

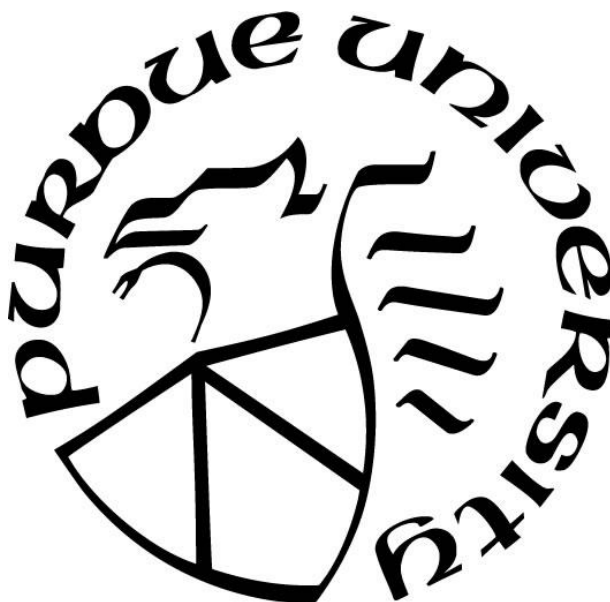
**CONVERSION OF POLYOLEFIN WASTE INTO USEFUL PRODUCTS
VIA HYDROTHERMAL PROCESSING (HTP) AND SEQUENTIAL
SELECTIVE EXTRACTION AND ADSORPTION (SSEA)**

by
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To my father and mother.

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ABSTRACT

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Title: Conversion of Polyolefin Waste into Useful Products via Hydrothermal Processing (HTP) and Sequential Selective Extraction and Adsorption (SSEA)

Committee Chair: Nien-Hwa Linda Wang

There has been an exponential increase of plastics being produced, used, and disposed of over the last 60 years. Most of plastic waste (76%) is consigned to landfills, 12% is incinerated, 3% ends up in the oceans while only 9% is recycled. If the current trend continues, more than 30 billion tons plastic waste will be generated on this planet and more plastic than fish will be in the oceans by 2050. Plastics take more than 100 years to degrade into plastic debris, microplastics, and toxic chemicals, which pose serious threats to the ecosystems, water and food supply, and eventually human health.

Polyolefins (Type 2 HDPE, Type 4 LDPE, and Type 5 PP), which are the majority (63%) of global plastic waste, are targeted in this study. Two methods, Hydrothermal Processing (HTP) and Sequential Selective Extraction and Adsorption (SSEA) were developed and tested.

HDPE was converted into wax and oils using supercritical water under HTP at reaction temperature 400- 450 °C with reaction time 0.5- 3 hr. PP was converted into oils under supercritical water at 425 °C with reaction time 1- 3 hr. The oil products from HDPE and PP via HTP were composed of paraffins, olefins, cyclics, and aromatics with carbon numbers from C6 to C31. Reaction intermediates were analyzed using two-dimensional gas chromatography with a flame ionization detector (GC × GC-FID). The results were used to establish potential reaction pathways of HDPE and PP, respectively. PP was found to react faster than HDPE under the same HTP conditions while generating more olefins and cyclics than HDPE. Clean wax was obtained from PE waste via HTP. Its Fourier-Transform Infrared Spectroscopy (FT-IR) spectrum was almost identical to the one of commercial paraffin wax. Oils converted from PE waste via HTP was distilled into three fractions. The diesel-like fraction ($170\text{ }^{\circ}\text{C} \leq \text{b.p.} < 300\text{ }^{\circ}\text{C}$) has similar properties as No.1 ultra-low-sulfur diesel. It also can be used as a blendstock for No2. Ultra-low-sulfur diesel.

SSEA methods were developed to recover pristine polymers from polyolefin waste via extraction and adsorption. Mixed solvents with higher selectivity, reduced toxicity, and lower costs

were found based on their Hansen Solubility Parameters. Extraction conditions were investigated using model polyolefins. Selective mixed solvents were found for the separation of LLDPE from LLDPE/PP blend. Pristine PE polymers were recovered from dark green PE waste pellets.

Preliminary analyses indicated HTP and SSEA have a higher energy efficiency and lower greenhouse gas (GHG) emissions than incineration, mechanical recycling, and pyrolysis. A combination of these two methods has the potential to convert 63% of the plastic waste into useful and profitable products. It also helps transform current linear path from crude oil to plastics to landfills, to a more sustainable circular path.

CHAPTER 1. INTRODUCTION

1.1 Plastic Waste Problem

Plastics have become an inseparable part of people's daily lives. They are widely used in packaging, electrical and electronic, transportation, and building and construction materials because of their high strength to weight ratio and low synthesis cost.¹ An exponentially increase of the production of plastics was observed during the last 60 years.¹ In 2015, 380 million ton of plastics were produced globally while only two million ton in 1950.² A major fraction of plastics is of single-use and has a lifetime less than one year.^{1,3} It then becomes waste and is disposed of. The plastic waste generated by 2015 was about six billion tons (Figure 1). The majority of plastic waste (76%) was landfilled. About 12% of the plastic waste was incinerated, while only 9% was recycled. The rest 3% ended up in the oceans.¹ A floating plastic waste gyre of the same size of Texas called the "Great Pacific Garbage Patch" was found in Pacific Ocean.⁴ If the current trend continues, there will be more than 30 billion tons plastic waste generated on this planet by 2050.⁵ And the ocean will become a giant "plastic soup" as more plastic than fish is in the oceans.⁵

Besides the fast generation of plastic waste, the slow natural degradation exacerbates the waste accumulation. Most plastics take more than 100 years to degrade in the environment while posing serious threats to the ecosystems.⁶ More than 267 animal species were found being suffered from plastic debris because of the entanglement and ingestion.⁷ Millions of birds and fishes were killed by the plastic debris annually.⁷ Microplastics and toxic chemicals are released during degradation and they cause pollutions to lands, surface and ground water, and oceans.^{3,6} Microplastics cannot be digested by animals and thus accumulate along food chain, which eventually cause health hazards to humans.⁸ Bisphenol A, one of the toxic chemicals released during plastic degradation was reported causing growth and reproduction problems of aquatic organisms.⁹

Being such a great hazard to the ecosystems and human health, the plastic waste pollution is an urgent global problem, and must be addressed before the waste is further dispersed into the environment. The state-of-the-art technology for separating plastic debris, microplastics, and released toxic chemicals from sea water is \$0.003/gallon water. To purify the oceans (3.5×10^{20} gallon), it will cost about $\$10^{18}$, which is 10,000 times of global GDP. This is already unaffordable

and will only become worse if the plastic waste accumulation grows. Effective and economically feasible solutions must be developed to reduce the amount of plastic waste.

