# An Evaluation of Mixed Feedstocks for Producing Bio Crude Oil Through Hydrothermal Liquefaction and Its Potential Use at WPI

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## Abstract

With the current climate crisis going on around the world, the need for sustainable energy sources have never been greater. Using waste products from everyday life as feedstock for sustainable biofuels helps reduce the greenhouse gas emissions from fossil fuel usage and from landfills across America. Colleges and Universities are in a unique position due to having a relatively consistent population every year that uses electricity and heat while producing a consistent amount of waste. Using the food and green waste generated on campus at Worcester Polytechnic Institute (WPI), the campus could generate biofuels to replace fossil fuels for heating and campus run vehicles. The goal of this project was to combine food waste and green waste, like landscaping waste, in a feedstock for hydrothermal liquefaction to determine which feedstock created the most biofuel and using data from WPI on waste generated annually to predict how much biofuel could be created and utilized at WPI and how many carbon emissions could be offset by using these fuels.

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## Introduction

Human activities over the past 150 years are the main source responsible for the global increase in temperature of approximately 2 °C (National Ocean and Atmospheric Administration (NOAA), 2020) (Solomon et al., 2007) due to the increase of greenhouse gas (GHG) emissions. The heat trapped in the atmosphere is causing ice caps to melt, sea level to rise, and causes catastrophic natural disasters across the globe; renewable energy sources with limited emissions are necessary to stop the temperature rise and help stop the detrimental effects. Fossil fuel usage is the largest source of GHG emissions in the United States (Environmental Protection Agency (EPA), 2018).

Although Carbon Dioxide is the main GHG that causes the warming, Methane emissions are 30 times more effective at trapping heat (Gabriel Yvon-Durocher et al., 2014). Methane's main source is from decomposing organic matter like post-consumer food waste in landfills and other organic materials, like green wastes from landscaping and agriculture (Environmental Protection Agency (EPA), 2020) which occurs in landfills. In the United States, 10% of all the GHG emissions is from methane (Environmental Protection Agency (EPA), 2018). Along with large amounts of emissions coming from landfills, the large amounts of land needed, stench, and leachate are all secondary forms of pollution from landfills that are harming the environment as well (Cao, Luo, Zhang, & Chen, 2016). Finding a way to utilize the waste organic matter will help to both decrease carbon and methane emissions in the U.S., it will also reduce the impact of one of the largest pollution sources: landfills.

Bio-oil is a up and coming green energy source that can be used in addition to fossil fuels to reduce the GHG emissions in the United States. Bio-oil is a net zero carbon emission fuel source (W. H. Chen et al., 2019), especially when using biomass as the components in the bio-oil makes it carbon neutral. Food and green waste are two sources of biomass that can be used to create bio-oil and help to both reduce emissions due to fossil fuels and landfills. Using bio-gasoline has a 71% reduction of emissions from traditional fossil fuel sources (Zhu et al., 2011).

Food and green waste separately have already shown to produce high amounts of bio-crude that need only slight upgrading to be used in place of traditional fossil fuels (Gollakota, Kishore, & Gu, 2019; Maag et al., 2018). Mixing the feedstocks to include both food and green waste is thought to benefit the overall oil yield. In a hydrothermal environment, proteins and lipids have a higher conversion rate than cellulose and lignin (Gai, Li, Peng, Fan, & Liu, 2015). Studies with just lignocellulose based feedstocks, like green waste for example, produced low amounts of oil due to the higher thermal resistance of cellulose, hemi-cellulose, and lignin (W. T. Chen et al., 2014; Gai et al., 2015). Combining both the food waste with high protein and lipid content with the green waste containing the more thermal resistant lignocellulose compounds will allow for the co-liquefaction of both to promote efficient means of conversion into sustainable biofuels (Gai et al., 2015). The ash created by the thermal conversion of green waste is also thought to act as a catalyst with the food waste to help promote even more conversion into biofuels.

Hydrothermal liquefaction (HTL) is a thermochemical process that has been extensively studied to create bio-oil that is both cheap and uses less energy than other methods (Patel, Zhang, & Kumar, 2016). HTL is the direct conversion of biomass to energy as it does not require a drying step for the biomass, which is necessary for the conversion of green wastes to bio-oil in other processes, the drying step is omitted as the water is used as a reaction medium inside the reactor (W. H. Chen et al., 2019). HTL has already shown to be a successful method of producing bio-oil as it as high liquid fuel yields compared to other methods (Zhu et al., 2011). HTL does not take as much energy to perform, and the byproducts produced during this method can be used to offset pollution and GHG emissions; these uses are shown in Figure 1.

