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HYDROTHERMAL LIQUEFACTION OF SPECIALTY PLASTICS

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ABSTRACT

Hydrothermal liquefaction (HTL) was performed on Nylon 6 (NY), Nylon 6,6 (NY 6,6), Polysulfone (PSU), Polystyrene (PS), Polylactic acid (PLA), and Poly(styrene-*co*-acrylonitrile) (SAN) for 30 minutes to produce oil. Each plastic underwent HTL at 350°C and 425°C to examine temperature effects on oil yield. At 350°C, NY, PS, SAN, and PSU produced oil yields above 20%, and only PS, PSU, and SAN produced oil yields above 20% at 425°C. Increasing the HTL temperature from 350°C to 425°C resulted in many of the plastics producing decreased oil yields which is likely a result of decomposition and the formation of gaseous products. GC-MS analysis showed that the oil phases of NY contained caprolactam (the monomer form of NY), NY 6,6 contained cyclic ketones, PS, SAN, and PSU contained aromatic compounds and PLA contained alcohols, esters, and carboxylic acid containing compounds. HTL of mixtures containing 50 wt% of each plastic with polypropylene (PP) and cellulose were examined to see if interactions between the plastics with PP and cellulose would affect the oil yields obtained. It was determined that interactions between PP and the plastics were not significant at 350°C, but both synergistic and antagonistic interactions between mixtures of these plastics and cellulose were both observed under HTL conditions at 350°C.

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Chapter 1

Introduction

There is over 292.4 million tons of municipal solid waste (MSW) containing 12.2 wt% plastics produced each year in the United States.¹ Single-use disposable consumer items, such as take-out containers, make up 50% all plastic waste.² Only a small portion of plastic waste is recycled (13.6%) or combusted (16.9%).¹ There are large costs associated with plastic collection, transportation, and the recycling process itself.³ Besides costs, there are many concerns with recycling plastics including the immiscibility of different plastics (which require extensive separation) and various contaminants present in colored plastics (which make them unable to be recycled).² Incineration is also used decrease plastic waste, but this process has negative impacts such as the release of various toxins and ash into the environment.^{4,5} One viable option for plastic waste is energy recovery. Several pathways for plastic waste combustion to obtain energy have been explored in the past including direct combustion, gasification, and pyrolysis. Combustion of plastics is comparable to combustion of coal and wood but burning plastic can release chlorine and other heavy metals into the environment.^{6,7} Pyrolysis converts plastic into waxy products that can be further cracked into oil.⁸ Products resulting from the pyrolysis of plastics are typically rich in hydrocarbons and are nearly ideal for oil refineries.⁹ Although pyrolysis of plastics lead to high-density oils, there are several downfalls associated with this thermochemical process. Pyrolysis reactants must be pretreated to ensure no metal is present, moisture and oxygen must be removed, and the plastic must be sieved into uniform pieces prior to reacting.⁹ Gasification can also be used to produce oil from plastics, but this process requires excessive amounts energy and is expensive.¹⁰

Hydrothermal liquefaction (HTL) is thermochemical depolymerization process that is typically used to convert wet biomass into biocrude. HTL has a pressure range of 10-25 MPa and a temperature

range of approximately 200-400°C for biomass.¹¹ HTL is performed at subcritical or supercritical water conditions. At supercritical conditions, the dielectric constant of water is lowered allowing for non-polar organic molecules to be dissolved in water.¹²

There has been prior research on HTL depolymerization of polyethylene terephthalate (PET) and polycarbonate (PC).¹³ Surface conditions (hydrophobic properties, hydrophilic, e.g.), first order structures (chemical structure, molecular weight distribution, e.g.) and second order structures (melting temperature, glass transition temperature, e.g.) are shown to play a significant role in the degradation of polymers and plastics.¹⁴ Polymers containing ester, ether, or amide linkages can decompose via hydrolysis near supercritical water conditions.¹⁵ For example, PET is depolymerized into ethylene glycol and terephthalic acid at supercritical water conditions and the HTL of PC showed high conversions for producing its monomer form, Bisphenol-A.¹⁵ Free radical depolymerization reaction pathways are also observed at supercritical conditions.¹⁶ These past experiments emphasize decomposition pathways that occur under HTL. Further experimentation and analysis must be done to characterize the components present within the oil phase to gain a further understanding of reaction pathways.

Most research related to the HTL of plastics has focused on biomolecule and plastic mixtures. One study experimented with the HTL of microalgae mixtures with individual plastics (PE, PP, and NY).¹⁷ Under HTL conditions, these plastics were shown to interact with biomass leading to compositional changes in the oil phase.¹⁷ This same study determined that increasing the plastic loading rate had different effects on the product yields.¹⁷ As the plastic loading rate increased, the solid yields increased for PE and PP while the aqueous yield increased for NY. Only slight decreases in oil yield were observed as the plastic loading rate for these mixtures of microalgae with PE, PP, and NY increased up to 25 wt%.¹⁷ Another study was performed on the HTL of synthetic polymer and biomolecule mixtures. A mixture of starch, lignin, cellulose, soy protein, stearic acid, PP, PC, and PET, simulating MSW, underwent HTL at various temperatures for 30 minutes.¹⁸ At 300°C, the oil yield obtained (31.6 %) was estimated to have

been twice as high as the oil yield that would have been obtained from the HTL of the individual components.¹⁸

Only sparse studies have been performed on the oil yields obtained from the HTL of single plastics. The plastics that have been previously researched are PC, PET, and PP. One study looked at the oil yields obtained from the HTL of PC and PP at different temperatures. HTL of PC (425°C, 30 min) and PP (425°C, 30 min) gave high oil yields of 60% and 32% , respectively.¹³ For this study, supercritical water conditions were achieved. A study involving the supercritical water liquefaction of high-impact styrene (HIPS) also produced a high oil yield of 88.4% (350°C) and contained compounds with aromatic structures.¹⁹

There are only a few plastics that have been utilized in HTL research. Much of this research focuses on plastic mixtures with biomolecules, and there is a lack of different plastics being utilized for HTL. There are variety of plastics presents within MSW, and the HTL of these plastics must be explored to compare oil composition, reaction pathways, and overall conversion of these plastics.

This research reports effects of temperature on the HTL of NY, NY 6,6, PLA, SAN, PSU, and PS at 350°C and 425°C. These plastics were selected due to their wide use in consumer good products such as textiles (NY), artificial fibers (NY 6,6), 3D filament (PLA), medical devices (PSU), and packaging (PS). The oil phase for each plastic and their compositions were analyzed to understand possible reaction pathways and determine whether the HTL of these plastics could be useful in future oil production. HTL of these plastics with mixtures of polypropylene and cellulose were also examined to see if interactions between the plastics and PP or cellulose would affect oil yields.

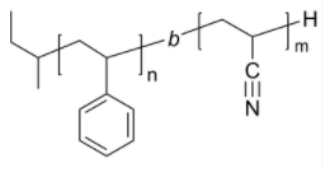
Chapter 2

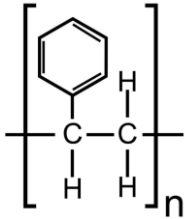
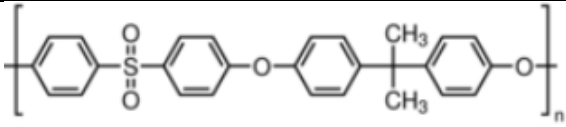
Experimental Method

Materials

HTL was performed on several plastics in their pellet form. The plastics utilized for these experiments and their structures can be found in **Table 1**. Cellulose (microcrystalline, Alfa Aeser) and polypropylene (Sigma Aldrich) were used in subsequent mixture experiments.