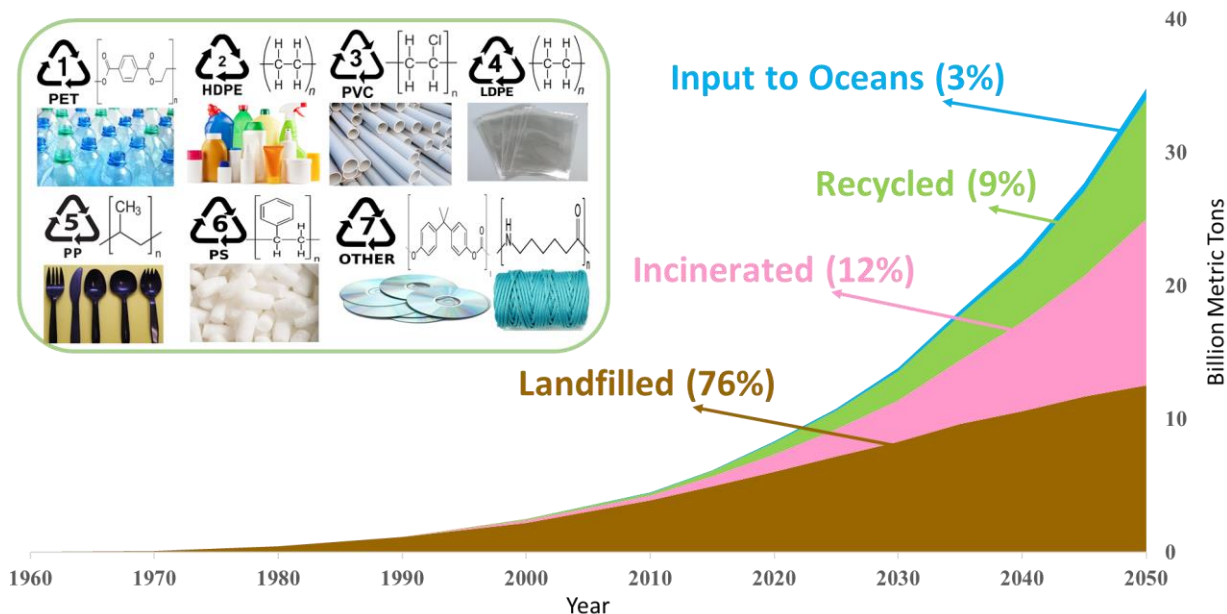


Figure 1. Global Plastic Waste Accumulation/Disposal and Projection, modified from Geyer et al. 2017¹

1.2 Methods to Address Plastic Waste

Landfilling is the most adopted method for waste plastic disposal because of its lowest cost. However, the cost is also increasing as less landfilling space is available.¹⁰ In addition, toxic chemicals leach from the plastic waste stored in landfills. This pollution also raises concerns.¹¹

Currently recycling methods mainly include incineration, mechanical recycling, and pyrolysis. Incineration is the most mature technology to reduce the amount of plastic waste. It recovers energy for power generation.¹² However, the energy efficiency is low. Conventional coal power plants have an energy efficiency up to 55%. But power plants using plastic waste can only have an efficiency up to 25%.¹³ To generate the same amount of power, plastic incinerators emit more GHGs than conventional power plants. In addition, carcinogens like dioxins and other air-pollutants are generated during mixed plastic waste incineration. Those gases are released into air if not treated.¹⁴ As a result, little power is generated at a high cost of generating a large amount of GHGs and toxic gases. Because of the little profit from incineration of plastic waste, incineration facilities heavily rely on “tipping fees” from municipalities for their revenue.¹⁵

Mechanical recycling has been a widely used method to recycle plastic waste. It requires washing, crushing, melting, and molding. However, polymers degrade during processing, resulting in a lower product value.¹⁶ Mechanical recycling cannot accept mixed plastics as feedstock because of the immiscibility between different plastics.^{10,17} In addition, additives like dyes cannot be removed and they accumulate during mechanical recycling. For this reason, the recycled polymers can only be used for manufacturing color-insensitive products like trash bin and trash bags.¹⁷

Pyrolysis is a thermo conversion process that converts plastic waste mainly into oils. Its condition usually requests high temperature (450- 800 °C).¹⁴ If without catalyst, the oil yield can be low while more gas and char are generated.¹⁴ Mixed plastic waste was commonly used as feedstock resulting in low fuel qualities of the oils.¹⁸ Thus, further upgrading is needed. Few products other than oils have been produced, indicating pyrolysis as an inflexible process.¹⁸ Whether pyrolysis can make profit depends on crude oil and fuel prices.

Researchers have also been developing alternative solutions. Biodegradable plastics like Polyhydroxyalkanoates (PHAs) and Polylactic acid (PLA) were believed to help reduce plastic accumulation.^{19,20} They have a shorter degradation time compared to petroleum-based plastics. But the cost for manufacturing biodegradable plastics is still too high, making it less competitive to petroleum-based plastics. Other researchers found that biodegradable plastics do not degrade as claimed.²¹ Furthermore, producing more and new plastics and mixing the waste with petroleum-based plastics will make the recycling even more challenging.

In summary, current recycling methods cannot address the plastic waste problem in an economic way. Thus, new economically feasible technologies are urgently needed.

1.3 Targeting Polyolefin Waste

Plastic is divided into 7 types (PET, HDPE, PVC, LDPE, PP, PS, and Others, Figure 1). Each type has different chemical structures and properties. Producing high value products from complex mixtures can be very difficult and costly because of the varied feed compositions and uncontrollable product quality. Thus, sorted or simple mixture (binary or ternary) of plastic waste is a better feedstock for developing efficient and economically feasible solutions. Polyolefins, including Type 2 High Density Polyethylene (HDPE), Type 4 Low Density Polyethylene (LDPE), and Type 5 Polypropylene (PP) were chosen for this study. Common products of HDPE include

grocery bags and liquid containers. LDPE is widely used for producing flexible films, like Ziploc bags. PP is used for products like disposable tableware and automobile parts. The reason for targeting polyolefin waste is that it accounts for 63.1% of total global plastic waste.²² HDPE, LDPE and PP accounts for 17.4%, 23.1%, and 22.6% respectively.²²

1.4 Proposed Solutions

In this study we propose to convert polyolefin waste into useful and profitable products including clean fuels, clean waxes, specialty chemicals, and pristine polymers via Hydrothermal Processing (HTP) and Sequential Selective Extraction and Adsorption (SSEA) (Figure 2). Instead of the linear path of polyolefins from crude oil to plastics to landfills, a closed loop can be formed for the hydrocarbons. In addition, the production of clean fuels and clean waxes from polyolefin waste can reduce the crude oil consumption and is more sustainable.