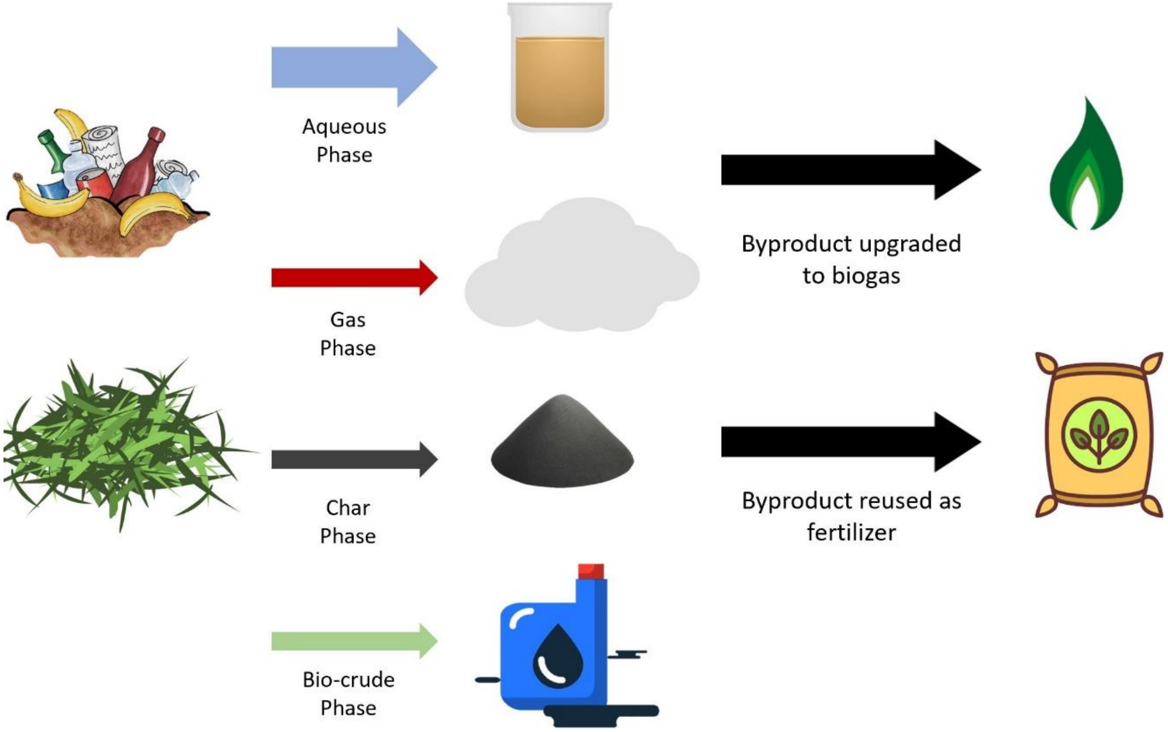

**Figure 1:** Carbon cycle of the HTL process. Starting at the mixed feedstocks and ends at potential products that the byproducts of this process could be used as. The size of the arrow corresponds to how much carbon is in each phase.

Replacing traditional fertilizers will help reduce runoff and pollution from these systems. Hydrochars have also proven to be beneficial for remediating soils that have been contaminated with pollutants like lead (Fang, Gao, Chen, & Zimmerman, 2015). Biogas can be used as an alternative to natural gas benefitting the environment because less fracking would be needed and lower the GHG emissions that are released from burning natural gas.

Colleges and universities have opportunities to use renewable energy systems, such as bio-oil, due to the consistent population of students that return on a yearly basis that uses electricity, heat, and produces food waste (Ebner et al., 2014). These institutions also landscape their campuses which produces a consistent amount of green waste as well. Worcester Polytechnic Institute (WPI) is a small engineering school in Central Massachusetts, and it would be well suited to start implementing bio-oil on the campus. WPI has already successfully implemented many sustainability initiatives on campus that are backed by the student population, like a bike share system. With a student body that supports sustainability initiatives, a relatively consistent food and green waste production of 100 tons per year and 62 tons (50 cubic yards) respectively, and a powerhouse on campus, WPI would benefit from using bio-oils to curb their emissions and cut spending costs.

## Materials and Methods

**Food and Green Waste Materials** A food waste mixture was prepared using data from Mainstream Engineering which was based on commonly found food waste. The components in the mixture were: applesauce, canned chicken, green beans, rice, instant potatoes, American cheese, butter, and DI water. The food was then blended together and stored at refrigeration temperatures until use. Green waste was obtained from a local landscaping company who donated their used mulch. This mulch was filtered to ½” first in order to take out any large sticks, wood pieces, or other unwanted material. The filtered mulch was then chopped in a coffee grinder to get the pieces small, and sieved to 0.85 mm.