Table 1. Utilized plastics and their structures.

Plastic	Compound	Manufacturer
NY	$\left(\begin{array}{c} \text{H} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{---N---(CH}_2\text{)}_5\text{---C---} \\ \\ \text{---} \end{array} \right)_n$	Sigma Aldrich
NY 6,6	$\left(\begin{array}{c} \text{H} \quad \quad \quad \text{H} \quad \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \quad \quad \quad \quad \\ \text{---N---(CH}_2\text{)}_6\text{---N---C---(CH}_2\text{)}_4\text{---C---} \\ \\ \text{---} \end{array} \right)_n$	Sigma Aldrich
PLA	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---C(=O)---O---} \\ \\ \text{---} \end{array} \right]_n \text{H}$	Good Fellow
SAN		Sigma Aldrich

PS		Sigma Aldrich
PSU		Sigma Aldrich

The mini batch reactors used for this experiment contained an internal volume of 10.0 mL and were constructed from stainless steel 316 Swagelok parts (a 3/4 inch port connector and two caps) as seen in **Figure 1**.



Figure 1. 10.0 mL Swagelok Batch Reactor.

Before running the experiments, the reactors were scrubbed with warm water and soap. The reactors were then rinsed several times with both acetone and water before receiving distilled water rinses. The reactors were then dried for 30 minutes at 150°C in an oven (Thermo Scientific Thermolyne). Afterwards, the reactors were cooled to room temperature before loading.

Experimental Procedure

Each reactor was loaded with 0.3962g of plastic pellets. For the plastic and PP or cellulose mixtures, the reactor was loaded with 0.3962g of reactants on a 50 wt% basis. Enough distilled water was added to achieve an internal pressure 25 MPa inside the reactor for running HTL at 350°C (4.96 mL) and 425°C (1.0 mL). Triplicates of each reaction were performed simultaneously.

After loading, the reactors were sealed using a wrench. The reactors were submerged in a Techne Industrial Fluidized Sand Bath (Techne IFB-51) for 30 minutes as seen in **Figure 2**. The temperatures used for the reactions were 350°C and 425°C. After 30 minutes, the reactors were immediately submerged into a cold water bath for five minutes to quench the reaction and to allow reactor to reach room temperature. The reactors were set aside for at least 3 hours to allow any water remaining on the reactor to evaporate.



Figure 2. Techne Industrial Fluidized Sand Bath.

Extraction

With a wrench, the reactors were carefully opened to allow the gaseous products to escape. The reaction products were extracted with 10 mL of dichloromethane (VWR Chemicals) to dissolve the organic phase and 10 mL of distilled water to dissolve the aqueous phase as seen in **Figure 3**. The reactors were rinsed with these solvents until the extracted reactor contents ran clear. A 10 mL syringe attached to a 10 μ m filter (Tisch Scientific) was utilized to capture any solids floating within the aqueous or organic phases. The organic and aqueous phases were then placed in a 50 mL centrifuge tube (VWR Chemicals) and were centrifuged at 4000 rpm using an Eppendorf tabletop centrifuge (Model: 5810) for 8 minutes. The organic and aqueous phases were each separated into separate pre-weighed 15 mL test tubes (VWR Chemicals) by a 5-3/4 in. pipette (VWR Chemicals).

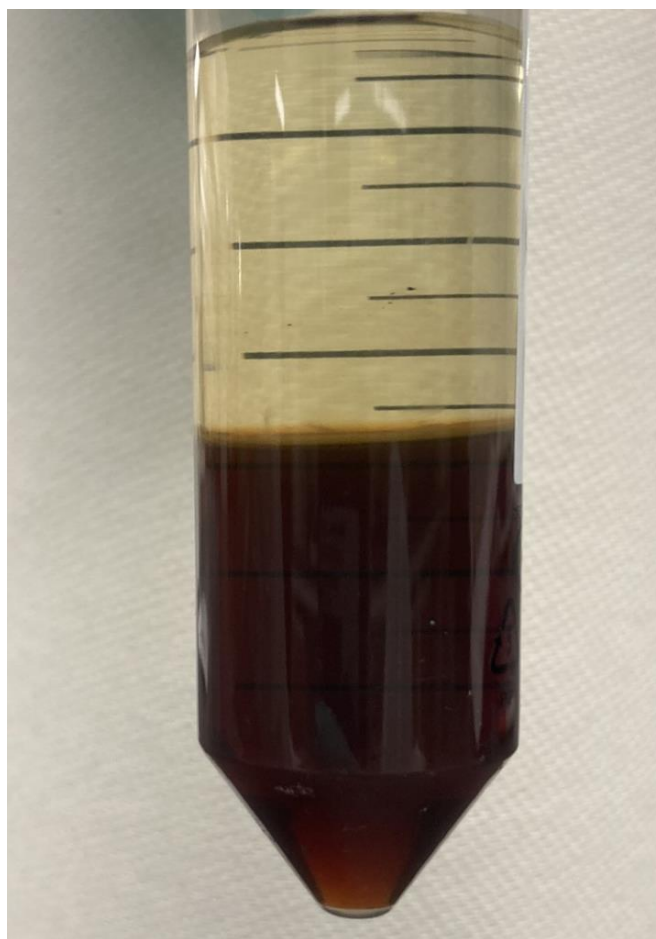


Figure 3. Extraction of the organic layer (bottom) and the aqueous layer (top).

Drying

The test tube containing the organic phase was placed into a test tube oven (LABCONCO RapidVap Vertex Evaporator) for approximately one day to ensure any remaining dichloromethane was evaporated as seen in **Figure 4**. The aqueous phase was placed into an oven (Fisherbrand Isotemp Microbiological Incubator) to allow the water to evaporate. Drying the aqueous phase took approximately one month. The reactor, pipette, filter, and centrifuge were placed into a separate oven (Thermo Scientific

Precision) for approximately one day to obtain the remaining solids. The mass of the oil and aqueous phases were calculated by subtracting the mass of the empty test tubes. The mass of the solid phase was calculated by subtracting the masses of the empty reactor, filter, syringe, centrifuge tube, and pipette. The yields of each phase were calculated using **Equation 1**.

$$\% \text{ Yield} = \frac{\text{mass (oil or aqueous or solid)}}{\text{mass of materials}} \times 100\% \text{ (Equation 1).}$$

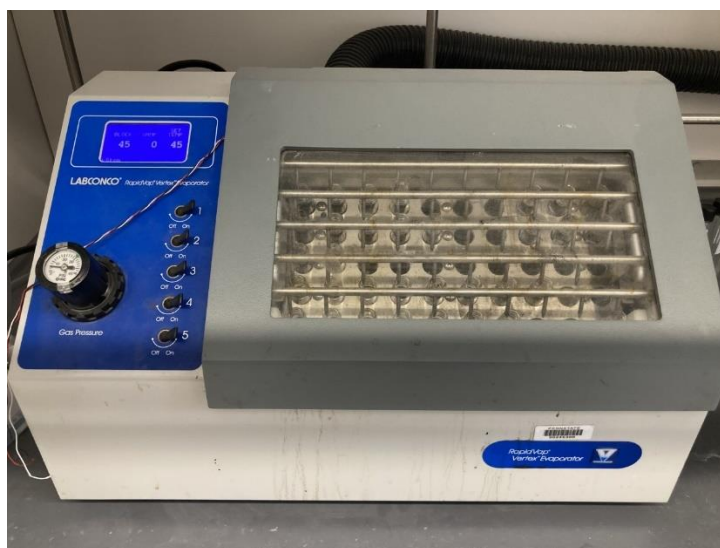


Figure 4. LABCONCO Rapid Vex Vertex Evaporator.