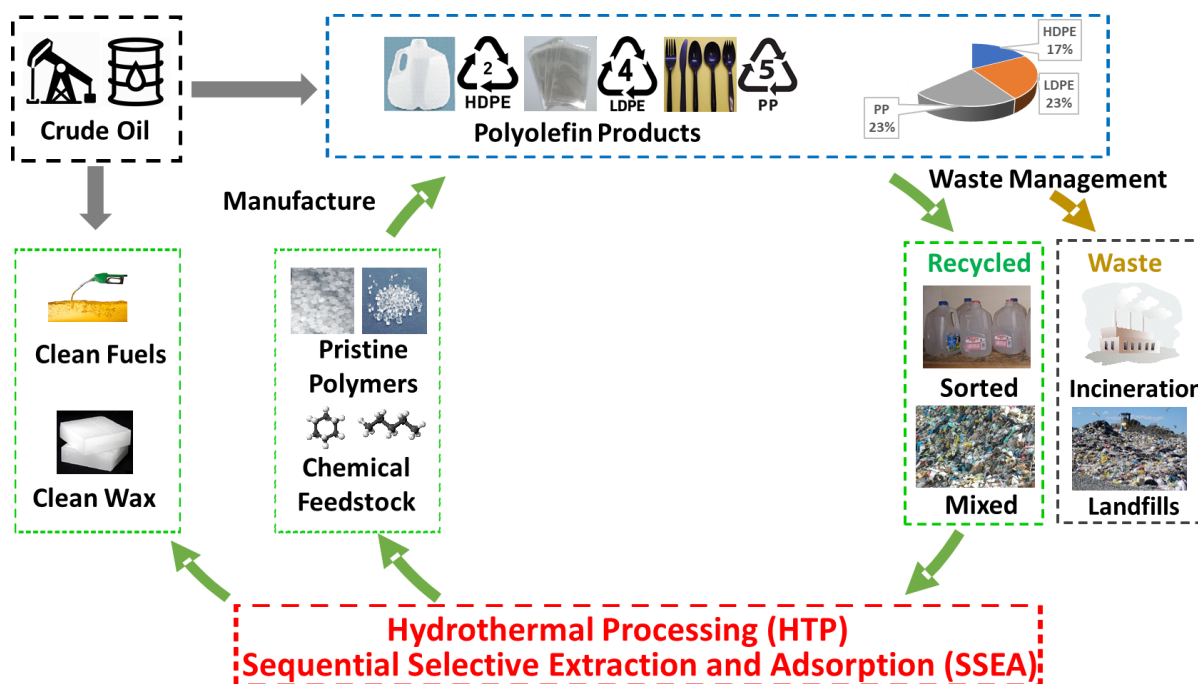


Figure 2. Producing useful products include clean fuels, clean wax, specialty chemicals, and pristine polymers from polyolefin waste via HTP and SSEA

1.5 Objectives and Approaches

The objectives of this study are:

1. To develop HTP method to convert polyolefin waste into useful products including waxes, fuels, and specialty chemicals
2. To develop SSEA method to recover pristine polymers from polyolefin waste
3. To show the feasibility of using a combination of HTP and to treat both sorted and mixed polyolefin waste

The following approached were used in this study:

1. Understand the fundamental principles of HTP and SSEA using model polyolefins first;
2. Develop HTP and SSEA methods for polyolefin waste and test the technical feasibility
3. Evaluate the energy demand, energy efficiency, GHG emissions, and profit potentials of HTP and SSEA

1.6 Highlights of this study

Comprehensive potential reaction pathways for the conversion of PP and HDPE in HTP were proposed for the first time. Clean paraffin wax was obtained from PE waste after HTP and adsorption. PE waste was converted into diesel blendstock via HTP and distillation. For SSEA, mixed solvents were proven to be better than single solvents, in terms of selectivity, solvent toxicity, and cost. Pristine PE polymers were recovered for the first time from dark-colored PE waste. Preliminary cost analyses indicate HTP and SSEA are economically feasible. HTP and SSEA have higher process energy efficiency (E_{out}/E_{in}) and lower GHG emissions than incineration, mechanical recycling, and pyrolysis. A more flexible recycling method is proposed to handle various polyolefin waste streams by the combination of SSEA and HTP.

CHAPTER 2. HYDROTHERMAL PROCESSING (HTP)

2.1 Introduction

Hydrothermal processing (HTP) is a thermal depolymerization process that can convert organic feedstocks into gas, oil, and solid.²³ A schematic for HTP is shown in Figure 3. HTP occurs in an enclosed reactor. Subcritical or supercritical water serves as a solvent, catalyst, or reactant depending on HTP conditions.²³ The range of HTP temperature is 250 to 500 °C and the range of HTP pressure is 4 to 30 MPa.^{23,24} HTP is used to convert wood waste, agricultural crops, aquatic plants, and municipal and animal waste into oil products, with the potential to be used as fuels and chemical feedstocks.^{25,26,27} HTP was also applied to upgrade heavy fractions of crude oil into light hydrocarbons.²⁸

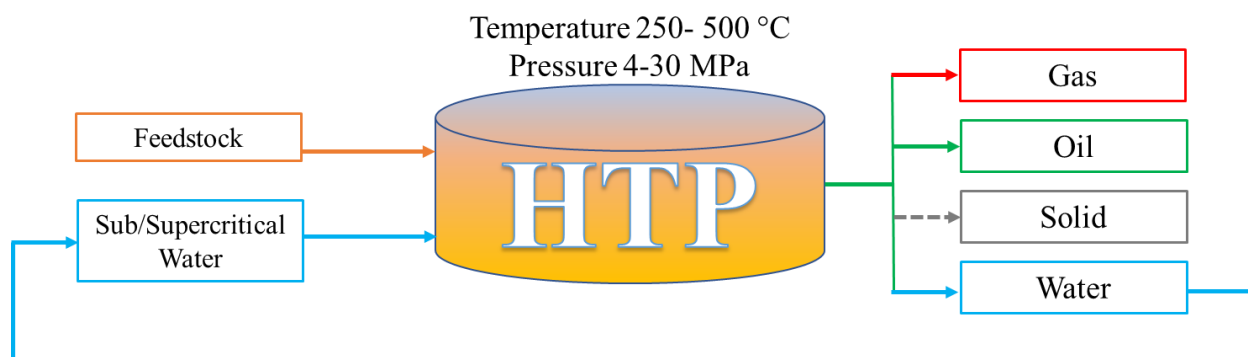


Figure 3. A schematic of HTP

The physical and chemical properties of water change significantly as water approaches to and goes beyond the critical point (374 °C, 22.1 MPa, Figure 4). Water at room temperature is a polar solvent as it has a high dielectric constant (79) and ion product ($\sim 10^{-14}$). However, at 450 °C, supercritical water has a reduced dielectric constant (2) and ion product ($\sim 10^{-19}$) and thus, behaves similar to nonpolar organic solvents.²⁸ One key characteristic of HTP is the manipulation of water's properties by tuning reaction temperature and pressure. It allows different reactions catalyzed by $[H^+]$ and $[OH^-]$ or free radicals to occur selectively.^{29,30}

Supercritical water is used in this study rather than other nonpolar solvents, as it is safer and less toxic. Water is one of the most accessible solvents with a low price. The high dielectric constant of water at room temperature enables water to automatically separate from oil products, which avoids extra separations. Water also helps extract hydrophilic products, for example,

alcohols and ketones produced in biomass HTP.³¹ In addition, feedstock drying, which is an energy intensive process, can be avoided if using water.

