HYDROTHERMAL LIQUEFACTION OF FOOD WASTE AND MODEL FOOD WASTE COMPOUNDS

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Abstract

Solid waste is generated at a rate of more than 4 lb per person per day. A significant portion of the non-recyclable waste is food waste, with high water content and low energy density. While most thermochemical conversion processes require a relatively dry feedstock, hydrothermal liquefaction uses subcritical water as the reaction medium and is therefore compatible with high-moisture feedstocks. We have studied the viability of converting high-moisture food waste into a liquid fuel. A surrogate food waste stream was formulated and the yield and bio-oil quality were measured at various process conditions. Yields as high as 45% on a dry mass basis were observed at a reactor temperature of 315 °C.

To further understand hydrothermal liquefaction of food waste, three model food compounds were studied—starch, soybean oil, and casein. The reaction mechanism, product distribution, and product yields for each compound were investigated at reactor temperatures ranging from 250–315 °C, using a sodium carbonate catalyst and a syngas head gas. The pure-component data were compared to data collected for the surrogate food waste under the same operating conditions. A lumped kinetic model describing the hydrothermal liquefaction of starch is also proposed.

Introduction

In 2011, the United States generated 250 million tons of municipal solid waste. Approximately 25% was recycled, leaving 163 million tons to be placed into landfills. Most landfilled material is organic, with the largest component of the non-recycled portion being food waste [1]. This waste occupies valuable space and emits harmful greenhouse gases, but is also a largely untapped source of renewable energy.

Military field bases are a prime example of a location with waste biomass accumulation challenges. Studies have shown that solid waste is generated at a rate of 3–4 lb/person/day for base camp operations [2]. A typical maneuver battalion of 550 soldiers will produce about 2000 lb of waste per day. Much of this waste is food waste, which is generated by field feeding kitchens and has a high water content and low energy content. In addition to the environmental problems mentioned above, these wastes generate objectionable odors and gases, and can contribute to the spread of disease.

The waste stream from an Army base camp was characterized and shown to be composed of roughly 38% paper and cardboard, 24% food waste, 17% slop, 12% plastic, 3% metal and glass, and 7% miscellaneous [2]. The majority of the waste is organic, and is therefore a candidate for renewable energy production. The organic portion of the waste can further be separated into higher energy materials (generally dry) and lower energy materials (wet). Food waste and slop are significantly lower in energy content as opposed to the other biomass materials. Although they have the lowest energy density, they are the highest risk constituents to leave untreated.

Hydrothermal liquefaction (HTL) is a promising technology to treat the wet waste stream because water is used as the reaction medium and easily separated from the product. In contrast, most other biomass conversion routes generally require dry feeds or distillation to remove water from the
product [3]. As a result, HTL is more energetically favorable for processing wet feedstocks such as food waste and slop. The result of treating waste with hydrothermal liquefaction is a reduction in the overall volume of waste on-site, sterilization of waste and the production of a renewable fuel.

Hydrothermal liquefaction has been studied extensively in the past [3–5] with feedstocks such as lignocellulose, biowaste and algae. Few studies [6], however, have been conducted on hydrothermal liquefaction of food waste streams. A number of studies on individual components of food waste have been performed (e.g., glucose, amino acids, fatty acids) [6], but there is minimal data available using food as a feedstock to produce bio-oil. Minowa et al. [7] analyzed the conversion of a garbage stream composed of cabbage, boiled rice, sardines, butter and clam shell into oil. Reaction temperatures between 250–340 °C were investigated. The highest oil yield obtained, 27.6%, was obtained at 340 °C with a residence time of 30 minutes and using a sodium carbonate catalyst. Nitrogen was used as the process gas; however, nitrogen is not available at remote military locations.