Green waste and food waste combinations were planned based on 100 g of total weight in the reactor per run. DI water was added to the ratios to keep the solids content inside the reactor at 15 wt%. This was done to make comparisons between the biocrude produced consistent with that of the only food waste runs. The 15 wt% figure was chosen based on previous food waste HTL work.

Acetone was used for biocrude oil extraction and for cleaning purposes. This acetone was also used as a solvent for GC-MS analysis. Pure $N_2$ gas was used to pressurize the reactor to 900 psi for the experiments.

**Hydrothermal Liquefaction of Food and Green waste** HTL experiments were carried out in a 300 mL stainless steel Parr reactor rated at 3500 psi and 350 °C with a magnetic stirrer. Once the food and green waste was loaded into the reactor, it was sparged using Nitrogen gas three times and then finally pressurized to 900 psi. The reactor was then heated to 300 °C using an external heater over the course of one hour. Once temperature was reached, the HTL reaction proceeded for one hour before being quenched. The reactor was weighed before HTL and after in order to ensure mass balance closure; the reactor was kept between ±1.0 g of its cleaned weight so a majority of the HTL products made it to the extraction phase.

After reaction, the reactor was opened, and the products were placed into a filter for vacuum filtration. Aqueous and Solid products were separated through this process and the aqueous phase was collected and kept for further analysis. The solid product was then washed with 1 L of acetone to extract the oil phase. The solid char was then air dried and collected for elemental analysis. The acetone and oil phase were roto vaped at 65 °F for approximately 40 minutes with breaks at 10, 15, and 25 minutes so samples of the acetone and oil phase could be taken for GC-MS analysis. The biocrude oil was then scraped from the flask and kept for higher heating value (HHV) and elemental analysis. A sample of the stripped off acetone was collected as well for GC-MS analysis.

### @Risk Model

Once the preliminary data from the HTL processes was complete, this data along with the waste and energy data for WPI was used in a model predicting how much energy could be offset using bio-oil produced with the university's waste. This model was produced in the @Risk software in Excel. @Risk was chosen for this as it can encompass multiple types of uncertainties in the predictions and can predict energy yield and use the predictions to give emissions offset. @Risk is also very versatile and can help in future work by predicting money saved and emissions offset by the usage of HTL byproducts as well.

Food waste was the limiting factor in producing the bio-oil, therefore it was the main variable that was tested in the model. The food waste produced on campus as mentioned previously is about 100 tons a year. But this figure can vary based on the number of students on campus using a meal plan as it is not required for most upperclassmen students. To account for this, an @risk triangular uncertainty distribution on the student population was performed. Values for this were obtained from WPI's admissions data which is published online. In the past 5 years, WPI's incoming first year student population has not been beneath 1,100 students, therefore the low number of first year students was picked to be 900 as this is unlikely and would give a wide distribution in the lower range. The most likely amount of students on a meal plan would be approximately 1,100 first year students and 1,500 upperclassmen students as this is the amount of students that can fit in the upperclassman dorms that require meal plans, bringing the most likely total to 2,600 students on a meal plan. The maximum number of students on a meal plan would be the entire undergraduate population at WPI, which is approximately 6,600 students also obtained from the published admissions data online.

Once the triangular uncertainty distribution was obtained for the number of students, this distribution was used in the following equation from the Connecticut Department of Environmental Protection (CDEP):

$$Food\ waste = 0.16\frac{kg}{meal} * 405\frac{meals}{student} * x\frac{students}{year}$$

Where x is the triangular uncertainty distribution. WPI did provide us with their average food waste data and using the most likely value from above in this equation gave a result very close to their food waste data reported to us. Therefore, this equation was accurate and able to be used in the model.

WPI currently donates their post-consumer food waste to a local pig farm to help feed their animals. This program significantly helps the farm and was an initiative set up by the students, which is something WPI might not want to get rid of completely. Due to this, the amount of total food waste used for HTL needed to have uncertainty as well. A uniform uncertainty distribution was included which varied from 70 – 100% of the food waste generated on campus being used for HTL.

Other values used in the model were HHV values for the oil ratios, average fuel price for 2019, and various conversion factors to get the values into corresponding units.

## Results and Discussion

The goal of this study was to determine which combination of food and green wastes produced the most biocrude oil, what compounds made up the biocrude, ensure carbon and mass balance closure, and determine the potential usage of biofuels at WPI.

