Bachelor of Science

in

Chemical Engineering

By:

Daniela Fraga

Carla Romo

Date: April 25, 2019

Project Advisor: Professor Michael Timko

Abstract

This project addresses two of today's major challenges: waste management and reduction of greenhouse gases (GHG). Food waste, that otherwise ends up in landfills contributing to methane production, can be converted into a biofuel, a fuel that emits less GHG, via the hydrothermal liquefaction process (HTL). The goal of our project was to investigate the effectiveness of nickel based catalytic hydrogenation for HTL. Results show that oxide catalysts improve bio-oil yield, high heating values, and energy recovery. Nickel based catalysts were more effective improving oil quality and reducing solids formation compared to non-nickel based catalysts; Ni/ZrO_2 was the best catalyst forming only 2 g of solids while producing a bio-oil with a HHV close to that of crude. Overall, catalytic hydrogenation is a promising technology for HTL and future studies on catalyst reusability and treatment of byproducts will be useful to determine if its economically feasible in a commercial scale.

Acknowledgments

Table of Contents

List of Figures

List of Tables

Introduction

In the United States over 90% of the fuels used for transportation are petroleum fossil fuels based [14]. The burning of fossil fuels represents approximately 76% of the human caused greenhouse gas emissions in the Unites States [11, 12]. The need to reduce greenhouse emissions along with the increasing depletion of fossil fuels, has pressed scientists to investigate different forms of renewable. Among these methods, a promising and widely investigated alternative is the conversion of biomass into biofuels. In 2017, biomass fuels provided 5% of the total energy use in the United States [11]. Currently a variety of different biochemical and thermochemical methods have been investigated to convert food waste into biomass. The most common methods are pyrolysis, gasification, and hydrothermal liquefaction. In all these methods, biomass is converted to liquid and gaseous products at high temperatures and pressures [32].

Among all these techniques, hydrothermal liquefaction (HTL) is a promising method since it requires a wet feedstock slurry eliminating the costly step of drying biomass. In HTL biomass is depolymerized at moderate temperatures (280 – 370°C), high pressures (10-25 MPa) during residence times ranging from 20-60 minutes; at these conditions, water remains in liquid state and acts both as a reactant and catalyst. The products of HTL are bio-oil with high heating value, and byproducts in the gaseous, solid and liquid phases [32]. To optimize conversion, catalysts are added into the reaction. In previous work, several homogenous catalysts in form of alkali salts have shown positive results in improving carbon yield. More widely used, however, are heterogeneous catalysts which not only improve carbon yield but also have the potential to improve process economics since they can be recovered and reused [22, 32].

Different biomasses have different components which generate bio-oil of different qualities. Biomasses that have been studied include swine manure, garbage, sawdust, beech wood, Spirunella algae, and microalgae [22]. A recent type of biomass that has been studied and shows promising results is food waste. In 2017 the United States Department of Energy estimated that 15.4 million tons of dry food waste and 61.20 million tons of wet food waste were generated; the United States Department of Agriculture (USDA) estimates that 30-40% of the food supply in the country ends up as food waste from which 92% ends up in landfills [9, 33]. As waste decomposes, it contributes to the greenhouse gases released into the atmosphere; thus, HTL is a suitable method to repurpose food waste.

In previous studies, both homogenous and heterogeneous catalysts have been studied in HTL of food waste. Homogenous catalysts such as Na_2CO_3 and heterogeneous catalyst such as CeZrOx, red mud, metal oxides, and hydroxyapatite have been tested. Results show that heterogeneous catalysts improve oil yield and oil high heating value (HHV) while reducing the organic content lost into the aqueous phase [2, 22]. Despite the promising results shown by these catalysts, there is still opportunity to improve the quantity and quality of the bio-oil while minimizing the formation of byproducts. Currently, the oil produced contains carbon, hydrogen, nitrogen and trace amounts of oxygen and sulfur. To improve oil quality, the bio-oil can be treated by subsequent hydro-treatment however, this will increase the operational costs [32].

Another alternative to improve oil quality is through catalytic hydrogenation were hydrogen gas is added as a reactant in presence of a metal supported catalysts such as nickel, palladium or platinum. The addition of hydrogen enhances reduction reactions such as saturation of carbonyl groups and carbon double bonds, and hydrodeoxygenation [4]. Through these reactions, bio-oil with higher carbon-hydrogen ratio and less nitrogen and oxygen can be

generated. A drawback to hydrogenation, is the higher cost of noble metal-based catalysts in comparison to the low budget catalysts previously investigated. Thus, a considerable improvement in bio-oil quality and/or quantity is required to justify the additional costs of hydrogenation.

The goal of this project is to investigate the effectiveness nickel based catalytic hydrogenation for hydrothermal liquefaction of food waste using nickel-based catalysts. We tested 3 oxide catalysts both nickel supported and non-nickel supported: $Ni/CeZrOx$, $CeZrOx$, $NiCeO_2$, CeO_2, $NiZrO_2$, and ZrO_2. After an analysis of the formed products, we were able to determine which catalysts was the most efficient by improving oil quantity and quality while reducing the formation of char. The results of this project will be compared to previous food waste studies by Worcester Polytechnic to understand the benefits of hydrogenation.

Background

This section provides an overview on biomass, current methods to produce biofuels, and previous studies of hydrothermal liquefaction.

Biomass

Biomass is any waste material from plants or animals and composed of organic matter mostly carbon, hydrogen, and nitrogen [12]. Although the composition of biomass varies widely its main components are carbohydrates, proteins, lipids and lignin [32]. Biomass is a rich energy source that can be used via direct to produce power or converted to fuels for transportation via several thermochemical and biochemical processes [12]. Biomass energy is a promising renewable energy source with the potential to reduce greenhouse emissions while also finding alternative uses for wastes that would otherwise end up in landfills.

Common types of biomass are wood, municipal waste, agricultural waste, animal manure, sewage waste, and forestry residues. The primary biomass sources for energy production are wood and cow manure that can be converted to biogas via anaerobic digestion. For biofuels generation, the most common sources are corn grain for ethanol and soybean oil for biodiesel. Over the last decades its popularity has stagnated primarily due to the high costs of biomass production, transportation, and storage [12]. Hence, cheaper, more accessible and abundant feedstocks, such as municipal solid waste, are a suitable solution to make bioenergy and biofuels production more economically feasible.

Municipal solid waste (MSW) is a broad term that includes all residential and industrial waste streams destined to incineration or landfills. MSW components suitable for biofuel production include paper, plastics, rubber and leather, textiles, food waste and yard trimmings. In 2015, approximately 262 million tons of MSW were generated. As seen in Figure 1, only 68 million tons (25.8%) were recycled and 33 million tons (12.8%) combusted for energy; the majority, 137 million tons (52.5%) ended up in landfills [14]. MSW in landfills contributes to the generation of greenhouse gases as it decomposes through anaerobic digestion. Figure 2 shows the MSW composition by materials; in 2015, the second largest material disposed were 39.6 million tons of food waste (15.1%). Due to the large amounts MSW generated annually and the low tipping fee, MSW and specifically food waste, is an attractive feed for bioenergy production [14].
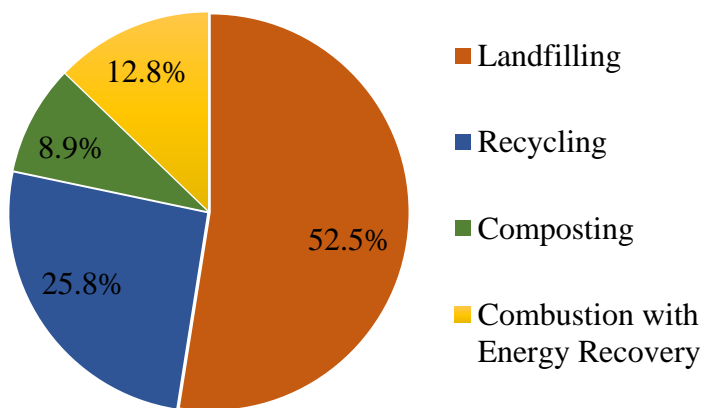
Figure 1. *Management of MSW in the United States in 2015. From the 262 million tons of MSW generated in 2015 over half of it, 137 million tons, ended up in landfills [14]. Waste in landfills is detrimental for the environment since it decomposes releasing greenhouse gases like methane.*
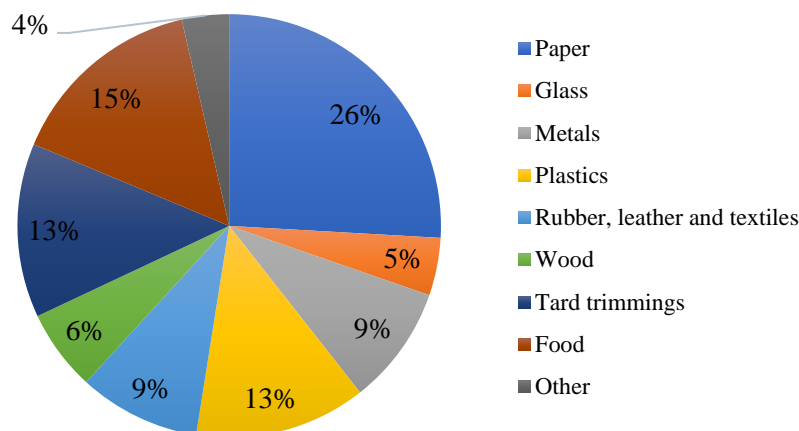
Figure 2. *Total MSW generated in the United States in 2015 classified by material. Out of the total of 262 million tons generated in 2015, the largest material was food waste which made up 39.6 million tons of waste [14]. Food waste has a high composition of organic material with the potential to be reused as a feedstocks to produce biofuel.*

Food Waste

Food waste encompasses plate waste, spoiled food, or peels and rinds that are considered to be inedible [14]. The Food and Agriculture Organization of the United Nations (FAO) estimated that a third of the food generated for human consumption ends up as waste; this represents 1.3 billion tons of food waste generated globally [15]. In the United States, in 2017, 15.4 million tons of food waste were generated from which 92% ended up in landfills; food waste has become the largest component of landfills in the United States [9, 10]. Once food waste is disposed in landfills, it decomposes through anaerobic digestion releasing greenhouse gases into the environment making landfills the third largest source of methane in the United States. Moreover, the energy, labor, time, land and water required to process, store, transport, and dispose food waste aside from representing a high economic cost, have a negative impact in the environment [33].

Over the past decades, efforts to reduce, recycle and repurpose food waste have been made to reduce the amount that ends up being disposed in landfills. The USDA and EPA support several programs to increase awareness about best practices to reduce food waste. Among these practices successful projects include donating food to shelters, initiatives to shop and store food wisely, and reducing overproduction of food [33]. Another suitable alternative, is repurposing food waste as feedstock for bioenergy production; due to the high organic content in food waste, it can be readily converted to biofuels or biogas through different thermochemical technologies. This in turn, will help reduce the environmental impact of landfills and reduce reliance on fossil fuels for energy production.

Methods of Conversion of Biomass

Biomass can be converted into liquid energy by using thermochemical methods such as gasification, pyrolysis, and liquefaction. The following section provides an overview of the most common methods used to convert food waste.

4

Gasification

Gasification is a process of converting organic compounds into a synthetic gas by using a limited amount of oxygen under high pressure and high temperature. This reaction takes place inside of a gasifier and produces mainly carbon monoxide, hydrogen, methane, and some light hydrocarbons [24]. A side product of this reaction is char, a combination of unreacted biomass, carbon, inerts, and ash. The mechanisms of gasification are oxidation, drying, pyrolysis, and reduction. During the oxidation step carbon compounds and water are formed, all the moisture is removed during the drying step, and at a temperature range of 250-700 ºC pyrolysis takes place and the heavy molecules decompose into lighter molecules that form a solid, liquid, and gas product. Finally, during the reduction step, the gas and the char react to produce the synthetic gas or "syngas" at a temperature range of 880-1100ºC. The gas produces can then be burned for heating or cooking or converted to electricity or mechanical work.