Therefore, the current study was designed based upon the previous studies [7], but also addressed requirements for a fielded military application. A surrogate feed was developed and reacted under hydrothermal conditions to produce bio-oil. Temperature (250, 280, 315 °C), residence time (10, 30, 60 min), catalyst (no catalyst, sodium carbonate, potassium hydroxide), process gas (no process gas, air, syngas) and initial solids loading (5, 10, 15%) were optimized to maximize the liquid bio-oil yield and minimize char produced. Syngas was assumed to be locally available from a gasifier on base that would process the higher energy dry waste stream. Model food waste compounds were then selected (starch, casein, soybean oil) and subjected to the optimal conditions found for the surrogate stream. Further, a global reaction mechanism was postulated for starch, and kinetic rate constants were determined.

**Experimental Methods**

**Feeds**

A surrogate waste stream based upon data gathered from the analysis of actual military waste was formulated. The surrogate waste stream consisted of 8 items in the following concentrations: American cheese (12.8%), chicken breast (14.9%), brown gravy (2.1%), mashed potatoes (10.6%), green beans (14.9%), white rice (19.1%), apple dessert (22.3%) and butter (3.2%). The moisture content of this stream was found to be 69.3%. Nutritionally, this stream was composed of 54% carbohydrate, 19% fat and 27% protein by mass. Many of these items (chicken breast, gravy, white rice, apple dessert) were directly sampled from military Unitized Group Rations (UGRs).

The model compounds selected were starch (carbohydrate), casein (protein) and soybean oil (fat). Larger model molecules were chosen as opposed to monomer-sized molecules to more accurately represent the actual waste encountered in the field. Also, hydrothermal liquefaction involves a complex network of elementary reactions, and selecting larger model molecules allowed for a more representative data set for comparison against the surrogate waste results.

**Hydrothermal Liquefaction**

A 300 mL stainless steel Parr Instruments bench top reactor, Model 4561, was used to conduct all hydrothermal liquefaction experiments. The contents of the reactor were stirred at 515 RPM throughout all of the experiments. A PID controller was used to control a heater that was capable of heating the reactor at approximately 6 °C per minute. Temperatures were maintained within 5 °C of the set point. Process gas, when necessary, was introduced through a pressure valve in the reactor cover plate before heating was initialized. Upon completion of a reaction, the reactor was placed in a room temperature water bath, which provided a cooling rate of approximately 40 °C per minute.

At the beginning of each trial, the reactor was loaded with catalyst (when used), deionized water,
and food waste. Once the reactor was sealed, the reactor was pressurized with a process gas, if necessary. All experiments that involved catalysts used 5 mass % loadings (based on dry mass of feed in reactor) of the respective catalyst. Three process gases were tested: ambient-pressure air (0.1 MPa), pressurized air (1.5 MPa) and pressurized syngas (1.5 MPa). For trials that required the use of a process gas, the appropriate gas was injected prior to the onset of reactor heating at 25 °C. The syngas mixture was composed of 43% carbon monoxide (CO), 24% hydrogen (H₂) and 33% carbon dioxide (CO₂).

**Product Separation and Analysis**

The products were collected and separated according to the procedure in Figure 1. Gas was collected with evacuated sample cylinders after the reactor contents cooled to 35 °C. The reactor was then opened and the liquid and solid contents were poured into a vacuum filtration funnel. Water and dissolved organics passed through the 1.2 µm glass filter. This water mixture was transferred to a separatory funnel and a solvent (diethyl ether) was added to extract any water insoluble components. Drying was performed at 60 °C for the water insoluble fraction (WISF) and 105–110 °C for the water soluble fraction (WSF). Oil and solid remaining on the filter paper were separated using an acetone wash. The reactor and agitator propeller were rinsed with acetone and scraped with a spatula to collect all residual material on the metal surfaces. The acetone soluble fraction (ASF) was dried at 60 °C and the solid char was dried at 105–110 °C. Yields were calculated as follows:

- **Gas yield** = \( \frac{\text{mass of gas collected} - \text{mass of process gas feed}}{\text{mass of dry biomass}} \)
- **Char yield** = \( \frac{\text{mass of solid residue}}{\text{mass of dry biomass}} \)
- **Oil yield** = \( \frac{\text{mass of ASF} + \text{mass of WISF}}{\text{mass of dry biomass}} \)

Several reactor runs were performed in duplicate and selected reactions were performed in triplicate to analyze experimental errors.