## Carbon Balance

In order to make sure that we were accounting for all of the carbon in the process; the starting amounts and that created in the HTL process, all samples were tested for carbon content. The aqueous phase was diluted and sent for TOC analysis on site. The biocrude and hydrochar were both sent to Midwest Laboratories for elemental analysis. Gas samples were collected while depressurizing the reactor and analyzed on site. Figure 2 below shows the overall carbon balance for all combinations.

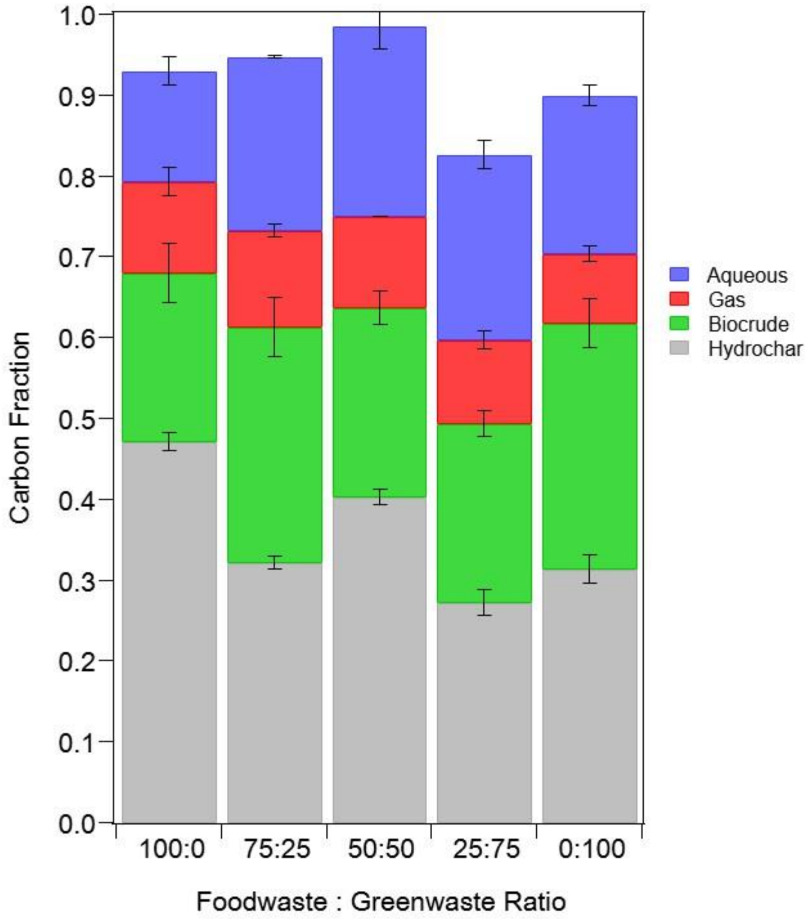

**Figure 2:** Carbon fraction per HTL component for all ratios of food and green waste

All feedstock combinations were run at minimum 3 times to ensure quality data was gathered and was correct for each combination. Multiple samples from different runs were sent out for elemental analysis to see if the carbon content was similar from run to run. Every combination closed the carbon balance above 80%. This is showing that most of the carbon is accounted for, carbon losses can be attributed to reactor losses when extracting contents of the reactor post HTL.

### Mass Balance

Table 1 below shows the mass balance for each feedstock combination, split up by component

**Table 1:** Mass balance of the HTL process for each mixed feedstock. The components are in mass fraction out of 1.

| Food to green waste ratio | Aqueous | Gas | Solid | Oil | Total |
|---|---|---|---|---|---|
| 100 : 0 | 0.828 ± 0.03 | 0.031 ± 0.006 | 0.053 ± 0.002 | 0.023 ± 0.005 | 0.935 ± 0.043 |
| 75 : 25 | 0.845 ± 0.01 | 0.028 ± 0.003 | 0.033 ± 0.01 | 0.026 ± 0.009 | 0.932 ± 0.032 |
| 50 : 50 | 0.851 ± 0.005 | 0.024 ± 0 | 0.036 ± 0.01 | 0.019 ± 0.003 | 0.93 ± 0.018 |
| 25 : 75 | 0.827 ± 0.03 | 0.022 ± 0.004 | 0.026 ± 0.01 | 0.018 ± 0.001 | 0.893 ± 0.045 |
| 0 : 100 | 0.811 ± 0.08 | 0.018 ± 0.003 | 0.033 ± 0.007 | 0.025 ± 0.003 | 0.887 ± 0.093 |

As shown in the total column of the mass balance, all of the feeds close the mass balance within 89%. The losses of mass are due to char sticking to the inside of the reactor after HTL, mass left on the spatula used to scrape the reactor after reaction, and losses to pouring the contents into the filter for extraction. In order to minimize the losses as much as possible, the reactor was weighed when clean and empty, and then during the extraction process the reactor after HTL was weighed multiple times. Extraction of the reactor contents was stopped once the weight post reaction and pre cleaning was within ± 0.5 g of the original cleaned weight.