Oil Analysis

The oil yields produced during the HTL of each plastic at 350°C and 425°C was analyzed using a Shimadzu gas chromatograph mass spectrometer (GC-MS) (Model: PQ210 Ultra GC-MS). Each oil phase was dissolved using approximately 5 mL of dichloromethane, and a NIST mass spectral library was utilized to identify volatile components present within each oil phase.

Chapter 3

Yields (%) from the HTL of Single Plastics

Temperature Effects

HTL was performed on several plastics at two different temperatures (350°C and 425°C) for 30 minutes. These temperatures were chosen to ensure supercritical water conditions are achieved during HTL.²⁰ Past research also suggests liquefaction typically occurs at around 200-400°C, and gasification occurs at 400-700°C for many biomolecules.²¹ Oil, solid, and aqueous yields at these two temperatures were then calculated. During HTL, gaseous products were also produced and lost upon opening the reactor, but they also make up a part of the overall product yield.

Both PS and SAN produced high oil yields at supercritical temperatures as seen in **Figure 5**. Both polymers produced the highest oil yields at 350°C. At this temperature, HTL of PS and SAN produced oil yields of $81.6 \pm 1.3\%$ and $83.9 \pm 1.7\%$, respectively. Control experiments performed on these plastics showed that PS and SAN can be dissolved with dichloromethane at room temperature. Dissolving the same sample size of PS and SAN used during the HTL experiments showed that 54% of PS and 57% of SAN was able to be dissolved. The oil yields obtained from the HTL of PS and SAN at 350°C were higher than the amounts of PS and SAN that were dissolved using dichloromethane during the control experiments indicating that depolymerization occurred during HTL of these plastics. Past research suggests that random scissions are a major thermal degradation pathway for PS.²² Further degradation can occur through propagating β -scission reactions and chain end scissions.²³ As the HTL temperature increased to 425°C, the oil yields of PS ($44.26 \pm 2.5\%$) and SAN ($44.5 \pm 3.0\%$) decreased significantly. This decrease in oil yields with increasing temperature corresponds to the total thermal degradation of PS which occurs at approximately 425°C leading to the formation of gaseous products.²⁴ This could explain

the large decrease in total yield (%) of the solid, aqueous, and oil products. There is limited information on the thermal degradation of SAN, but it likely undergoes similar thermal degradation pathways as PS due SAN being a co-polymer containing both styrene and acrylonitrile repeat units. Therefore, the HTL of these polymers yields have comparable results. Small solid yields resulted from the HTL of both plastics at both temperatures. Any unreacted PS or SAN would likely be dissolved with DCM. The HTL of both PS and SAN produced minimal aqueous yields. SAN produced a larger aqueous yield than PS at both 350°C and 425°C. The increased aqueous yields obtained from the HTL of SAN is likely due the nitrile group being soluble in water. PS is insoluble in water as it is non-polar and therefore has smaller aqueous yields.²⁵ Interestingly, the addition of the nitrile group did not appear to affect the depolymerization of SAN as the oil yields obtained from PS and SAN were nearly the same at each HTL temperature.

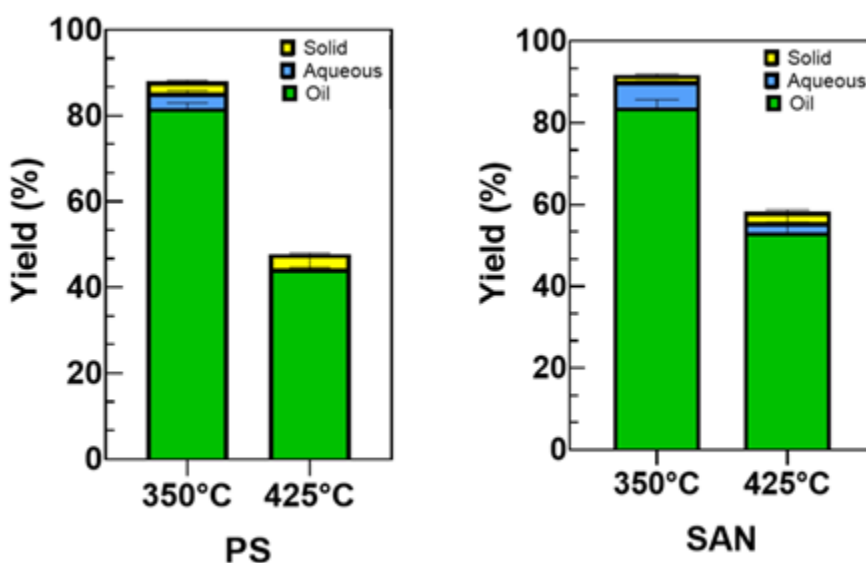


Figure 5. Yields (%) of products from the HTL of PS and SAN at 350°C and 425°C.

HTL of NY and NY 6,6 at both 350°C and 450°C produced significant aqueous yields as seen in **Figure 6**. The aqueous yields obtained were $69.7 \pm 2.5\%$ (NY at 350°C), $47.0 \pm 2.6\%$ (NY at 425°C),

$58.7 \pm 2.1\%$ (NY 6,6 at 350°C), and $53.9 \pm 2.4\%$ (NY 6,6 at 425°C). In past studies, NY has been shown to decompose in both subcritical and supercritical water conditions.²⁶ Hydrolysis of NY leads to the formation of ϵ -aminocaproic acid which can undergo cyclodehydration to yield caprolactam (the monomer of NY) which is highly soluble in water thus leading to large aqueous yields.²⁶ Past research has reported two major pathways of NY decomposition.²⁷ One involves the scission of the C-N bond in the beta position to the amide group during a hydrogen transfer reaction and the other involves intramolecular back-biting leading to the formation of caprolactam.²⁷ High aqueous yields for NY, at both temperatures, suggests that that nylon was decomposed to caprolactam or further components which were then dissolved in water due to hydrogen bonding. The decrease in aqueous yields at 425°C is due to further thermal degradation of NY which occurs from a range of 350 - 500°C .²⁸

In a control experiment, only 0.9% of NY and 1.3% of NY 6,6 was able to be dissolved with dichloromethane at room temperature. If any NY or NY 6,6 remained unreacted, it would likely remain within the solid phase which could explain the small solid yields observed for both NY and NY 6,6 at both temperatures. The oil yield produced during the HTL of NY decreased from $20.1 \pm 1.2\%$ at 350°C to $3.0 \pm 0.7\%$ at 425°C . The opposite trend was observed for the HTL of NY 6,6. For NY 6,6, the oil yield increased from $4.8 \pm 0.2\%$ at 350°C to $14.8 \pm 2.0\%$ at 425°C . The increased oil yield produced during the HTL of NY 6,6 at 425°C suggests that thermal degradation only begins at exceedingly high temperatures.