![Figure 1. Inputs to HTL reactor and experimental product separation process](image)

Gas chromatography was used to analyze both the gas and liquid products collected from liquefaction reactions. The gas was analyzed with a GC-TCD (gas chromatograph with thermal conductivity detector) and a GC-MS (gas chromatograph with mass spectrometry detector). The liquid fractions (both organic and aqueous) were analyzed only with the GC-MS. Additional analyses performed on the ASF included bomb calorimetry and elemental analysis.
Results and Discussion

HTL of Surrogate Food Waste

Two sets of experiments were designed to optimize reaction conditions for the hydrothermal treatment of military field feeding waste. Catalyst and process gas optimization was performed first. A series of reactions at varying residence times with a reactor temperature of 280 °C and a solids loading of 10% were performed with the food waste surrogate as the feed. The use of syngas resulted in the highest yield of oil and lowest yield of char. The char yield was higher and the oil yield lower when high pressure air was used as a process gas. Trials run in the absence of catalyst also experienced similarly poor oil yield and increased char production. In contrast, charging the reactor with ambient pressure air did not significantly alter yields from what was obtained using syngas. Comparisons of the catalysts tested (KOH and Na$_2$CO$_3$) showed sodium carbonate consistently resulted in a 10% greater yield of oil under the conditions tested.

Following the optimization of the catalyst and process gas, residence time, reaction temperature and solids loading were optimized (using sodium carbonate and syngas). Reactions performed at 250 °C produced high concentrations of char. Conversely, reactions performed at 315 °C resulted in high concentrations of oil and low yields of char. In general, as residence time increased, char yields increased and oil yields decreased. The maximum yield of oil achieved was 45% at reactor conditions of 315 °C, 10 minute residence time and 10% solids loading. The solids loading to the reactor had a minimal impact on yield. A 10% solids loading led to the highest oil yields; however, for batch processes, higher solid feed rates are beneficial to the process energetics. Therefore, a 15% solids loading was determined to be preferable. The results from the 15% solids loading trials are shown in Figure 2.

![Figure 2. Bio-oil and char mass yields (dry basis) from liquefaction of military surrogate waste at 15% solids loading. All trials used syngas as the process gas and 5 mass % sodium carbonate as the catalyst.](image)

HTL of Model Food Waste Compounds

Each model compound was investigated under the optimal reaction conditions identified for the surrogate food waste stream. Reactor temperature and residence time were varied using 5 mass % sodium carbonate as the catalyst, 1.5 MPa of syngas and a 15% solids loading. The results between the three model compounds were drastically different. Starch (Figure 3) followed a similar trend compared to trends obtained from liquefaction of the surrogate. The highest oil yields and lowest char yields were obtained at 315 °C and a residence time of 10 min. Oil yield decreased as residence time increased, while both the char and gas yields increased, indicating a secondary reaction was occurring where the oil
was breaking down into solid and gas byproducts. Gas production from liquefaction of starch was significant. Gas yields ranged from 19% at 250 °C to over 25% at 315 °C. Details on the production and consumption of CO₂ and CO, respectively, are shown in Figure 3. Hydrogen was also analyzed, but was found to remain nearly unchanged in concentration at all conditions tested. Total hydrogen gas production rates ranged between 0.2–0.3 g. Large amounts of CO₂ are produced within the first 10 minutes of reaction, suggesting that the majority of decomposition and decarboxylation is complete by that time.

