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Waste to Energy: Understanding the Effects of Radical Initiators, Hydrothermal Liquefaction Pathways

A Major Qualifying Project submitted to the faculty of WORCESTER POLYTECHNIC INSTITUTE in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemical Engineering

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April 22, 2024

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Abstract

The central focus of this project is to promote a circular economy by converting waste to energy. Utilizing energy dense waste feeds: green waste and food waste —namely, lignocellulosic matter, carbohydrates, and proteins— converting these into a valuable bio-crude precursor for fuel, thus achieving clean energy production. In this way, addressing the UN Goals 7 and 12 by tackling various issues such as the need for sustainable energy, and responsible consumption and production. To achieve this the technology utilized was Hydrothermal Liquefaction, a sustainable method, and more energy efficient than competing technologies. The focal point was targeted towards optimizing reaction times, temperatures, determining the effects of hydrogen peroxide (when used as a promoter for the reactions), and finding the ideal feedstocks. Overall, the main goal is to devise an optimal system for HTL, maximizing the yield and quality of the produced biocrude. The main findings from this research were that the radical initiator hydrogen peroxide reduced the amount of biochar but had no substantial impact on the biocrude. The optimal conditions for the best production of biocrude were found to be: HTL with the mix of food waste and green waste, more specifically PKFW+AGW, in a 3:1 ratio, with a temperature of 300°C, and a reaction time of 60 minutes. This is on account of it having an average organic oil and mass yield, while simultaneously having a high carbon percentage (of about 70%) in the oil. Note that this research experience was translated into lesson plans for high school level chemistry.

Keywords: Hydrothermal Liquefaction (HTL), waste to energy, circular economy, biocrude, biochar, renewable energy

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Acknowledgements

Thank you: Advisors, CHE partners, RET fellow teachers and staff, for all the help and guidance throughout the research, without you this wouldn't have been attainable. This material is based upon work supported by the National Science Foundation under Grant No. EEC-2055507, and the U.S. Department of Energy.

1. Introduction

Biomass consists of organic matter from plants and animals, stands as our planet's sole source of renewable carbon (Serrano-Ruiz, 2020). It's a natural alternative to fossil fuels in producing a wide range of chemicals, but more specifically fuel precursors. Biomass components (such as starches, sugars, lipids, and lignocelluloses) are rich in oxygen, highly reactive, and energy dense. Combining feedstocks has demonstrated to have a greater capability of diverting a larger volume of waste (LeClerc, 2022). Which reduces transportation costs associated with a larger range of co-located waste feeds, and addresses feedstock variability by “engineering” a more consistent blended waste.

There are multiple viable sources of biomass, but this research's central aim is established on waste sources (such as food and green waste) as a raw material. Given that waste is a result of an error in design, our society has been stuck in the mentality of “we do not have to reinvent the wheel”, but it is time we do for more conservation efforts. The prevailing waste crisis reflects unsustainable practices, urging for reinvention and conservation (HADJIOSIF, 2020). While climate change's severity is sometimes downplayed by corporations protecting their interests, marginalized communities bear the brunt of its impacts, as evident by the environmental injustice (Keane, 2020; PSCI Patnaik et al., 2020). Addressing these disparities aligns with the United Nations Sustainable Development Goals (UN SDGs), especially UN SDG 7 and 12.

This project focuses on converting food and green waste into clean energy (bio-crude), contributing to UN SDG 7's aim of accessible and sustainable energy, thereby mitigating climate change and fostering equity in environmental matters. UN SDG 12 emphasizes the significance of changing consumption and production behaviors, with a focus on the growing problem of Municipal Solid Waste (MSW) generation. Furthermore, the process utilized to convert the waste into energy is Hydrothermal Liquefaction (HTL), since it provides a compelling solution for biomass conversion due to its innovative approach and numerous advantages. Notably, HTL excels in efficiency, surpassing competing techniques for converting low-value biomass into renewable energy and chemicals, being a step closer towards reduced reliance on fossil fuels.

Nonetheless, there is still a research gap regarding the impact of adding hydrogen peroxide (H_2O_2) as a promoter (also described through this paper as HTL+) to the HTL method and evaluating its effects with different feedstocks. There is much inquiry as to how different types of

green waste behave on its own and combined with diverse food waste. The information presented above prompted the project's initiation, and there is still further investigation needed to achieve an optimal system for HTL.

2. Background

2.1) Waste-to-energy & United Nations Sustainable Goals

For many years, we have continued with the same unsustainable practices which have exponentially been consuming all the Earth's resources and our planet as a whole, erasing life gradually. Large corporations have been known to fund misinformation campaigns or downplay the severity of climate change to protect their interests and avoid regulatory changes that could impact their profits (Keane, 2020). However, they are not the ones that get directly affected by climate change, because there is no environmental justice. Hence, this climate crisis disproportionately affects marginalized and vulnerable communities around the world, often exacerbating existing inequalities (PSCI Patnaik et al. 2020). In view of the fact that such communities have limited resources to adapt to the changing climate. For example, areas with lower socioeconomic status have elevated pollution levels in comparison to wealthier neighborhoods, which also demonstrates a larger benefit in minimizing the risk of exposure to pollutants (Brazil, 2022).

Moreover, recognizing these environmental and social disparities is essential to achieve the UN SDGs which purpose is to eradicate poverty, conserve the environment, and guarantee a more equitable sustainable future for all (United Nations, n.d.). This project brings us a step closer by focusing primarily on the UN SDG 12 "Responsible Consumption and Production", and UN SDG 7 "Affordable and Clean Energy". UN SDG 12 highlights the need to modify our consumption and production habits to make them more sustainable and effective. This is crucial considering the data which shows that in 2018, the total amount of MSW produced reached 292.4 million tons, up 23.7 million tons from the 268.7 million tons produced the year before and a significant increase from the 208.3 million tons produced in 1990 (EPA, 2022). MSW is a problem because of the excessive production and inadequate management of garbage, which has many harmful causes such as: resource depletion, environmental degradation, health concerns, greenhouse gas emissions, economic hardship, and social inequalities.

Additionally, of all the solid waste accounted in 2018 more than 30% was made up of food waste and green waste which are sources of renewable energy due to their chemical composition. For these reasons, to lessen the damaging effects MSW has on the environment and society, this project uses food and green waste as a raw material for clean energy (xbiocrude) generation. The production of energy also ties back to the UN SDG 7 which focuses on providing access to clean, affordable, and sustainable energy. This is another key factor in mitigating climate change and promoting environmental equity since despite many advances it is expected that by 2030 there will still be 679 million people without electricity. Also, the current reliance on traditional polluting energy options requires the burning of fossil fuels for energy production. This is a major contributor to greenhouse gas emissions, leading to global warming, and its adverse effects. Therefore, there is a pressing need for innovative sustainable alternatives.

2.2) Hydrothermal Liquefaction (HTL)

This section delves onto the HTL variations and parameters that can be altered for optimization of its reactions to obtain a greater biocrude quality and yield.

2.2.1) What is HTL?

HTL is a water aided process that uses elevated temperatures from 250°C to 400°C and pressures above 400psi (LeClerc, 2022). It can convert wet biomass such as waste into energy-dense-biocrudes or other valuable products, following the law of conservation of mass. The elevated temperatures and pressures break down the organic material into four phases: liquid, solid, gaseous components, and bio-crude oil. This bio-crude can then be refined into transportation fuel or used as a raw material in other chemical processes. HTL has increasingly developed as a means of converting wet and low value biomass into renewable energy and chemicals, offering greater efficiency, and versatility compared to traditional processes. Thus, it's an energy production source that reduces the dependency on fossil fuels.

The HTL procedure is ecologically sustainable as it avoids the use of detrimental solvents and achieves high energy efficiency (Aarhus University, 2013). This elevated temperature liquefaction technique consumes merely around 10-15% of the energy contained within the initial biomass due to the efficient recycling of heat energy during both the heating and cooling stages of the process medium. It is advantageous given that it operates under such conditions that allow for high moisture content feedstocks, which prevents energy-intensive feedstock drying. Previous

research has proven that this allows HTL to have a greater energy recovery, hence being more energy-efficient, and cost-effective than competing technologies (Yang, 2017). Although HTL has benefits in terms of the moisture content of the feedstock, it still needs energy to attain the elevated temperatures and pressures required for the conversion process. However, this has a great potential to be a circular economy, since it follows the waste hierarchy rule, has demonstrated to be a sustainable, and a resource-effective method for turning wastes of organic material into biocrude (Govindasamy et al., 2022). The circular economy is strengthened by decreasing waste, environmental impact, and adding value to underused resources that are renewable.

2.2.2) Radical Initiators

The weak bond of a molecule is what makes it a radical initiator because it enables it to break more easily by homolytic cleavage. The radical initiator doesn't involve any of the propagation steps (Chemistry LibreTexts, 2016). Its main purpose is the startup of a chain reaction, thus being the reactant in the initiation step. Only negligible amounts of radical initiator are utilized to promote a reaction, because it only needs to create the initial radical in the reaction to then be depleted.

For this research, the radical initiator used was hydrogen peroxide H_2O_2 . Peroxides are good for this matter given that the oxygen bond can undergo homolytic cleavage with ease. This is identified by the bond dissociation energy. The enthalpy for the bond dissociation of the oxygen bond in peroxide was determined to be 45 kcal/mol (Bach, 2020). Hence, H_2O_2 serves as a thermal radical initiator in this project. Due to it having a low bond dissociation enthalpy, meaning the bond is weak, and it can create free radicals as well as enabling radical reactions.

2.2.3) What is HTL+?

HTL+ is an attempt to achieve an upgraded version of HTL, using the radical initiator - H_2O_2 as a promoter. Since it was expected that the H_2O_2 will alter the partitioning of molecules, lowering char formation and increasing bio-crude oil yield. The amount of H_2O_2 added to the reactor must be carefully considered to ensure that the ratio between the moles of carbon to the moles of oxygen is appropriate, because if there is too much oxygen it can lead to gasification of CO_2 . Nevertheless, if it is well balanced there is the capability to break the chemical components of the feed, to produce more bio-crude.

Furthermore, in earlier studies H_2O_2 has been proven to improve the byproducts' characteristics, such as activating the biochar. Enhancing it in such a way that allows it to be an efficient sorption medium in filters and reactive barriers to clean water, for example eliminating lead (Xue et al., 2012). In addition, it has also shown effectiveness in achieving higher biocrude yields, and accelerating liquefaction rates (Wu, 2022). The GC-MS analysis has illustrated the formation of new substances providing a path for turning biomass into valuable fine chemicals.

2.2.4) Feedstocks

The inputs of HTL create an impact in the outputs, especially the solids loadings that go into the reactor. Multiple feeds of biomass can be used for the HTL process, some examples include algae, green waste, sewage sludge, food waste, poplar sawdust, manure, among others; but some can produce a higher oil yield and quality. What makes a good feedstock is their chemical composition, for example carbon sources are great energy producers because it can achieve a higher percentage of carbon in the bio-crude oil, hence a better oil quality. In this research the focus was directed towards green waste and food waste, given that we want to contribute to achieving the UN SDG 7 and 12, reducing waste and producing energy.

Green waste is predominantly comprised of cellulose, hemicellulose, and lignin. In a previous study, from the lignocellulosic biomass the lignin composition in it has exhibited a correlation to biocrude formation (Wang, 2023). The limitation of green waste is that it is more resistant to heat, due to higher thermal resistance of cellulose, hemi-cellulose, and lignin (Murphy, 2020). On the other hand, food waste generally consists of around 40–60% carbon, mainly found in starch, proteins, and particularly lipids (LeClerc, 2022). The lipids were found to be the primary influencer in the synthesis of biocrude (Kumar, 2022). Within a hydrothermal setting, proteins and lipids undergo conversion at a more rapid rate compared to cellulose and lignin.

2.2.5) What is Co-HTL?

It refers to the co-processing of feedstocks, for an optimized HTL. In prior research, the combination of green waste and food waste has been analyzed, when food waste and green waste are co-processed in the reactor, their interaction appears to result in distinct individual effects rather than a combined effect, leading to the production of similar components as evident from the GCMS analysis (Murphy, 2020). As shown below in figure 1, mixed feedstock HTL shows promising results, since combining high lipid food waste with cellulose rich green waste in HTL

yields biocrude quantities above 45% and achieves higher than 50% energy recovery (LeClerc, 2022).

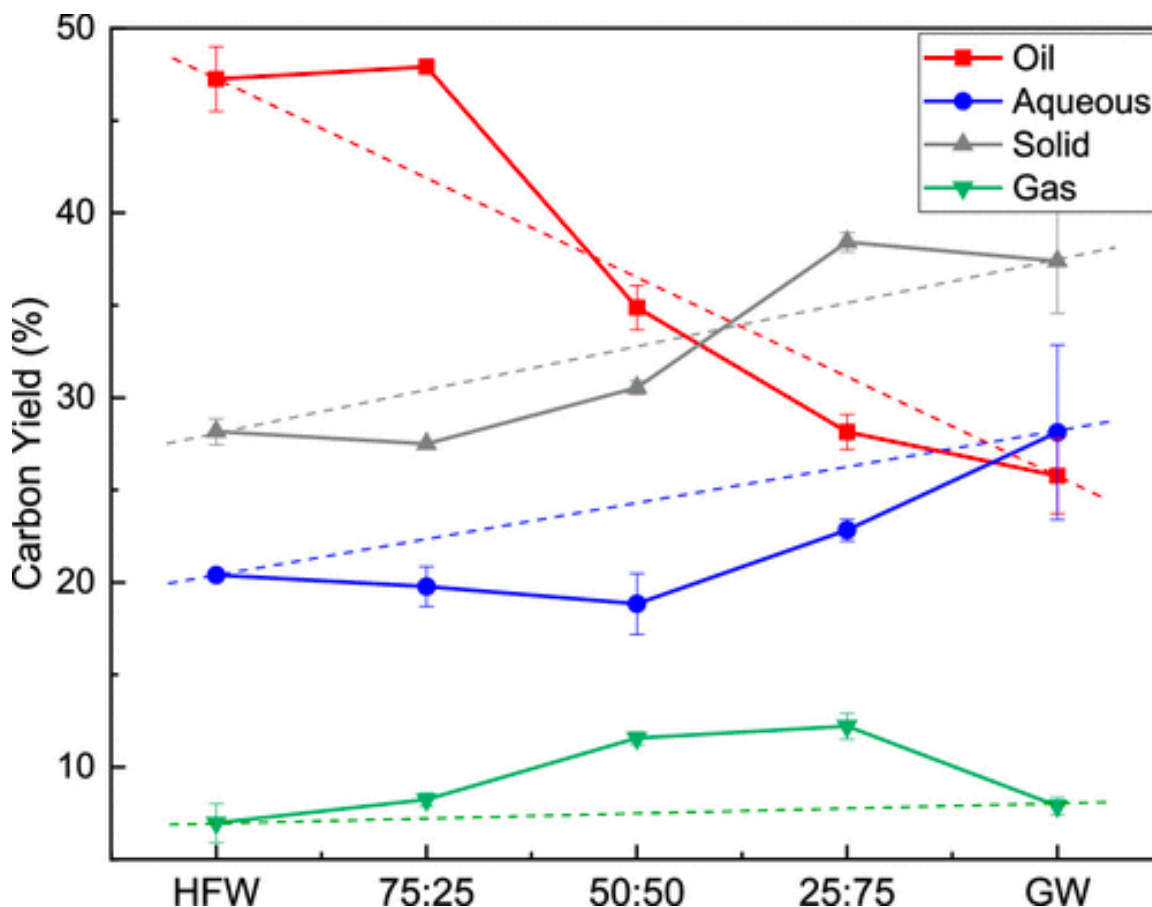


Figure 1. HTL carbon product yields, for mixtures of food (HFW) and green waste (BDP), greater oil yield was found utilizing a food waste to green waste ratio of 75:25 sample (LeClerc, 2022).