## GCMS Analysis

The composition of the biocrude oil made from food waste and green waste needed to be understood since the feedstock mixture is a combination of cellulose, hemicellulose, and lignocellulose from the green waste and carbohydrates, lignin, and proteins from the food waste. Due to the mixture of compounds in the bio-crude the reaction chemistry is complex as various reactions take place to transform the feedstock into the bio-crude and other byproducts (Gollakota et al., 2019). Characterization of the final compounds is necessary to help understand and quantify the reactions taking place during HTL.

It was thought that the food and green wastes would create different compounds in the oil due to the different macromolecule makeup of food versus mulch. Samples of biocrude oil mixed with pure acetone were taken at 10-minute time intervals in the extraction process to see how the concentrations of the compounds changed with evaporation and which ones did not get stripped off with the acetone.

The GCMS graph for biocrude oils from 100% food waste, 100% green waste, and 50 50 food and green waste are shown in figure 3.

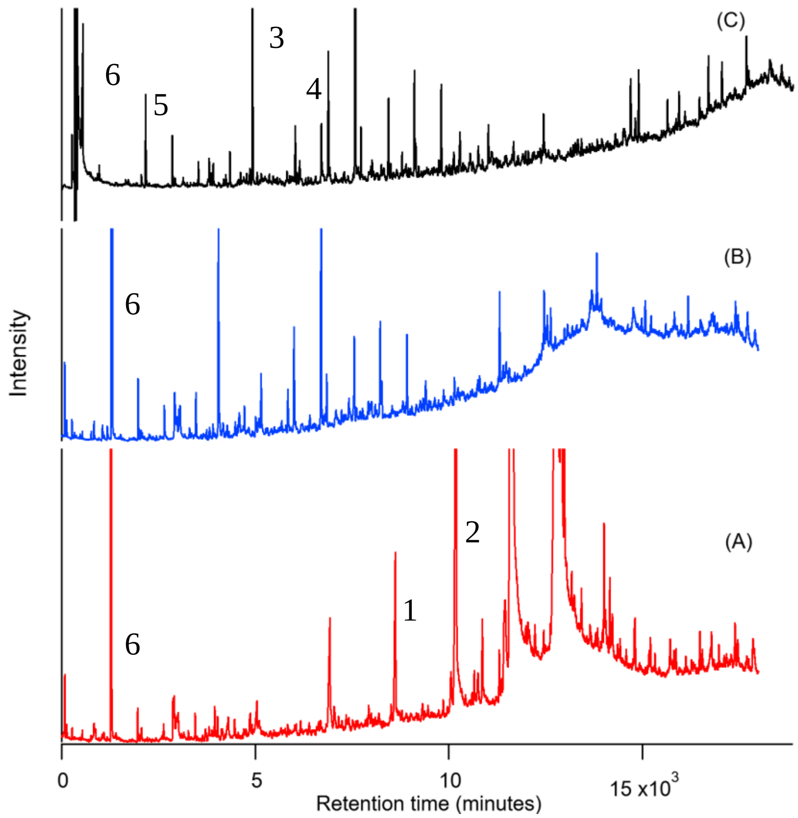

**Figure 3**: GCMS analysis for three different combinations. (A) 100% food waste (B) 50 50 food and green waste (C) 100% green waste

The GCMS shows that the compounds in the biocrudes differ depending on the waste used. For the 100 % food waste runs, the main compounds shown in the GCMS in Figure 3 (A) were long chain fatty acids and amides, shown by peak 1 and 2 respectively. This can be attributed to the large amounts of cellulose, hemi-cellulose, and starches present in the food waste. 100 % green waste demonstrated some of these compounds, but very little as their peaks are smaller in Figure 3 (C). The main components in the green waste was aromatics, phenols, and ketones, shown by peak 3, 4, and 5 respectively. These compounds are present due to the different carbohydrates found in the green waste which are cellulose, hemi-cellulose, and lignocellulose. Peak 6 shown in

Figure 3 A-C is due to impurities in the acetone used as a solvent for the GCMS, since there are needed characterization peaks near by the impurities, it is very difficult to try to use the timing on the method file to cut out these impurities while keeping the nearby peaks. The 50 50 food and green waste run in Figure 3 B has peaks that are similar to the green and food waste runs above and below it. This demonstrates that while going through the HTL process, the food and green waste interact both together and separately, creating new compounds and keeping ones the same. With large similarities in the 50 50 GCMS, it is thought that the two compounds tend to react separately more than together during HTL.