**Figure 3.** Effect of residence time on liquid and solid yields (left) and net gas production (right) for starch

Casein and soybean oil resulted in low yields of char (<3%) at all temperatures. Yields for oil were low for casein (<14%) and high for soybean oil (50–95%). Oil yields were difficult to characterize for both casein and soybean oil due to inefficient separation processes. At low temperatures and residence times, a portion of the casein feed appeared unreacted and passed into the oil phase during product recovery. This was not observed at 315 °C. Soybean oil was difficult to separate due to the lack of conversion at the reaction temperatures investigated; therefore, the product retained a relatively low viscosity, allowing a portion of the product oil to pass through the filter. This also led to a significantly higher error associated with the soybean oil yield. Gas production for casein was fairly constant ranging between 6–10% while soybean oil resulted in negligible consumption or production of gas. For both feeds, as was the case for starch, hydrogen appeared to have little impact on the reactions as indicated by negligible changes in H₂ concentration.

A comparison for the results obtained with hydrothermal liquefaction of the surrogate military waste and model compounds at 315 °C are summarized in Figure 4. A mixture of starch, casein and soybean oil at the prescribed ratio contained in the surrogate (54% carbohydrate, 19% fat and 27% protein) was also reacted at 315 °C with a 30 minute residence time. The result of this test was in reasonable agreement with the surrogate feed results. The char yield was within 1% of the surrogate experimental value and the oil yield was approximately 5% higher than the surrogate experimental value. However, if the results of the individual model compound oil yields are used to calculate the theoretical oil yield of a weighted average mixture, a significantly lower yield is calculated. This result suggests that higher oil yields are promoted by the interaction between the different constituents. This was verified by performing binary reactions with each pair of model compounds. The addition of soybean oil to both casein and starch significantly increased the oil yield as compared to the yield expected based the weighted average of individual yields.
Bio-Oil Analysis

Hydrothermal liquefaction of the surrogate food waste stream resulted in a black, viscous oil as the main liquid product. Starch and casein produced an oil phase similar to the oil produced from the surrogate food waste. Soybean oil appeared mostly unreacted as only a slight darkening of the oil was observed. Each feed and oil product was analyzed to determine the higher heating value and elemental composition. These data, shown in Table 1, established the degree of upgrading that occurred during the hydrothermal treatment. The average higher heating value of the HTL oil, generated at the ideal conditions for the surrogate food waste, was 35.1 MJ/kg. Process conditions using a blanket of air at atmospheric pressure yielded similar quality oil products compared to using syngas. Solids loading and residence time also did not appear to have a significant effect on the energy content of the oil. Comparisons between the raw starch and casein feeds and their respective bio-oil clearly show upgrading occurred. Elemental analysis demonstrates that the oxygen content of these feedstocks is reduced by over 50% after reaction. Also, the concentration of carbon increased drastically for both feeds. Reaction of soybean oil, based on both the heating value and elemental analysis, resulted in no upgrading of the raw feed. In fact, no appreciable reaction appeared to occur as the elemental composition remained unchanged.

Gas chromatography for each oil product was also performed. Individual molecules obtained in the highest percentages for starch reacted at 315 °C included acetic acid (5%), methylated 2-cyclopenten-1-one (25%), 3-methylpyridazine (5%), methylated phenol (18%) and 2,3-dihydro-1H-indene-1-one (3%). High concentration molecules for casein reacted at 315 °C included 1-pentyl-piperidine (3%), phenols (46%) and indole (19%). The gas chromatograph was not equipped with a column capable of reaching the temperatures needed to detect fatty acids present in the bio-oil derived from soybean oil.
Table 1. Summary of Bio-oil Properties Obtained for all Feedstocks