These feedstock combinations revealed specific chemical behaviors that improve oil production at reduced blend ratios via esterification, Maillard reactions, and polymerizations. The synergistic energy created by the mixture of food and green waste in a ratio of 75:25 surpasses that of the theoretical trend, as observed in figure 1. Based on these previous results the ratio of food and green waste was kept the same for this research.

2.2.6) Byproducts and Implementation

In a large-scale production of bio-crude, it would be ideal to implement a continuous process with continuous stirred tank reactor (CSTR), plug flow reactor (PFR), and/or recyclers, where the gas that the reaction produces can be collected and used in future HTL runs, and nutrients from the aqueous phase can be utilized in the making of the bio-crude add value by enhancing its

quality. Multiple iterations of what this would look like have been analyzed in the scientific article “Best Practices for Bio-crude Oil Production at Pilot Scale Using Continuous Flow Reactors” (Cheng et al., 2022). For this research, HTL is performed in a smaller scale batch reactor. To give the byproducts a second life, a carbon cycle was evaluated in a prior Major Qualifying Project (MQP) by Caroline Murphy, as illustrated in figure 2.

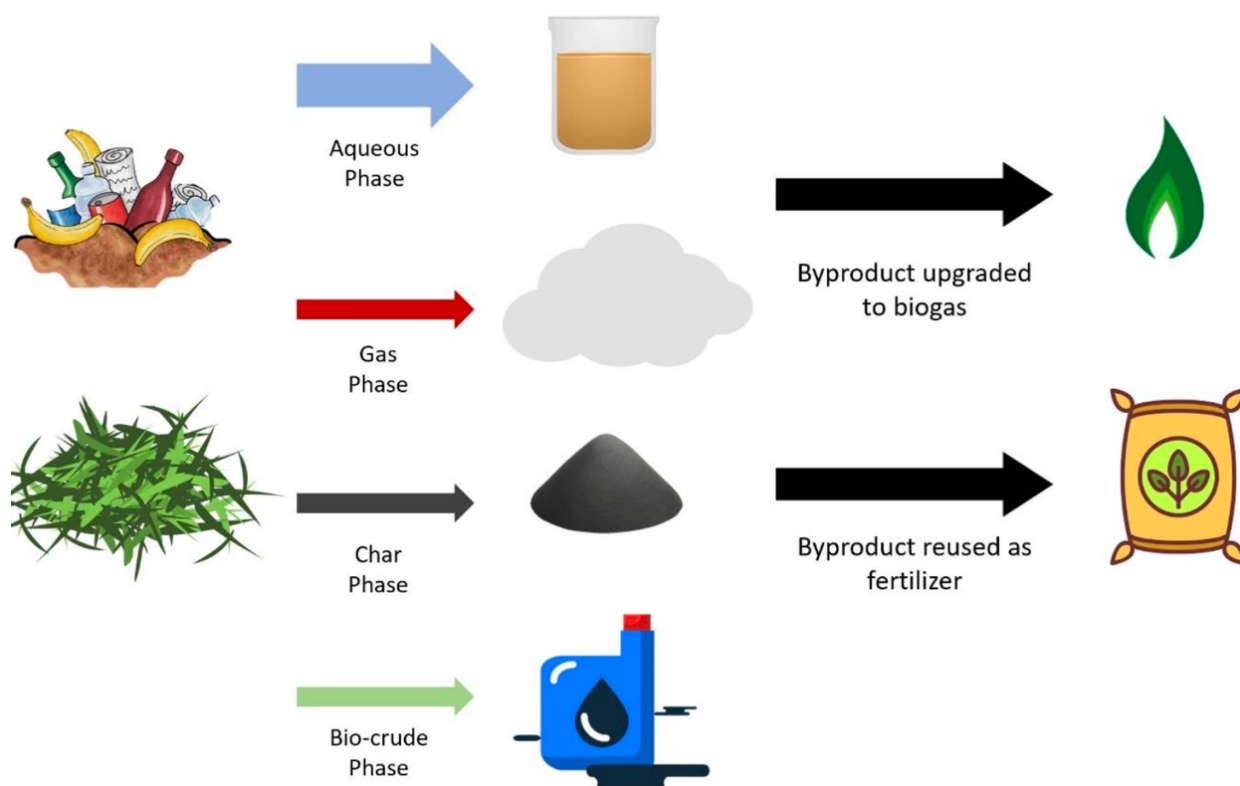


Figure 2. Byproducts and implementations, tracing of the carbon cycle with the arrows size being representative of the amount of carbon pertaining to that phase (Murphy, 2020).

The applications of these byproducts are many more and have been carefully reported in multiple research papers (Liu et al., 2019). The aqueous phase can be converted into biomethane by anaerobic conversion, strengthening the retrieval of energy and nutrients while advancing the commercial adoption of hydrothermal liquefaction. Also, the aqueous phase offers the potential for transforming carboxylic acids into chemicals through condensed phase ketonization using catalysis, along with various methods for converting it to hydrogen gas (Lopez-Ruiz et al., 2019). The gas phase byproduct as depicted in the diagram above it can be upgraded to biogas, and this

can be then applied to produce both electricity and heat for use in power plants, rather than for use in vehicles because that would require further processing (U.S. Department of Energy, n.d.).

Nevertheless, the char phase has more applications which could benefit our environment. For example, it promotes redox reactions which contribute to environmental restoration of the soil by absorption of heavy metals and dye (Kumar Ponnusamy, 2020). The biochar is known to be capable of cleaning hazardous chemicals from the wastewater such as: COD, nitrate, ammonia, and phosphate. Hence, is a favorable and economical substitute for addressing remediation needs, that can also be implemented in anaerobic reactions. It's important to note that biochar produced through HTL at lower temperatures, as opposed to higher temperatures could be suited for other energy applications.

2.3) Competing Technologies

This section delves into the HTL competing technologies, which also enable a Thermo-Chemical Conversion (TCC) for fuel production from biomass. The primary technologies encompass pyrolysis, torrefaction, gasification, direct combustion, and supercritical fluid extraction (Dimitriadis et al., 2017). In 2022, biomass contributed nearly 5% to the total primary energy consumption in the U.S., serving roles in heating, electricity generation, transportation fuel, and being a crucial energy source for cooking and heating in developing nations (U.S. Energy Information Administration, 2023). An attempt to increase sustainability is done by implementing HTL and the following technologies:

2.3.1) Pyrolysis

Pyrolysis breaks down biomass with the primary goal of producing liquids for fuel or chemical applications, achieved through the decomposition of complex hydrocarbons into smaller molecules in the absence of oxygen (Basu, 2018). This process for biomass is usually conducted within a temperature range spanning from 300 to 650 degrees Celsius. Pyrolysis is a rapid heating process where biomass or feedstock is subjected to high temperatures without air, resulting in the formation of non-condensable gases, solid char, and liquid product. This breakdown is influenced by factors such as temperature and heating speed, involving reactions in both gas and solid phases that lead to the formation of smaller molecules and permanent gases. It plays a crucial initial role in gasification, producing a denser solid product compared to the original biomass, while generating less energy-dense liquid and gas products. A pyrolysis plant using a fluidized bed

system employs heated solids to warm the biomass, extracting both condensable and non-condensable vapors, ultimately yielding biooil and product gas, respectively.

Table 1: Pyrolysis vs. HTL, contrast of their main variations (Dimitriadis et al., 2017).

	Pyrolysis	Liquefaction
Drying	Necessary	Unnecessary
Pressure (MPa)	0.1–0.5	5–20
Temp (°C)	370–526	200–400
Catalyst	No	Sometimes
Heating Value	Low (~17 MJ/Kg)	High (~30 MJ/Kg)
Oxygen content	High	Low
Water Content	High	Low

Drying the feedstock is necessary for pyrolysis, thus it suffers from reduced economic returns due to the higher energy consumption it requires to dehydrate the wet feeds. In addition, pyrolysis rarely involves catalysts, while HTL employs solvents as catalysts leading to higher-quality products. HTL products contain lower oxygen and moisture content and a higher heating value compared to pyrolysis products, resulting in decreased handling and storage costs, hence making HTL a more viable option for biomass conversion to fuels.

2.3.2) Torrefaction

A subtle variant of pyrolysis is torrefaction, a process in which biomass is heated within a specified temperature range from 200–300°C using an appropriate heating medium to increase the energy density of the biomass (Basu, 2018). The product that is torrefied retains a higher percentage of the original energy of the biomass. The heating medium used in a torrefaction process may be a hot material or gas. The commercial method is usually dry, but wet (or hydrothermal) torrefaction uses compressed hot water to heat biomass. The process proceeds through stages of drying, heating, and chemical degradation, resulting in color change and mass loss. The final product is more energy dense but less energy yielding.

2.3.3) Additional practices

Other techniques for converting biomass into energy include direct combustion, gasification, and Supercritical Fluid Extraction (SFE). Direct combustion of biomass is often utilized to generate energy and is one of the most common methods (Dimitriadis, 2017). To generate high-pressure steam, biomass is burnt in a boiler using temperatures from 800–1000°C. This steam pours over a set of turbine blades, spinning them. The turbine's spin powers a generator, which generates energy (U.S. Department of Energy, n.d.). The biomass must be pretreated and for this reason it has a high energy consumption (Kee Lam, 2019).

Another process is biomass gasification, which typically occurs in temperatures from 800–900°C that allows it to convert biomass into synthesis gas, which mostly consists of hydrogen, carbon monoxide, carbon dioxide, and methane (Basu, 2018). While it is adaptable to many types of biomasses, the result is a gas that requires more processing, such as Fischer-Tropsch synthesis, to be converted into fuel. Additionally, Supercritical Fluid Extraction (SFE) is a process for separating components that uses supercritical fluids as a solvent. This approach is used in a variety of sectors, including separating biological fluids, extracting petroleum, processing coal, and purifying perfumes and oils from diverse items. The utilization of high pressures in SFE, on the other hand, results in increased operating and capital costs for the companies that execute this process.

3. Methodology

This project's aspiration was to convert waste into energy in a sustainable manner to be a step closer in attaining the UN goal number seven, which focuses on providing low cost and modernized green energy. As well as promoting the UN goal number 12, for responsible production and consumption. While simultaneously having a positive impact primarily in students completing high school chemistry; given that the research experience was translated into the chemistry classroom with different activities to expand the awareness of climate change, UN goals, and participation of the students in engineering together with real world problems. To accomplish the final goal the following objectives were addressed:

1. Conduct experimentation in the lab performing HTL at different temperatures and times, for optimization of the biocrude production utilizing green waste.

- Convert the research performed in the lab into lesson plans following the standards of high school chemistry for interactive learning.

This chapter depicts and justifies the strategies utilized to attain these objectives.

3.1) Objective 1 – HTL Transformation of Energy

Transformation of Energy

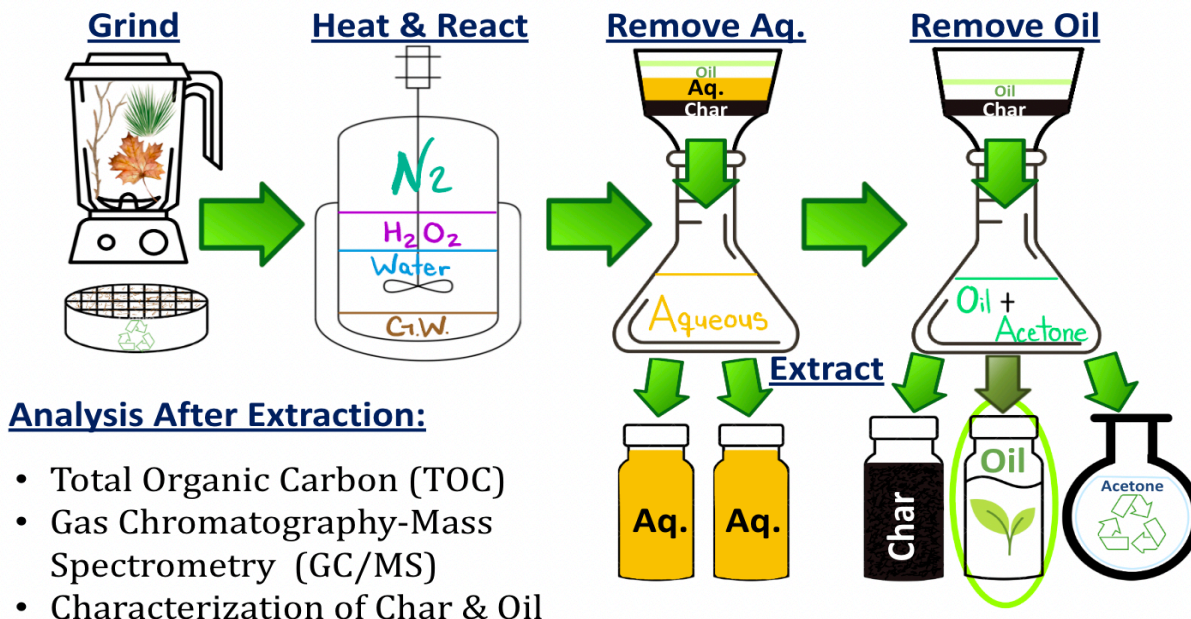


Figure 3. Visual description design of the methodology utilized to achieve the transformation of energy.

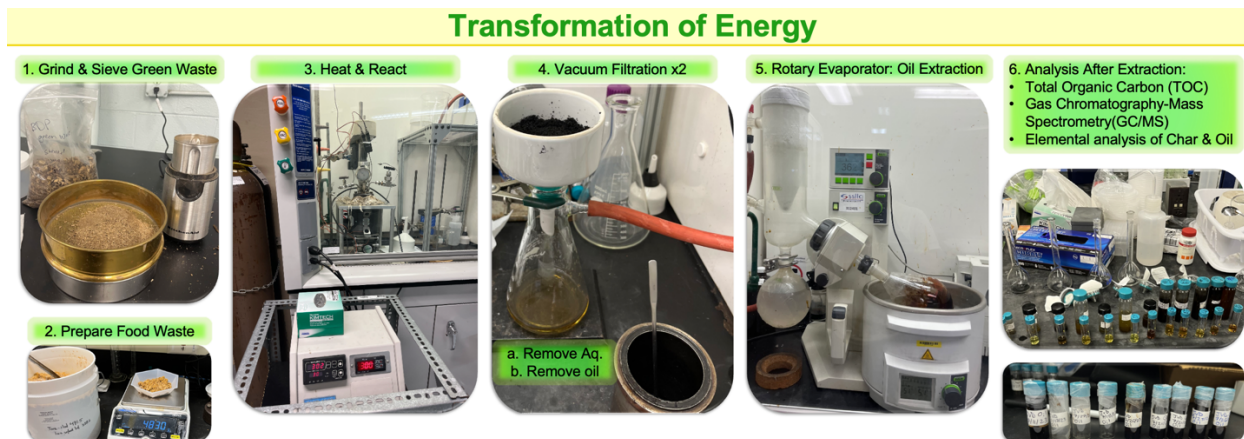


Figure 4. Visual description with images of the lab illustration the methodology used to transform energy.

3.1.1) Materials

This section discusses the main materials utilized for this research:

- BDP – BDP Industries Green Waste (composed mainly of wood chips/sticks)

The green waste, referred to as BDP in this paper, was acquired from BDP Industries Inc., in Greenwich, NY. This green waste is composed of mainly woods chips and sticks; it has a carbon percentage of 42.2%. It was initially placed in air-tight bags and stored in a freezer at a temperature of $-20\text{ }^{\circ}\text{C}$. To prepare the green waste it was dried, ground, and sieved to a particle size of $<0.85\text{ mm}$, since a higher particle size has proven to be less effective (Carlson REU, 2022).