### @Risk Model Predictions

Once the @risk model was run, the prediction curve shown in Figure 4 was obtained.

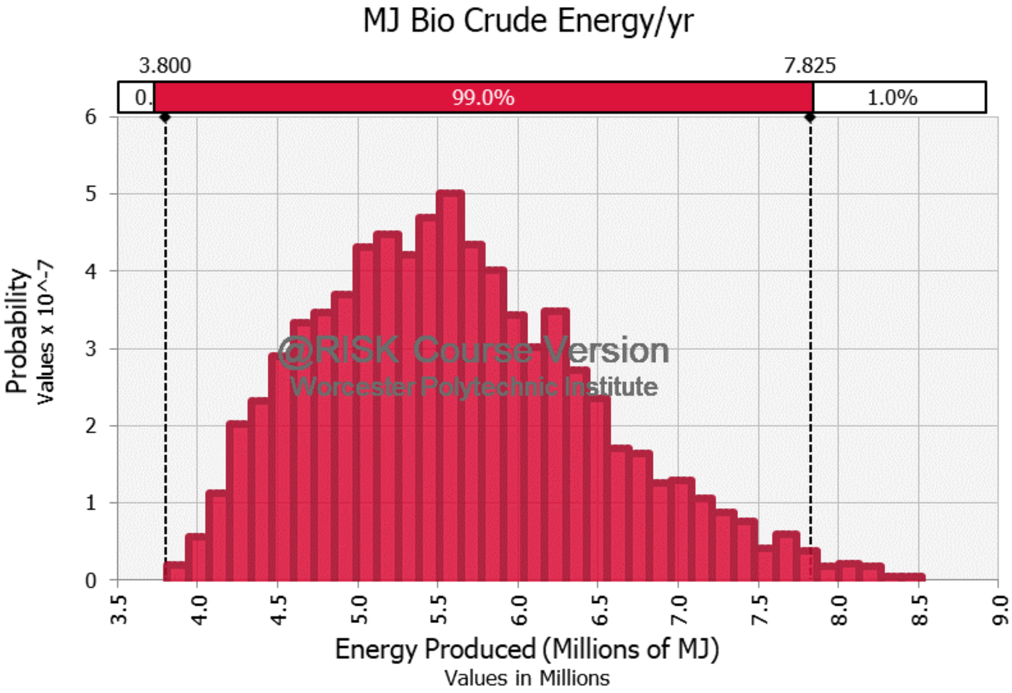

**Figure 4:** @risk prediction histogram of MJ bio-crude energy/ yr that can be made at WPI assuming 100% of the food waste created on campus is used. The y-axis is the probability, and the x-axis is MJ energy/yr.

From this histogram, the mean value is 5,610,893 MJ energy produced/ yr. This would offset all the fossil fuel usage from WPI’s leased and owned vehicles for a year. Saving the university $91,000 annually on fuel costs and offsetting their GHG emissions by 27 million lbs. $CO_2$ per year.

Although these figures are fantastic and would help WPI and the planet, it is unlikely that this value would be seen. As WPI is making the energy, unused bio-crude that is created does not help the university since it will not be used for the vehicles and takes time and energy to create. Therefore, the probability curve shown in Figure 5 was generated from the histogram in Figure 4 to see the probability of producing just enough for WPI to use.