Pyrolysis

Pyrolysis is the process of decomposing organic compounds under high temperatures. It does not require oxygen unlike gasification and combustion and it forms three products: a non-condensable gas, a pyrolytic oil or bio-oil, and a solid residual or char [29]. This chemical reaction usually takes place around temperature values of 400 ºC to 1000 ºC, this amount of heat decomposes heavy hydrocarbons into lighter molecules. There are two types of pyrolysis, fast and slow pyrolysis. Fast pyrolysis operates as at a rate of 500 ºC per second and the main product is a bio-oil. Slow pyrolysis is used to produce bio-char, a powerful fertilizer [29]. It takes place around temperatures of 300 ºC and usually has long reaction times[28]. Pyrolysis is a very expensive process due to the equipment required to endure the high temperatures and it produces a low-quality biofuel that requires an upgrade.

Liquefaction

Liquefaction is the thermochemical conversion of biomass into liquid fuel. This process requires a catalyst to initiate the chemical reaction and it decomposes heavy molecules into lighter ones. Unlike pyrolysis, combustion, and gasification liquefaction does not require to dry the biomass for the reaction to take place. The operating temperature is around 250ºC to 330 ºC at a pressure range of 5 MPa to 20 MPa [6]. Many aspects of liquefaction are being studied to improve the oil yield by testing different catalyst, varying operating conditions, or adding side chemical reactions like hydrogenation.

Hydrothermal Liquefaction in Depth

Hydrothermal liquefaction is the thermochemical process of converting wet biomass into liquid fuel by breaking down heavy hydrocarbons under a high temperature and pressure in absence of oxygen. It usually requires a catalyst to enhance the reaction and increase the yield of the bio-oil. It produces four products: char, bio-oil, gas, and a water-soluble substance. The mechanisms of conversion of biomass via HTL are biomass depolymerization, cleavage of C-C bonds, dehydration, decarboxylation, deamination, and recombination of reactive fragments [34].

Process Conditions of HTL

Hydrothermal liquefaction, unlike other conversion methods, does not require a drying step. Instead, the water found in the biomass stays in a liquid state and becomes a supercritical fluid hence it consumes less energy. At this state, water can act as a reactant and a catalyst. For

water to become a supercritical fluid, as seen in the phase diagram in Figure 3, it is necessary to carry out the hydrothermal liquefaction process at the critical point of water which occurs at a temperature range of 280 ℃ to 370 ℃ and a pressure range of 10MPa to 25 MPa[32, 34]. At these operating conditions, the viscosity of water decreases, and water behaves as a nonpolar fluid that is highly soluble [22]. Water disassociates in H^+ and OH^- ions that combine with the components found in the biomass that decompose and undergo hydrolysis.
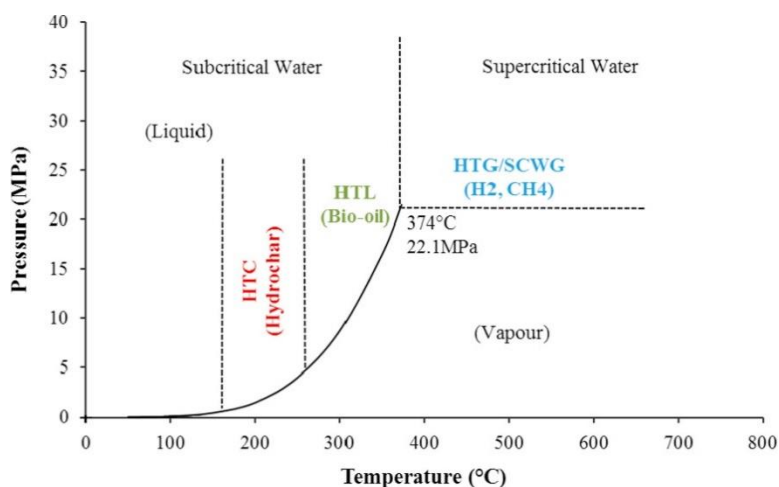
Figure 3. *Phase diagram of water and the classification of hydrothermal liquefaction [19]. Hydrothermal liquefaction must take place between 280 ℃ to 370 ℃ and 10MPa to 25 MPa. At these parameters, the water molecules from the wet biomass disassociate and dehydration takes place.*

The residence time of this process varies according to the used biomass, catalyst and operating conditions. It affects the biomass conversion, gas production, and residuals yield [8]. HTL reactions take place in a short period of time since the biomass does not have to be dried. The residence time can vary from 15 up to 60 minutes. Increasing the residence time can increase the yield of the bio-oil however an extended residence time can limit the bio-oil yield by turning the liquids into gases and forming a greater amount of char which is an undesirable product [8]. Additionally, the residence time is affected by temperature. At lower temperature, a longer residence time will be necessary to increase the biomass conversion while at a high temperature the residence time can vary [8].

In order to enhance the reactions, increase bio-oil yield, reduce char formation, and improve gasification efficiency, catalysts can be added to the reaction. Homogenous catalysts increase the bio-oil yield from 17% to 33.7% by accelerating the gas shift and suppressing the formation of char [32]. However, they corrode the equipment and they are hard to recover for further reuse [4]. Heterogeneous catalysts have recently been studied for HTL; since heterogeneous catalyst are metal based and are in the opposite phase of the biomass, they do not dissolve with the high temperature water. Heterogeneous catalyst like non-noble transition metal-based catalyst or metal oxides are useful to increase oil yield and improve its quality. Studies of

6

metal oxides like CeZrOx, can retain their crystal structure in supercritical water, maintain the oxidation state of active metal, and retain active metal in the surface area.

Chemistry of Hydrothermal Liquefaction

The exact chemical pathways of hydrothermal liquefaction are unknown although some mechanism may provide an insight of the possible reaction pathways [35]. Under high temperatures the long chain of hydrocarbons undergoes depolymerization which is the process of breaking a large compound into a monomer. The monomers then decompose, and the oxygen atoms react with the hydrogen atoms to form water. This known as dehydration. In a particular study, model compounds characteristic of food waste were reacted with CeZrOx to understand the exact chemical reactions that occur. The main chemical reactions found were aldol condensation, decarboxylation, ketonization and esterification.

Products Overview

Hydrothermal liquefaction produces four main products: a solid, bio-oil, water soluble substance and gas as seen in Figure 4. The solid, also known as char, is the product of unsaturated compounds that repolymerized due to the lack of hydrogen. It forms towards the end of the reaction when the higher temperatures have been reached. As the temperature and residence time increases so will the formation of char [8]. Char is an undesirable product of HTL since it reduces the yield of the bio-oil. The quantity of char produced depends of the type of biomass used and its lignin concentration hence, catalyst and optimization of operation conditions can be studied to minimize char formation [17]. The water-soluble solution forms during the dehydration step where the water is removed from the biomass. The non-polar compounds like glycerol stay in the water solution and do not convert into the bio-oil. A gas containing mostly carbon monoxide, carbon dioxide, and methane forms in the overhead of the reactor and its yield increases with temperature and residence time.

The bio-oil generated has a low oxygen and moisture content, yet it is very viscous, corrosive, and unstable. The characteristics of the bio-oil are dependent of the biomass used in the process. For example, Bamboo wood biomass produced a bio crude with a heating value range of 20.07 MJ/kg to 23.81 MJ/kg and rice stalk gave a heating value of 28.95 kJ/kg [8]. Hydrothermal liquefaction is known for producing a biocrude with a higher heating value than pyrolysis or combustion; however, in order to make the bio-crude a more suitable transportation fuel it is necessary to upgrade the product via hydrogenation, hydro-deoxygenation, and the use of a solvent to improve stability.
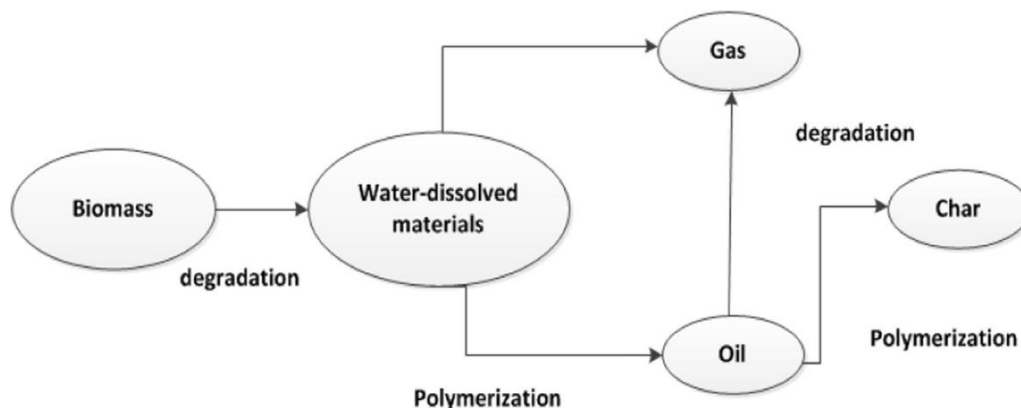
Figure 4. *Products od hydrothermal liquefaction: oil, water, solid, and gas.* *[19].*

Literature Review on Hydrothermal Liquefaction of Food Waste

The study of HTL of food waste has mostly focused on the use of different catalysts to improve bio-oil yield and quality. On study compared the effectiveness the homogenous catalyst Sodium Carbonate (Na_2CO_3), and the heterogonous catalyst Cerium Zirconia ($CeZrO_X$). Na_2CO_3 had been reported to improve carbon yield by suppressing coke formation; however, a drawback of homogenous catalysts is the costly steps to recover and reuse the catalyst. $CeZrO_X$ is a suitable catalyst due to the stability of metal oxides, ability to catalyze the desired reactions, and easiness to recover catalyst after reaction. The results demonstrated that $CeZrO_X$ improved oil yield by 59% when compared to non-catalytic HTL while Na_2CO_3 had no effect. Not only was the yield higher but the use of $CeZrO_X$ also resulted in oil with increased carbon content and high heating value (HHV). Moreover, $CeZrO_X$ was found to be a more cost-effective catalyst due its reusability of at least 25 times [22].

The high cost of $CeZrO_X$, has led to the investigation of cheaper catalysts with similar catalytic activity. A suitable substitute are metal oxide catalysts because they perform similar base chemistry to $CeZrO_X$, catalyze dehydration and decarboxylation reactions, are insoluble in water at supercritical water temperatures, and can be reused several times. Another study the effectiveness of red mud and its pure metal oxide components: Iron Oxide (Fe_2O_3), Calcium Oxide (CaO), and Alumina (Al_2O_3). Red mud is a waste product of the industrial production of alumina; due to its abundance, low price, and metal oxide-based composition it has been investigated as a catalyst [2].

The results of this study showed that red mud produced the highest yield of oil in comparison to the metal oxides, non-catalyzed HTL, and $CeZrO_X$. All catalysts increased the oil yield when compared to the non-catalytic HTL reaction. The highest yield was of 73.4% when using red mud followed by 65.3% when using alumina. Despite the highest yield, red mud bio-oil had a lower HHV than $CeZrO_X$. Another limitation of red mud was that 20-30% of the catalyst was lost through the reaction limiting its reusability. However, due to red mud's overall higher yield and energy recovery it was determined to be the best catalyst in the study followed by alumina [2].