- AGW – Athens Green Waste

The Athens Green Waste referred to in this paper as AGW was acquired from Athens Services, in Irwindale, CA. This green waste is composed mainly of yard clippings and has a carbon percentage of 45.9% (BETO Project, 2022). It was received in a bag already dried.

- PKFW – Prison Kitchen Food Waste

The prison kitchen food waste referred to in this paper as PKFW was acquired from Coyote Ridge Correction Center. The PKFW was stored in a freezer at $-20\text{ }^{\circ}\text{C}$ prior to use, it wasn't dry hence it had a moisture content of 77%, and a carbon percentage of 49.3%.

- HFW – Hospital Food Waste

The hospital food waste was acquired via Greener Chemistry LLC from a veteran's hospital cafeteria. To grind and dry the food waste an Ecovim dehydrator was utilized. The HFW was also stored in a freezer at $-20\text{ }^{\circ}\text{C}$ prior to use and had a carbon percentage of 56%.

Table 2: Chemical composition of the feedstocks utilized mentioned above (BETO Project, 2022).

	Green Waste (BDP)	Green Waste (AGW)	Prison Kitchen Food Waste (PKFW)	Hospital Food Waste (HFW)
Proximate Analysis (wt.%)				
Moisture	0.10 ± 0.05	4	76.7	0.7 ± 0.1
Ash	14.7	1.20	5.83	1.9 ± 1.9
Elemental Analysis (wt.%)				
Carbon	42.2	45.9	49.32	56
Hydrogen	5.2 ± 0.3	5.9± 0.2	7.27	7.5 ± 0.2
Nitrogen	0.2 ± 0.1	0.5± 0.2	3.5	4.3 ± 0.1
Sulfur	0.7 ± 0.2	0.5± 0.1	1.2	1.0 ± 0.1
Oxygen	52.0 ± 2.0	51.2	32.88	33.2 ± 2.1
Biochemical Analysis (wt.%)				
Total carbs	52.1	54.40	53.9	29.8
Glucan	34.1	39.50		21.9
Xylan	18.0	14.90		1.1
Starch				6.8
Lipids			18.6	38.9
Protein			21.7	26.8 ± 0.6
Lignin	29.6	30.00		
HHV (MJ/kg)	8.8 ± 0.6 (wet) 21.4 (dry)	21.1	21.1	23.6 ± 3.0

□ Additional Reagents

Additional reagents include the following: the water utilized for the reactions was deionized water of an electrical resistivity greater than 18.0 MΩ. Pure acetone >99.5% was used to extract the biocrude, dilute the oil samples (for preparation to perform GC/MS) and cleaning the equipment after the whole HTL procedure was completed. To eliminate the oxygen (flush) and pre-pressurize the reactor nitrogen gas (purity > 99.9%, Airgas) was utilized. If the reaction was HTL+, hydrogen peroxide (30% solution) was added as a promoter. For the GC/MS helium (grade 5.0, Airgas) was used as the carrier gas.

3.1.2) HTL Reaction and Extraction

First, before adding anything to the reactor, the top and bottom part of it were measured. Note all the observations and measurements of the reactions ran were recorded in the “run sheet” (Appendix A, Figure A1). For all the reactions 15%wt of solids was utilized and a mass balance

of approximately 100g. Depending on whether the reaction was HTL+, Co-HTL, or solely HTL, the components added to the reactor would have varied between food waste and/or green waste, and hydrogen peroxide, but all the reactions included DI water with no exception. These were measured to then be added to the bottom part of the reactor, starting with the solids to finally add the liquids. Thereafter, the reactor was assembled and measured the total weight of it as whole. For accuracy all the measurements were taken 3 times. The reactor was clamped tightly in star formation, to ensure the screws get placed evenly in the ring. Then it was placed inside the hood in its stand, attaching to it the heater, stir bar, thermocouple, water-cooling lines, and nitrogen line. The reactor was flushed 3 times before being pre-pressurized to 400psi or 1000Psi with nitrogen gas, to be able to maintain the oxidation level the same in all the trials since it removes the oxygen that might be in the ambient air. After this the reactor was heated up to the desired temperature (ranging from 250°C to 350°C). At the desired temperature, it could react until it ran for the needed time (varying from 20 to 60 minutes).

With the purpose of time efficiency while the reaction was ongoing the materials (funnel+filter paper+stopper, empty aqueous flask, and empty round-bottom flask) needed for the future step of the extraction were measured in the meantime, while simultaneously supervising the reactor and ensuring everything is operating without any issues. Once the reaction was completed the reactor was quenched with an ice bath immediately, lowering its temperature to 30°C or less, to then be depressurized slowly and making sure the fume hood is closed. Having allowed the reactor to cool down, drying the outside of it, and removing the clamps, the reactor was measured again to contrast its weight with the initial one before the reaction was done this allowed to gravimetrically calculate the gas produced.

To proceed with the extraction process, the empty aqueous flask was connected to the vacuum, and set up with the funnel and its components to perform a vacuum filtration. The reactor was opened and the components inside were mixed to then be poured into the funnel, some char stayed stuck in the walls of it thus it had to be scraped with a spatula. After the reactor was empty and there was no more of the aqueous phase emerging with the vacuum the first vacuum filtration was finalized, and the full aqueous flask was measured to then place the liquid in vials for analysis. Around 1000 mL of acetone was acquired for the second vacuum filtration, and a clean bigger flask was attached to the vacuum. Some acetone was added to the bottom of the reactor and the

stir rod to remove and pour into the funnel any additional char that might have remained on such. With the objective of releasing the organic phase of the char in the funnel, an acetone wash was performed allowing for the separation of the compounds. To ensure there wasn't any liquid remaining on either of the vacuum filtrations, it was permitted to operate for some additional time, and in the meantime the reactor top and bottom were measured again to note if there was any remaining yield in it, which can be accounted for in the losses. Later when the funnel was dry, the char product in it was measured. This bio char was placed into gram vials, measured, and placed in the oven to be measured the next day again once it was dry. In this manner the moisture content was calculated by deducting the weight of the char after being dry from the weight before drying.

For the purpose of extracting the acetone from the oil the rotary evaporator (rotovap) was utilized. Beforehand the acetone and oil mixture were poured into the empty round-bottom flask that was previously measured, assuring that it does not get filled up above $\frac{3}{4}$. This flask was screwed lightly on to the rotovap, and then acetone was chosen from the solvent library setting the reactor bath to 50°C. Dry ice was added to the tower until it was completely full (note that the bigger the ice pieces are the harder is for the acetone to be extracted and it will take a longer amount of time). After completing the setup, the rotovap was started with the rotation at level 3. The rotovap had to be performed until there wasn't any more acetone with the oil in the round-bottom flask, this acetone extracted was recycled and used in future runs. When this was completed the outside of the round-bottom flask was dried, and it was weighted now with the oil. However, it is worth noting that sometimes water will remain with the oil, and this had to be placed in a vial to then be put in the oven so that there was an accurate measure of the oil yield. Finally, the oil was collected and placed in a small gram vial for characterization.

3.1.2.1) Run Matrix and Measurements

Table 3: Reactions with green waste alone and the measurements of the inlets for the two types of green waste (BDP and AGW).

Reaction	Feed	Green Waste(g)	Water(g)	H₂O₂(g)
HTL	BDP	15	76.63	0
HTL+	BDP	15	76.63	11.96
HTL	AGW	15	76.63	0
HTL+	AGW	15	76.10	12.70

Note that there was an error in the calculations and for the HTL + reactions presented in this table had 16wt% of solids instead of 15wt%. However, as seen in previous research this doesn't have much impact (Biando, 2022).

Table 4: Reactions with food waste and green waste co-fed in a 3:1 ratio and the measurements of the inlets for the various combinations (PKFW+BDP, PKFW+AGW, HFW+AGW).

Reaction	Feed (3:1)	Food Waste(g)	Green Waste(g)	Water(g)	H₂O₂(g)
Co-HTL	PKFW+BDP	48.30	3.70	47.90	0
Co-HTL+	PKFW+BDP	48.30	3.70	38.47	13.46
Co-HTL	PKFW+AGW	48.30	3.70	47.90	0
Co-HTL+	PKFW+AGW	48.30	3.70	38.30	13.60
Co-HTL	HFW+AGW	11.25	3.75	85.0	0
Co-HTL+	HFW+AGW	11.25	3.75	74.6	14.90

3.1.3) Total Organic Carbon (TOC) Test

For analysis of the aqueous phase TOC was performed, permitting to figure out how much organic carbon was in this phase and complete a carbon balance. To operate the machinery the TOC manual was followed (Appendix B). Nevertheless, the stock standard was already premade hence only the working standards needed to be done. The procedure for it required a 100mL volumetric flask, it was washed with acid (0.5 mL of HCl, rinse w DI 4-5 times) to avoid any impurities. Afterwards a small amount of the aqueous sample was filtered into a small vial to ensure that no small particles of char were carried on. The volumetric flasks were filled halfway with DI water, 50 mL of the sample was added, as well as 1 mL 6 M HCl, and it was filled to line with DI water to then be covered with parafilm and inverted 20 times. From the flasks prepared with the working samples the injector vials were filled.

The TOC machine takes hours to finalize testing the samples, for this reason it was run in the afternoon and the results were viewed the next day. With the results we obtained the Non-Purgeable Organic Carbon (NPOC) value in mg/L, and calculated the carbon content of the aqueous phase in grams as well as in percentage.

Table 5: Sample table of the Excel calculation of carbon content in the HTL+ aqueous phase.

Water Properties	HTL+ BDP 300°C 1hr
Total Water Dilution (wt fraction)	50
TOC Results NPOC (mg/L)	6.951
Undiluted HTL Water TOC (ppm)	$6.951 * 2000 = 13902$
Carbon Content (g/g)	$13902 / (1000 * 1000) = 0.013902$
Carbon Content (%)	$0.013902 * 100 = 1.3902$

3.1.4) Elemental Analysis

To obtain the characterization of the biochar and biocrude, samples of both phases were sent out to Midwest Micro Lab, in Indianapolis or to Micro – Analysis, Inc., in Delaware. Here specialists in the field tested the samples with the technology of CHNS(O) analyzers. When the results (Appendix A, Figures A2 and A3) were received these allowed for the calculation of the oil and char properties.

3.1.5) Gas Chromatography-Mass Spectrometry (GC/MS)

The GC separates the chemical mixture, and the MS identifies the chemical components. The biocrude samples were evaluated using a Shimadzu GCMS-QP2010 SE Gas Chromatography Mass Spectrometer equipment with helium as the carrier gas. The biocrude samples were diluted in acetone to roughly 1wt% (0.1g of biocrude and 10g of acetone), before being inserted into the machine to determine the composition of the light portion. Standards were pre-made to confirm identifications of both retention time and mass spectra match.

When the GC/MS is operated the lighter materials show up faster, hence it must be carefully adjusted so that it does not present the incorrect compounds. For this reason, the method used to test the samples started with a temperature of 35°C and was held for 4min. Allowing the temperature to increase at 5°C/min until it reached 290°C which was the injection temperature and was held for 40min. The total program time was 95min, and the injections were of 1µL. Compounds that eluted from the GC/MS are illustrated by peaks in a graph of intensity vs residence time that's obtained as a result. The peaks are what allows to determine what is the biocrude composed of, must be of 90% accuracy or above when compared to known calibrations of other chemicals, because if not it might be an error due to the GC coeluting with other compounds.

All these previous steps that encompass the objective number one were repeated multiple times to have a set of trials and determine the most optimal conditions for better production of oil, analyzing the data to increase the oil yield and quality.

3.2) Objective 2 – Teaching and Research

This project consisted of two summers of work as well as some sessions during the academic year with different cohorts of Research Experiences for Teachers (RET), which provided the project experience with a variety of perspectives and teaching techniques from diverse expert educators. Over twelve weeks, I attended weekly professional development three hours workshops. Overall, these workshops included, but not limited to: reviewing the Sustainable Development Goals of the United Nations, looking at the elements of high-quality Integrated STEM education, familiarize with the engineering design process and develop ideas about how to include problem-solving in my teaching, identifying the STE standards that are compatible with their study and develop learning objectives, considering the most recent culturally responsive teaching (CRT) techniques and develop plans for incorporating CRT into their lessons, and identifying different STEM occupations and the numerous routes that may be followed to target climate change.

Moreover, I was immersed in numerous academic fields and discovered more of the research being done in other labs of WPI, since as part of RET we had scheduled visits to the locations of Practice Point, Sagamore Labs, Scarlet Shell's lab, among others. Additionally, we had weekly meetings, gatherings and focus groups, where we would all present our progress, learn from each other, have discussions about the lesson plans, and gain feedback. All of this was crucial for professional as well as my personal growth, it allowed me to obtain substantial knowledge from in-service teachers from the Worcester Schools District, by having many conversations about techniques for providing an enhanced education to students.

3.2.1) Lab Experience = Lesson Plans

The lab research aspect of this project was directly connected with the standard PS1: Matter and its Interactions. Therefore, it provided an easier path for the translation of it into the chemistry classroom. The first lesson plan (Appendix D) developed was regarding separation methods, the learning target was the following HS-PS1-11: Design strategies to identify and separate the components of a mixture based on relevant chemical and physical properties (DESE, 2016). The

second lesson plan created was about energy, covering the learning target HS-PS1-4: develop a model to illustrate the energy transferred during an exothermic or endothermic chemical reaction based on the bond energy difference between bonds broken (absorption of energy) and bonds formed (release of energy).

3.2.2) Present and Enhance

Following the principles of participatory action research this objective was achieved. The work accomplished during the first summer was presented on the RET presentation day, where multiple teachers and professors of different areas meet. Nevertheless, throughout the academic year the RET cohort continued to meet for improvements and more professional development meetings.

Furthermore, the presentation and poster were also delivered at the Worcester State University (WSU) STEM Expo, informing the students of what I had done during my first summer in the lab and implementing the second lesson plan which is related to energy. Conducting the activity of inflating the balloons with yeast, and the students connected it to biocrude/bio-alcohols production, the RET project, and the UN SDG. There, I gained valuable feedback after and before the activity since we had previous meetings to discuss the material.

This work was also presented on Project Presentation Day 2023. Where teachers, professors, and the RET cohorts of 2022 and 2023 gathered, providing feedback, and having meaningful discussions about education to enhance teaching practices and lesson plans. During the last semester of the academic year 2023-2024, the lesson on separation techniques and chromatography was presented to students at a high school in the chemistry classroom. This was part of the student teaching, more information about it can be found in section 4.4, and in my WPI independent study paper titled: Implementation of Culturally Responsive Teaching & Asset Based Pedagogy.

4. Results and Analysis

In this segment, the information acquired from all the experiments trials will be evaluated and graphically represented. The section will assess how alterations in HTL vs HTL+, reaction duration, temperature, and feedstocks influence factors such as: overall mass yields, organic yields, quality of biocrude and biochar, and the chemical composition of the oil.

To start an evaluation of the different temperatures and reaction times is needed, these reactions were carried out by HTL+, meaning that hydrogen peroxide was added to our reaction as a promoter. In previous studies 300°C and 60minutes had been proven to have the best performance, with a higher oil yield and carbon percentage. Nevertheless, adding the hydrogen peroxide proved to be key in improving the oil yield for a reaction time of 20minutes. As illustrated on appendix C, figure C1, the 20 minutes reactions had a higher oil yield, and of all of them the temperature of 275°C had the greater mass yield of oil. Since the 20 minutes reactions had enhanced efficiency compared to the 60 minutes reactions, more reactions were carried out at 20 minutes but at different temperatures as seen on appendix C, figure C2. Increasing the temperature above 300°C wasn't beneficial given that it resulted in a lower oil yield, but below 275°C didn't show any significant impact either. Also, the greatest yield was at the 275°C reaction, but there was more loss in the 300°C reaction which could have had an impact if there would have been less loss the oil yield could have been higher. Therefore, the ideal temperature at which the reaction should be carried out is between 275°C to 300°C. Nevertheless, the quality of the oil also must be considered, and it will be discussed in the following section about the carbon yields.