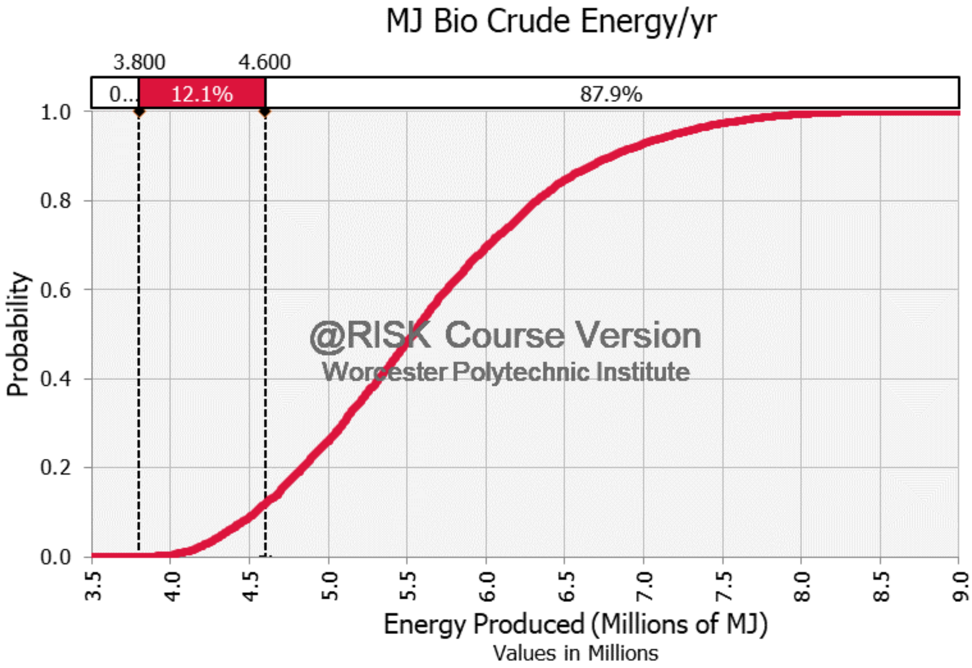

**Figure 5:** Probability curve generated in @risk showing how likely it is to create enough energy to off-set WPI's vehicle fuel usage without creating more than is needed. The x-axis is amount of energy produced in millions of MJ, and the y-axis is the probability

There is a 12.1% probability of WPI producing enough bio-crude to cover just their vehicle fuel usage. This probability is extremely low and does not seem likely, although as shown in Figure 4, there is a high probability of creating enough bio-crude to cover 5.5 million MJ of energy annually. To raise the probability of covering the fuel usage entirely more sources that could use bio-crude should be added to the study, for example furnaces used to heat buildings. If these sources are considered as well, WPI's energy need goes up and the probability of producing just enough to cover the need would be greater.

Additionally, this simulation was run using bio-crude oil yields, for this bio-crude to be used in vehicles it would have to be upgraded. Although the HHV for the upgraded bio-crude would only be better, some of the upgraded biofuel should be used to power both the reactor and the upgrading process to not increase electricity usage at WPI.

The biogas produced from the HTL process and the solid char that is a waste byproduct can be used as well. The biogas can be upgraded as well to use as heating gas for the reactor or the university. Again, some of this gas should be used to power the process and a future analysis on how much biogas can be produced by this process should be done to ensure that it is feasible when it comes to energy production. The char byproduct can be used as a fertilizer on campus instead of the traditional nitrogen-based fertilizers. Hydrochar from HTL has been studied as a fertilizer in the past and

## Conclusions

From the mixed feedstocks, the 75 % food waste 25 % green waste ratio was the most optimal for producing large amounts of oil yield. HHV from ratio to ratio did not differ drastically and carbon content in all components was within the same range for each ratio as well. The high green waste ratios, 50 50 and 25 75, were the worst when it came to bio-crude yield. This could be due to the high amounts of ash produced by the green waste during HTL and the low amounts of food waste present to react with it.

The mass and carbon balances closed within 89% and 85% respectively which shows that during the process a majority of the components are accounted for. Most of the mass is lost due to transfer from the reactor to the filter in the extraction process. Minimizing this by using a spatula with a covering to stop the solid products from sticking to it or by pouring washing with acetone would help but would ultimately not completely get rid of this loss. Reactor losses could be minimized by washing the reactor with acetone before filtering but there is a risk that aqueous phase would be in the acetone and end up in the evaporating flask. This is not ideal as the acetone evaporates faster than the water and leaving the bio-oil on the roto vape for too long results in the oil getting burnt and stuck to the sides of the flask.

WPI has the potential to drastically reduce its fossil fuel consumption using the food and green waste generated annually on campus in HTL. A 100% reduction in the carbon dioxide emissions and reducing the methane emissions from the food and green waste decomposing in landfills will minimize WPI’s carbon footprint and help to save the campus money. With the average amount of food waste generated on campus currently, WPI over produces the amount they need to just cover vehicle fuels. The probability of producing just enough with no extra is very small, so to overcome this WPI should try to use the extra fuel produced in other places on campus like in furnaces to heat the buildings and to power or heat the HTL reactor.