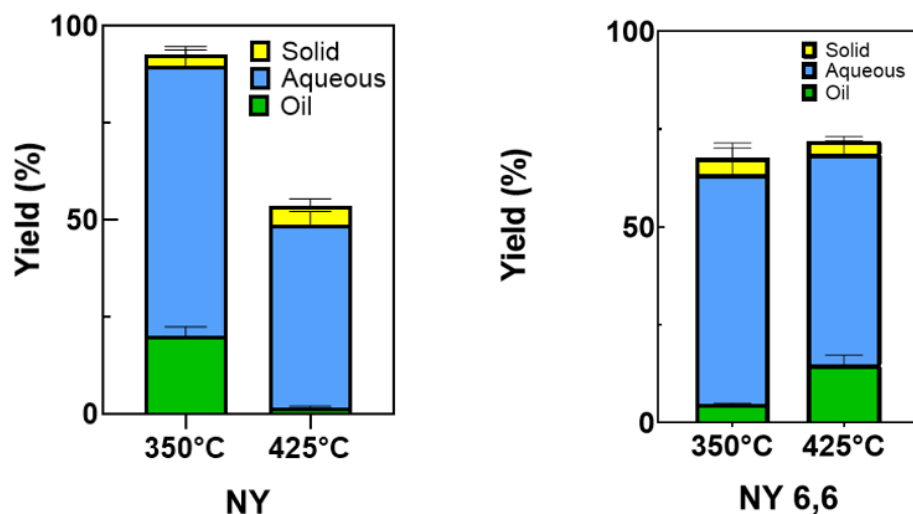


Figure 6. Yields (%) of products from the HTL of NY and NY 6,6 at 350°C and 425°C.

PLA contains ester groups which can undergo degradation via hydrolytic cleavage. Hydrolytic scissions of the ester bonds lead to the formation of carboxylic acid end groups.²⁹ The formation of these carboxylic end groups via hydrolysis can explain why the HTL of PLA leads to small aqueous yields of $8.3 \pm 0.6\%$ (at 350°C) and $4.8 \pm 0.5\%$ (at 425°C) as carboxylic acids are soluble in water as seen in **Figure 7**. The decrease of aqueous yield from 350°C to 425°C is likely due to thermal degradation becoming the dominating pathway. If long carbon chains are formed, attached to carboxylic groups, these products would slightly soluble present in the organic layer which could explain small oil yields of $4.2 \pm 0.5\%$ (at 350°C) and $3.0 \pm 0.5\%$ (at 425°C). The formation of carboxylic acids can also further increase the degradation of PLA due to a decrease in pH leading to auto catalyzation.³⁰ From 350°C to 425°C, the solid yield decreases $15.3 \pm 1.0\%$ to $10.8 \pm 2.0\%$. Past TGA analysis of PLA showed that decomposition of PLA, under nitrogen gas, occurs at 335°C.³¹ Volatile products such as carbon dioxide, carbon monoxide and cyclic oligomers are produced during the thermal degradation of PLA at high temperatures.^{32,33} This could explain why solid, aqueous, and oil yields decreased at 425°C as more gaseous products were being formed. The formation of gas was also indicated by a fruity smell that was emitted from the reactors upon opening them after HTL of PLA at both 350°C and 425°C.

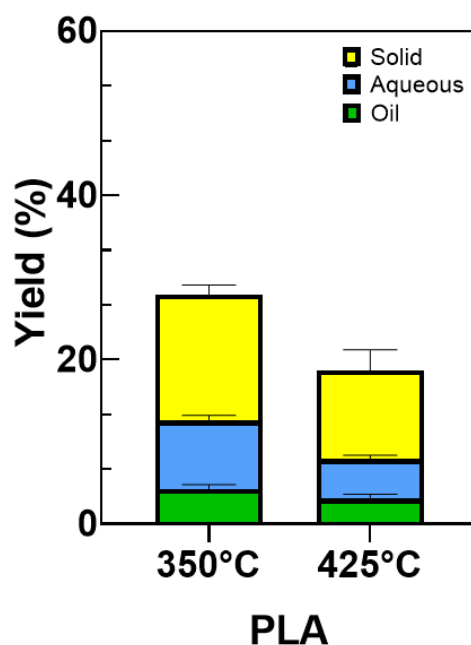


Figure 7. Yields (%) of products from the HTL of PLA at 350°C and 425°C.

PSU is resistant to high temperatures and has a high glass transition temperature of 185°C.³⁴ At high temperatures, the thermal degradation of PSU can lead to the formation of volatile products which can explain the significant overall yield decrease from 350°C to 425°C.³⁵ When the reactors were opened, there was a pungent smell possible indicating that sulfur dioxide gas or hydrogen sulfide gas was produced during the HTL of PSU at 425°C. This pungent smell was not present upon opening the reactors for the 350°C trials. One possible pathway for the formation of sulfur dioxide gas is via the scission of S-C bonds.³⁵ At both temperatures, a minimal amount of aqueous product was recovered. This result is not surprising as main chain random scission, which occurs at elevated temperatures, leads to the formation of bulky products containing phenyl groups which are insoluble in water.³⁶ Oil yields were shown to increase from $23.3 \pm 2.3\%$ at 350°C to $44.5 \pm 3.0\%$ at 425°C. As temperature increases, the thermal degradation of PSU increases. Due to PSU being highly resistance to temperature, depolymerization of

PSU is more prominent at 425°C. From 350 °C to 425°C, solid yields decreased significantly. One explanation for decreasing solid yield is that some of the PSU did not react during the HTL at 350°C. The blank experiment performed showed that the extraction process performed on PSU would lead to 56.6% solid yield. If unreacted PSU were present in the reactor, it would likely remain within the solid phase.

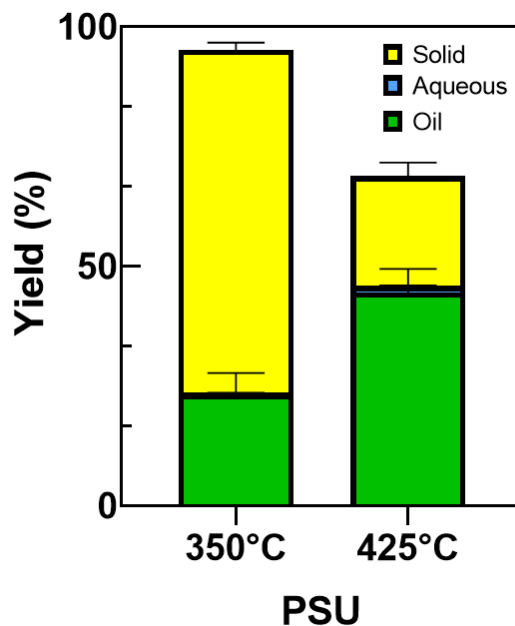


Figure 8. Yields (%) of products from the HTL of PSU at 350°C and 425°C.

GC-MS Analysis of The Oil Phase

GC-MS analysis was performed on the oil yields produced from the HTL of each plastic at 350°C and 425°C. This section will summarize the types of molecules found within the oil phases. The results obtained from the GC-MS analysis confirm the pathways previously discussed and tables containing the top four compounds present within each oil phase can be found in the **Appendix**.

The HTL of NY at both 350°C and 425°C produced substantial amounts of caprolactam (the monomer of NY). Past pyrolysis research of NY suggests two major reaction pathways for degradation: scission of the C-N bond in the beta position to the amide group during a hydrogen transfer reaction and

intramolecular back-biting.²⁷ The GC-MS analysis of oil phase produced from the HTL of NY at 350°C showed the presence of long chain alcohols, long chain aliphatic, and long chain esters compounds, which was an unexpected result. This result could be due to contamination within the GC-MS column. The GC-MS analysis of the 425°C oil phase produced from the HTL of NY showed the presence of aromatic compounds and nitriles which was unexpected and is likely due to contamination from the previous GC-MS sample (SAN).