In consideration of the previous reactions performed and the results, additional experimentation was conducted at 275°C to determine the effect of adding hydrogen peroxide, and the impact of the feedstock. For both BDP and AGW the best results were without the hydrogen peroxide given that it had a greater oil yield, but HTL+ did seem to reduce the amount of char (as depicted in appendix C, figure C3). However, the expected outcome was that HTL+ would increase the oil yield while simultaneously reducing the biochar, thus it didn't meet the hypothesis. Moreover, the HTL reaction with AGW produced the most yield of oil with the highest amount of reproducibility as shown by the error bars. Consequently, further reactions were performed using AGW for the majority. When considering the quantity of organics in the two green waste feedstocks, the BDP had almost the same organic oil yield for both HTL and HTL+. Nevertheless, the organic char yield had a decrease in the HTL+ BDP reactions, but on the AGW the decrease was seen in the oil (note that only one reaction of HTL+AGW was performed, and the reproducibility is unknown).

There is a need to evaluate the impact of the mixtures of feedstocks, with this objective in mind three different combinations of food waste with green waste in a 3:1 was analyzed.

Unfortunately, the hypothesis of HTL+ was again incorrect given that it didn't have any significant impact on the oil yield, except by a little on the HFW+AGW reaction. Nonetheless, HTL+ did demonstrate a substantial difference in the gas produced for all the waste combinations, this has potential for utilizing the gas byproduct for production of biogas. From the reactions seen in the figure above the HTL PKFW+BDP and PKFW+AGW had the higher oil yield, but the PKFW+BDP had a greater loss and less reproducibility. The highest organic oil yield in the reactions of food waste and green waste combined was the HTL PKFW+AGW. In contrast, the HTL+ had a reduced amount of organic oil as well as char, but in the HFW+AGW it was the opposite. Therefore, HTL+ didn't make a large difference and did not contribute to increasing the organic oil yield.

4.1) Carbon yields

Considering that the primary valuable outcomes derived from hydrothermal liquefaction (HTL) reactions encompass the biocrude and biochar, this carbon analysis is distinctly centered upon these pivotal constituents. The core objective of this analysis resides in the meticulous assessment of the carbon content across varying temperatures, reaction durations, and feedstock variations. This section aims to elucidate the distribution of carbon within these phases, showing the effects of variable conditions. Furthermore, by undertaking this comprehensive assessment, the aim is to ascertain the optimal conditions that yield the utmost quality in terms of carbon distribution, thus unlocking insights crucial for enhancing the overall process efficacy.

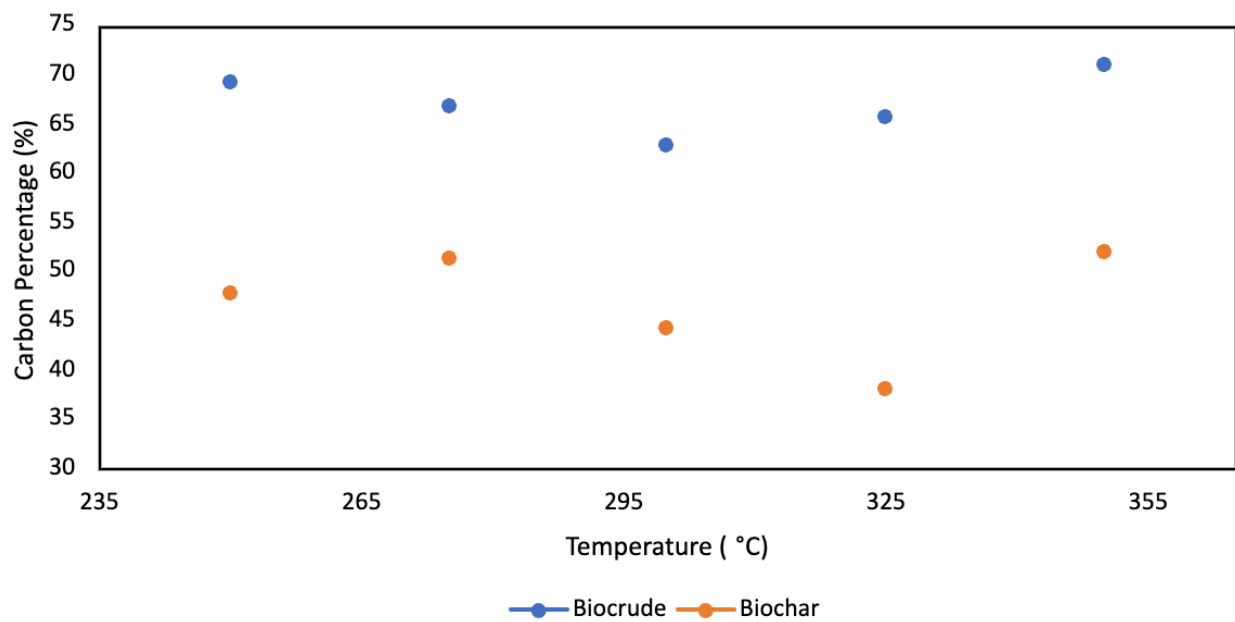


Figure 5. BDP green waste carbon percentages (%) of the biocrude and the biochar, for all the reactions carried out at 20 minutes using HTL+ at various temperatures ranging from 275°C to 350°C.

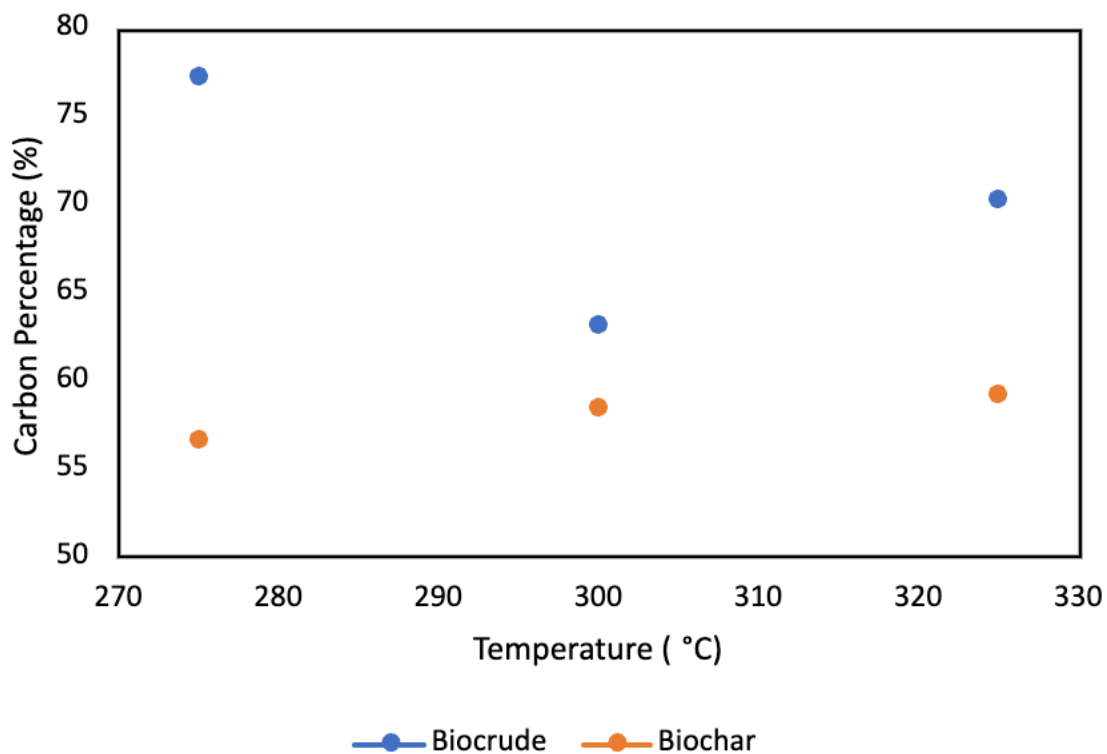


Figure 6. BDP green waste carbon percentages (%) of the biocrude and the biochar, for all the reactions carried out at 60 minutes using HTL+ at various temperatures ranging from 275°C to 325°C.

In the two figures presented above the carbon percentages are shown for the 20 minutes and the 60 minutes reactions. The trend that they both share is that the extremes in the graph have a higher carbon percentage in the oil than the reactions in between. Nevertheless, at a temperature of 275°C the carbon percentage in the oil is almost as high as in the greater temperatures. For example, as observed in figure 5 for the reactions of 20 minutes the carbon in the oil for the 350°C reaction is 71% and the percentage of carbon in the 275°C is 67%. The same trend was observed when the reactions were performed at 60 minutes. As for the carbon percentage in the biochar it is very similar on the 20 minutes reactions, except on the 275°C it is slightly higher. In contrast, the carbon percentage in the biochar for the 60 minutes reactions is almost linear. Based on these results, further experiments were carried out at 275°C for 20 minutes, these produce a good oil quality meaning that the oil has a high carbon percentage, consuming less energy, and being more time efficient allowing to perform more trials.

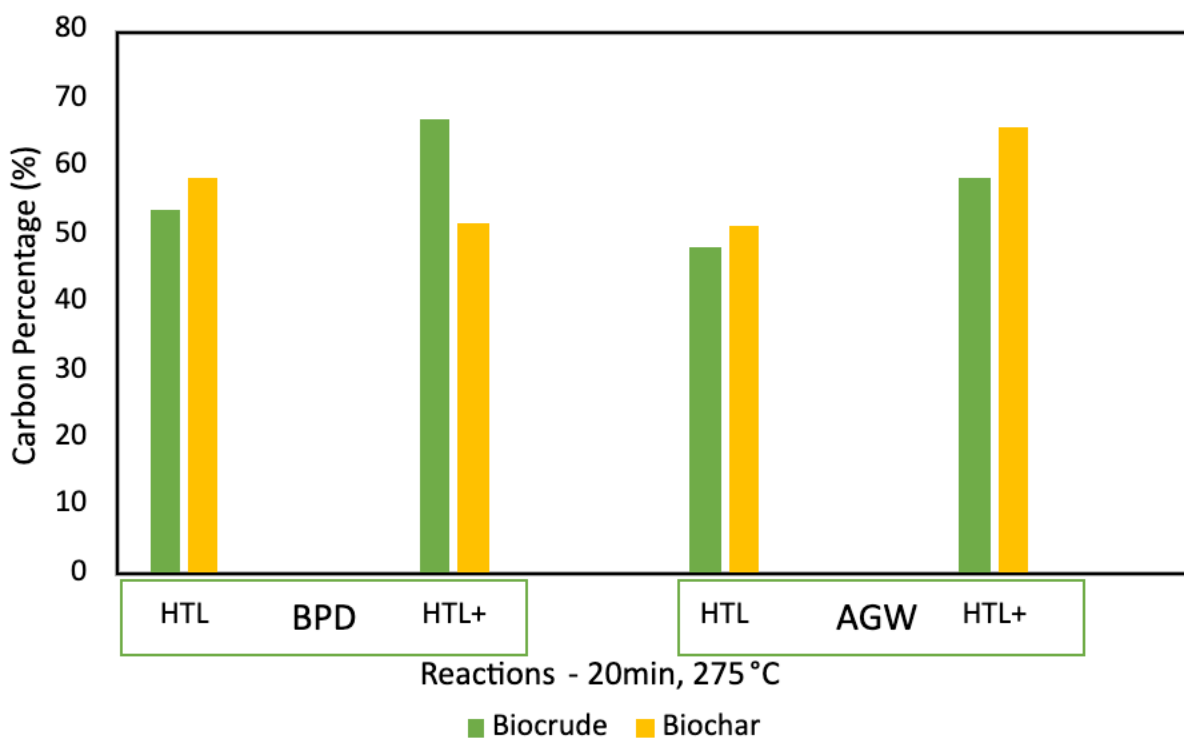


Figure 7. Carbon percentages (%) in the biocrude and biochar, comparison of the different types of green waste. These reactions were carried out at 20 minutes and at 275°C, comparing HTL vs HTL+, and different types of waste.

Two different types of green waste BDP and AGW are compared at the reaction of 275°C and 20 minutes, using HTL and HTL+. Despite HTL+ not having a significant impact in the oil mass yields, in the carbon percentage of BDP it had a great effect which is shown in the graph

above. Affecting the partitioning of the molecules in such a way that decreased the amount of carbon in the biochar and increased it in the oil. Nevertheless, in AGW HTL+ increased the carbon percentage for both the char and the oil, when compared to HTL.

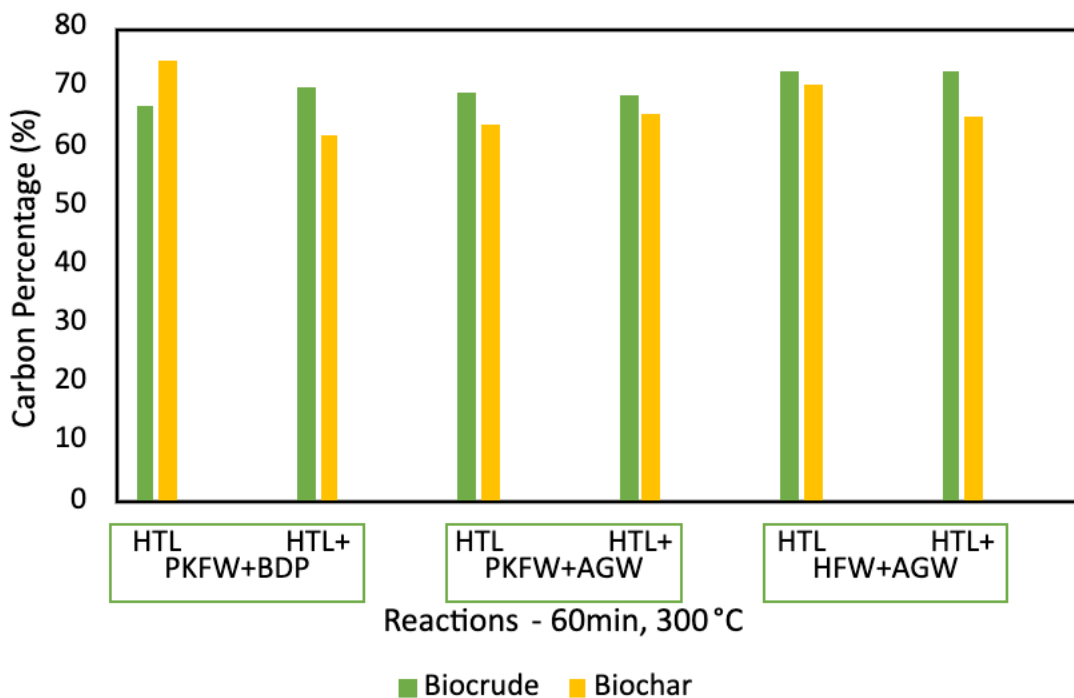


Figure 8. Food waste and green waste combinations (3:1) carbon percentages (%) in the biocrude and biochar. All these reactions were carried out at 60 minutes and at 300°C, comparing HTL vs HTL+, and different types of waste.

In previous research, it was proven that the ideal reaction parameters for food and green waste was at 300°C for 60 minutes in a 3:1 ratio. These results filled the gap of what occurs when different types of food and green waste are used, and the effects of the radical initiator. For the combinations of waste in the figure above, HTL+ didn't have a meaningful effect given that it increased the carbon in the oil and decreased it in the biochar only for the PKFW+BDP reaction. The reaction with the greater amount of carbon was the HTL HFW+AGW, but it had the least oil yield.