A more recent catalyst under study is hydroxyapatite. Hydroxyapatite is a mineral commonly found in bones. It can be widely used as a catalyst due to its strong adsorption ability, surface acidity or basicity and ion-exchange ability [27]. Current work with hydroxyapatite has shown a slight increase in oil yield and quality in comparison to red mud and $CeZrO_X$.

Hydrothermal Hydrogenation Liquefaction

A modification to HTL to improve oil quality is adding hydrogen gas as a reactant. The excess of hydrogen will enhance hydrogenation and hydrodeoxygenation reactions to saturate hydrocarbons and yield bio-oil of a higher quality. To catalyze these reactions, a metal-based catalyst, such as nickel, palladium, or platinum is needed.

Hydrogenation

Hydrogenation is a chemical reaction that saturates carbon chains by adding hydrogen atoms. In the industry, hydrogenation is used to solidify liquid oils or increase the heating value. Hydrogenation takes place in several steps [16]. First, the sigma bond of the H_2 molecule breaks and it is absorbed to the surface of the catalyst forming a metal-hydrogen bond. The pi bond of the carbon compound also breaks and attaches to the surface of the catalyst. The weak bond formed between the hydrogen and metal catalyst breaks and the hydrogen atoms then transfer to the carbon compounds forming carbon-hydrogen bonds. After two hydrogen bonds have attached to the carbon compound, it forms a saturated product [20, 26].

Hydrogenation is a thermodynamically favorable reaction however it is necessary to add a catalyst for the reaction to take place if not it will be required an extremely high temperature. Heterogenous catalyst, like insoluble metals, are most commonly used at the industrial level for the process of hydrogenation. Highly reactive catalyst includes platinum, palladium, rhodium, and ruthenium however they are very expensive. Hence, the usage of nickel-based catalyst has popularized in the industry due to its low cost and ability to absorb hydrogen [31].

Hydrodeoxygenation

Hydrodeoxygenation is a chemical process that removes oxygen atoms in the form of water. It requires the presence of hydrogen to take place since it is a hydrogenolysis process. Hydrogenolysis is a chemical reaction that breaks a carbon-carbon bond, removes an oxygen, nitrogen, or sulfur atom and attaches a hydrogen atom to the cleavage bond. Hydrodeoxygenation is mainly used in the upgrade of bio-oil since a high oxygen content reduces the heating value of the fuel [1].

Experimental

The following section outlines the preparation of reactants, reaction, and product retrieval and analysis for the conversion of food waste to biofuels via HTL.

Feedstock Preparation

For all experiments, we used a feedstock made of common food items including dairy products, vegetables, fruit, meat, and carbohydrates. To prepare the feedstock, food was blended with deionized water (DI water) to create a slurry that consisted of 15 wt.% solids. The amount of each food item added was calculated based on their moisture content to achieve 85% water content. 100 grams of slurry were used for every run and the slurry was stored in a jar and refrigerated in between runs. The food items used and their respective moisture content are described in Table 1.

Table 1: Moisture content of the food items used to prepare food slurry. DI water was added to the food mixture to create a slurry with 15wt.% content.

Food Item	Moisture Content [%]
American Cheese	0.00
Canned Chicken	64.9
Instant Potatoes	0.00
Green Beans	93.52
White Rice	0.00
Apple Sauce	88.24
Butter	0.00

Catalysts

In this project we used 3 different oxide catalysts: cerium zirconium oxide (CeZrOx), zirconia oxide (ZrO_2), and Cerium Oxide (CeO_2). All these catalysts were tested by themselves and loaded in nickel. The preparation procedures are outlined below.

Non-Ni Loaded Catalyst Preparation

CeZrOx nanopowder of 99% purity was purchased from Sigma Aldrich. The ZrO_2 and CeO_2 catalysts were prepared by the method of calcination of nitrates for 3 hours at 500°C in an air flow of 50 mL/min and a heating and cooling ramp rate of 5°C/min.

Ni-Loaded Catalyst Preparation

The nickel based catalysts were prepared via incipient wetness impregnation following Liao et.al procedure. 15 grams of the oxide catalyst was wetted with the corresponding volume of $Ni(NO_3)_2$. $6H_2O$ solution to obtain a theoretical 10% nickel loading. The precursor was dried overnight at a temperature of 120°C and then calcined at 500°C for 3 hours. The product was NiO/oxide which was then reduced at 350°C for 3 hours at a hydrogen flow of 15 mL/min to produce the Ni(10wt%) [21].

Catalyst Characterization

The nickel loaded catalysts were characterized using X-ray diffraction (XRD). A Rigaku automatic instrument with the Bragg-Bretano theta-theta configuration was used to obtain

diffraction patters of non-Ni loaded catalysts and Ni-loaded catalysts after reduction. XRD patterns were obtained with a Cu K(alpha) radiation at 27.5 kV and 25 mA. The scans were taken over the range of 2θ angles from 6° to 80° at a speed of 0.02°/s. These scans allowed us to verify the calcined catalysts was completely reduced. All scans for the catalysts used can be found in Figures 5-7.
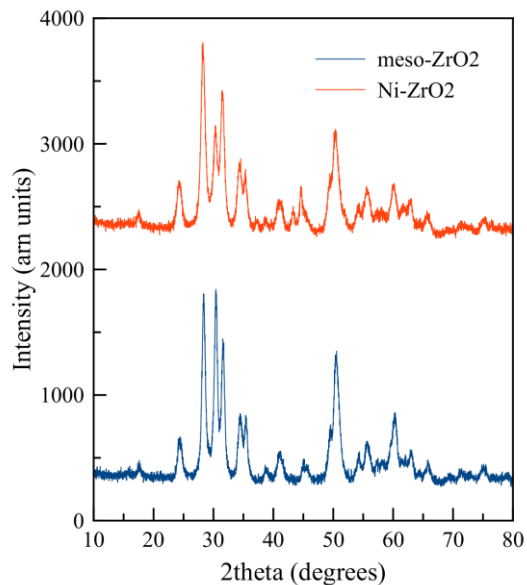
Figure 5. *XRD pattern for Ni/ZrO2. The prepared catalyst, orange line, is compared to meso-ZrO2, blue line, to verify the catalyst was completely reduced.*
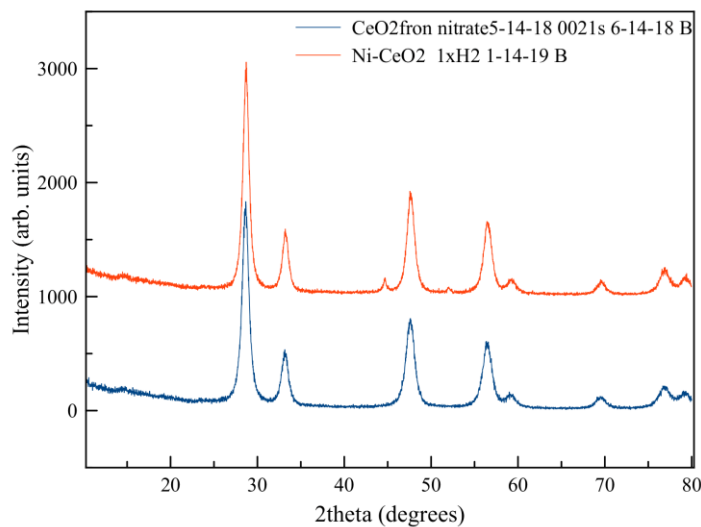
Figure 6. *XRD scan for Ni/CeO2. The prepared catalyst, orange line, is compared to CeO2, blue line, to verify the catalyst was completely reduced.*
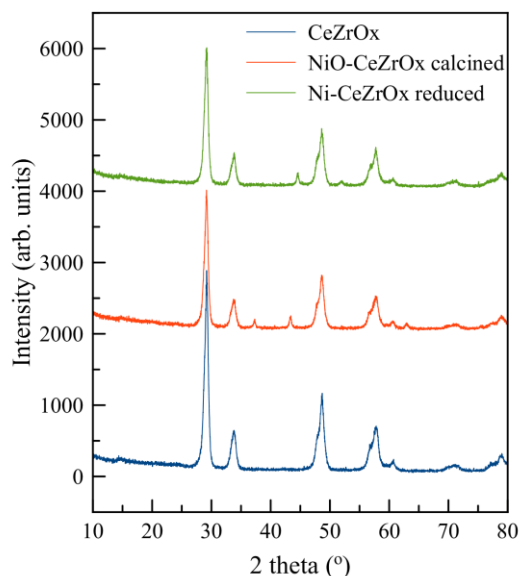
Figure 7. *XRD scan for CeZrOx. The prepared catalyst, green line, is compared to CeZrOx, blue line, and NiO- CeZrOx, orange line, to verify the catalyst was completely reduced.*

Food Waste Hydrothermal Liquefaction

HTL was carried out in a 300 mL Parr Instrument stainless steel bench-top reactor (see Figure 8) rated at a temperature of 350 ℃ and a pressure of 20.6 MPa. An external heating jacked was used to heat the reaction and the temperature was controlled using a Proportional-Integral-Derivative (PID) controller. The reactor was equipped with a thermocouple and a gas entrainment impeller. The temperature of the reaction was read from the PID's display as well as the speed of the impeller. A water circulator was used to regulate the temperature of the reactor and prevent it from overheating. The pressure gauge located at the reactor's head was utilized to monitor the pressure inside the reactor and a pressurization valve allowed for the insertion and removal of gases.

The experiments were carried out by adding 100 g of food slurry with either 5.0 g of the non-nickel loaded catalyst or 5.5 g of a nickel-loaded catalyst to the previously weighted bottom of the reactor. The reactor was properly sealed, massed, and purged three times with 1100 psi of nitrogen gas. For the hydrogenated runs the reactor was pressurized with 300 psi of hydrogen and for the non-hydrogen runs the reactor was pressurized with 1100 psi of nitrogen. The reaction was then heated for approximately 1 hour until it reached 300 ℃ and then this temperature was maintained for 1 hour. At the end of the reaction period, an ice water bath was used to cool down the reactor to approximately 35- 40 ℃. The pressure was recorded, and the overhead gas was collected in a gas bag for later analysis. The reactor is depressurized and weighted. The initial and the final weight of the reactor were compared to track for any loses. Finally, the products were extracted by different methods.
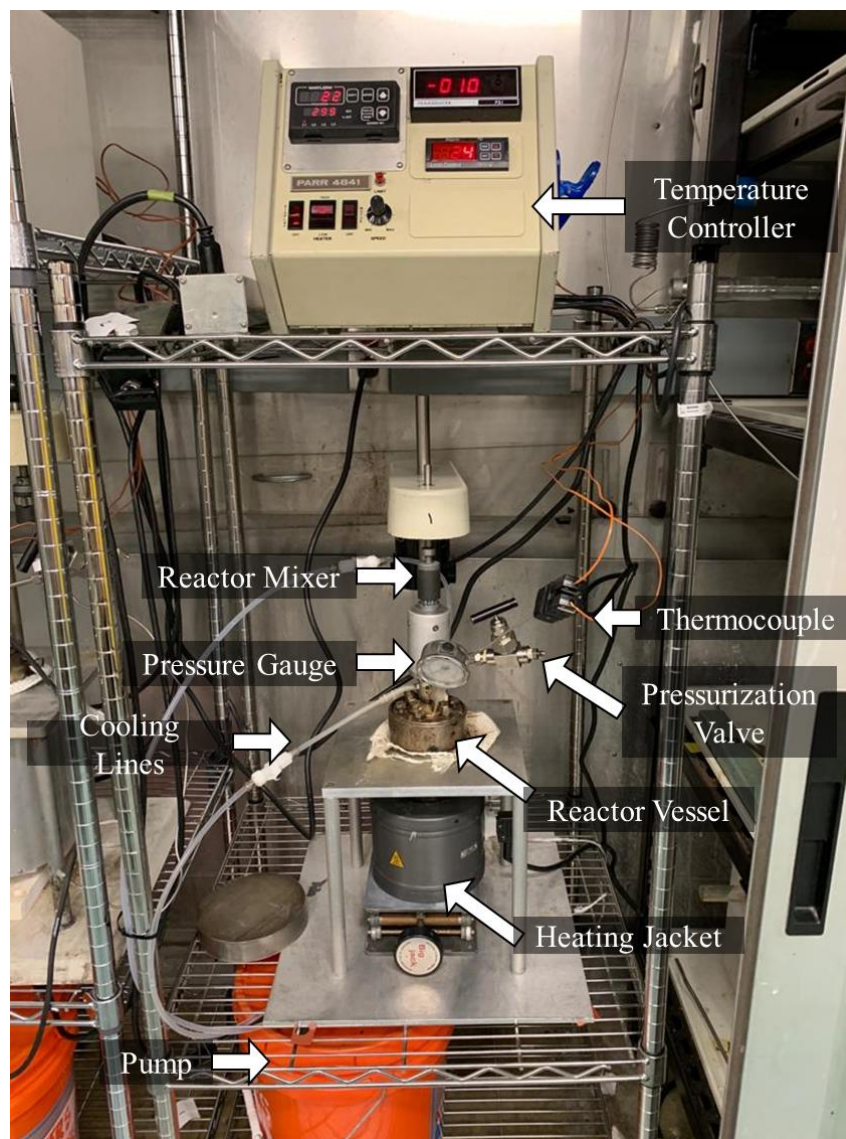
Figure 8. *Reactor set up: a PID controller was used to adjust the temperature and the speed of the reactor mixer; the pressure was read from a pressure gauge found at the top of the reactor; the reactor was pressurized or depressurized through the pressurization valve; a heating jacket heated the reactor and a cooling line was installed as a safety precaution against overheating.*