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Temperature (°C)</th>
<th>Higher Heating Value (MJ/kg)</th>
<th>Elemental Analysis (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Starch feed</td>
<td>–</td>
<td>17.0</td>
<td>38.3</td>
</tr>
<tr>
<td>Casein feed</td>
<td>–</td>
<td>23.6</td>
<td>47.6</td>
</tr>
<tr>
<td>Soybean oil feed</td>
<td>–</td>
<td>39.3</td>
<td>77.7</td>
</tr>
<tr>
<td>Starch bio-oil</td>
<td>250</td>
<td>28.2</td>
<td>66.4</td>
</tr>
<tr>
<td>Starch bio-oil</td>
<td>315</td>
<td>31.0</td>
<td>73.4</td>
</tr>
<tr>
<td>Casein bio-oil</td>
<td>315</td>
<td>33.6</td>
<td>71.3</td>
</tr>
<tr>
<td>Soybean oil bio-oil</td>
<td>315</td>
<td>38.2</td>
<td>76.0</td>
</tr>
<tr>
<td>Surrogate food bio-oil</td>
<td>315</td>
<td>35.1</td>
<td>75.2</td>
</tr>
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</table>

**Kinetic Modeling of Starch HTL**

Modeling of the liquefaction kinetics of starch was performed due to the high concentration of carbohydrates in field feeding waste. Multiple reaction schemes were examined to determine the model that best fit the data collected for HTL of starch. The mechanism proposed below was found to be most representative of the data. Biomass decomposes into water soluble components, acetone soluble components, gas and solid residue. As residence time increases, the acetone soluble components further degrade into additional gases and solid residue. The activation energy and pre-exponential factor for the Arrhenius rate expression were optimized for each assumed first-order reaction. The rate constants and Arrhenius parameters are reported in Table 2. These rate constants and Arrhenius parameters are comparable to those reported by Zhang, Huang and Ramaswamy [8] for reaction of other feedstocks under hydrothermal conditions. The predicted model was compared to the data collected at 250 °C and 315 °C in Figure 5. The model agrees well with both data sets. Differences in the predicted and actual WSF yields are due to the mass balance not closing completely. Approximately 90% of the mass was recovered during the experiments. The remaining 10% of unrecovered mass was most likely lost during the high-temperature WSF drying process.

![Kinetic Model Diagram](image)

Table 2. Summary of Rate Constants for the Liquefaction of Starch

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (min⁻¹)</th>
<th>Ea (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>315 °C</td>
<td></td>
</tr>
<tr>
<td>k₀</td>
<td>0.799</td>
<td>0.917</td>
</tr>
<tr>
<td>k₁</td>
<td>0.223</td>
<td>0.359</td>
</tr>
<tr>
<td>k₂</td>
<td>0.157</td>
<td>0.288</td>
</tr>
<tr>
<td>k₃</td>
<td>0.039</td>
<td>0.057</td>
</tr>
<tr>
<td>k₄</td>
<td>0.0017</td>
<td>0.0017</td>
</tr>
<tr>
<td>k₅</td>
<td>0.0036</td>
<td>0.0036</td>
</tr>
</tbody>
</table>
Hydrothermal liquefaction of food waste and model food waste compounds (starch, casein, soybean oil) were studied. The highest yield of bio-oil obtained from the surrogate food waste stream was 45% at a reaction temperature of 315 °C using a sodium carbonate catalyst and a syngas process gas. At the same conditions, starch and casein had bio-oil yields of 25% and 14%, respectively. Very little conversion was observed at the reaction conditions studied for soybean oil. Similar yields of bio-oil and char were obtained for the mixture of model compounds and surrogate stream verifying the model compounds represented the food waste stream well. Properties of the bio-oil were found to be mostly dependent upon the type of feed and reaction temperature, whereas process gas, catalyst type, residence time and solids loading did not affect bio-oil properties significantly. The average heating value of the bio-oil obtained for the food waste surrogate at optimal reaction conditions was 35 MJ/kg. A reaction mechanism for the hydrothermal liquefaction of starch was proposed, and a kinetic model was developed for this mechanism. The agreement between the model and experimental results is within the experimental error. Hydrothermal liquefaction is promising pathway to treat wet food waste streams with high yields and minimal solid residue. Further research should focus on upgrading the bio-oil product to a more refined fuel and treating the aqueous byproduct stream.

References