4.2) Van Krevelen Plots

The Van Krevelen Plots for this research present the relationship between the feedstocks and the products (biocrude and biochar) from the hydrothermal liquefaction reactions. It allows to evaluate the stoichiometric ratios of the components, by having the ratios of O/C vs H/C. Providing

insight into the heating value of the products as well. Hydrogen and carbon are the main components of fuel, for the most common transportation fuels the H/C ratio is equal to approximately 2 (UBC, n.d.). Hence this allows us to observe how close these products are to reaching that ratio, the parameters that are best, and if further upgrading is required.

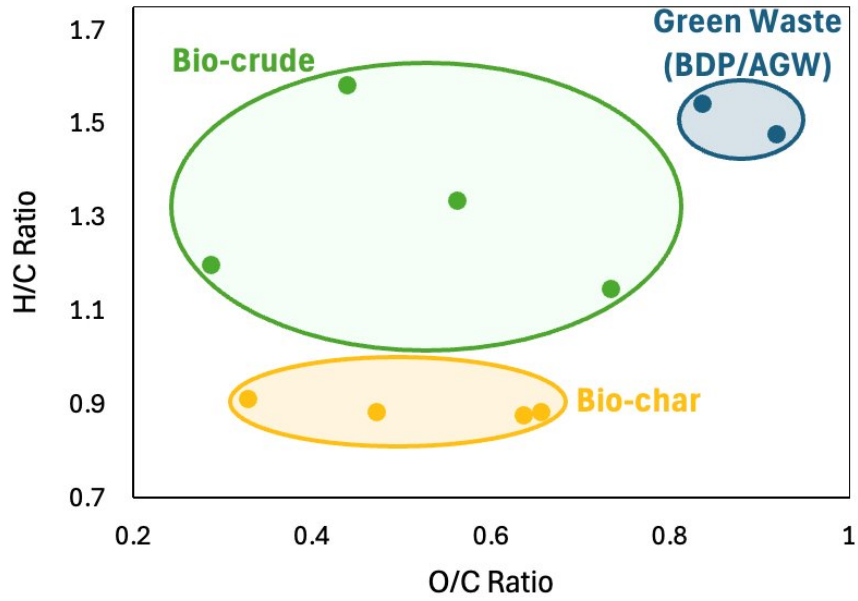


Figure 9. Van Krevelen Plot illustrating the ratios of O/C vs H/C, for green waste (BDP vs AGW), all 20 min reactions at 275°C.

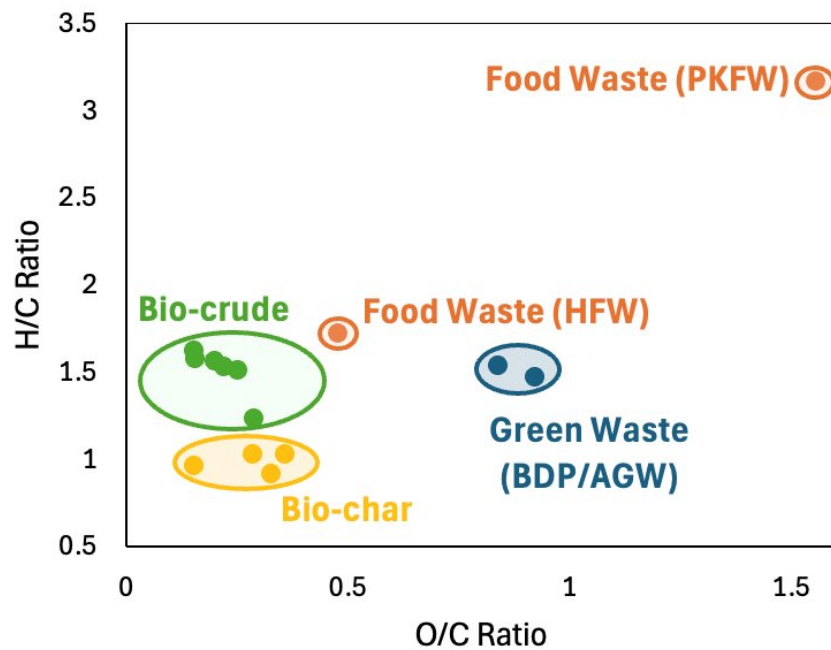


Figure 10. Van Krevelen Plot illustrating the ratios of O/C vs H/C, for different food and green waste blends in a 3:1 ratio, all 60 min reactions at 300 °C.

Deoxygenation of the feedstocks is observed in both plots presented above. As the reactions were carried out the oxygen reduced, having smaller trace of it in the products. The same trend was observed for food waste on its own and for the mixtures with food waste. Except PKFW is a less oxygenated feedstock, being in a different range from the other feedstocks utilized.

The greater the H/C ratio the better the heating value of the material. The bio-crudes heating value are very similar for all the reactions, yet the best ones were with the combination of HFW and the AGW which in regular HTL produced an H/C ratio of 1.6. This is the closest to that of common transportation fuels, and further upgrading will be required to be used for these purposes.

4.3) GC/MS

The GC/MS provides insight into what biocrude is composed of. Allowing for understanding of the diverse array of chemical species encapsulated within the biocrude matrix. This holds the potential to be harnessed in innovative ways, as it not only informs us of the biocrude's inherent composition but also enables the identification of specific chemicals that could serve as promising precursors for the synthesis of novel compounds. Note that silicones compounds can be disregarded because those are just impurities.

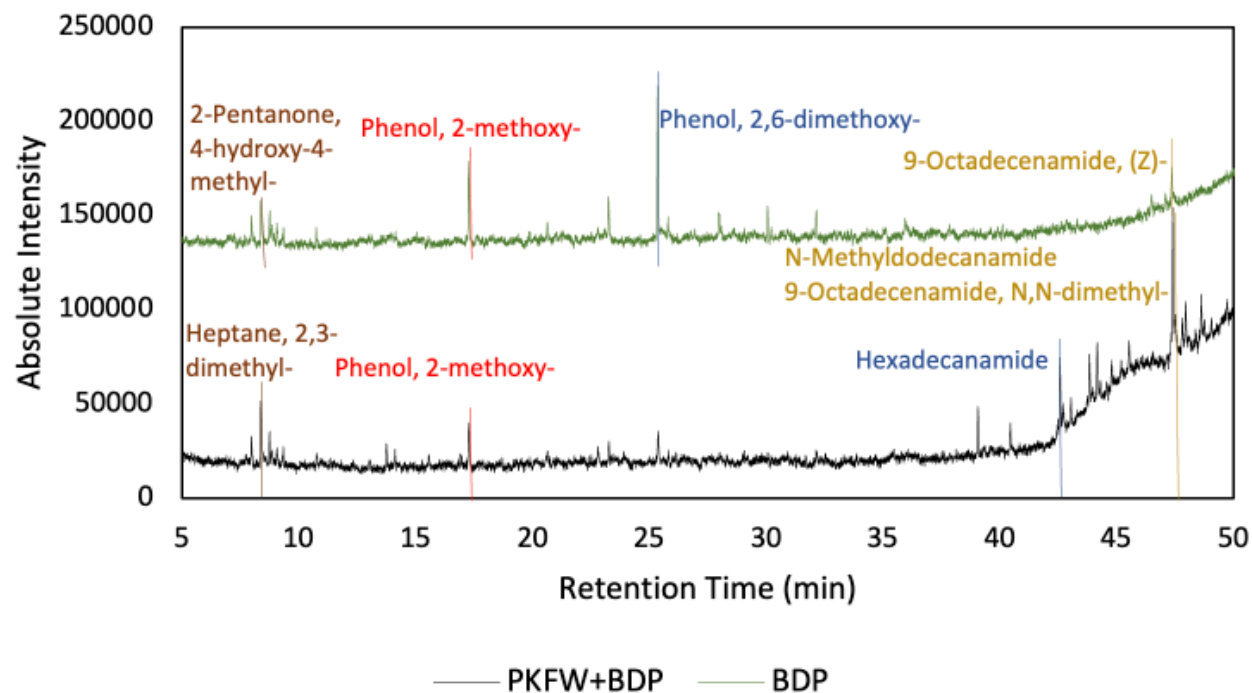


Figure 11. This graph illustrates the retention time vs. absolute intensity of the GC/MS. Performing a sample comparison of food waste and green waste combinations (3:1), as well as just the green waste on its own, both reactions are of 60minutes and 300°C.

The main peaks of PKFW+BDP and BDP have some similarities given that around 17 minutes they both indicated the presence of Phenol,2-methoxy and around 47.5 both exhibited a peak for 9-Octadecenamide. However, petroleum is mainly composed of hydrocarbons and in the GC/MS test above there is only one hydrocarbon and that is for the PKFW+BDP. Identifying the other chemicals that are present helps in determining in what other ways this biocrude could be used. For example, the BPD green waste is mainly made up of phenols and could be used for making synthetic fibers such as phenolic resins and nylon (PubChem, n.d.). Also, 9-Octadecenamide is a bioactive chemical that could have multiple applications such as in medicine (Kandeepan, 2022).

When comparing the PKFW mixtures with the green waste, their peaks are almost identical, and the same compounds showed up at the same time in all of them HTL and HTL+. Thus, the feedstock combination and HTL+ didn't have a significant impact on the chemical composition of the final biocrude. Potentially, it is a result of having a greater ratio of food waste (PKFW) and it being the constant, since the amount of green waste in the feed was smaller and it was the variable, it's expected that it wouldn't have a large impact. Nevertheless, some of these peaks looked relatively smaller when compared to the other reactions. For example, the peak of

N-Methyldodecanamide and 9-Octadecenamide, N,N-dimethyl-, is much smaller in the PKFW+BDP reaction than in all the other reactions. This could have been due to the long refrigeration periods causing the concentration to decrease given that the PKFW+BDP experiment was performed earlier than all the others. Further GC/MS analysis is required to be able to tell the exact concentration of such compounds and all samples should be evaluated withing the same time frame so that there isn't a change while the biocrude is stored.

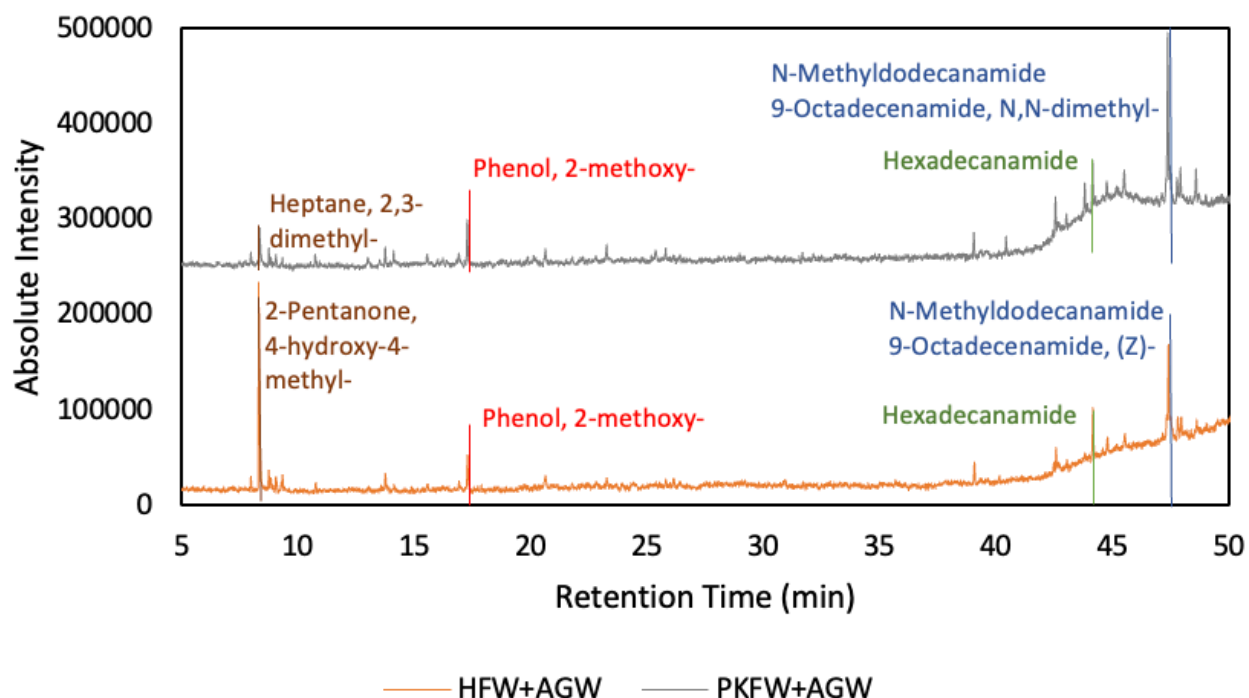


Figure 12. GC/MS retention time vs. absolute intensity for sample comparison of food waste and green waste combinations (3:1). These reactions were carried out at 60 minutes and at 300°C, comparing the different types of waste.

Considering that green waste as a variable didn't have an impact in composition, in the graph above the opposite is examined (food waste as a variable). The earlier peak around 8 minutes revealed that there was a different compound, 2-Pentanone, 4-hydroxy-4-methyl-, in the HFW+AGW this was the highest peak meaning that it's most certain the chemical it indicates. On the other hand, both HFW+AGW and PKFW+AGW exhibit the same peaks and compounds after 8.5 minutes.

4.4) Teaching Component

To bring this research into the chemistry classroom, the most successful lesson was the one where first the students were presented with the question of what research is, they discussed it, and then they learned about the engineering design process. This was then tied to the chemistry

standard PS1. Matter and Its Interactions, HS-PS1-11(MA) which states that students need to design strategies to identify and separate the components of a mixture based on relevant chemical and physical properties. Based on the objectives from the lesson the students were able to: do authentic research on the classroom following the engineering design process; identify and separate components of a mixture; be aware of the effects of polarity and use it to their advantage when separating compounds and identify the polarity of compounds; and understand how to perform chromatography by TLC (Thin-layer chromatography) to separate compounds.



Figure 13. Chromatography from the mystery greens, which are those in the beakers.

The problem given to the students was the following: there is a lot of waste in the landfills that comes from the food waste and green waste, and we need to be able to remove it. For this reason, your task is to perform a separation technique - chromatography, and you need to find out which are the chemicals in your waste that your pigments show, are there any applications where we can use this. Students were given a mystery green waste as shown in the figure above and conducted the chromatography in groups. Based on what they knew they identified the pigments present in the mixture (of the unknown leafy green and isopropyl alcohol), then with their knowledge about polarity they determined the polarity of the components in the mixture. Thereafter students made further questions they wanted to research or recommendations on what can be sustainable alternatives to deal with waste. They made this into a poster as shown in figure 14 and presented it in class.

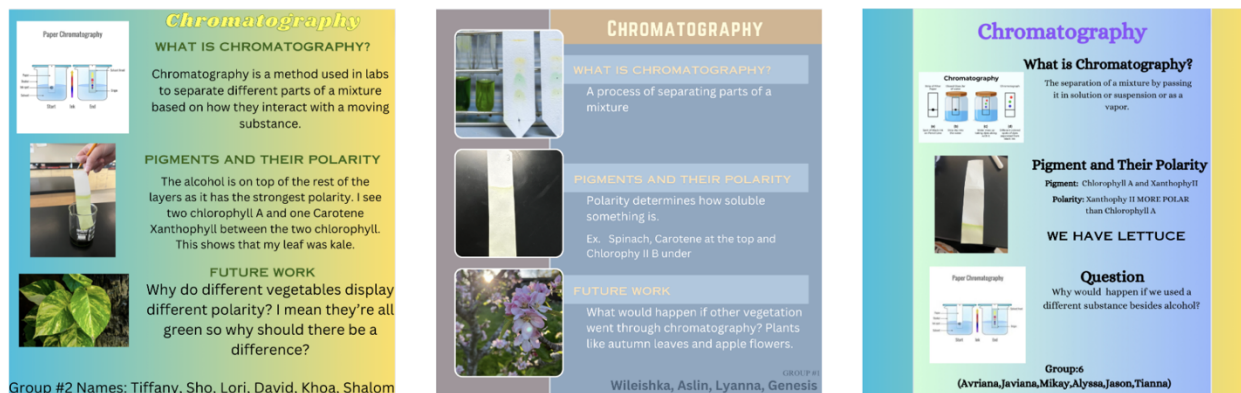


Figure 14. Posters created by the students from the chromatography lesson.