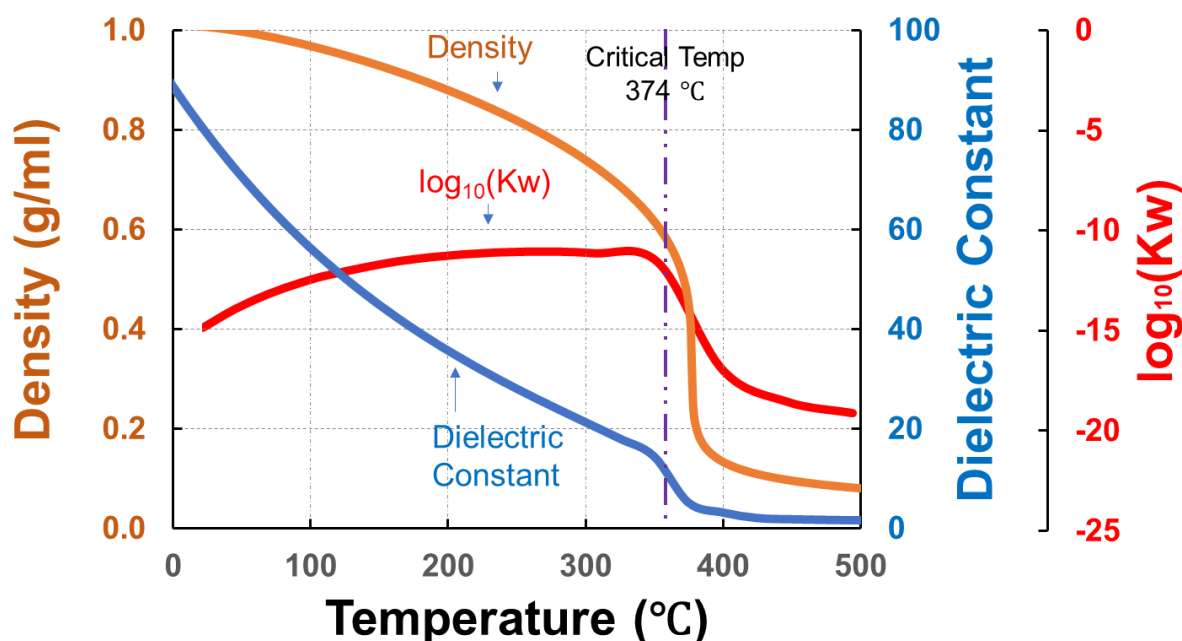


Figure 4. Density, dielectric constant, and ion product as a function of temperature of water at 23.4 MPa, data obtained from NIST³²

HTP was intensively studied for the conversion of wet biomass materials to bio-crude oil. Aspen wood and glycerol were co-liquefied under HTP at 400 °C and 29.6 MPa.³³ Bio-crude oil with a Higher Heating Value (HHV) of 34.3 MJ/kg was collected.³³ Another study used HTP to convert swine manure and mixed-culture algal biomass.²⁶ The produced crude oil has an HHV of 27.5 MJ/kg.²⁶ HTP was also applied to convert other organic feedstocks like plastics. Funazukuri conducted HTP experiments for polyethylene terephthalate (PET) and polycarbonate (PC) subcritical water with ammonia.³⁴ These condensation polymers were found to be decomposed into monomers via hydrolysis.³⁴ Terephthalate acid and ethylene glycol were collected from PET experiments, and bisphenol A was found in PC experiments.³⁴

HTP is also used for polyolefins as well. A co-liquefaction of biomass and HDPE under subcritical and supercritical water was reported.³⁵ But the focus was on how to improve the bio-oil product yield by adjusting feedstock mixing ratio. How hydrocarbon structures affect the reaction was not investigated. Also, no comprehensive reaction pathways were developed in such a complex system. Representative studies of HTP on polyolefins were listed in Figure 5 along with

their reaction temperatures and reaction pressures. Watanabe et al. conducted experiments to decompose LDPE via pyrolysis and HTP with supercritical water.³⁶ They found HTP has a higher oil yield and a higher olefin/paraffin ratio in oil than pyrolysis. They concluded that it is because of the different reaction phases. Moriya et al. and Su et al also reported higher oil yields and more olefins in oil of HTP than pyrolysis.^{37,38} Zhao et al. carried out HTP for PP using subcritical water at reaction temperatures of 250- 350 °C.³⁸ Oil yields of 10-30% were reported. Another study used water vapor at 500 °C under hydrogen atmosphere to convert HDPE and PP into oils. Paraffin, olefins, and aromatics were detected in the oils.³⁹ Although, many studies have been conducted for HTP of polyolefins, no comprehensive reaction pathways were reported. In addition, no detailed identification of the product applications was conducted. Whether HTP is technically and economically feasible to treat polyolefin waste still remains unclear.