Product Retrieval and Analysis

This section describes the techniques used to sperate products and the tests carried to analyze each product, see Figure 11. The gas, solids, water and oil were retrieved once the reaction was over. A description of the retrieval methods will be outlined below.

Extraction of the Gas

A gas bag was purged three times with helium gas. Once the reaction had ended and the reactor was cooled to approximately, the overhead gas was retrieved by attaching the gas bag to the pressurization valve as seen in Figure 9.
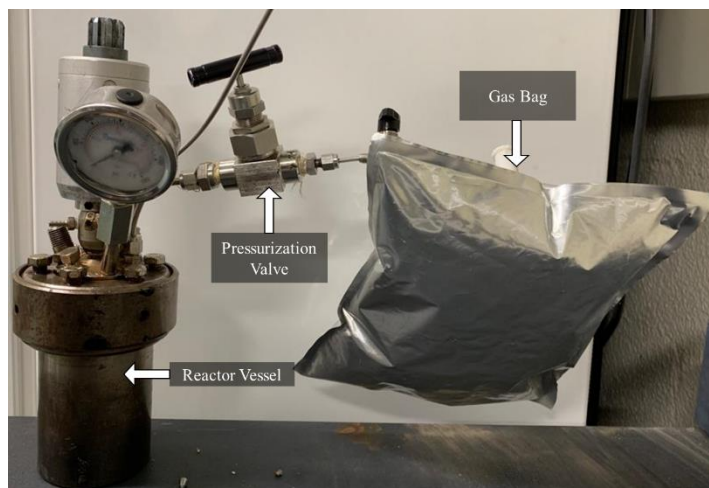
Figure 9. *The gas produced was extracted from the reactor vessel after the reaction has taken place and the reactor was cooled to 40°C. A gas bag was attached to the pressurization valve and it was slowly opened to let the gas be collected in the bag.*

Extraction of the Water Phase, Solid, and Bio-oil

The reactor was depressurized and massed to take into account for losses. The contents of the reactor were poured into a previously massed ceramic funnel containing a Whatman 125 milimteres filter paper. The solid and bio-oil were separated from the aqueous phase via vacuum filtration. The Erlenmeyer flaks containing the aqueous phase were massed and a sample was saved into a 10 mL vial for later analysis. The contents remaining in the filter paper were washed with acetone until a light brown color was observed (approximately 1 L of acetone) to separate the bio-oil from the solid. The ceramic funnel containing the solid was weighted and a sample of the solid was saved in a 5 mL vial for later analysis. The acetone was distilled from the bio-oil using a rotary evaporator maintained at a temperature range of 45-60ºC (see Figure 10). Once all the acetone was removed, the evaporating flask was weighted to determine the yield of the bio-oil. The bio-oil was retrieved from the flask and saved for later testing.
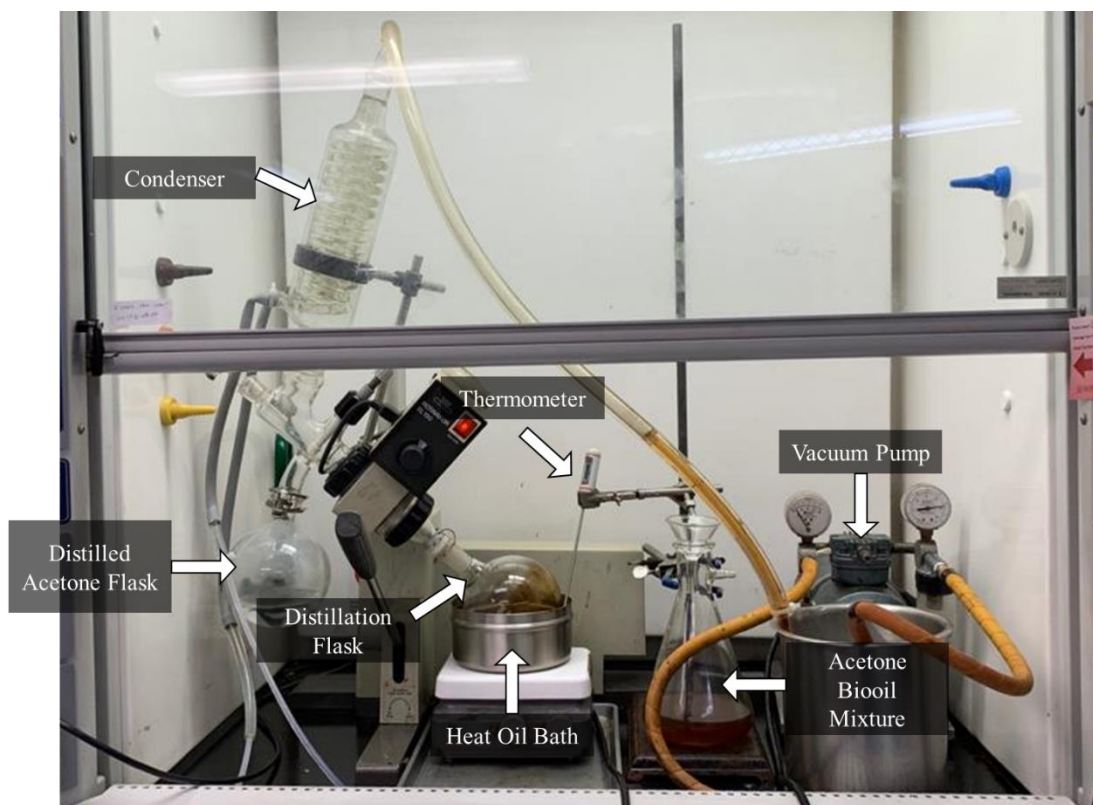
Figure 10. *The solid and oil products were separated from the water phase via vacuum filtration. The oil was washed off the solids using 1 L of acetone. The acetone was separated from the bio-oil via distillation using a rotary evaporator.*

Bio-oil Analytical Analysis

The bio-oil from each run was analyzed for their elemental composition and high heating values (HHV).

Elemental Analysis

A small sample of approximately 0.20g of bio-oil was sent to MidWest MicroLab for an organics (CHON) elemental analysis. This analysis was useful to determine the oil composition, theoretical HHV, and energy recovery for each catalyst.

Higher Heating Values

To quantify the energy density of the oil, we analyzed each sample's HHV. HHV is a measurement of the amount of heat is released when a unit quantity of fuel is completely combusted. Theoretically, we calculated the HHV using Demirbas equation that is "derived from the oxidation heats of C and H and the reduction heat of O assuming that the effect of the N content of a biomass fuel on its HHV was negative" [7]. The equation used was the following:

$$HHV = \{33.5[C] + 142.3[H] - 15.4[O] - 14.5[N]\} \times 10^{-2}$$

To obtain the actual HHV of each fuel, we sent a 0.25g sample of each bio-oil to MidWest MicroLab. The HHV values of the oil were obtained with a semimicro calorimeter. A food waste sampled that was dried overnight was also sent for HHV analysis.

The HHV values were useful to understand the energy recovery meaning how much of the energy in the feedstock is recovered in the oil phase. To calculate the energy recovery we used the following equation:

$$\text{Energy recovery} = \frac{(\text{HHV}_{oil} \times \text{Yield}_{oil})}{\text{HHV}_{feed}} \times 100$$

Solid Analytical Analysis
The bio-oil from each run was send for an elemental analysis to quantify the elements in the char.

Elemental Analysis

Samples of 0.5g of the solids were sent to MidWest MicroLab for an organics (CHON) elemental analysis. The analysis of the solid was useful to determine the composition of the solid and the amount of carbon atoms that repolymerized and turned into char (undesirable product). The catalyst was not removed from the solid before being sent for testing. To determine the amount of char and catalyst in the solids we followed a decoking method. We used a quartz tube furnace to blow the coke off slowly over a period of 24 hours from a known mass of the solid sample. During this time period the coke is combusted and the solid that remained consisted of catalyst only.

Liquid Analytical Analysis
For analysis of organic content, the liquid samples were sent to the Civil Engineering Department for TOC analysis. This analysis helped us understand the organic composition of the aqueous phase to better understand the carbon distribution of the products. The aqueous phase was diluted to 4 ppm of TOC assuming the aqueous phase initially had 500,000 ppm of TOC. For the dilutions, DI water was used and 0.5 uL/mL of solution of 12M HCl were added to the dilutions to adjust the pH.

Gas Analytical Analysis
The gas samples were tested in GC-2014 Shimazu Gas Chromatography instrument running helium as the carrier gas. The samples were injected to a VICI actuator valve into a 102 µL sample loop. The method utilized to test the samples had an initial temperature of 30 ℃. The temperature was increased at 5℃/min until it reached 90℃ and was held for 20 minutes. Once again, the temperature was ramped at a rate of 5 ℃/min until it reached 130 ℃ and immediately after it was ramped at 10℃/min until it reached 150℃. The run was finalized by holding temperature of 150 ℃ for 40 minutes. The area of the peaks produced by the test were compared to previously known calibrations to identify the compounds formed in the gas phase.

Prepare catalyst and food slurry.

Add 100 g of food slurry and 5.5 g nickel-loaded catalyst or 5.0g of non-nickel loaded catalyst to the reactor.

Purge reactor three times with 1100 psi of N_2 gas.

Load the reactor with 300 psi of H_2 gas and heat up to 300 ° C.

Leave the reactor for 1hr at 300 ° C.

Cool down and depressurized the reactor, collect gas.

Use vacuum filtration to remove aqueous phase from solid and oils.

Aqueous Phase

Solids and Biooil

TOC Analysis

Acetone wash to remove biooil from solid.