The GC-MS analysis of the oil phases produced from the HTL of NY 6,6 at both 350°C and 425°C both showed the presence of cyclic ketones, cyclic amides, and amides. Unsaturated cyclic ketones result from intramolecular cyclisation of adipic acid groups within a carbon chain.³⁷ Cyclization can occur during the reformation of an amide bond between a carboxylic acid group. The presence of both cyclic ketones indicate that depolymerization of NY 6,6 has occurred.

The GC-MS analysis of the 350°C and 450°C oil phases produced from the HTL of SAN both contained aromatic structures and compounds with nitrile groups. GC-MS analysis of the oil yields produced from the HTL of PS at 350°C and 425°C also contained compounds with aromatic structures. The presence of aromatic structures indicate random chain scissions and chain-end scissions were major degradation pathways that occurred during HTL of PS and SAN.²² These reactions occur due to the presence of weak C-C links within the carbon back bone.³⁸ It is likely that both polymers undergo the same reaction pathways as the oil phases contain similar compounds. The acrylonitrile repeat unit within in SAN did not appear to have an impact on thermal degradation.

Analysis of the oil phase produced from the HTL of PLA at 350°C showed the presence of ester and carboxylic acid containing compounds. The presence of ester containing compounds indicates that transesterification reactions occurred during the HTL of PLA, and the presence of carboxylic acid indicates that hydrolytic degradation of PLA occurred under HTL conditions at 350°C.³⁹ The oil phase produced from the HTL of PLA at 425°C contained long chain alcohols which was an unexpected result. It is possible that products from the oil yield were less volatile and not detected during GC-MS analysis.

The analyses of the oil phases produced during the HTL of PSU at 350°C and 425°C differ from each other. Long chain aliphatic and long chain alcohol compounds were detected in the oil phase produced from the HTL of PSU at 350°C. These compounds are from some sort of contamination and are not indicative of PSU degradation. The GC-MS analysis of the oil yield produced from the HTL at 425°C contained compounds with aromatic rings which are consistent with chain scissions of PSU.

Chapter 4 Oil Yields (%) from the HTL of Plastic Mixtures

Co-HTL was performed on 50 wt% mixtures of the previously tested plastics with PP and cellulose. HTL was performed for 30 minutes at 350°C. This temperature was chosen as the HTL of many of these plastics at 425°C led to decreased oil yields compared to the oil yields produced during the HTL of these plastics at 350°C. To determine whether interactions between these plastics and PP or cellulose had significant effects on the production of oil yields, the p-values between the oil yields produced from the HTL of the single plastics and the oil yields produced from the HTL of the plastic mixtures were evaluated. Interactions were considered to be significant if the p-values are less than 0.05.

Plastic and PP Mixtures

The oil yields produced from the HTL of 50 wt% mixtures of each plastic with PP can be seen in **Figure 9**. The HTL of mixtures of PS, SAN, PSU, PLA, NY 6,6 with PP exhibited no signs of interactions as the p-values calculated for these mixtures all exceeded 0.1, and the experimental oil yields did not vary from the estimated oil yields that would have been produced from the HTL of the individual components. Past research showed that HTL of PP at 350°C resulted in minimal thermal degradation which could explain why no interactions were observed.¹³ It is possible that interactions between PP and these plastics may change with temperature as seen in previous research investigating the HTL of plastic and biomolecule mixtures in which exhibited both synergistic and antagonistic effects at different temperatures.¹⁸ Interactions between the plastics and PP may also be affected by loading weight.

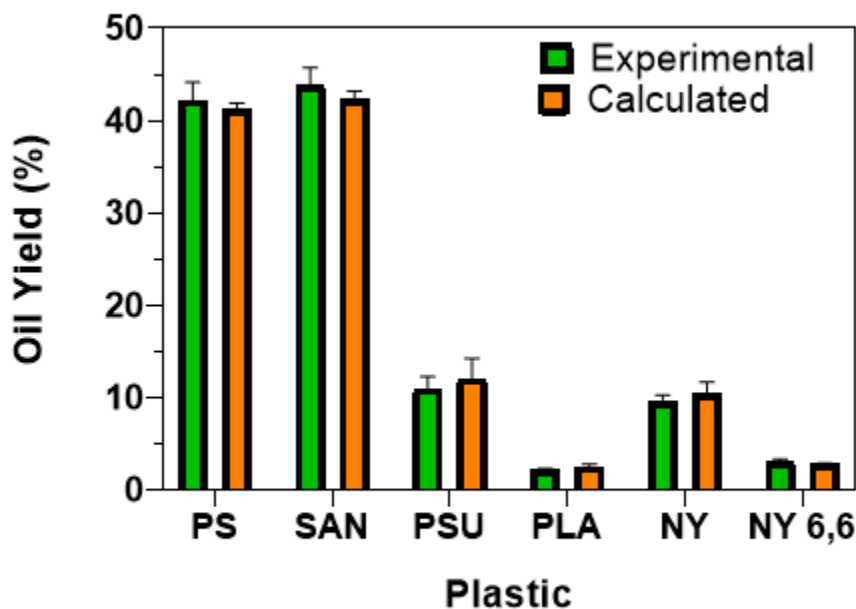


Figure 9. Oil yield (%) from the HTL (350°C, 30 min) of equal mass mixtures of each plastic and PP.

Plastic and Cellulose Mixtures

The oil yields produced from the co-HTL of 50 wt% mixtures of cellulose with each plastic showed that both synergistic and antagonistic interactions between the plastics and cellulose. The interactions between PS, SAN, PSU, and PLA with cellulose under HTL conditions were synergistic and the experimental oil yields of these mixtures were higher compared to the calculated oil yields of the mixture components being processed individually through HTL. The HTL of the NY, NY 6,6, with cellulose mixtures exhibited antagonistic interactions at HTL conditions which lead to smaller oil yields of these mixtures being produced compared to the calculated oil yields of the components being individually processed through HTL as seen in **Figure 10**.

The most significant synergistic interactions were observed between PLA and cellulose under HTL conditions. The oil yield produced from the HTL of PLA and cellulose ($24.4 \pm 0.7\%$) was

significantly higher than calculated oil yield of the mixture components being processed individually ($6.6 \pm 0.5\%$). At high temperatures, the thermal degradation rate of cellulose increases leading to the formation of hydroperoxide groups and carboxyl groups.⁴⁰ The formation of these groups could lead to lower pH conditions. It is possible that these slightly acidic conditions accelerated the degradation of PLA leading to increased oil yields.³⁹ The oil yields produced from the HTL of cellulose mixtures with PS ($59.9 \pm 1.8\%$) and SAN ($60.0 \pm 2.3\%$) were also larger than the calculated oil yields of the plastics being processed individually through HTL (PS ($45.2 \pm 0.7\%$), SAN ($46.3 \pm 0.9\%$)). The thermal degradation of cellulose leads to the formation of free radicals which can then be capped by PS and SAN through hydrogen atom transfer which could increase the oil yields produced.⁴¹ The oil yield produced from the HTL of PSU and cellulose was $19.3 \pm 0.7\%$ which was larger than the calculated oil yield of the mixture components being individually processed through HTL ($16.1 \pm 1.6\%$). Only slight synergistic interactions were observed between PSU and cellulose. One explanation could be from the cleavage of the C-O bond which leads to the formation of phenol after hydrogen abstraction.³⁶ The formation of phenol could have slightly increased the thermal degradation of cellulose which is sensitive to slight pH effects.