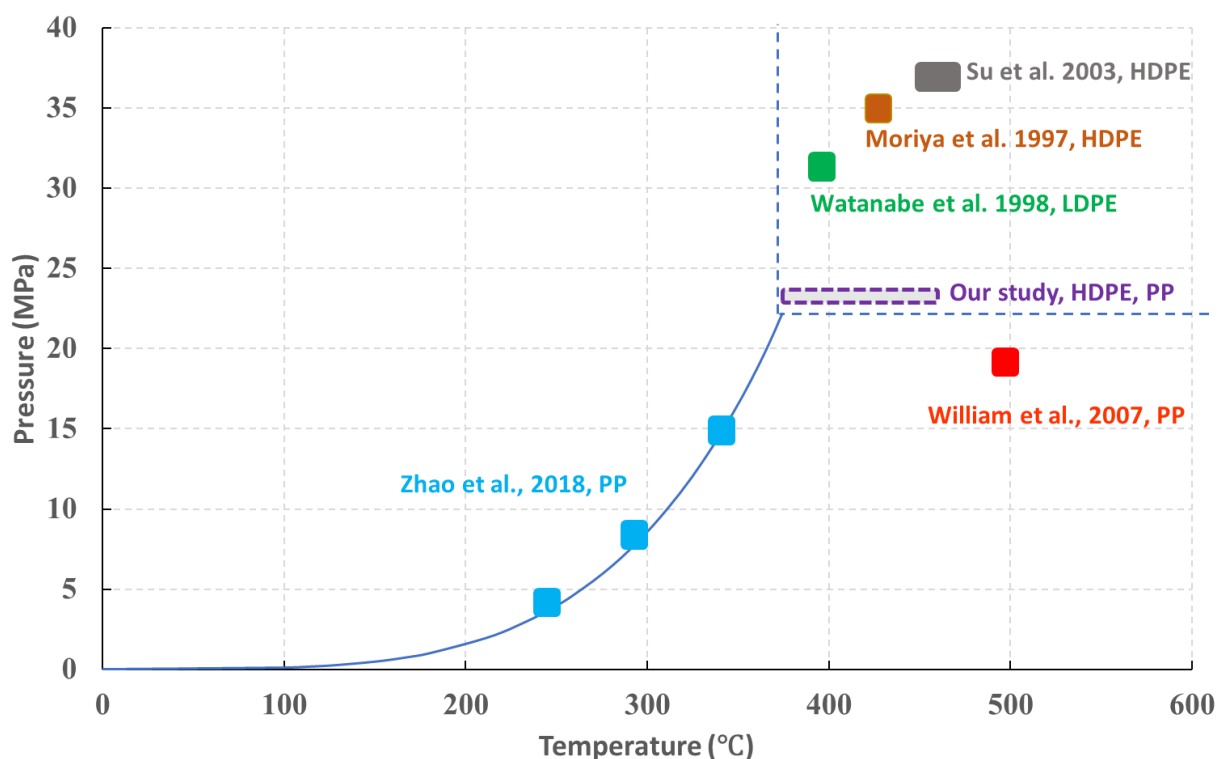


Figure 5. Literature studies on HTP for polyolefins^{36,37,40-42}

The long-term goal of this study is to develop HTP as an effective method to convert polyolefin waste into useful products including wax and oils. The oil products have the potential to be used as fuels and chemical feedstocks. The effects of reaction temperature, reaction time and

feed loading on product yields, compositions and properties were investigated. Model polyolefins were tested to help understand the reaction mechanisms. HTP technical feasibility was tested by experiments using polyolefin waste in a lab scale. GC $\times$ GC-FID was used to analyze the products. Potential reaction pathways of HDPE and PP were established based on the analytical results. Detailed characterizations include FT-IR, flash point test, cloud point test, density and viscosity measurement, and water content measurement were carried out to identify whether products can be qualified as commercial wax and transportation fuels. Preliminary cost analyzes were also conducted to investigate the economic feasibility.

This is the first study to propose detailed reaction pathways of HDPE and PP in supercritical water under HTP. The pathways are proposed based on detailed analyzes of reaction intermediates. Under the same HTP conditions, PP reacts faster and generates more olefins and cyclics than HDPE. Clean wax is converted from PE waste under HTP for the first time. FT-IR results indicate the wax product as almost identical to commercial paraffin wax. The major fraction (50%) of the oil products from PE waste has similar properties as No.1 ultra-low-sulfur diesel and can also be blended into No.2 ultra-low-sulfur diesel. The preliminary cost analyzes indicate the wax and fuel production via HTP can be profitable.

2.2 Methodology

2.2.1 Materials

The polymers used in this study are shown in Figure 6. Model HDPE and PP polymer pellets were purchased from Sigma Aldrich (St. Louis, MO). The weight-averaged molecular weight ($\overline{M}_w$) were 180,000 and 250,000, respectively. EREMA (Ipswich, MA) provided PE pellets made of customer drop-off polyethylene shopping bags. The $\overline{M}_w$ of the PE waste pellets was approximately 270,000. Deionized Water used in experiments was from a Milli-Q water purification system and was degassed for 30 minutes before use.



Figure 6. From left to right are model PP and HDPE, and PE waste (EREMA)

Activated carbon used for wax adsorption was purchased from Calgon Carbon Corporation (Pittsburgh, PA). Heptane was purchased from Fischer Scientific (Waltham, MA), and used as received. Commercial paraffin wax sample was from VWR (Chicago, IL).

Five commercial diesel samples were purchased from local gas stations (West Lafayette, IN) including Speedway, Meijer, Marathon, and Family Express.

2.2.2 Experiment Descriptions

A 4570-benchtop high-pressure high-temperature reactor system manufactured by Parr Instrument Company was used in this study (Figure 7). This reactor system includes a 500 ml reactor cylinder (2.5" ID and 6.6" inside depth) and a reactor head equipped with magnetic drive (0-600 RPM), pressure gauge (0-34.5 MPa), safety rupture disc, gas inlet and outlet valve, liquid sampling valve, cooling coil, and thermowell with a Type J thermocouple. This reactor is rated up to 34.4 MPa at temperatures up to 500 °C. The cylinder, head, and internal parts are made of Alloy C276 while valves and external fittings are made of stainless steel. An electric heater assembly (110V) is equipped for heating.



Figure 7. Parr series 4570 benchtop high pressure high temperature reactor (500ml)

HTP experiments were conducted at reaction temperature of 400-450 °C with reaction time of 0.5-3 hr. Each test requires 20-80 g polymer feedstock and 70 ml water. The relationship between supercritical water pressure, temperature, and water loading was obtained from NIST Chemistry WebBook, SRD 69.³² After feed-loading, the reactor was subsequently sealed, and purged with nitrogen twice to remove any residual air. A 0.62 MPa nitrogen gas blanket was again added to the reactor to build an inert atmosphere. The heating process usually takes 40-60 minutes to reach the set temperature point. Reaction time starts once the set point was reached. Initial and final pressures were recorded. Once completed, the reactor is air-cooled. Stirring at 300 revolutions per minute (RPM) was performed throughout the heating, reaction, and cooling process. After cooling the reactor to room temperature, the gas pressure was

measured, and the gas was sampled. The reactor was then disassembled. The mixture of oil, water, and solids (if any were present) was decanted into a glass flask for weighting. Filtration was conducted to separate solids from the liquid, and liquid-liquid separation was carried out to separate water from oil. Solids were weighed after drying.

Yields of oil, solids, and gas were calculated using Equation 1,2,3 (based on dry weight, d.w.):

$$\text{Oil product yield (d. w \%)} = W_{\text{oil}}/W_{\text{feedstock}} \times 100 \quad (1)$$

$$\text{Solid yield (d. w \%)} = W_{\text{solid}}/W_{\text{feedstock}} \times 100 \quad (2)$$

$$\text{Gas product yield (d. w \%)} = 100 - (\text{solid residue} + \text{oil}) \quad (3)$$

Under some specific conditions, wax product was obtained. It was further purified by dissolution, adsorption and reprecipitation. First, 5 grams of crude wax were weighted and collected in a 100 ml flask. 50 ml n-heptane was decanted into the flask and a stir bar was placed in. The flask was then sealed and placed in a 50 °C water bath with stirring for 1 hr. Filtration was then carried out to separate the insoluble from the solution. About 2.5 grams of activated carbon were added into the flask and the mixture was stirred for another 2 hr at 50 °C. Afterwards, activated carbon was separated out by centrifugation. The solution was cooled to low temperature (4 °C). The wax then precipitated out and was collected by centrifugation.