Solid Phase

Biooil and Acetone Mixture

Organic elemental analysis sent to MidWest MicroLab.

Distill acetone using rotary evaporator

Collect biooil

Organics elemental and HHV analysis.

Figure 11. *Overview of experimental procedure; a 100 g of food slurry was reacted with 5.0 g of non-nickel loaded catalyst or 5.5 g of nickel loaded catalyst. The reactor vessel was pressurized with 300 psi of H_2 and heated to 300°C. After 1 hour, the reactor was cooled down and the products were extracted. Each product was analyzed respectively.*

Results

We first carried out uncatalyzed runs/ thermal runs as a control for our experiments. We did two types of thermal runs one without hydrogen hereafter referred as Thermal (N) and one with hydrogen hereafter referred as Thermal (H). For the nickel loaded catalysts we completed two runs per catalyst; for the non-nickel loaded catalysts we completed three runs per catalysts; all these runs were hydrogenated. The rest of this section will present and discuss the results of these project. The product distribution for each run can be found in Appendices B and C.

Product Distribution

This section presents two types of product distribution: a mass balance which takes into account the mass produced of each product and a carbon balance that quantifies how carbon is distributed among products.

Mass Yields

For each run, we assumed that we recovered all the catalysts, either 5 g or 5.5 g. We then assumed that the 100g of slurry were converted into products; in all the runs we could not close the mass balance exactly at 100 g and this mass difference we considered losses. We kept track of the reactor losses, the product we were unable to manually remove from the bottom of the reactor and impeller, by weighing the reactor before and after extracting the products; we assumed that 10% of the reactor losses were oil and 90% were solids. Table 2 summarizes the average weigh distribution of the products for all the runs we completed.

Table 2: Average mass distribution of products for each catalyst used.

	Thermal (N) [g]	Thermal (H) [g]	Ni/CeZrOx [g]	Ni/ZrO$_2$ [g]	Ni/CeO$_2$ [g]	CeZrOx [g]	ZrO$_2$ [g]	CeO$_2$ [g]
Oil	2.47 ± 0.56	3.18 ± 0.42	2.95 ± 0.5	3.41 ± 0.11	3.19 ± 0.02	3.10 ± 0.21	2.75 ± 0.11	2.75 ± 0.06
Water	83.99 ± 5.00	80.49 ± 1.79	87.34 ± 0.05	87.83 ± 0.83	86.10 ± 3.73	81.82 ± 1.80	84.00 ± 2.52	84.69 ± 0.64
Solid	4.45 ± 1.94	5.64 ± 0.14	2.05 ± 0.05	1.60 ± 0.06	3.26 ± 0.13	4.47 ± 0.60	5.09 ± 0.37	5.28 ± 0.36
Gas	3.00 ± 0.50	2.50 ± 0.50	2.50 ± 0.5	2.50 ± 0.00	1.25 ± 0.50	3.50 ± 0.50	2.83 ± 0.29	2.17 ± 0.58
Losses	6.10 ± 2.72	8.19 ± 2.04	5.16 ± 0.05	4.67 ± 0.54	6.20 ± 3.88	7.11 ± 1.89	5.33 ± 2.62	5.12 ± 1.08

The product we want to produce is the bio-oil; water, solids, and gases are considered undesirable side products that need further treatment to be disposed. However, the least desirable product are the solids. Water can be treated and discharged or reused within the process and the gases can be treated until they are safe for discharge. The catalyst and solids are mixed and in order to recover the catalysts the char needs to be incinerated; in an industrial scale this is a very energy intensive process which is why we want to produce the least amount of solids.

As seen in Table 2, hydrogenation increased oil yields; nickel loaded catalysts decreased solids formations while increasing water yields; non-nickel loaded catalysts decreased the amount of water and oil formed while increasing the amount of solids. An ideal catalyst increases oil yield and decreases solid, water, and gas yield. From the results obtained, the catalyst that exhibited a consistent high oil yield and the lowest solid yield was Ni/ZrO_2 however it produced the largest amount of the water product compared to other catalysts. Without nickel, ZrO_2 produced a lower oil yield and increased almost four times the solid product. The greatest quantity of solid product was produced by the uncatalyzed hydrogenated runs (Thermal H) which also had the lowest amount of the water product. This can potentially suggest that most carbons repolymerized towards the end of the reaction and converted into char instead of forming hydrocarbons that increase the oil yield. The thermal non-hydrogenated run (Thermal N) produced the lowest oil demonstrating that the addition of hydrogen is useful to enhance formation of bio-oil. The amount of gases produced varied within in runs; overall Ni/CeO_2 yielded the least amount of gas. Overall, the most suitable catalyst tested was Ni/ZrO_2 since it produced the highest oil yield, 3.41 g, while reducing the formation of solids to 1.60g.

Oil Yields
The oil yields were calculated by determining the organic composition (12.6%) and the water content (87.4%) of the food slurry. The oil yield is the ratio of oil produced by the reaction to the organic content in 100g grams of food slurry. As seen in Table 3, hydrogenated runs using Ni/ZrO_2 as the catalyst resulted in the highest oil yield (27.0%) while the non-hydrogenated and non-catalyzed run produced the lowest oil yield (19.6%). Furthermore, the oil yields of all the hydrogenated experimental runs produced a higher quantity of oil compared to the non-hydrogenated runs. Thus, suggesting that hydrogenation in enhances oil production.

Table 3 also compares the oil yield improvements by the addition of hydrogenation and catalysts. Oil yield improvement by hydrogenation is defined as the ratio of HTL bio-oil yield obtained by using a catalyst and hydrogenation to HTL bio-oil yield obtained in uncatalyzed and non-hydrogenated runs; oil yield improvement by catalysis is defined as HTL biooil yield obtained by using a catalyst and hydrogenation to HTL biooil yield obtained only by hydrogenation. Hydrogenation itself improved the oil yield by 29% , furthermore the addition of a catalyst such as Ni/ZrO_2 improved the oil yield by a higher percentage of 38%. On the other hand, some catalysts such as CeO_2 and ZrO_2, decreased the oil yield by 13-14% when compared to the hydrogenated non-catalytic runs (Thermal H). Hydrogenation and nickel bases catalysts are shown to considerably improve oil yields.

Table 3: Average oil yields, oil yields improvements by hydrogenation and oil yield improvements by catalyst for all the runs conducted in this study.

Catalyst	Oil Yield [%]	Oil Yield Improvement by Hydrogenation $\frac{Yield_{hydro\ with\ cat}}{Yield_{Thermal\ N}}$	Oil Yield Improvement by Catalysis $\frac{Yield_{hydro\ with\ cat}}{Yield_{Thermal\ H}}$
Thermal (N)	19.6	1.00	0.78
Thermal (H)	25.2	1.29	1.00
Ni/CeZrOx	23.4	1.20	0.93
Ni/ZrO$_2$	27.0	1.38	1.07
Ni/CeO$_2$	25.4	1.30	1.01
CeZrOx	24.6	1.26	0.97
ZrO$_2$	21.8	1.11	0.86
CeO$_2$	21.8	1.12	0.87

Carbon Balance

To complete a carbon balance, we first quantified the initial carbon available. Table 4 shows the elemental (CHON) composition of the dried food slurry; with these results we estimated that our food waste contained 7.08 g of carbon. We assumed that all of this carbon was distributed among the products to then estimated the carbon content in the bio-oil, gas, liquid and char. Figure 12 shows the average carbon distribution for all the product phases. We assumed that 10% of the carbon that was lost in the reactor, because it couldn't be manually removed, was oil and 90% was solids. This graph is normalized, ignoring losses that would close that mass balance at 1, since we are certain most carbon is lost while distilling acetone from the oil; the unnormalized graph and be found in Appendix B.
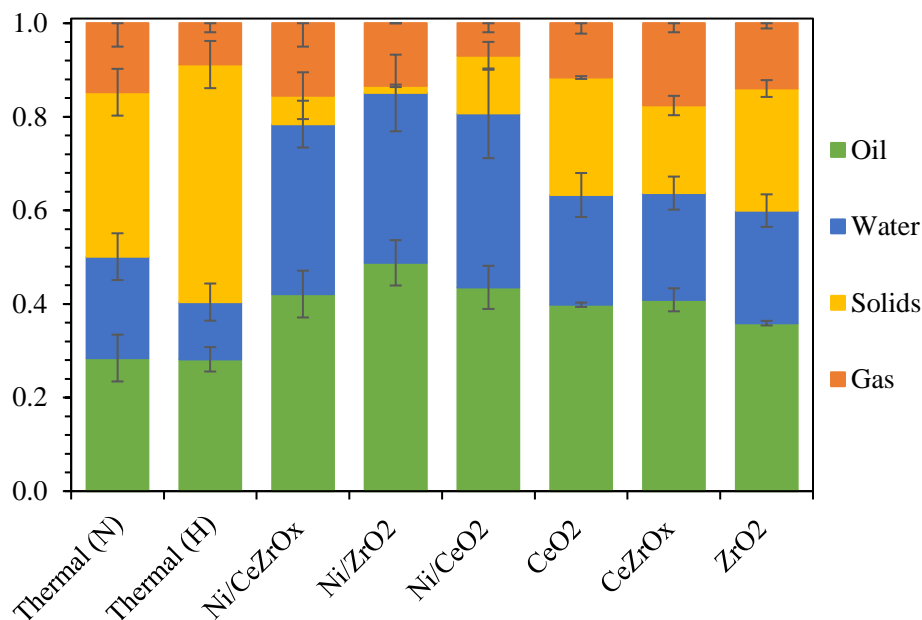
Figure 12. *Normalized average carbon distribution for thermal runs and each catalyzed run. Hydrogenated catalyzed runs considerably increase the amount of carbon in the oil; nickel-based catalysts reduce the formation carbon in the solids phase while non-nickel catalysts decrease carbon distributed in the water phase. The most efficient catalyst was Ni/ZrO_2 where 50% of the carbon was in the oil and only 2% in the solids.*

In both thermal runs with and without hydrogen the oil had 28% of the carbon. The water phase in the thermal (H) runs has less carbon than in the thermal (N) runs, 12% vs 21%, at the cost of increasing the carbon content of the solids, 51% vs 35%. Overall, all catalysts increase the carbon content of the oil while reducing the formation of solids; the carbon content in the water and gas varies per catalysts. The oils produced using the nickel loaded catalysts have the highest carbon content ranging from 42% - 49%. Nickel loaded catalysts can also considerably reduce the carbon content in solids to ranges as low as 2% - 12%. The oils produced using non-nickel loaded catalysts have higher carbon content than thermal runs ranging between 36% – 41%. With these catalysts, the carbon in the solids was reduced in comparison to thermal runs but not in comparison to the nickel runs. The most efficient catalysts is Ni/ZrO_2; the oil for this catalysts contained 49% carbon while the solids only had 2% carbon. Compared to runs using non-nickel loaded catalysts and thermal runs the carbon in water was higher, 36%. To reduce operating costs in an industrial scale reusing the catalyst is crucial; to do so, the organic portion of the solids needs to be removed by combusting the organics. Hence the less char that is formed the less energy required to recover the catalyst. On the other hand, the water could potentially be reused by mixing it with the food waste slurry. Since there is a larger economic benefit in reducing the formation of solids nickel loaded catalysts, especially Ni/ZrO_2, are efficient for HTL.

Bio-oil Analysis

Besides looking into the oil mass and carbon yield, we also analyzed the quality of the oil. Table 4 summarizes the dried elemental composition, HHV and energy recovery for each catalyst that was used. Compared to the initial food waste, all HTL runs had an increase in carbon content in the oil phase. Between both thermal runs and the catalyzed runs, there is no considerable increase in the in either carbon content, which ranges between 62.9% – 72.9%, or hydrogen content, which ranges between 7.8% - 9.3%.