5. Conclusions and Recommendations

Aiming to achieve the UN sustainable development goals, HTL's potential for creating a renewable fuel precursor and other chemicals contributes to assuring clean energy, responsible consumption, and climate change mitigation. HTL has potential as a crucial contribution to a more sustainable future, working towards the pressing need to tackle climate change while striving toward global growth and a circular economy. Considering that HTL is a promising technique as a sustainable energy solution, enabling the transformation of waste materials. Nevertheless, various conditions for the system were evaluated to determine the optimal parameters for the reactor.

In view of the results and analysis, the optimal conditions for the best production of biocrude are: HTL with the mix of food waste and green waste, more specifically PKFW+AGW, in a 3:1 ratio, with a temperature of 300°C, and a reaction time of 60 minutes. This is on account of it having an average organic oil and mass yield, while simultaneously having a high carbon percentage (of about 70%) in the oil. Considering that even though other reactions might have a higher oil mass and organic yield their carbon percentage is lower; in others the carbon percentage in the oil is just slightly higher but the oil yields are lower. Hence, the conditions mentioned earlier are the ideal midpoint. If we just consider the green waste on its own the best conditions for it will be in HTL+ given that it significantly increases the carbon percentage in the oil, BDP at 275°C, and 20 minutes reaction time. Under these parameters the oil mass and organic yield were higher than the one for the food waste and green waste combinations, but the oil carbon percentage was lower (of about 66.7%). Therefore, the waste mixture in a 3:1 ratio is preferable for HTL, because

the quality of the oil is better, it has less viscosity being easier to manage, doesn't require the use of hydrogen peroxide as a promoter, and allows to utilize as raw materials two forms of waste at the same time for a responsible production of sustainable energy. Furthermore, it's important to highlight that when contrasting HTL vs HTL+, the only meaningful impact was for the feed of only green waste given that HTL+ created a higher amount of carbon percentage in the oil. Nevertheless, HTL+ had no substantial effects on the Co-HTL.

5.1) Limitations

This project had some setbacks and learning experiences which will be discussed in this section. In consequence of the TOC machine being in a separate building (Kaven Hall) at WPI, rather than in where the Timko lab is in Goddard Hall, it was more difficult to be able to perform the TOC analysis thus it wasn't possible to test all the aqueous phases to conclude the carbon balance. Moreover, some of the samples had long refrigeration periods which could have caused a decrease in concentration affecting such TOC results as well as the ones for GC/MS. Due to financial constraints not all the samples of oil and char were sent out for elemental analysis, but the ones sent were carefully considered after evaluating the organic yields. Additionally, from around 40 reactions that were performed issues presented in around 4 of them. For example, some of these had spills (data had to be discarded, because it wasn't reliable), and others because of the filter for the vacuum filtration had apertures too large it caused a char loss because it went through (this was solvable by repeating the filtration).

5.2) Future Work

Continued investigation should be conducted to aim for an upgrading from a batch reactor to a continuous system with a recycler where the byproducts can have a second life. This could initially be more costly, but it is more efficient and in order to move this process to a big-scale production it will be essential. It will also contribute to achieving a circular economy with zero waste. In addition, keeping in mind the possible use of the byproducts the biochar has the most potential based in other studies, and additional research is needed in the optimization of it depending on which area it will be applied (Xue et al., 2012). For example, if it's going to be used for cleaning chemicals from soil, it will be useful to explore its ability to regenerate.

Moreover, TOC measurement is required to complete the carbon balance and advance the uses of the aqueous phase byproduct. The gas byproduct should be further investigated, as

characterizing it is difficult but can improve biogas production. contribute Refrigeration time and concentration of compounds also needs to be further studied, to examine the longevity of the HTL phases. Finally, it's crucial to continue finding new pathways for HTL optimization with the goal of being even more sustainable and energy efficient, hence having lower reaction times and lower temperatures.

As for the teaching component of this research, with the lesson students were very interested in the research and asked further questions about it leading to engaging conversations about STEM. They started to visualize themselves as scientists, they were very excited to conduct the experiment and find out what was in their mixture. Therefore, more variations of these lessons will be carried out to motivate the students to go into STEM careers and see themselves as agents of change.

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7. Appendices

Appendix A. Figures

Date: _____

Run Name: _____

Operator(s): _____

Reactant Identities:

Feed (name):	Catalyst (name):
--------------	------------------

Input Mass (g):

Organic Feed:	Water:	Catalyst:
---------------	--------	-----------

Pre-Run Measurements (g):

Reactor Top:	Reactor Bottom:	Whole Reactor:
--------------	-----------------	----------------

Reaction:

	Initial	Start	End	Quenched
Time (XX:XX)				
Temp (C)				
Pressure (psi)				

Post-Run Measurements (g):

Whole Reactor:		
Filter Paper, Funnel, Stopper:	Filter Paper, Funnel, Stopper, Oil, Char:	Filter Paper, Funnel, Stopper, Char:
Empty Aqueous Flask:		Full Aqueous Flask:
Empty Round-Bottom Flask:		Full Round-Bottom Flask:
Reactor Top:		Reactor Bottom:
Empty Vial, Label:	Char, Vial, Label (undried):	Char, Vial, Label (dried):

Notes:

Figure A1. Sample run sheet for the experiments conducted illustrates all that was measured.



JVD Char
 7/11/23
 SAMPLE IDENTIFICATION ON Vial

Analysis Requested: CHN Elemental Analysis

Single Duplicate Triplicate

Submitter Name:	Geoffrey Tompsett
Business or Institution:	WPI
Lab Group:	TIMKO
Results email and Phone #:	gtompsett@wpi.edu
Invoice email and Phone#:	accountsPayable@wpi.edu
Invoice Address:	Worcester Polytechnic Institute- WPI Attn: Accounts Payable 100 Institute Road Worcester, MA 01609-2280
Purchase Order Number:	23070542

Analysis Requested	Customer Theory	Office Use Only: Results are total % Found		
C	60			
H	5			
N	5			

Molecular Formula:	C6H5N0.4O1.3	
Air Sensitive/ Glove Box:	YES <input type="checkbox"/>	NO <input checked="" type="checkbox"/>
Hazardous/ Explosive:	YES <input type="checkbox"/>	NO <input checked="" type="checkbox"/>
Hydroscopic:	YES <input type="checkbox"/>	NO <input checked="" type="checkbox"/>
Vacuum Drying Requested:	Temp: _____ °C	
Yes <input type="checkbox"/>	Time: ___ Hr. ___ Min.	
No <input checked="" type="checkbox"/>		
Sample Return Address:		
Yes <input type="checkbox"/>		
No <input checked="" type="checkbox"/>		

Shipping address:
 Midwest Microlab
 Attn: Valerie Guzzetta
 7212 N. Shadeland Ave., Suite 110
 Indianapolis, IN 46250
 Phone: 317-849-6606
 Fax: 317-849-8534
 Email: info@midwestlab.com
 Website: www.midwestlab.com

Submitter Comments:

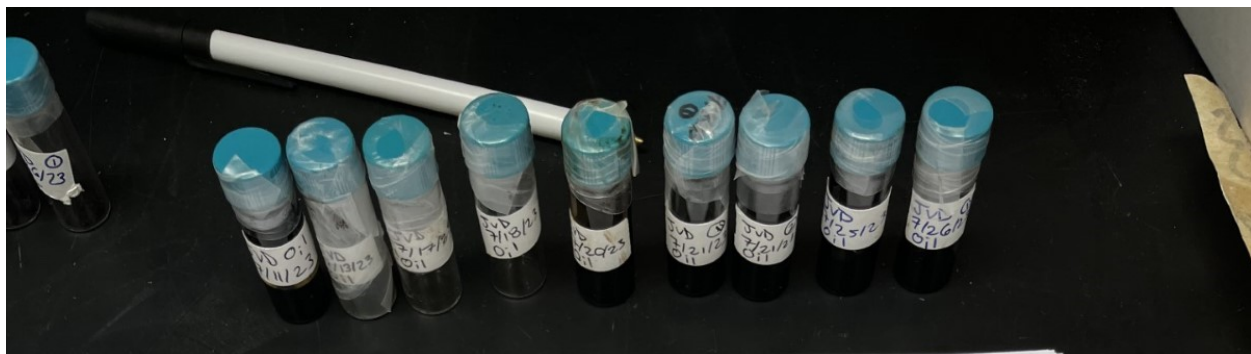
sample is char solid containing carbon, hydrogen, oxygen and nitrogen with trace sulfur and ash

Office Use Only

Please include 1 submission form per sample.

We appreciate your business.

Figure A2. Bio char CHN Elemental Analysis, sheet for submission to the Midwest Microlab.



JVD Oil
7/11/23
SAMPLE IDENTIFICATION ON Vial

Analysis Requested: CHN Elemental Analysis

Single Duplicate Triplicate

Submitter Name:	Geoffrey Tompsett
Business or Institution:	WPI
Lab Group:	TIMKO
Results email and Phone #:	gtompsett@wpi.edu
Invoice email and Phone#:	AccountsPayable@wpi.edu
Invoice Address:	Worcester Polytechnic Institute-WPI Attn: Accounts Payable 100 Institute Road Worcester, MA 01609-2280
Purchase Order Number:	23070542

Analysis Requested	Customer Theory	Office Use Only: Results are total % Found		
C	70			
H	5			
N	5			

Molecular Formula:	C6H5N0.4O1.3
Air Sensitive/ Glove Box:	YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>
Hazardous/ Explosive:	YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>
Hydroscopic:	YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>
Vacuum Drying Requested:	Temp: _____ °C
Yes <input type="checkbox"/>	Time: ____ Hr. ____ Min.
No <input checked="" type="checkbox"/>	
Sample Return Address:	
Yes <input type="checkbox"/>	
No <input checked="" type="checkbox"/>	

Shipping address:
Midwest Microlab
Attn: Valerie Guzzetta
7212 N. Shadeland Ave., Suite 110
Indianapolis, IN 46250
Phone: 317-849-6606
Fax: 317-849-8534
Email: info@midwestlab.com
Website: www.midwestlab.com

Submitter Comments:
sample is oil containing carbon, hydrogen, oxygen and nitrogen with trace sulfur and ash

Office Use Only

Please include 1 submission form per sample.

We appreciate your business.

Figure A3. Bio oil CHN Elemental Analysis, sheet for submission to the Midwest Microlab.

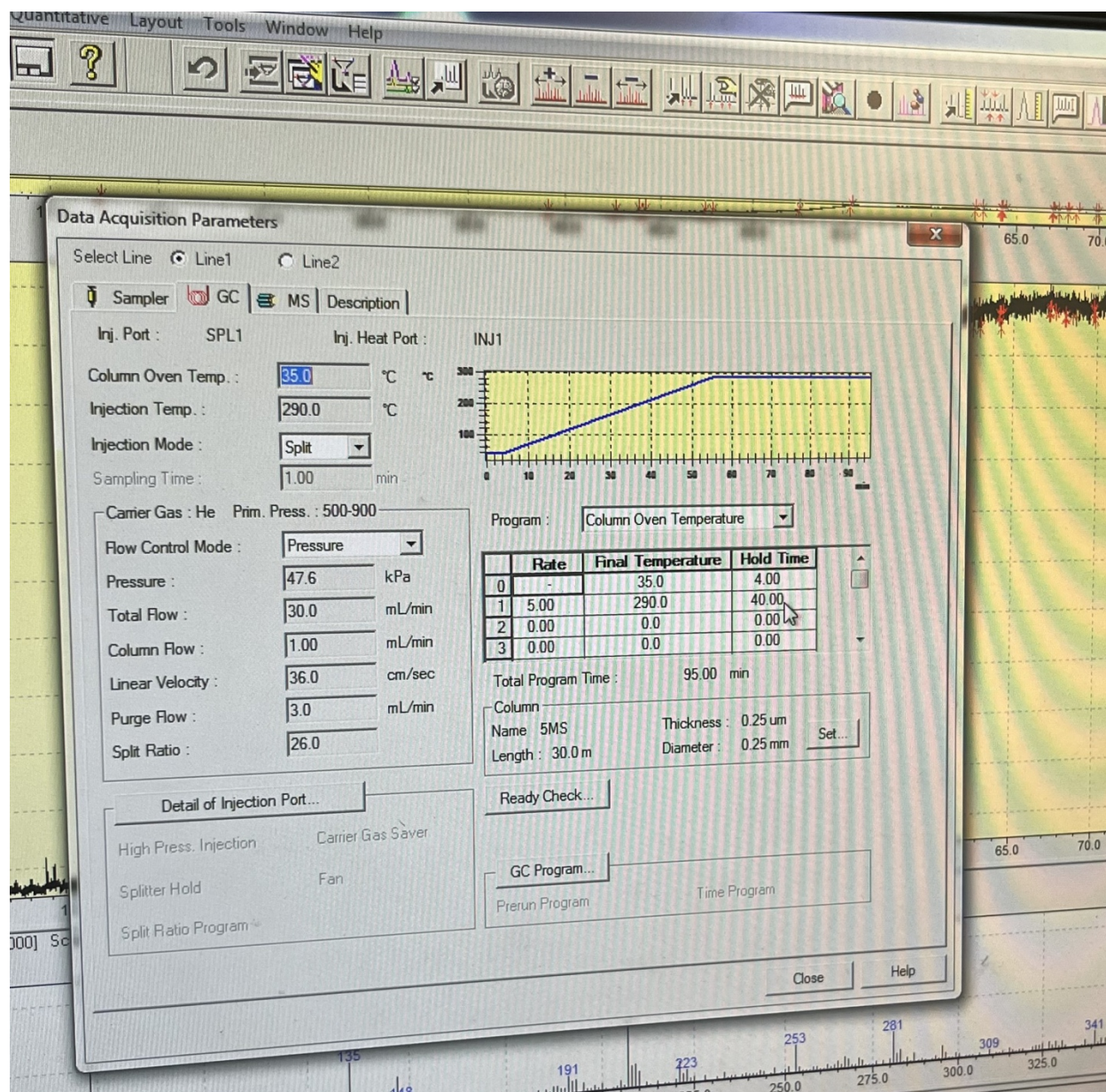


Figure A4. Parameters set for the GC/MS, which helped to identify the components present in the biocrude.

Appendix B. TOC Manual

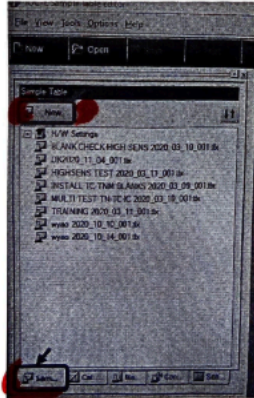
NPOC ANALYSIS

Verify the following

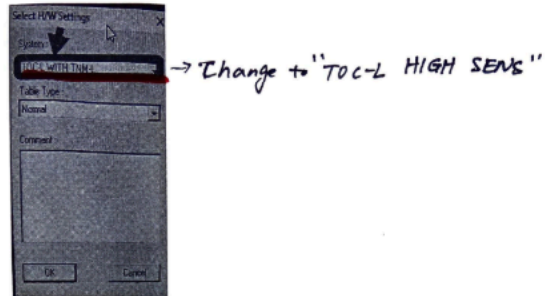
- i) Gas cylinder pressure is above 500psi
 - ii) Regulator pressure is between 70-85 psi
 - iii) Rinse water bottle (located behind autosampler) is full and end of the tubing is at the bottom of the bottle. If not full, fill with DI water.
 - iv) Water level humidifier is above "Lo" mark. If not, replenish by adding DI water through the port on top of the vessel until "Hi" mark is reached.
- A. Turn on instrument
When the power button is orange, press the button to start up the instrument.
- B. Place Standards and samples in autosampler
- 1) Take off the sample cover and sample tray
 - 2) Add standards and samples in sample tray and place sample tray back. Gently spin tray until it sits in the right position.
 - 3) Put sample cover back until it clips.
- C. Edit the Sample Table Editor






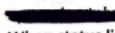



- 1) Start "TOC-L Sample Table Editor" on desktop → Type in your Initials → click OK
- 2) Click "New" in the Sample Table tab of the file viewer



- 3) In "Select H/W settings" window: select **TOC-L HIGH SENS** in system dropdowns → Click OK.