Distillation was carried out following ASTM D86 method⁴³ to separate oil products. Three fractions were collected, the light oil (b.p. <170 °C), diesel-like oil (170 °C < b.p. < 300 °C), and heavy oil (b.p. >300 °C).

2.2.3 Characterizations

2.2.3.1 Oil Product Analysis

The oils produced from polyolefins are a complex mixture of different hydrocarbons. One-dimensional gas chromatography (GC) cannot provide good analytical results because of the limited resolution. Two-dimensional GC with a flame ionization detector (GC × GC-FID) (Figure 8) was used in this study to quantitatively analyze the chemical compositions of the reaction intermediates and products. Two-dimensional GC has two individual columns with different stationary phases. The two columns were connected by a modulator which captures effluents from the primary column (first dimension) and injects them into the secondary column (second dimension). The primary and secondary column used in this study are DB-17ms and DB-1ms,

respectively (Figure 9). The stationary phase of DB-17ms is (50%-Phenyl)-methylpolysiloxane, which separates hydrocarbons based on their volatility and aromaticity. Less volatility and higher aromaticity result in longer retention time in DB-17ms column. The stationary phase of DB-1ms is 100% dimethylpolysiloxane which separates hydrocarbons based on their volatility solely. Light hydrocarbons elute earlier than heavy ones. The separation resolution is significantly improved in two-dimensional GC owing to its two distinct separation mechanisms.

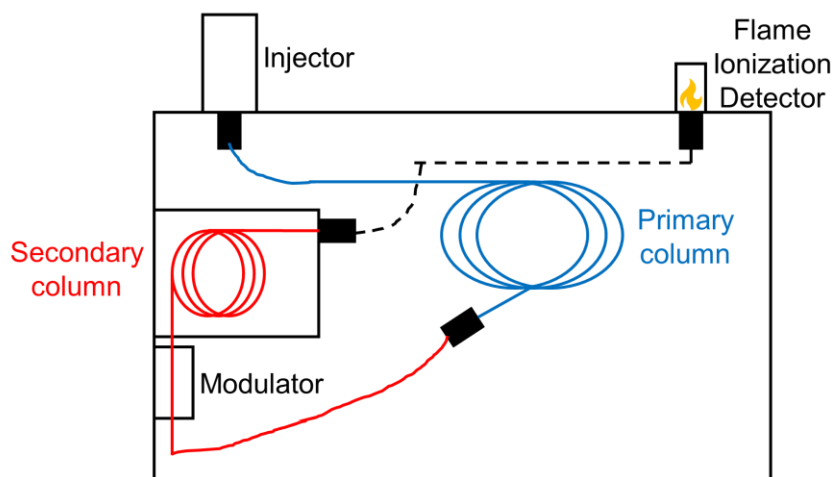


Figure 8. GC × GC-FID instrument

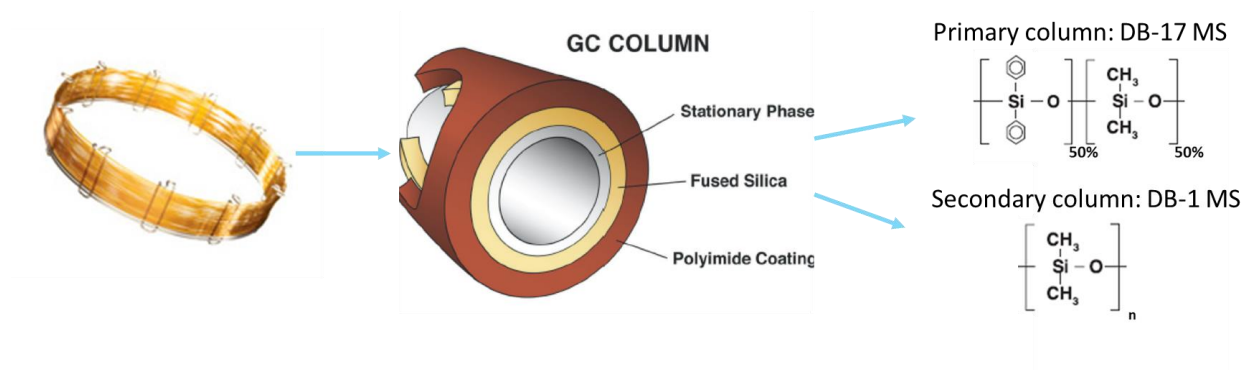


Figure 9. GC column and stationary phases [modified from internet source^{44,45}]

FID (Figure 10) is commonly used for GC because of its low cost and wide detection range. It is mass sensitive as it corresponds to ions per unit time. However, FID reads the same signals for hydrocarbons with the same carbon number regardless of their chemical structures. As a result, FID itself cannot provide qualitative identification for each kind of hydrocarbon. In addition, hydrocarbons with a high carbon number can have numerous kinds of isomers. For example, isododecane has 355 isomers. It is impractical to distinguish each isomer. Thus, classification is introduced in this study. A classification refers lumping hydrocarbons based on their carbon numbers and chemical categories including *n*-paraffins, isoparaffins, olefins, monocycloparaffins, dicycloparaffins, tricycloparaffins, alkylbenzenes, cycloaromatics, naphthalenes, biphenyls, anthracenes and phenanthrenes, and pyrenes.⁴⁶ Olefins, monocycloparaffins, dicycloparaffins and tricycloparaffins can be further grouped as olefins plus cyclics. Alkylbenzenes, cycloaromatics, naphthalenes, biphenyls, anthracenes and phenanthrenes, and pyrenes can be further grouped as aromatics. The classification method was established based on GC $\times$ GC-FID tests of a mixture of 24 standard compounds (Table 1) as the representatives of different carbon numbers and chemical categories.⁴⁶ The detailed development of the classification was introduced in previous study.⁴⁶

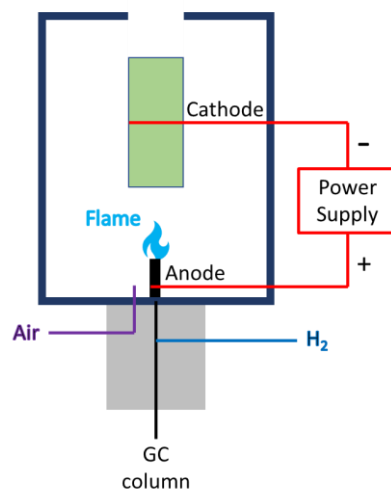


Figure 10. Flame Ionization Detector
[modified from internet source⁴³]