The HHV of the oil was found to be 24.60 MJ/kg; all bio-oils from both catalyzed and uncatalyzed runs had a higher HHV than the original food waste. Comparing the non-hydrogenated thermal run and hydrogenated thermal run the HHV with hydrogenation is 11% higher suggesting the addition of hydrogen plays a crucial role on oil energetics. All catalyzed runs yielded oils with higher HHV and energy recoveries than the non-hydrogenated thermal run; all catalyzed runs, besides Ni/CeO_2, had higher HHV than the hydrogenated thermal run but the energy recovery was not always higher. Ni/ZrO_2 and ZrO_2 had the highest HHV and energy recovery these being 39.3 MJ/kg and 40.3 MJ/kg respectively and 35.5% and 30.7% respectively. Crude has a HHV ranging between 40 – 46 MJ/kg and zirconia catalysts can efficiently yield bio-oil that approximates crude's energy.

Table 4: Dried food waste, catalyzed and uncatalyzed bio-oil elemental composition, high heating value and energy recovery. Elemental analysis of oil carried out on a dry basis. Nickel based catalysts considerably increase oil' HHV and energy recovery.

	C [%]	H [%]	N [%]	O [%]	HHV (MJ/kg)	Energy Recovery (%)
Food Waste	47.2	6.7	4.6	41.5	24.60	N/A
Thermal (N)	70.0	8.4	3.8	17.9	32.4	21.5
Thermal (H)	68.8	9.0	4.3	18.0	36.1	30.7
Ni/CeZrOx	62.9	7.8	4.6	24.7	37.3	27.9
Ni/ZrO2	72.9	9.3	5.5	12.2	39.3	35.5
Ni/CeO2	66.7	8.1	4.3	20.8	34.6	28.8
CeZrOx	71.7	8.7	3.8	15.8	37.6	30.7
ZrO2	72.4	9.3	3.8	14.5	40.3	28.9
CeO2	73.7	8.8	4.4	13.1	38.8	27.5

Based on these results, hydrogenation is beneficial to improve oil quality and quantity. Nickel loaded catalysts are useful to reduce solids formation but do not improve oil properties considerably when compared to non-nickel loaded catalysts. Zirconia seems to be a better catalyst for HTL than cerium; we believe that the cerium in both CeZrOx and CeO_2 enhances chemical reactions that reduce oil formation and HHV values. Previous work reported non-hydrogenated HTL with CeZrOx catalysts can produce oil with HHV of 31.2 MJ/kg but an energy recovery as high as 38.8% [22]. Perhaps the presence of some different chemistry occurs with cerium and hydrogen that increases oil's HHV at the cost of reducing the amount produced.

Figure 13 shows a Van Krevelen diagram comparing the H:C and O:C atomic ratios for different types of biomass, the bio-oils from this study, and crude. HTL is a suitable method to upgrade food waste biomass into a bio-oil with reduced oxygen content. However, hydrogenated

HTL seems to be limited by the amount of hydrogen that can be added into the bio-oil. As seen in Table 4, the HTL bio-oils had 50% or less oxygen content than food waste but only a 20-30% higher hydrogen content. Overall, hydrogenated HTL is useful to decrease oxygen in oil but it is limited by the amount of hydrogen that can be added. By adding hydrogen as a reactant and using nickel loaded catalysts, we were expecting to enhance hydrogenation reactions to achieve higher saturation of hydrocarbons. It seems however that they additional hydrogen is being consumed in hydrodeoxygenation reactions which is why perhaps, the catalyzed runs with nickel produce more water.
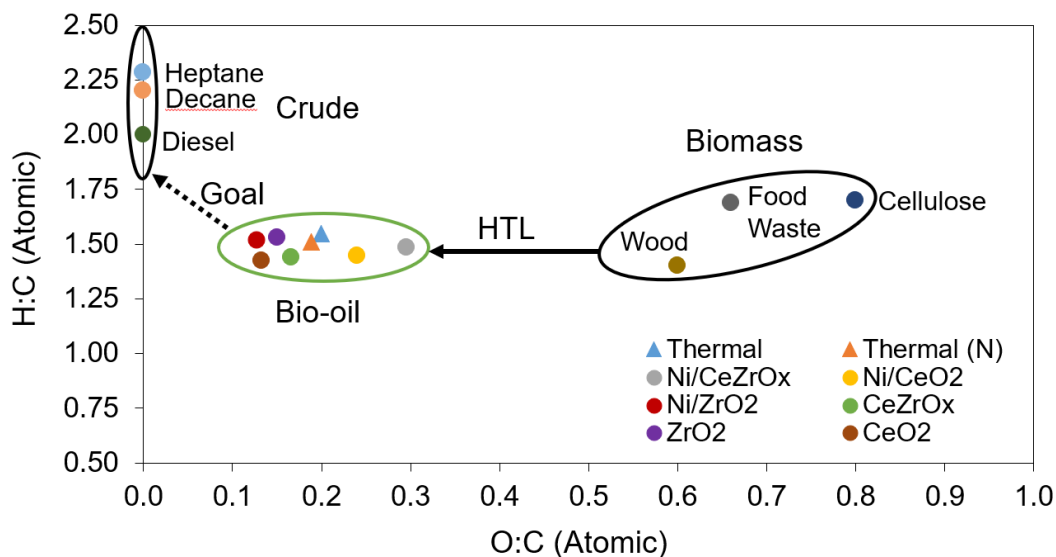
Figure 13. *Van Krevelen plot comparing the atomic O:C ratio and H:C ratio of different biomass, bio-oils produced in this project and different compounds of crude. Hydrogenated catalytic HTL can yield oil with low O:C ratio but cannot increase H:C ratio past the initial ratio in food waste; this suggests hydrogenation might not be the main reaction taking place.*

Gas Analysis

To find the gas composition we analyzed the gases in a GC/MS to identify and quantify the compounds produced as seen in the GC/MS scan in Figure 14. For the hydrogenated reactions, the reactor was pressurized with 300 psi of H_2 (approximately 0.38 g of H_2). The main gases produced via HTL were hydrogen, methane, carbon dioxide, carbon monoxide, and ethylene. As seen in Figure 15, hydrogeneration and the addition of catalysts seems to increase the production of carbon dioxide; as contrary non-catalyzed and non-hydrogenated runs, Thermal (N), increase the production of carbon monoxide. All the catalyzed hydrogenated runs had hydrogen in the gas product, these might indicate that not all the hydrogen gas fed was consumed in hydrogenation reactions; perhaps competing dehydrogenation and hydrodeoxygenation reactions are occurring at a faster rate increasing the volume of hydrogen produced.
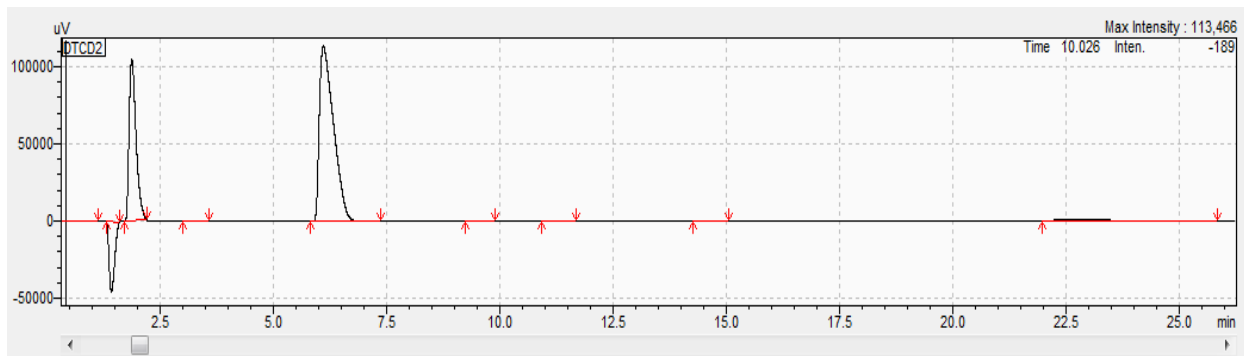
Figure 14. *GC/MS Scan for CeZrOx. The most prominent gases can be observed at the following times are: 1.65 min Hydrogen, 1.87 min Carbon Monoxide, 6.12 min Carbon Dioxide, 21.94 min Ethylene.*
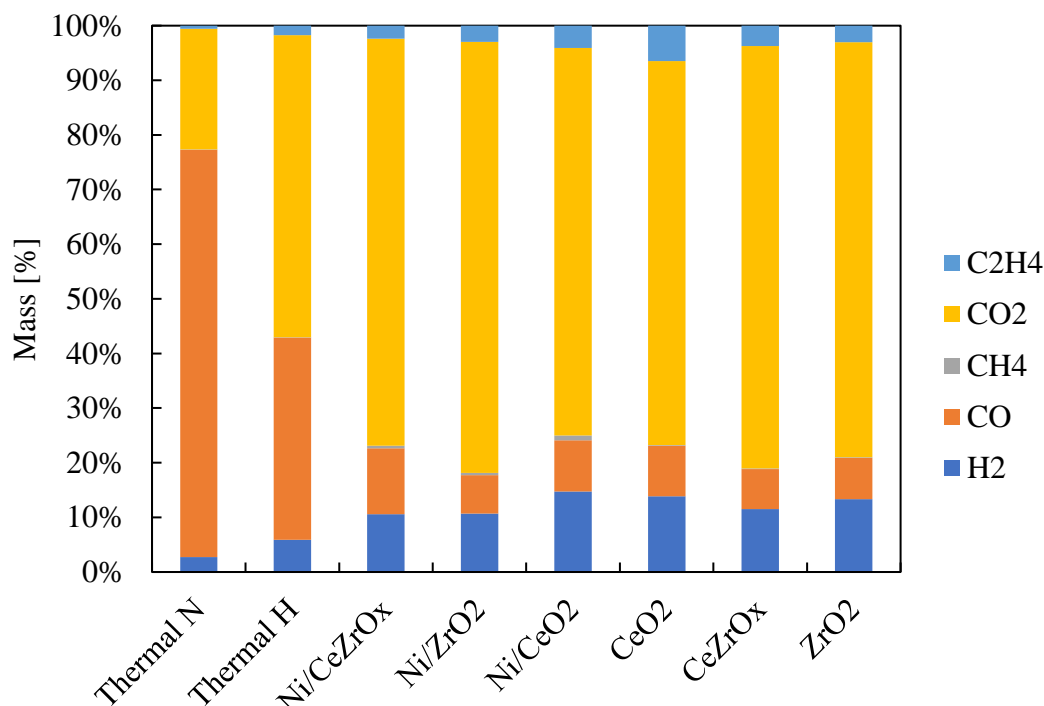
Figure 15. *Weight percentage comparison of the gases produced via HTL. The most prominent gases produced were ethylene, carbon dioxide, methane, carbon monoxide, and hydrogen. Carbon dioxide was the most abundant gas in all the hydrogenated runs while for the Thermal N runs (non-catalyzed and non-hydrogenated) carbon monoxide was the most abundant. This suggests that dehydrogenation and hydrodeoxygenation reactions might be taking place increasing the production of hydrogen.*

The gas compositions indicate that hydrogenation does occur in hydrogenated catalytic HTL but competing reactions also take place. Previous work modeling chemistry for HTL reactions showed that the main reaction occurring include adol condensation, esterification, and

ketonization [22]. Determining the catalytic role of the catalysts used with the complex mixture in food waste is complicated; however, future work testing simple molecules will be useful to better understand the reactions that occur during HTL.