- 4) Calibration: Click Calibration Curve tab of the file viewer.
 
 Drag the right calibration file to the first line in the sample table
- 5) Samples: Click Method tab of the file viewer.
 
 Drag the right method file to the following lines in the sample table. Copy and paste the line to insert multiple samples using the same method file.
- 6) Edit Sample Name in the sample table.
 
- 7) Vial Numbers: Click in  the sample table → Enter a standard and sample locations in Vial column → Click OK.
- 8) Connect: click the sample table to be used → click "connect" . Wait  for instrument to warm up.
- 9) When status light at the upright corner shows "Ready", click Start → Select "Shut down instrument" → Click Start to start analysis
- 10) To view result: click 
- 11) To output results: click "Print" → click "Sample Report-All"

GLASSWARE

All glassware used for standard preparation must be organic-free (acid washed).

Initial Cleaning

- A. Wash glassware with soap and hot water. Rinse Thoroughly
- B. Soak glassware in 20% sulfuric acid bath overnight
- C. Remove glassware from acid bath and rinse 3 time with DI water
- D. Air dry
- E. Label glassware with "organic free"

Subsequent Cleaning

Use organic-free glassware for TOC/NPOC only. After use, wash glassware with soap and water. Rinse thoroughly with tap water, then rinse 6 times with DI water. If glassware is used for high concentration samples, repeat acid wash procedure.

STANDARDS

Note: all glassware used for standard preparation must be organic-free (acid washed).

Sample concentrations should be exceed the highest concentration of the working standards. Dilute samples with DI water if needed.

- A. Stock Standard (1000ppm OC)
 - a. Dry about 0.75 g of Potassium Hydrogen Phthalate (KHP) in oven at 103-110°C for 30 min. Cool in desiccator for 20min.
 - b. Weigh exactly 0.5314 g using analytical balance. Add to a 250ml volumetric flask to mark with DI water
 - c. Store in amber glass bottle in refrigerator. Label well with name, date and "1000mg OC/L KHP standard". Discard after 1 month
- B. Working Standards
 - a. Prepare working standards that bracket the sample concentrations
 - b. Use 100ml or 50ml volumetric flasks. Fill halfway with DI water. Add 1% v/v of 6N HCl (acid addition for NPOC analysis to bring pH around 2) (don't add HCl, if use acid addition function in software)
 - c. Add desired volume of Stock Standard to each flask and fill to mark with DI water.

Appendix C. Additional Results

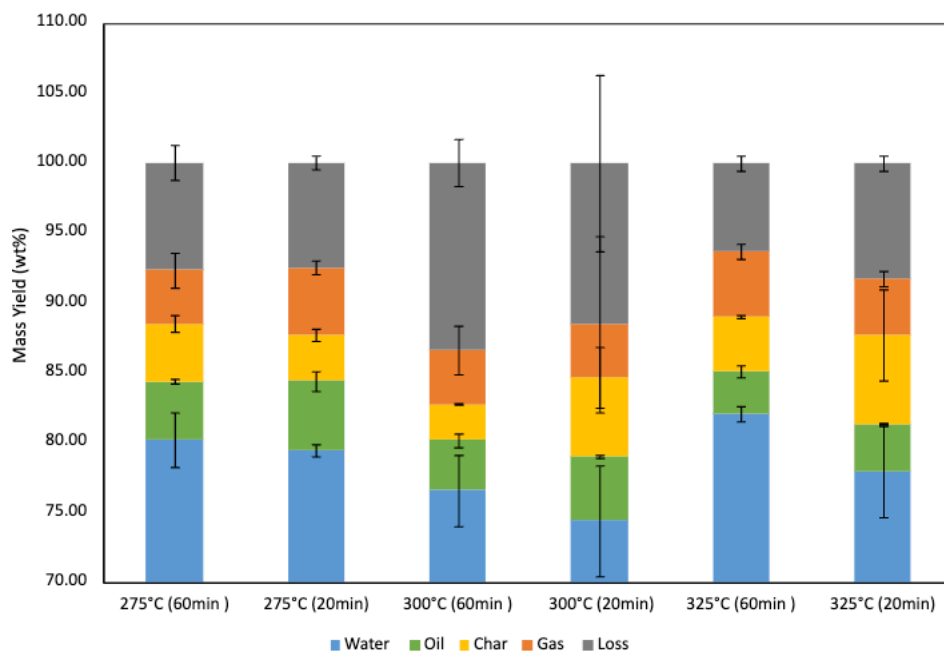


Figure C1: BDP green waste (0.85mm) mass yields (wt%) for all the HTL phases and the loss, at various temperatures ranging from 275°C to 325°C, HTL+ (adding hydrogen peroxide), and times of 20 minutes and 60 minutes respectively.

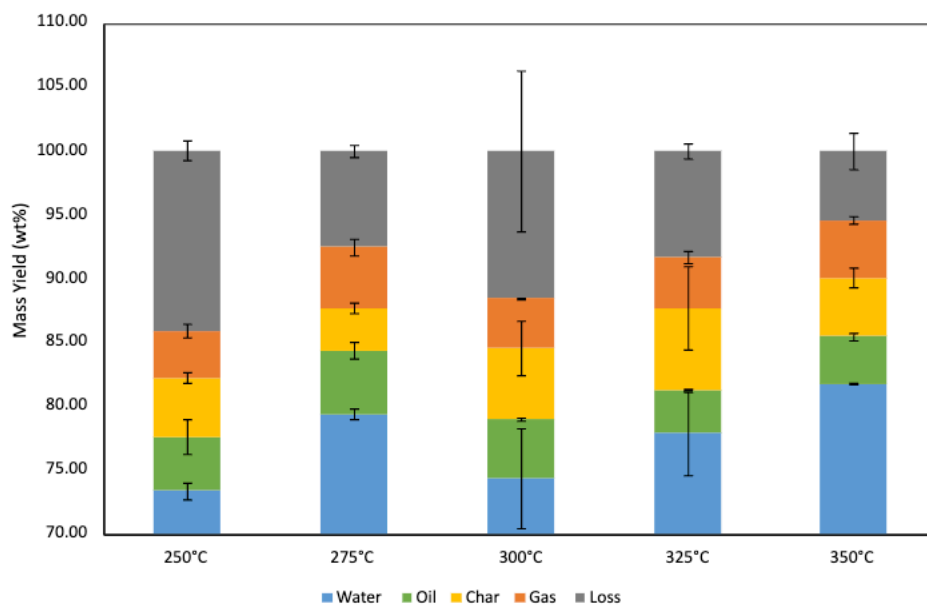


Figure C2: BDP green waste mass yields (wt%) for all the HTL phases and the loss, these reactions were carried out at 20 minutes, HTL+ (adding hydrogen peroxide), at various temperatures ranging from 250°C to 350°C.

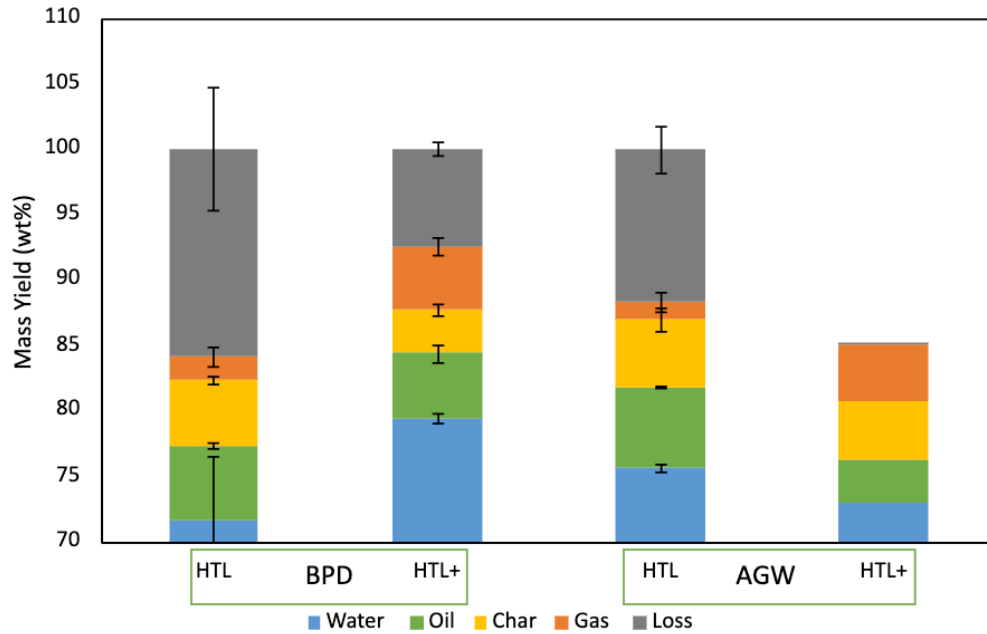


Figure C3: Mass Yield (wt%) in the biocrude and biochar, comparison of the different types of green waste. These reactions were carried out at 20 minutes and at 275°C, contrasting HTL vs HTL+, and different types of waste.

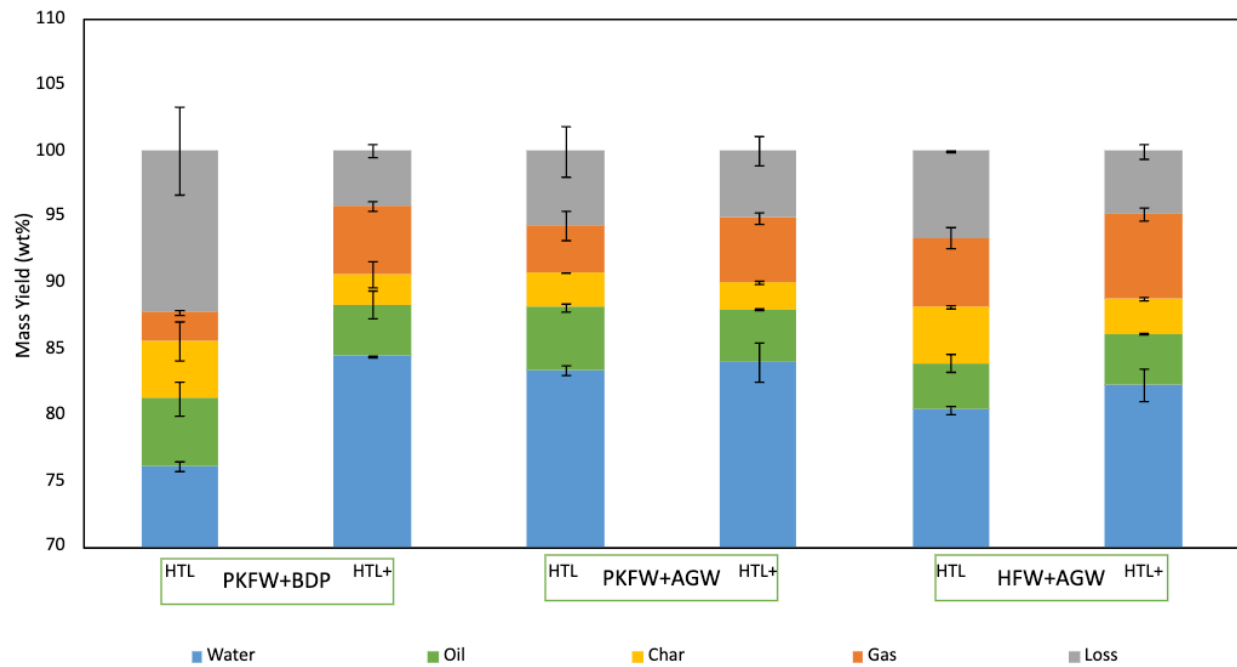


Figure C4: Food waste and green waste combinations (3:1) mass yields (wt%). All these reactions were carried out at 60 minutes and at 300°C, comparing HTL vs HTL+, and different types of waste.

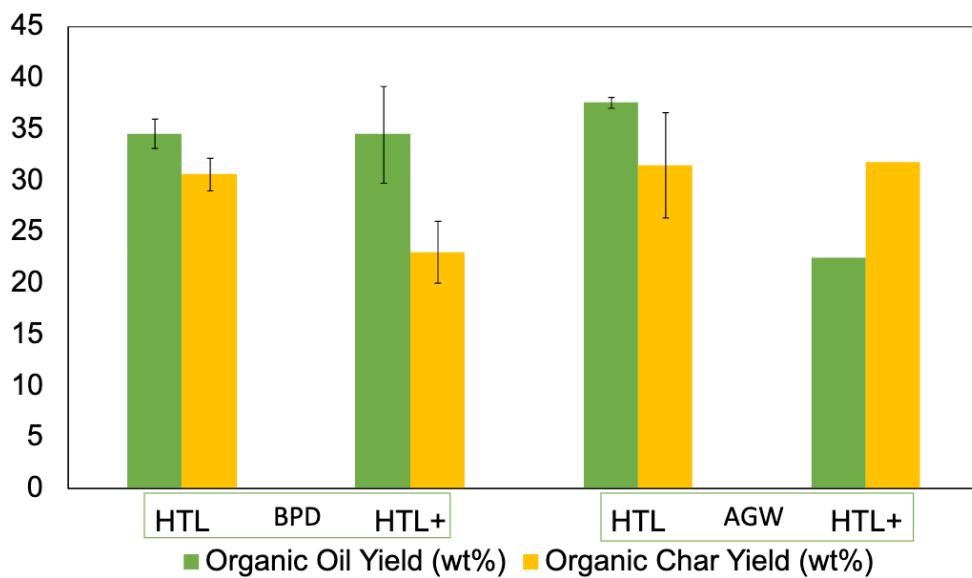


Figure C5: Organic yields (wt%) of the different types of green waste. These reactions were carried out at 60 minutes and at 275°C, comparing HTL vs HTL+, and different types of waste.

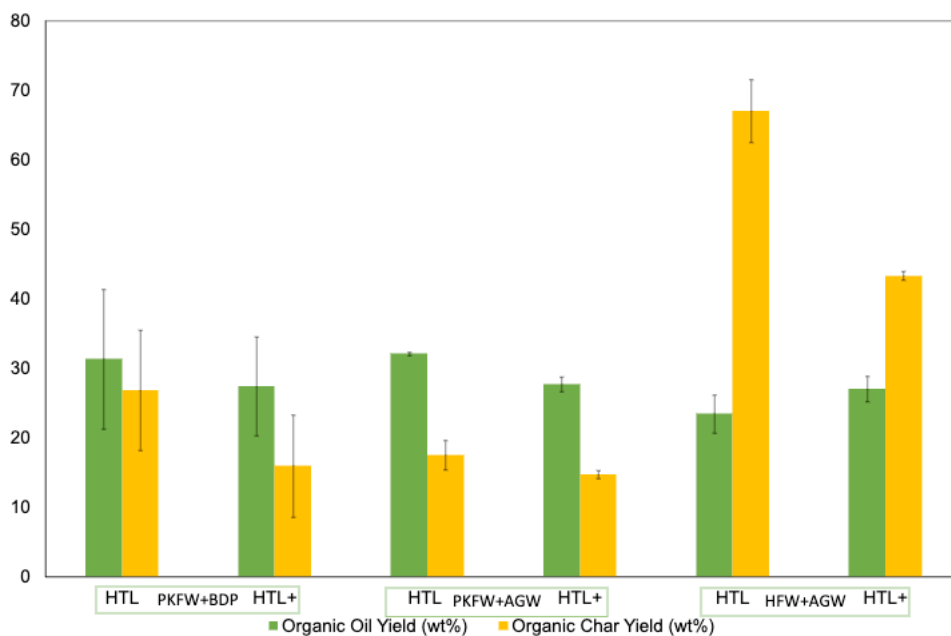


Figure C6: Food waste and green waste combinations (3:1) organic yields (wt%). All these reactions were carried out at 60 minutes and at 300°C, comparing HTL vs HTL+, and different types of waste.