Table 1. 24 standard compounds used for establishing the classification⁴⁶

CAS #	Substances	CAS #	Substances	CAS #	Substances
111-65-9	n-octane	104-51-8	n-butylbenzene	569-41-5	1,8-dimethylnaphthalene
112-40-3	n-dodecane	1077-16-3	n-hexylbenzene	92-52-4	biphenyl
544-76-3	n-hexadecane	496-11-7	indan	644-08-6	4-methylbiphenyl
2935-07-1	perhydrophenalene	6682-71-9	4,7-dimethylindan	613-33-2	4,4-dimethylbiphenyl
6596-35-6	tetradecahydroanthracene	1985-59-7	1,1-dimethyltetralin	85-01-8	phenanthrene
108-88-3	toluene	475-03-6	1,1,6-trimethyltetralin	610-48-0	1-methylanthracene
100-41-4	ethylbenzene	91-20-3	naphthalene	129-00-0	pyrene
103-65-1	n-propylbenzene	91-57-6	2-methylnaphthalene	2381-21-7	1-methylpyrene

More chromatographic details are in Table 2. ChromaTOF software (version 4.71) was used to collect and process data. The software was optimized for GC $\times$ GC-FID with a signal to noise

ratio of 75. Non-moving quad-jet dual stage thermal modulator was used for this Agilent chromatograph 7890B GC system. Liquid nitrogen was used for effluent capture and injection. *n*-pentane was used to dilute samples using a volumetric dilution ratio of 100:1 for *n*-pentane to sample. The injection split ratio was set to 20:1.

Table 2. Chromatographic Conditions for GC $\times$ GC-FID

Parameter	Description
Analytical column	Primary: DB-17ms Agilent (30 m $\times$ 0.25 mm $\times$ 0.25 μ m) Secondary: DB-1ms Agilent (0.8 m $\times$ 0.25 mm $\times$ 0.25 μ m)
Carrier gas	UHP helium, 1.5 mL/min
Oven temperature	isothermal 40 $^{\circ}$ C for 0.2 min, followed by a linear gradient of 3 $^{\circ}$ C/min to a temperature 260 $^{\circ}$ C being held isothermally for 20 min
Modulation period	2.5 s with 0.42 s hot pulse time
Offsets	Secondary oven: 50 $^{\circ}$ C Modulator: 15 $^{\circ}$ C
Temperatures	Inlet: 280 $^{\circ}$ C FID: 300 $^{\circ}$ C
Solvent	<i>n</i> -pentane (99.9% pure, Sigma Aldrich), 130 s delay

An example of GC $\times$ GC-FID chromatograms in 3-D view is shown in Figure 11. The two axes are the retention time in primary and secondary column, respectively. Each peak indicates an identified chemical substance and the peak height indicates the weight fraction. The chromatogram in the back is the one-dimensional chromatogram for the primary column. Figure 12 is the chromatogram projection in 2-D view, and Figure 13 is the projection with classification. Chemical categories were distinguished by different colors. Each region represents an individual classified group. The weight percentage of each group is calculated as the peak area of this group divided by the total peak area. GC $\times$ GC-FID with classification, provides detailed quantitative information of chemical substances in sample.