Discussion

Our results indicate that overall, catalytic hydrogenation for HTL can efficiently improve bio-oil quantity and quality. The most efficient catalyst was Ni/ZrO2 which yielded the largest amount of oil with the highest HHV and lowest oxygen content while considerably reducing the formation of solids. To better understand the benefits of hydrogenation and Ni/ZrO_2, we compared current results with those presented in literature. Table 5 presents the energy recovery, oil yield improvement and oil HHV improvement of catalytic HTL studies using food waste and other feedstocks under similar conditions.

Table 5: Comparisons of energy recoveries, oil yield and oil HHV using different feedstocks and catalysts for HTL.

Feedstock	Catalyst	Temp (°C)	Energy Recovery $\left(\dfrac{HHV_{oil} \times Yield}{HHV_{feed}} \right)$	Oil Yield Improvement $\left(\dfrac{Yield_{w/cat}}{Yield_{thermal(N)}} \right)$	Oil HHV Improvement $\left(\dfrac{HHV_{w/cat}}{HHV_{thermal(N)}} \right)$
Food waste [2, 22]	CeZrOx	300	38.80	1.59	0.88
	Na2CO3	300	21.30	1.12	0.68
	Red mud	300	93.70	1.78	0.88
	Ni/ZrO2	300	35.50	1.38	1.21
Rice Straw [4]	Ni/CeO2 (hydrogenated)	290	81.60	1.39	1.22
Spirunella Algae [18]	NiO	350	56.50	0.76	1.08
Microalgae [30]	Nano Ni/SiO2	250	28.90	1.49	1.05
Sawdust [23, 25]	NaOH (hydrogenated)	300	75.00	1.14	1.00
	MgO	300	48.6	1.60	0.93

We compared the results of food waste with rice straw, spirunella algae, microalgae and sawdust. Compared to other feedstocks, spirunella algae have the highest energy recoveries; this could be attributed to the high lipid content of these sources that facilitates conversion. Feedstocks like sawdust are harder to convert due to their high lignocellulosic composition. However, as seen in Table 5, hydrogenated HTL using sawdust can considerably increase energy recovery. Similarly, high energy recovery, oil yield and HHV were obtained with hydrogenated HTL using rice straw, which has high cellulose content that is recalcitrant to conversion. Food waste is mostly composed of carbohydrates; surprisingly, studies using food waste have resulted in energy recoveries and oil yields similar to those of microalgae and spirunella algae. Algae is one of the best feedstocks for HTL due to its abundance, easiness to grow and high energy content; however, other studies have shown that lower quality feedstocks can produce high quality oils using hydrogenation.

As seen in Table 5, HTL performance is based on the catalysts used. Previous studies have shown that heterogenous catalysts like red mud and CeZrOx improve oil yield and energy recovery

in comparison to thermal runs and homogenous catalysts like Na_2CO_3. The largest benefit of these catalysts is that they considerably increase oil yield but did not have a large impact on the oil's HHV. As contrary, using $NiZrO_2$ as a catalyst while adding hydrogen increased oil yield by 38% and HHV by 21% compared to uncatalyzed and non-hydrogenated HTL. Overall the addition of hydrogen using nickel catalysts in HTL is useful to improve oil quality when using relatively low-quality feedstocks.

Conclusion and Recommendations

This study demonstrated that hydrogenated nickel oxide catalytic HTL is a suitable method to convert food waste into bio-oil. All catalyzed runs improved bio-oil yields, energy recovery and bio-oil's HHV in comparison to uncatalyzed and non-hydrogenated runs. Catalytic hydrogenated HTL can successfully reduce the oxygen content of the bio-oil but cannot increase the oils' hydrogen to carbon ratio past the initial ratio that already exists in food waste.

Zirconia seems to be a better catalyst than Cerium. The most efficient catalyst was Ni/ZrO_2 which increased bio-oil yield by 38% and produced a bio-oil with a HHV of 39.3 MJ/kg which is really close that of crude. Aside from an increase in quality and quantity of bio-oil, another major benefit of $NiZrO_2$ was the reduction of solids. Using this catalyst only 1.60g of solids were produced; this is of particular importance at an industrial scale to lower the costs of catalyst reusability. Despite this reduction of solids, this process is still limited by the fact that over half of the organic content is being lost to the byproducts, especially the water phase which has a high content of carbon. This in turn compromises the economics of HTL in a large scale.

The main focus of future research should be finding ways to recover the carbon content of the liquid phase. We suggest analyzing the possibility of recovering hydrogen through gasification to then upgrade the bio-oil that is produced. Another alternative will be to mix the water phase with the food slurry to increase the initial carbon content of the feedstock and recycle byproducts within the process.

Another important area of research is an economic analysis of the process. Since nickel catalysts are expensive, it is crucial to further study catalyst reusability. Recovering the catalyst and reusing it is important to understand if catalyst is being lost throughout the reactions and if activity reduces after reuse. Hydrogen is also an expensive reactant which cost needs to be taken into account. A thorough economic analysis will determine if the increase of oil quantity and quality justify these additional costs. Aside from an economic analysis, a safety analysis should also be done to consider the safety risk associated with hydrogen use at an industrial scale.

We suggest to also explore different operating parameters using Ni/ZrO_2 as a catalyst. One parameter could be the retention time of the process. Towards the end of the process, molecules repolymerize to form solids; reducing the reaction time could further help reduce the formation of solids and other byproducts. Another parameter that could vary would be the amount of hydrogen added into the reactor. The addition of more hydrogen could increase the saturation of carbohydrates. On the other hand, adding less hydrogen could enhance other dehydration and deoxygenation reactions to further decrease the oxygen content of the bio-oil.

At last, we recommend studying the different reactions that might be taking place during HTL. We believed hydrogenation is one of the main reactions but the formation of other gases indicates that other reactions are taking place at a faster rate. Food waste is a complex feedstock so using model compounds and reacting them with nickel based catalysts and hydrogen can help us better understand the chemistry of HTL. This will also help us better understand the role of nickel catalysts and weather cheaper catalysts can perform similar chemistries.

Overall, we believe these are the main areas of research that will provide enough background to then design a plant at an industrial scale. All in all, hydrogenated HTL using

Ni/ZrO$_2$ seems like a promising technology to reduce waste, greenhouse gas emissions and our dependence on fossil fuels.

References

1. Asphaug, S. Catalytic Hydrodeoxygenation of Bio-oils with Supported MoP-Catalysts. *Norwegian University of Science and Technology.* **2013**.

2. Bailey, M.; Carabillo, N.; Hemingway, J. Hydrothermal Liquefaction of Food Waste. *Worcester Polytechnic Institute.* **2018**.

3. Boslaugh, S. Pyrolysis. *https://www.britannica.com/science/pyrolysis* (accessed November 25, 2018).

4. Chen, D.; Ma, Q.; Wei, L.; Li, N.; Shen, Q.; Tian, W.; Zhou, J.; Long, J. Catalytic hydroliquefaction of rice straw for bio-oil production using Ni/CeO2 catalysts. *Journal of Analytical and Applied Pyrolysis* **2018***, 130*, 169-180.

5. Cheng, D.; Wang, L.; Shahbazi, A.; Xiu, S.; Zhang, B. Characterization of the physical and chemical properties of the distillate fractions of crude bio-oil produced by the glycerol-assisted liquefaction of swine manure. **2014***, 130*, 251-256.

6. Demirbas, A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management* **2000***, 41*, 633-646.

7. Demirbaş, A. Calculation of higher heating values of biomass fuels. *Fuel* **1997***, 76*, 431-434.

8. Dimitriadis, A.; Bezergianni, S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renewable and Sustainable Energy Reviews* **2017***, 68*, 113-125.

9. EERE. Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities. *U.S. Department of Energy* **2017**.

10. EERE. From Feedstocks to Final Products *U.S. Department of Energy* **2016**.

11. EIA. Where Greenhouse Gases Come From. *https://www.eia.gov/energyexplained/index.php?page=environment_where_ghg_come_from*(accessed Nov 11, 2018).

12. EIA Biomass—renewable energy from plants and animals. *https://www.eia.gov/energyexplained/?page=biomass_home* (accessed Nov 11, 2018).

13. EPA Greenhouse Gas Emissions. *https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions* (accessed Nov 11, 2018).

14. EPA Advancing Sustainable Materials Management: Facts and Figures. *United States Environmental Protection Agency* **2018**.

15. FAO Food Loss and Food Waste. *http://www.fao.org/food-loss-and-food-waste/en/* (accessed Nov 11, 2018).

16. Food and Safety Authority of Ireland Trans Fatty Acids And Hydrogenated Vegetable Oils. *https://www.fsai.ie/faq/trans_fatty_acids.html*(accessed Nov 25, 2018).

17. Gollakota, A. R. K.; Kishore, N.; Gu, S. A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews* **2018**, *81*, 1378-1392.

18. Jena, U.; Das, K. C.; Kastner, J. R. Comparison of the effects of Na2CO3, Ca3(PO4)2, and NiO catalysts on the thermochemical liquefaction of microalga Spirulina platensis. *Appl. Energy* **2012**, *98*, 368-375.

19. Kambo, H. S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renewable and Sustainable Energy Reviews* **2015**, *45*, 359-378.

20. Lew, J. Catalytic Hydrogenation of Alkenes. *https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Alkenes/Reactivity_of_Alkenes/Catalytic_Hydrogenation* (accessed Nov 25, 2018).

21. Liao, X.; Zhang, Y.; Hill, M.; Xia, X.; Zhao, Y.; Jiang, Z. Highly efficient Ni/CeO2 catalyst for the liquid phase hydrogenation of maleic anhydride. *Applied Catalysis A: General* **2014**, *488*, 256-264.

22. Maag, A.; Paulsen, A.; Amundsen, T.; Yelvington, P.; Tompsett, G.; Timko, M. Catalytic Hydrothermal Liquefaction of Food Waste Using CeZrOx. *Energies* **2018**, *11*.

23. Malins, K. Production of bio-oil via hydrothermal liquefaction of birch sawdust. *Energy Conversion and Management* **2017**, *144*, 243-251.

24. Molino, A.; Chianese, S.; Musmarra, D. Biomass Gasification technology: The state of the art overview. *Journal of Energy* **2016**, *25*, 10-25.

25. Nazari, L.; Yuan, Z.; Souzanchi, S.; Ray, M. B.; Xu, C. Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils. *Fuel* **2015**, *162*, 74-83.

26. Reusch, W. Hydrogenation of Alkenes. *https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Alkenes/Reactivity_of_Alkenes/Stereoselectivity_in_Addition_Reactions_to_Double_Bonds/Hydrogenation_of_Alkenes* (accessed Nov 25, 2018).

27. Rodriguez, E.; Keller, C.; Mitchell, S.; Perez-Ramirez, J. Hydroxyapatite, an exceptional catalyst for the gas-phase deoxygenation of bio-oil by adol condensation. *Royal Society of Chemistry* **2014**.

28. Ronsse, D.; Nachenius, P. In *In Biomass Pyrolysis and Biochar Characterization;* 1st FOREBIOM Workshop; Department Of Biosystems Engineering, Faculty of Bioscience Engineering, Ghent University (Belgium): Vienna, April 4, 2013.

29. Roth, A. Pyrolysis | Student Energy. *https://www.studentenergy.org/topics/pyrolysis* (accessed Nov 25, 2018).

30. Saber, M.; Golzary, A.; Hosseinpour, M.; Takahashi, F.; Yoshikawa, K. Catalytic hydrothermal liquefaction of microalgae using nanocatalyst. *Appl. Energy* **2016***, 183*, 566-576.