Antagonistic interactions were observed from the HTL of cellulose with NY and NY 6,6. The estimated oil yields for HTL of the individual components being processed individually were $14.5 \pm 1.2\%$ (NY) and $6.9 \pm 0.3\%$ (NY 6,6). These calculated oil yields were larger than the oil yields produced from the HTL of these mixtures of NY ($7.6 \pm 0.6\%$) and NY 6,6 ($1.1 \pm 0.3\%$) with cellulose. The HTL of NY 6,6 by itself showed minimal decomposition and produced low oil yields in the previous experiments. One study suggests that NY 6,6, is an unreactive polymer that could potentially act as a barrier between water and biomass preventing the degradation of biomass through hydrolysis therefore leading to decreased oil yields.⁴² The result of NY 6 having antagonistic interactions with cellulose is rather surprising since both components are fairly polar.

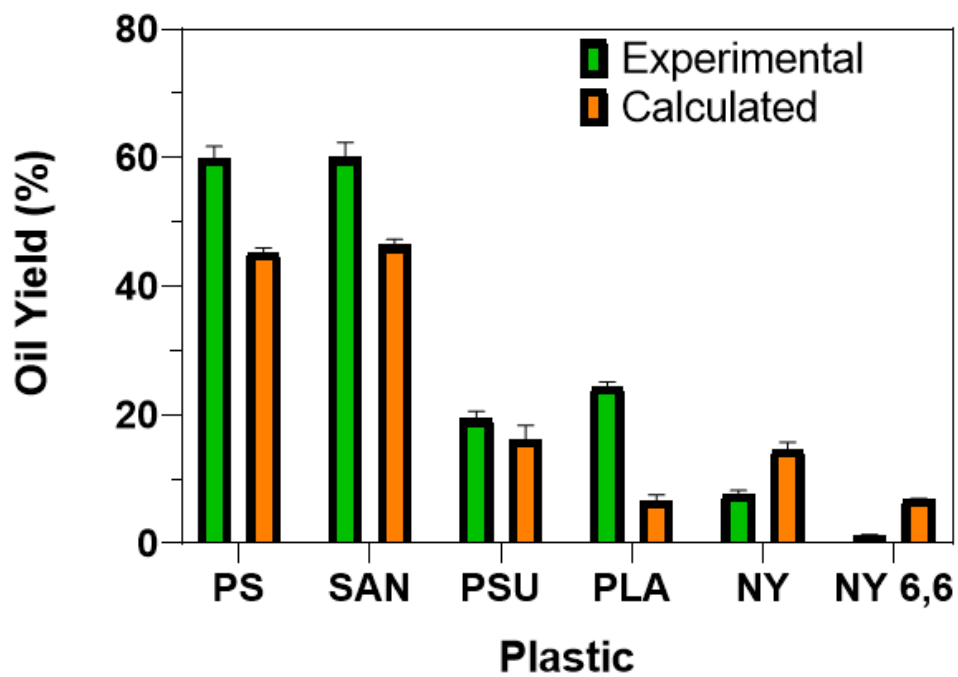


Figure 10. Oil yield (%) from the HTL (350°C, 30 min) of equal mass mixtures of each plastic with cellulose.

Chapter 5 Conclusion

The goal of this research was to utilize HTL on commonly used plastics to produce oil. Previous research on the HTL of plastics is minimal, and most research involving HTL primarily focuses on biomolecules. Performing HTL on plastic could be a solution for handling plastic waste which is expensive to recycle and is harmful to the environment if incinerated. This research involved conducting HTL on several plastics at 350°C and 425°C to examine whether temperature affected oil yields. It was found that HTL of NY, PS, SAN, and PSU yielded significant oil yields which were affected by temperature. Further research of using HTL on these plastics at higher and lower temperatures should be conducted. GC-MS was utilized to characterize compounds present within the oil phases produced from the HTL of these plastics at 350°C and 425°C to classify possible reaction pathways. Interactions between these plastics with PP and cellulose under HTL conditions were also investigated. HTL of mixtures containing 50 wt% of each plastic with polypropylene did not show significant interactions occurring under HTL conditions at 350°C. Interactions between the plastics and PP at different temperatures would have to be further explored. Both synergistic and antagonistic effects were observed in the oil yields produced from the HTL of the 50 wt% mixtures of each plastic and cellulose. This study has found that HTL of these plastics can produce significant oil yields and the mixture of plastics with biomolecules can have major effects on the production of the oil phase.

Appendix

GCMS Analysis

The tables below display the top four area peaks from the GC-MS analysis of the oil phases produced from the HTL of each plastic at 350°C and 425°C. Each peak contains a compound name, classification, a depiction of the compound detected, the area (%) of the volatile component identified within the oil phase, and a similarity index (SI) value. The SI value indicates the reliability of the identification of the volatile components within the oil phase.⁴³ For this research, a good identification was indicated by an SI value greater than seventy.

Table 2. Major products identified in the oil phase from the HTL of NY (350°C, 30 min).

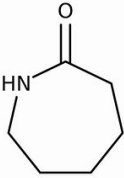

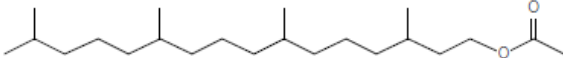

Name	Structure	Type	Area (%)	SI
Caprolactam		Cyclic Amide	68.2	75
Heptane,4,4-dimethyl		Long chain aliphatic	25.9	84
Acetic acid, 3,7,11,15-tetramethyl- hexadecyl ester		Ester	0.16	83
3-Eicosene, (E)-		Alkene	0.15	70

Table 3. Major products identified in the oil phase from the HTL of NY (425°C, 30 min).

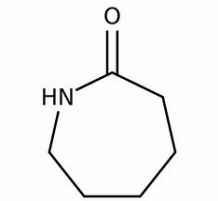
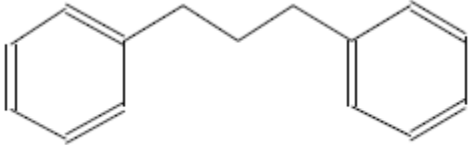
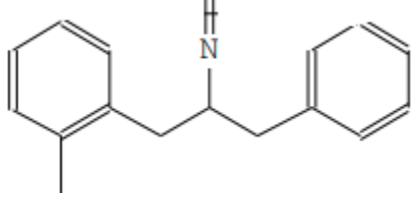
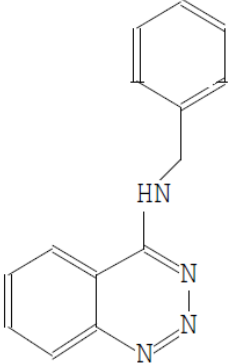
Name	Structure	Type	Area (%)	SI
Caprolactam		Cyclic Amide	16.75	71
Benzene, 1,1'-(1,3-propanediyl)bis-		Aromatic	10.28	91
(1-Benzyl-2-O-tolyl-ethyl)-is nitrile		Aromatic	6.97	77
4-[Benzylamine]benzo-1,2,3-triazine		Aromatic	5.02	77

Table 4. Major products identified in the oil phase from the HTL of NY 6,6 (350°C, 30 min).