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## Appendices

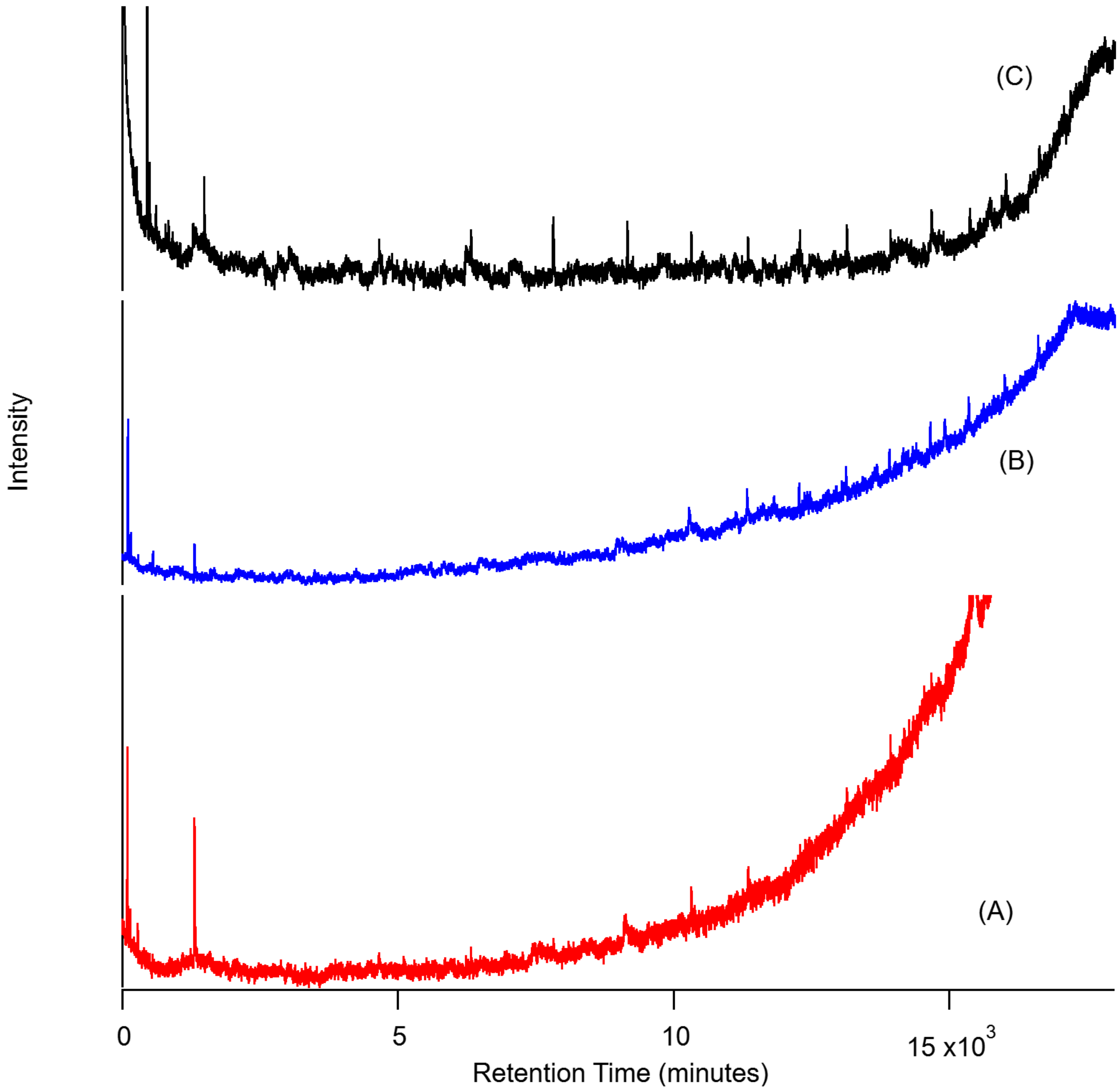
### Appendix A: Table of food waste preparation data

| | Weight (g) | Moisture Content (%) |
|---|---|---|
| American Cheese | 23.3 | 0 |
| Green beans | 415.5 | 93.5 |
| White Rice | 34.5 | 0 |
| Instant Potatoes | 19.2 | 0 |
| Butter | 9.8 | 0 |
| Applesauce | 342.6 | 88.2 |
| Canned Chicken | 82.3 | 67.3 |
| Water | 41.5 | 100 |

## Appendix B: Food to Green Waste Feedstock Combinations

| | Food waste (g) | Green waste (g) | Water (g) |
|---|---|---|---|
| 100:0 | 100 | 0 | 0 |
| 75:25 | 42.06 | 14.02 | 45.89 |
| 50:50 | 19.48 | 19.48 | 63.77 |
| 25:75 | 7.46 | 22.39 | 73.28 |
| 0:100 | 0 | 24.19 | 79.19 |

## Appendix C: Waste acetone GCMS data



GCMS data for stripped off acetone from evaporating. (A) is acetone from 100% food waste (B) is acetone from 50 50 food to green waste and (C) is 100% green waste