31. The Weinberg Group, L. The Importance of Nickel Compounds: Catalysts. *European Nickel Institute* **2007**.

32. Toor, S. S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011***, 36*, 2328-2342.

33. USDA Food Loss and Waste. *https://www.usda.gov/oce/foodwaste/faqs.htm* (accessed Nov 11, 2018).

34. Yim, S. C.; Quitain, A.; Yusup, S.; Sasaki, M.; Uemura, Y.; Kida, T. Metal oxide-catalyzed hydrothermal liquefaction of Malaysian oil palm biomass to bio-oil under supercritical condition. *The Journal of Supercritical Fluids* **2017***, 120*, 384-394.

35. Zhang, Y. *Biofuels from Agricultural Wastes and Byproducts;* Blackwell: United States, 2010; pp 201-228.

Appendices

Appendix A: List of Acronyms

Table 6: Glossary of acronyms used throughout this report

Name	Meaning
Al_2O_3	Alumina
CaO	Calcium Oxide
CeO_2	Cerium Oxide
CeZrOx	Cerium Zirconia Oxide
CHON	Carbon, hydrogen, oxygen, nitrogen
DI Water	Deionized water
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization of the United Nations
Fe_2O_3	Iron Oxide
g	Grams
GC-2014	Gas Chromatography
H_2	Hydrogen gas
HCl	Hydrocloric acid
HHV	High heating value
HHV	high heating values (HHV).
HTL	Hydrothermal liquefaction
kg	kilograms
kV	Kilovolts
L	Liter
mA	Mega Amps
min	minutes
MJ	Mega Joules
mL	milliliter
Mpa	Mega Pascals
MSW	Municipal solid waste
N_2	Nitrogen gas
Na_2CO_3	Sodium Carbonate
$Ni(NO_3)_2 . 6H2O$	Nickel(II) nitrate hexahydrate
Ni/CeO_2	Nickel Cerium Oxide
Ni/CeZrOx	Nickel Cerium Zirconia Oxide
Ni/ZrO_2	Nickel zirconia oxide
NiO	Nickel(II) oxide
ºC	Degree Celsius
pH	Potential of hydrogen
PID	a Proportional-Integral-Derivative controller
ppm	parts per million
psi	Pounds per inches

Thermal H	Hydrogenated non-catalyze run
Thermal N	Non-hydrogenated, non-catalyzed run
TOC	Total organic Carbon
USDA	United States Department of Agriculture
VICI	Valco Instruments Co. Inc
WPI	Worcester Polytechnique Institute
XRD	X-ray diffraction
ZrO_2	zirconia oxide
μL	microliter

Appendix B: Carbon Balance

The following tables show the distribution of carbon in grams for the products of HTL.

Table 7: Carbon Balance in grams for all the Thermal N runs.

Carbon Balance	Run 1	Run 2
Carbon in Oil	2.06	1.32
Carbon in Water	1.31	1.00
Carbon in Solid	4.24	1.62
Carbon in Gas	0.95	0.68
Total Carbon Loss	-1.49	2.05

Table 8: Carbon Balance in grams for all the Thermal H runs.

Carbon Balance	Run 1	Run 2	Run 3	Run 4
Carbon in Oil	3.78	2.39	2.06	2.07
Carbon in Water	1.32	0.99	0.64	1.20
Carbon in Solid	2.54	3.99	4.24	3.53
Carbon in Gas	0.95	0.55	0.68	0.82
Total Carbon Loss	-1.52	-0.84	-0.55	-0.55

Table 9: Carbon Balance in grams for all the Ni/CeZrOx runs.

Carbon Balance	Run 1	Run 2
Carbon in Oil	1.85	2.00
Carbon in Water	1.60	2.85
Carbon in Solid	0.27	0.24
Carbon in Gas	0.68	1.91
Total Carbon Loss	2.67	0.08

Table 10: Carbon Balance in grams for all the Ni/ZrO_2 runs.

Carbon Balance	Run 1	Run 2
Carbon in Oil	2.32	2.66
Carbon in Water	2.14	1.56
Carbon in Solid	0.07	0.09
Carbon in Gas	0.68	0.68
Total Carbon Loss	1.87	2.09

Table 11: Carbon Balance in grams for all the Ni/CeO_2 runs.

Carbon Balance	Run 1	Run 2
Carbon in Oil	2.30	1.97
Carbon in Water	1.48	2.16
Carbon in Solid	0.50	0.71
Carbon in Gas	0.27	0.41
Total Carbon Loss	2.53	1.83

Table 12: Carbon Balance in grams for all the CeZrOx runs.

Carbon Balance	Run 1	Run 2	Run 3
Carbon in Oil	2.09	2.42	2.15
Carbon in Water	1.12	1.07	1.53
Carbon in Solid	1.18	0.90	0.97
Carbon in Gas	0.82	1.09	0.95
Total Carbon Loss	1.88	1.60	1.47

Table 13: Carbon Balance in grams for all the ZrO_2 runs.

Carbon Balance	Run 1	Run 2	Run 3
Carbon in Oil	2.02	1.95	1.99
Carbon in Water	1.49	1.05	1.45
Carbon in Solid	1.48	1.55	1.30
Carbon in Gas	0.68	0.82	0.82
Total Carbon Loss	1.40	1.71	1.51

Table 14: Carbon Balance in grams for all the CeO_2 runs.

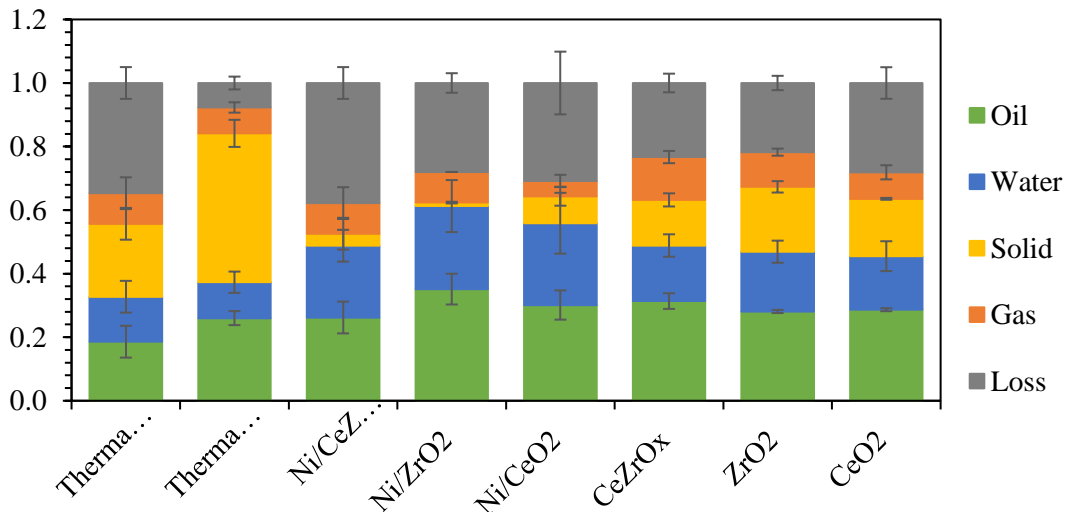| Carbon Balance	Run 1	Run 2	Run 3
Carbon in Oil	1.99	2.05	2.05
Carbon in Water	1.24	1.50	0.84
Carbon in Solid	1.26	1.27	1.30
Carbon in Gas	0.41	0.68	0.68
Total Carbon Loss	2.17	1.58	2.21

Figure 16. *Carbon balance taking into account losses to close the balance at 1.*

Appendix C: Mass Balance

The following tables show the distribution of products in grams for all the runs completed in this study.

Table 15. Product distribution in grams for all the Thermal N runs.

	Run 1	**Run 2**	**Run 3**
Oil (after extraction)	3.00	1.88	2.37
Water	79.00	88.98	84.64
Solid	6.00	2.45	5.60
Gas	3.50	2.50	3.00
Reactor Loss	0.00	0.50	0.50
Other Loss	8.50	3.69	3.89
Total	100.00	100.00	100.00

Table 16: Product distribution in grams for all the Thermal H runs.

	Run 1	**Run 2**	**Run 3**	**Run 4**
Oil (after extraction)	5.86	3.61	3.04	2.78
Water	80.06	78.70	82.28	80.48
Solid	3.71	5.70	5.71	4.62
Gas	3.50	2.00	2.50	3.00
Reactor Loss	0.00	0.00	0.50	0.50
Other Loss	6.87	9.99	5.97	8.62
Total	100.00	100.00	100.00	100.00

Table 17: Product distribution in grams for all the Ni/CeZrOx runs.

Product Distribution	**Run 1**	**Run 2**
Oil (after extraction)	2.90	2.61
Water	87.34	80.39
Solid	1.60	1.46
Gas	2.50	7.00
Reactor Loss	0.50	1.00
Other Loss	5.16	7.54
Total	100.00	100.00

Table 18:Product distribution in grams for all the Ni/ZrO$_2$ runs.

Product Distribution	**Run 1**	**Run 2**
Oil (after extraction)	3.22	3.44
Water	88.66	86.99
Solid	0.98	0.86
Gas	2.50	2.50
Reactor Loss	0.50	1.00
Other Loss	4.14	5.21
Total	100.00	100.00

Table 19:Product distribution in grams for all the Ni/CeO$_2$ runs.

Product Distribution	Run 1	Run 2
Oil (after extraction)	3.06	3.08
Water	84.23	87.96
Solid	2.07	2.20
Gas	1.00	1.50
Reactor Loss	1.50	1.00
Other Loss	8.14	4.26
Total	100.00	100.00

Table 20:Product distribution in grams for all the CeZrOx runs.

Product Distribution	Run 1	Run 2	Run3
Oil (after extraction)	2.80	3.21	3.03
Water	82.36	83.29	79.81
Solid	4.15	3.04	3.98
Gas	3.00	4.00	3.50
Reactor Loss	1.00	1.00	0.50
Other Loss	6.69	5.46	9.18
Total	100.00	100.00	100.00

Table 21:Product distribution in grams for all the ZrO$_2$ runs.

Product Distribution	Run 1	Run 2	Run3
Oil (after extraction)	2.57	2.60	2.77
Water	86.40	81.38	84.22
Solid	3.81	4.55	4.21
Gas	2.50	3.00	3.00
Reactor Loss	2.00	0.50	0.50
Other Loss	2.72	7.97	5.30
Total	100.00	100.00	100.00

Table 22: Product distribution in grams for all the CeO$_2$ runs.

Product Distribution	Run 1	Run 2	Run 3
Oil (after extraction)	2.55	2.64	2.66
Water	84.28	84.36	85.42
Solid	4.05	3.73	4.45
Gas	1.50	2.50	2.50
Reactor Loss	1.50	1.50	1.00
Other Loss	6.12	5.27	3.97
Total	100.00	100.00	100.00

Appendix D: Gas Balance

Table 23: Average amount of gas produced per run.

	Thermal N	Thermal H	Ni/CeZrOx	Ni/ZrO$_2$	Ni/CeO$_2$	CeO$_2$	CeZrOx	ZrO$_2$
H$_2$	0.24	0.13	0.22	0.22	0.27	0.35	0.36	0.39
CO	6.69	0.83	0.25	0.15	0.17	0.23	0.23	0.22
CH$_4$	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.00
CO$_2$	1.98	1.24	1.52	1.63	1.28	1.75	2.43	2.21
C$_2$H$_4$	0.05	0.04	0.05	0.06	0.07	0.16	0.12	0.09
Est. GC	8.97	2.25	2.04	2.07	1.81	2.49	3.14	2.91
Act. Gas	3.50	2.25	4.75	2.50	1.25	2.00	3.50	2.83