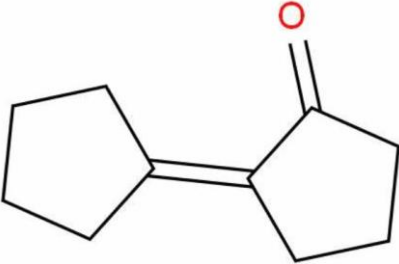
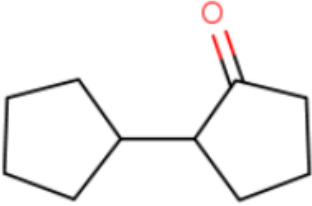
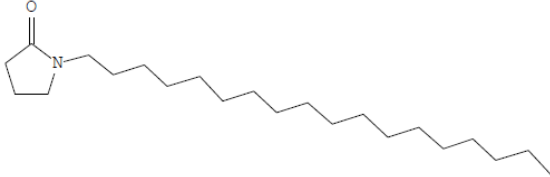
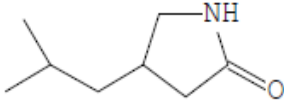
Name	Structure	Type	Area (%)	SI
Cyclopentanone, 2-cyclopentylidene-		Ketone	4.01	96
[1,1'-Bicycloptenyl]-2-one		Ketone	3.72	90
2-Pyrrolidinone, 1-octadecyl-		Cyclic Amide	3.35	74
4-Isobutyl-2-pyrrolidinone		Cyclic Amide	1.95	75

Table 5. Major products identified in the oil phase from the HTL of NY 6,6 (425°C, 30 min).

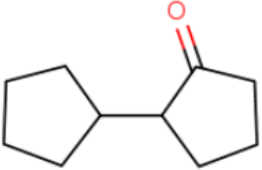
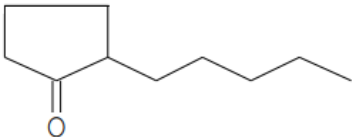
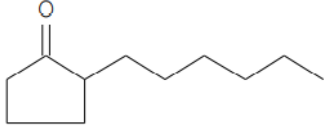
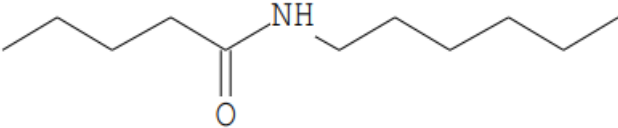
Name	Structure	Type	Area (%)	SI
[1,1'-Bicyclopentyl]-2-one		Ketone	3.90	76
2-Pentylcyclopentanone		Ketone	2.86	83
2-n-Hexylcyclopentanone		Ketone	2.54	83
Valeramide, N-hexyl-		Amide	2.06	86

Table 6. Major products identified in the oil phase from the HTL of SAN (350°C, 30 min).

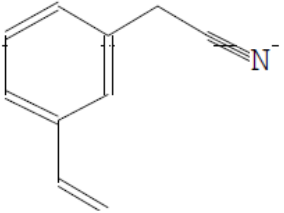
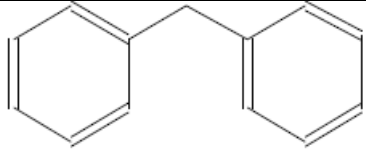
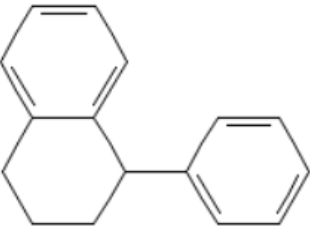
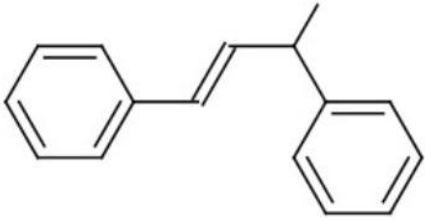
Name	Structure	Type	Area (%)	SI
Vinyl phenyl acetonitrile		Aromatic	12.31	84
Diphenylmethane		Aromatic	10.38	82
Naphthalene, 1,2,3,4-tetrahydro-1-phenyl		Aromatic	7.17	71
Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-		Aromatic	5.04	74

Table 7. Major products identified in the oil phase from the HTL of SAN (425°C, 30 min).

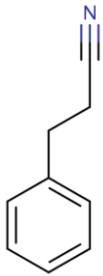
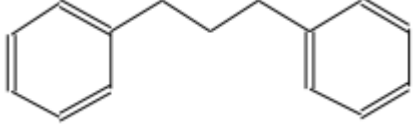
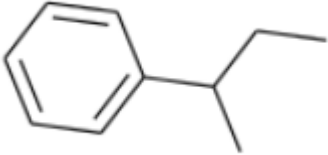
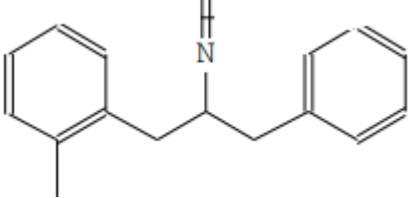
Name	Structure	Type	Area (%)	SI
Benzenepropanenitrile		Aromatic	21.31	75
1,1'-(1,3-propanediyl)bis-		Aromatic	9.36	95
Benzene, (1-methylpropyl)-		Aromatic	8.46	75
(1-Benzyl-2-O-tolyl-ethyl)-isonitrile		Aromatic	6.74	73

Table 8. Major products identified in the oil phase from the HTL of PS (350°C, 30 min).

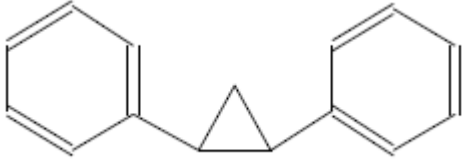
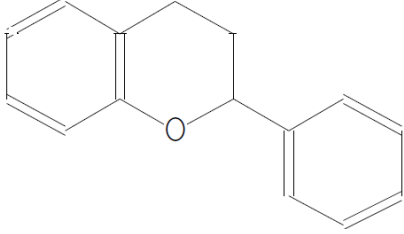
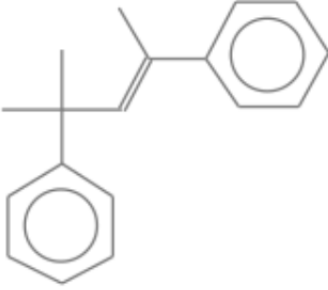
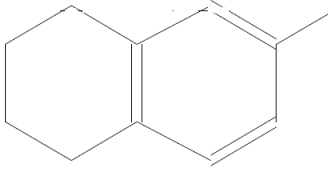
Name	Structure	Type	Area (%)	SI
1,2-Diphenylcyclopropane		Aromatic	31.78	85
2H-1-Benzopyran, 3,4-dihydro-2-phenyl-		Aromatic	6.33	73
2,4-Diphenyl-4-methyl-2(E)-pentene		Aromatic	4.43	72
Naphthalene, 1,2,3,4-tetrahydro-6-methyl-		Aromatic	3.13	70

Table 9. Major products identified in the oil phase from the HTL of PS (425°C, 30 min).