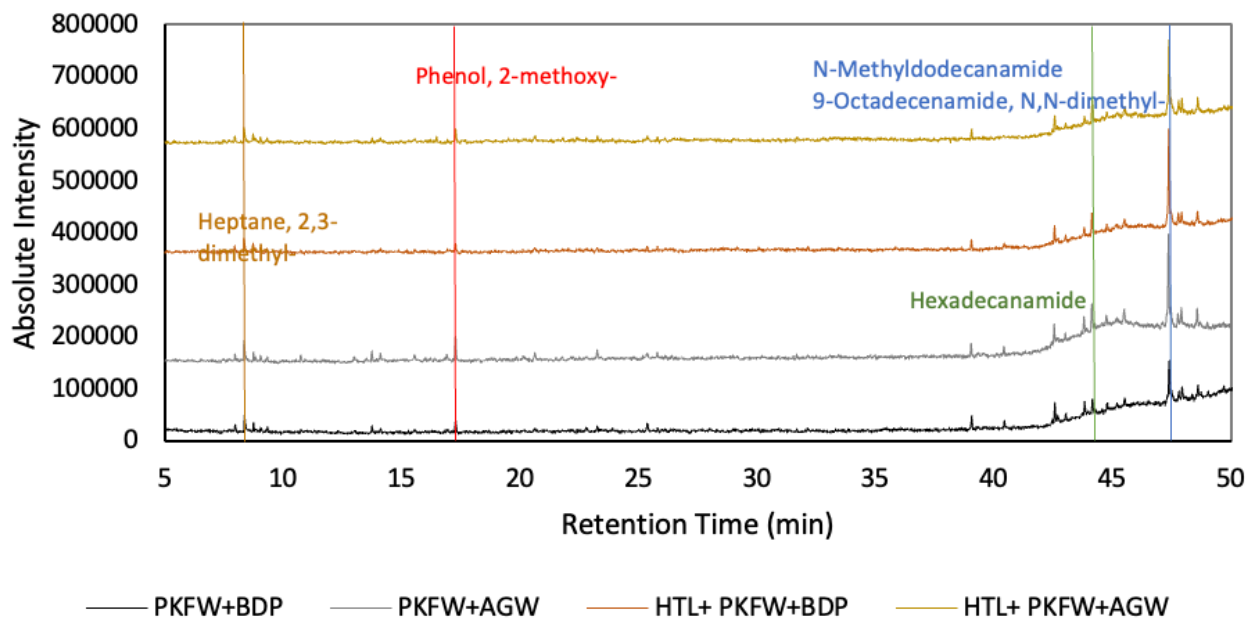


Figure C7: Retention time vs. absolute intensity of the GC/MS. It does a sample comparison of food waste and green waste combinations (3:1). All these reactions were carried out at 60 minutes and at 300°C, comparing HTL vs HTL+, and different types of waste.

Appendix D. Final Lesson Plans


Teacher Name(s): Joelis Velez Diaz

Subject/Course: Chemistry



Grade Level: High School - 10th grade

United Nations Sustainable Development Goal: *What UNSDG is the project related to?*

The research project precisely associates with the United Nations Sustainable Development Goal (UN SDG) number 7, “ensure access to affordable, reliable, sustainable and modern energy for all”; as well as goal number 12, “ensure sustainable consumption and production”. The students will be introduced to it, environmental justice, and sustainable energy, which will be tied directly with separation techniques.



Hydrothermal Liquefaction: Green Waste = Green Energy
 Presenter: Joelis M. Velez Diaz
 Advisors: Heather LeClerc, Professor Michael Timko, Professor Alex Maag
 Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA

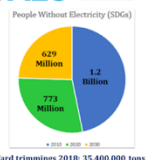



Social Impact

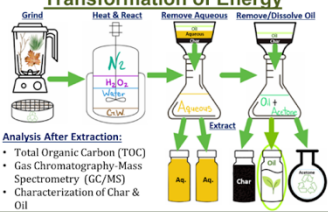
SUSTAINABLE DEVELOPMENT GOALS

SDG #7: “Ensure access to affordable, reliable, sustainable and modern energy for all”.

The project will also shape high schoolers in chemistry as the lab experience was transformed into a lesson plan for interactive learning.



Transformation of Energy



Analysis After Extraction:

- Total Organic Carbon (TOC)
- Gas Chromatography-Mass Spectrometry (GC/MS)
- Characterization of Char & Oil

Discussion

Reactions	20min	60min
275°C	35.9%	N/A
300°C	33.1%	25.9%
325°C	24.5%	N/A
350°C	26.5%	N/A

The results demonstrate that the procedure can be carried out at a lower temperature, it will be more energy efficient, economic, and less time-consuming.

Green Waste & HTL

The Hydrothermal Liquefaction (HTL) process that was used is sustainable, economically viable, and non-polluting, thus allowing to produce bio-oil (clean energy) from energy-dense green waste feeds (yard clippings and agricultural waste).

Fossil Fuels (with a red prohibition sign) → **Lignocellulose** (with a green checkmark)

The HTL phases were characterized to determine the best conditions to maximize oil production and quality. Various reaction times and temperatures were also evaluated, to achieve an optimal system.

Gas

Aqueous

Char

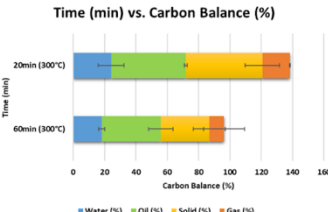
Oil

In the reaction Hydrogen Peroxide (the catalyst) acts as an oxidant to reduce the amount of char and produce more oil! More H₂O₂ results in gasification to CO₂

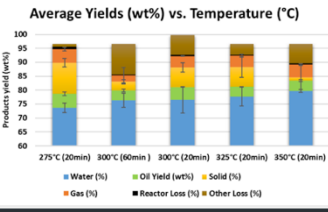
$$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}^{2-}$$

Increasing Oil Yield & Quality

Time (min) vs. Carbon Balance (%)



Average Yields (wt%) vs. Temperature (°C)



Future Work

Continuous research to achieve the most efficient system:


- Lower temperatures (lightning bolt icon)
- Lower cost (dollar sign icon)
- Shorter reaction time (stopwatch icon)

References

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Acknowledgements

- Thank you: Advisors, CHE partners, RET fellow teachers and staff, for all the help and guidance.
- This material is based upon work supported by the National Science Foundation under Grant No. EEC-2055507.



2022

What do students need to KNOW ?	<ol style="list-style-type: none"> 1. Students will use the following vocabulary words in context: Polar, non-polar, Chromatography 2. Students will be able to distinguish between polar and nonpolar
What do students need to DO ?	<ol style="list-style-type: none"> 1. Be able to identify and separate components of a mixture 2. Be aware of the effects of polarity and use it to their advantage when separating compounds, and identify the polarity of compounds 3. Understand how to perform chromatography by TLC (Thin-layer chromatography) to separate compounds
What will students CREATE ?	<ol style="list-style-type: none"> 1. Students will perform an experiment 2. Complete a write-up/lab report 3. Connection to real world problems <p>More specifically on the long version students will be able to do authentic research on the classroom following the engineering design process (there are 6 groups, and 2 groups have the same leafy green they are able to compare it - having two different trials now per each leafy green allowing them to have more evidence/data to back up their results while doing collaboration, students get to present their results). Students also carry out 2 different sets of experiments that involve a different procedure, which allows them to compare them.</p>

ELA Standard: Presentation of Knowledge and Ideas 4. Present information, findings, and supporting evidence clearly, concisely, and logically such that listeners can follow the line of reasoning and the organization, development, vocabulary, substance, and style are appropriate to purpose, audience, and task.

Red = Knowledge LTs

Orange = Reasoning/Skill LTs

Green = Product LT

Vocabulary	Tier 1	Tier 2	Tier 3
	<input type="checkbox"/> Information	<input type="checkbox"/> Evidence	<input type="checkbox"/> Findings
What do students need to KNOW ?	Students will use the following vocabulary words in context: <ol style="list-style-type: none"> 1. Information/data 2. Evidence/findings 		
What do students need to DO ?	<ol style="list-style-type: none"> 1. Students need to present their information gatherers through the lab experiment 		

What will students CREATE?	1. Student will create relevant data point and use as evidence to support their findings
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Assessment - *In what ways will the students demonstrate proficiency of the standards? Include a link to your rubric.*

<https://docs.google.com/document/d/14Og-oN2hxJoHEpdOUEdYC4dAbQyhHieTrSp-zYTDhuA/edit?usp=sharing>

Work samples from the students:

<https://www.canva.com/design/DAGBXLRI1Gw/7HyCupZvjmXuknspOjsiQg/edit>

Learning Plan

Real world problem: *What is the problem and how will it be presented to students?*

The bigger issue is climate change, it will be presented with a video of the UN Sustainable goals. For this specific experiment there is a need to separate the components in green waste, to be able to identify what chemicals these leafy vegetables are made of and find what we can do with those chemicals.

Connects to the examples of previous research conducting RET:

- Using green waste and food waste to make biocrude, we need to do chromatography to identify the chemicals/components of the biocrude we create and figure out its applications.
- Breaking down plastic into reusable chemicals.

The problem that is given for the students to solve is the following: there is a lot of waste in the landfills that comes from the food waste and green waste, and we need to be able to remove it. For this reason, your task is to perform a separation technique - chromatography, and you need to find out which are the chemicals in your waste that your pigments show, are there any applications where we can use this. Students will be given a mystery green waste and based on what they know they'll identify these pigments, then with their knowledge about polarity they'll determine the polarity of the components in the mixture. Thereafter students will make further questions they want to research or recommendations on what can be sustainable alternatives to deal with green waste or any other type of waste they want.

[RET lesson 1 - Unit 9 - Intermolecular Forces 5.pptx](#)

[Old RET lesson1 - Unit 9 - Intermolecular Forces 6.pptx](#)

https://docs.google.com/document/d/1Lw4wXe8xnyNTYMaRgCiViIo0EuoZK_W5QqAE4QPikpE/edit?usp=sharing

Prior Knowledge:

- Polar vs nonpolar
- How to determine the polarity based on electronegativity
 - Find the difference of electronegativity of the atoms involved.
 - If it was between 0.4-1.7 it's polar

- Below 0.4 is not-polar

Short Version - 1 Class Period (2022)

Materials/Resources:

[*Old RET lesson1 - Unit 9 - Intermolecular Forces 6.pptx*](#) - paper, scissor, cup, pencil, tape, water, ruler, sharpie (can be performed using recycled materials such as plastic water bottles which teaches students about recycling)

Timeline: *Complete the chart below.*

Note: Students should follow the problem solving/engineering design process to solve the problem presented to them. Be sure to include all the components.

Duration	Activity	Instructions	Product
10 minutes	Introduction	Share with the students RET project for them to gain insights on the project and ask them to identify separation methods utilized in it.	Learning of green waste conversation to green energy, and separation methods.
5 minutes	Do now	Image of oil not mixing with water having a discussion with students about the possible reasons why?	Allows students to create a connection with something they have previously seen
20 minutes	Problem + experiment	Present the problem to students and allow them to perform the experiment (teacher can also perform a sample experiment), where students get to simulate the chromatography of TLC plates as well as a gas chromatograph (which I used during my research to identify which compounds where in the aqueous mixture) but with water instead of a chemical and normal paper/napkin.	Gain lab skills, knowledge, and write lab report
10 minutes	Discussion	Class discussion about the lab, is our sharpie ink polar or nonpolar why? Also, show students how to calculate Rf values of our experiment and why it is important.	Reflect
5 minutes	Exit ticket	Did you obtain a good Rf value (should be between 0.2-0.8), what was it? Do you think the size of your paper matters? Why or why not?	Analyze

Long Version - 2 Class Periods (2024)

Materials/Resources:

[RET lesson 1 - Unit 9 - Intermolecular Forces 5.pptx](#) - Filter paper/ or coffee filter paper, scissor, cup/beaker, pre-made solutions of different leafy vegetables in isopropyl alcohol, isopropyl alcohol, coins (one per group), lettuce, spinach, and kale

Timeline: Complete the chart below. (*Designed for about two class periods*)

Note: Students should follow the problem solving/engineering design process to solve the problem presented to them. Be sure to include all of the components.

Duration	Activity	Description/Instruction	Product
4	Hook	What is research and why do we need it?	Students start think about the importance of scientific research, connection with basic research
10	I Do (demo)	Teacher share with the students the engineering design process and the RET project for them to gain insights on the project and research, with an emphasis on the separation techniques that were used in it.	Connection to careers and gain engagement from the students into the subject
10	We Do (guided and group practice)	Present the problem to students and allow them to perform the experiment (teacher performs a sample experiment), where students get to simulate the chromatography of TLC plates as well as a gas chromatograph (which I used during my research to identify which compounds where in the aqueous mixture and the oil samples) but with isopropyl alcohol as a solvent and filter paper. Students also get to try the chromatography with a different approach in which there is a pre-made mixture of the leafy vegetables and they just put the filter paper on it. This allows for two sets of experiments.	Students can carry out the chromatography by two different experiments.

30	We Do (partner or group practice)	<p>Creating their own TCL - having 6 groups, and 2 groups having the same leafy green students compare their results with those that had the same leafy vegetable - having two different trials now per each leafy green allowing them to have more evidence/data to back up their results while doing collaboration. Students also discuss with those that had a different leafy vegetable from them and ask about the results.</p> <p>For the pre-made mixture - students don't know which leafy green they have but they must figure it out by calculating Rf values or comparing to samples made and labeled by the teacher.</p>	Facilitates collaboration among students in a similar manner to that of the research scientific community.
20	You Do (individual practice)	<p>All students formulate future questions that can lead to additional research or find sustainable applications to reuse the green waste/food waste.</p> <p>Given a sample in Canva students create and present a poster where they explain in their own words what chromatography is, the pigments they saw, their mystery green, the polarity of the pigments, and the future work or other sustainable applications for waste.</p>	Shows understanding of the engineering design process and understanding of the separation technique - chromatography.
5	Closing	Allow students to make a personal connection by letting them choose which type of research they would like to do or find someone that is doing some research they like.	Diversity in STEM role models and careers - Research, could also have them do this at home and/or do now for the next day.

Attending to Equity - *What strategies will you use to best meet the needs of your students?*

Strategy	Explain how the strategy contributes/relates to the lesson/activity
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<i>Incorporate culturally relevant teaching</i>	Emphasizes social justice (climate change/environmental justice)
<i>Making it a safe place</i>	Students can feel free to share ideas and trial an error (room to fail)
<i>Adjusting to the students learning needs</i>	Get students from where they are to allow them to grow, instead of assuming they are supposed to know certain material already

Connections to STEM Careers - *In what ways will you connect the activity to STEM Careers?*

- By explaining students about research
- Project based learning
- Allow them to experience a hands-on activity/perform experiment
- Enhancing teamwork in the classroom
- Giving the space for them to discuss with their classmates and analyze