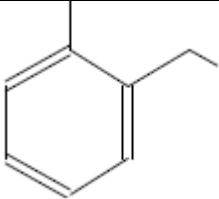
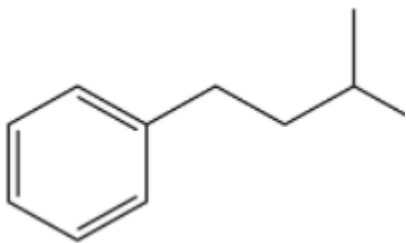
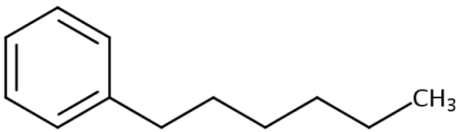
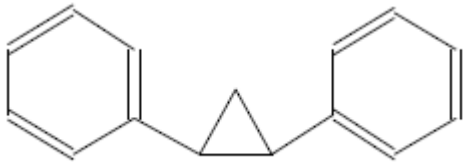
Name	Structure	Type	Area (%)	SI
Benzene, 1-ethyl-2-methyl-		Aromatic	10.81	95
Benzene, 1-methyl-3-(1-methylethyl)-		Aromatic	7.96	90
Benzene, hexyl-		Aromatic	6.42	78
1,2-Diphenylcyclopropane		Aromatic	5.38	91

Table 10. Major products identified in the oil phase from the HTL of PLA (350°C, 30 min).

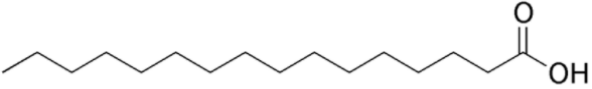
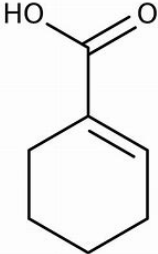
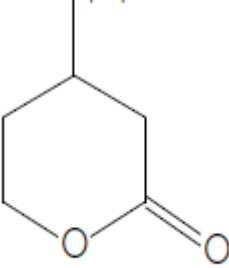
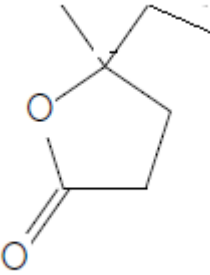
Name	Structure	Type	Area (%)	SI
n-Hexadecenoic Acid		Fatty Acid	9.78	95
1-Cyclohexene-1-carboxylic acid		Carboxylic Acid	6.37	80
2H-Pyran-2-one, tetrahydro-4-methyl-		Cyclic Ester	3.65	90
2(3H)-Furanone, 5-ethyl-5-methyl-		Cyclic Ester	3.41	90

Table 11. Major products identified in the oil phase from the HTL of PLA (425°C, 30 min).


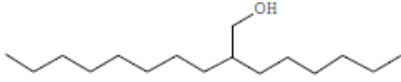
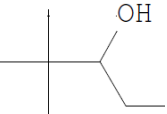
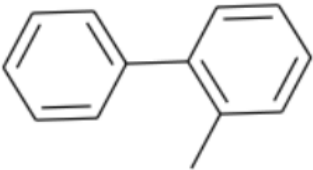
Name	Structure	Type	Area (%)	SI
n-Tridecan-1-ol		Alcohol	13.80	85
1-Decanol, 2-hexyl-		Alcohol	6.56	82
3-Pentanol, 2,2-dimethyl-		Alcohol	3.98	74
1,1'-Biphenyl, 2-methyl-		Aromatic	3.15	90

Table 12. Major products identified in the oil phase from the HTL of PSU (350°C, 30 min).

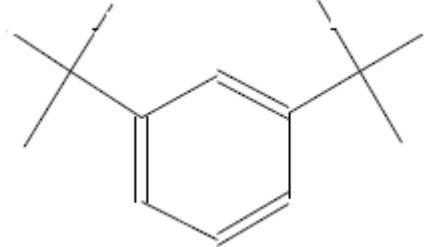


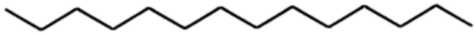
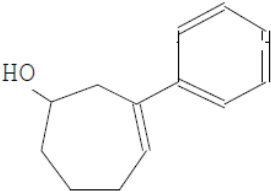
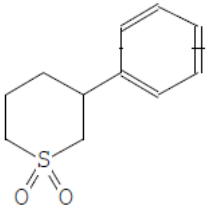
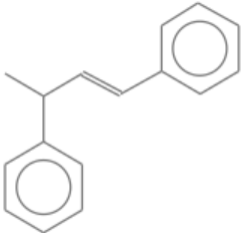
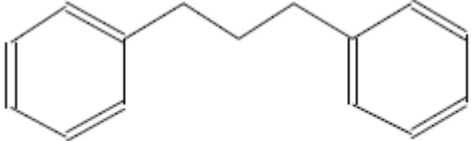
Name	Structure	Type	Area (%)	SI
Benzene, 1,3-bis(1,1-dimethylethyl)-		Aromatic	11.17	92
Dodecane		Long Chain Aliphatic	7.55	97
Decane		Long Chain Aliphatic	4.73	91
Tetradecane		Long Chain Aliphatic	3.97	96

Table 13. Major products identified in the oil phase from the HTL of PSU (425°C, 30 min).

Name	Structure	Type	Area (%)	SI
3-Cyclohepten-1-ol, 3-phenyl-		Aromatic	16.75	70
3-Phenylthiane,S,S-dioxide		Aromatic	15.67	80
Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-		Aromatic	11.71	75
Benzene, 1,1'-(1,3-propanediyl)bis-		Aromatic	2.78	95

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ACADEMIC VITA

BIANCA VILLACIS

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EDUCATION

The Pennsylvania State University | University Park

B.S. Chemical Engineering | Anticipated Graduation: May 2022

Schreyer Honors College

EXPERIENCE

Undergraduate Researcher (Dr. Phillip Savage Research Group)

August 2021 – Present

- Performed hydrothermal liquefaction processes on biomolecule and polymer mixtures to produce bio-crude.
- Utilized GC-MS to characterize the recovered bio-crude products.
- Researched the effects of temperature and plastic mixtures variations on bio-crude yield.

Chemical Engineering Grader

August 2020 – December 2020

- Graded homework for a chemical engineering computational tool course.
- Helped students troubleshoot issues on Microsoft Excel and Mathematica.

Math Peer Assistant

August 2019 – December 2019

- Tutored students in college algebra and analytical geometry courses.
- Facilitated exam and homework review sessions.

Engineering Peer Mentor

August 2019 – December 2019

- Aided in creating a lesson plan for an introductory engineering course.
- Created guides aimed to help first-year engineering students complete college tasks.

Chemistry Lab Assistant

January 2019 – May 2019

- Prepared and standardized solutions made for student usage.
- Set up and conducted experiments for organic and general chemistry lab courses.

EXTRACURRICULAR

Engineering Ambassadors (Engineering Ambassador Network)

March 2020 – Present

- Co-authored a proposal for nationwide program funding through Raytheon Technologies.
- Created the foundation for a new Engineering Ambassador Network website.
- Presented engineering and science related topics to K-12 students.

Abington Engineering Club (Secretary)

August 2018 – December 2019

- Coordinated a group of club members to work on a semester-long trebuchet building project.
- Catalogued incoming members and created informative weekly newsletters.

AWARDS

- Fick Honors Scholarship
- McVicker Chemical Engineering Scholarship
- Ayoub Mathematics Achievement Award
- James R. Donnelley Chemical Engineering Scholarship
- Outstanding Chemistry Freshman Award
- The President's Freshman Award