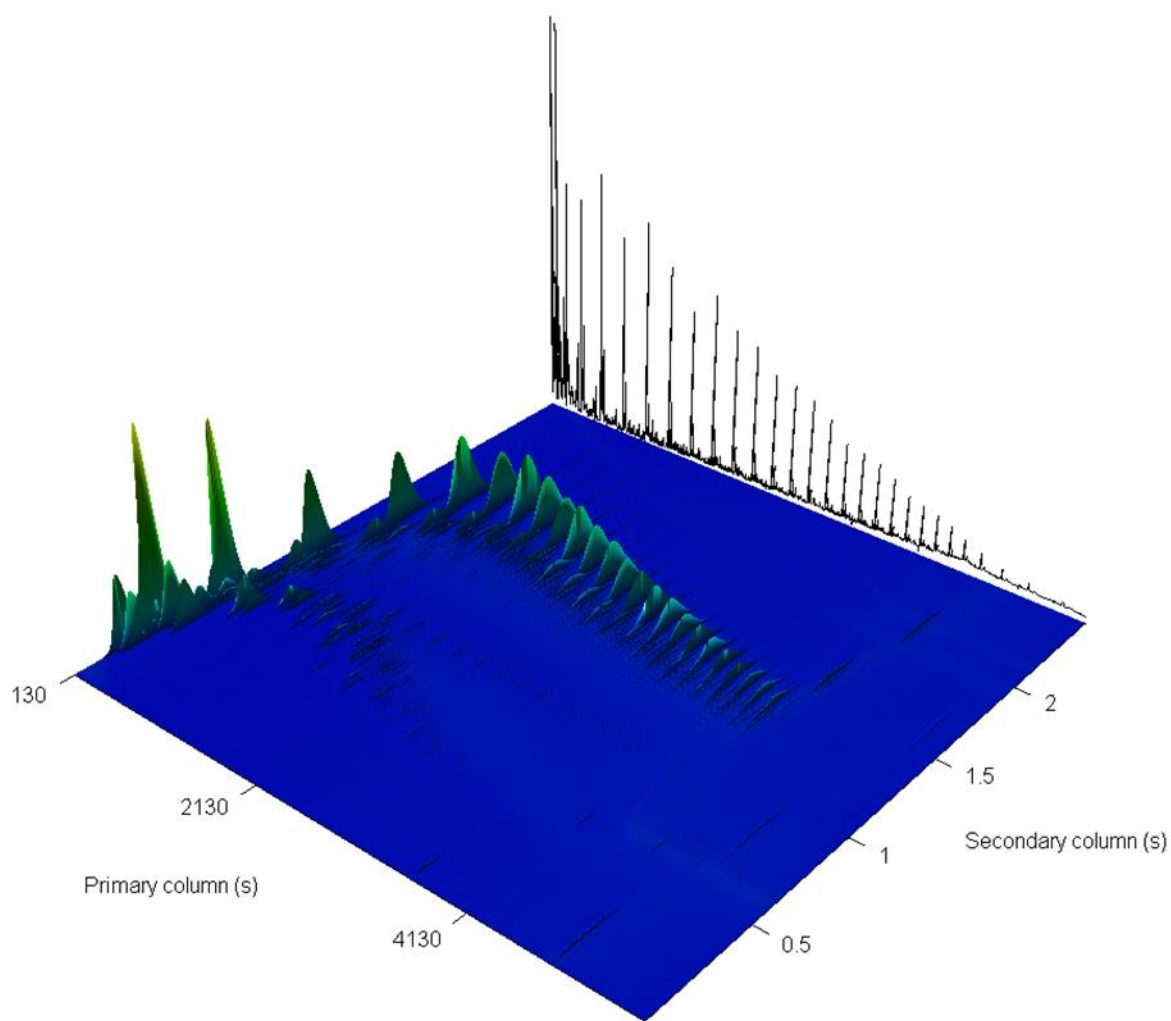


Figure 11. GC $\times$ GC-FID chromatogram in 3-D view

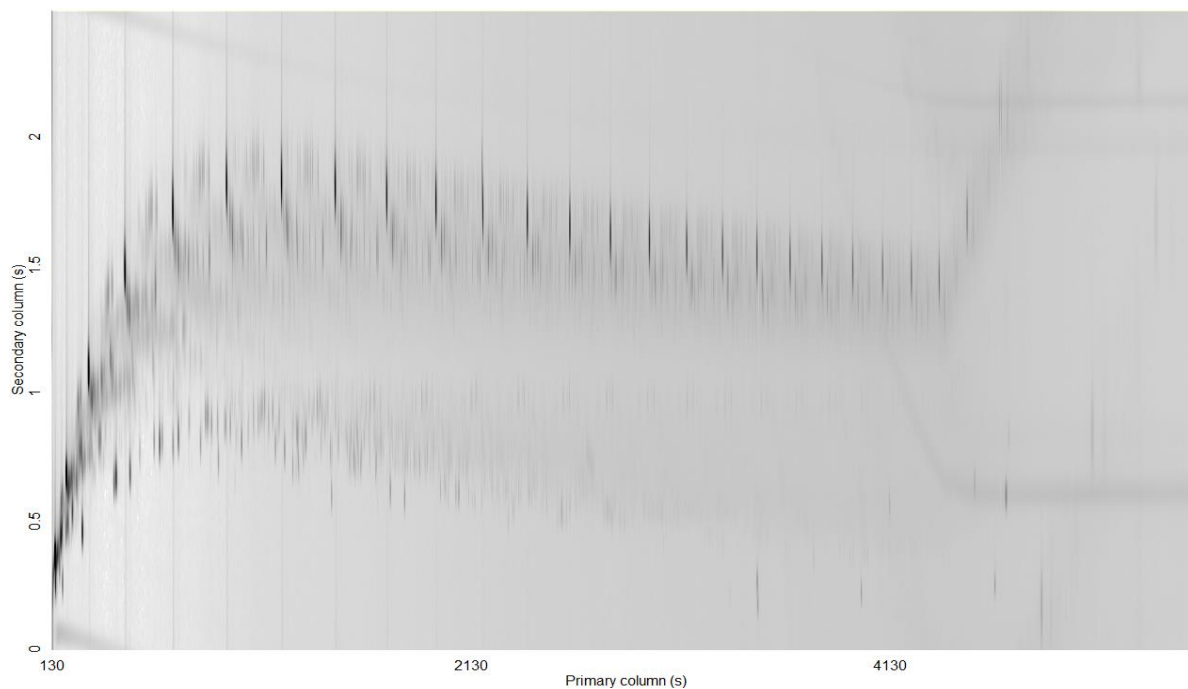


Figure 12. GC $\times$ GC-FID chromatogram projection

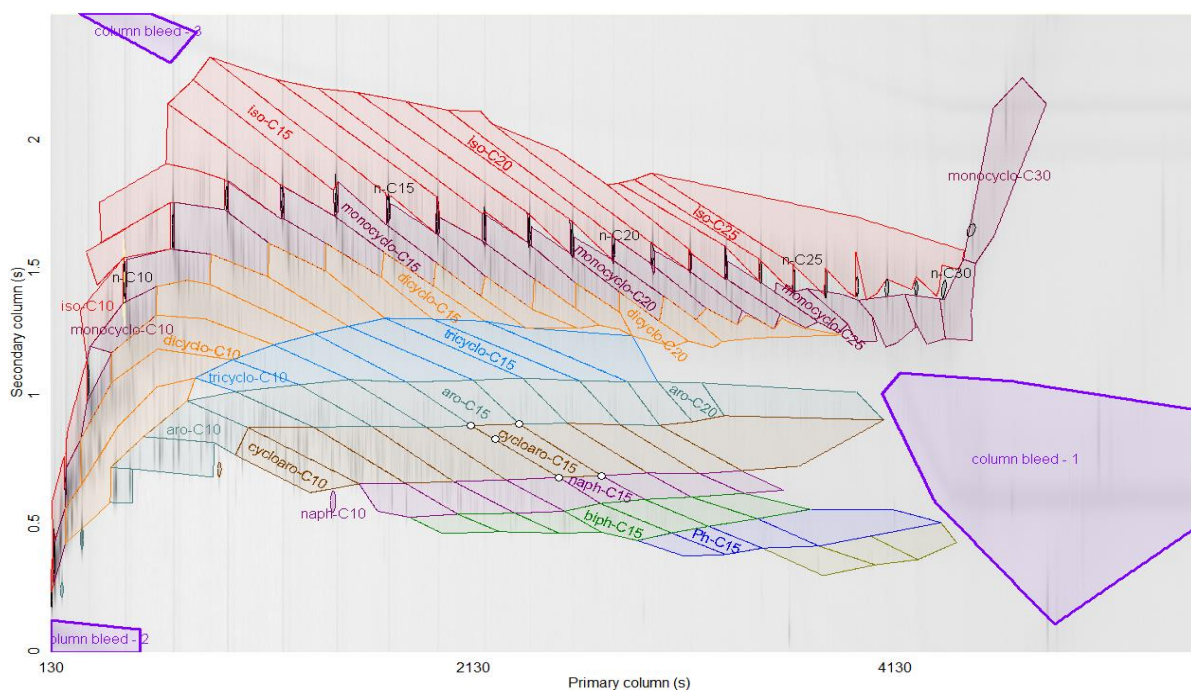


Figure 13. GC $\times$ GC-FID chromatogram projection with classification. Regions from top to bottom are isoparaffins (red), *n*-paraffins (black), monocycloparaffins (crimson), dicycloparaffins (orange), tricycloparaffins (azur), alkylbenzenes (dark green), cycloaromatics (khaki), naphthalenes (pansy), biphenyls (green), anthracenes and phenanthrenes (dark blue), and pyrenes (mustard). Column bleed region (purple) are at corners.

2.2.3.2 Solid Product Analysis

Chemical structure information of the solid wax products was obtained from Fourier-Transform Infrared Spectroscopy (FT-IR). Thermo-Nicolet Nexus 470 FT-IR with an ultra-high performance, versatile Attenuated Total Reflectance (ATR) sampling accessory (Figure 14) was used in this study. Resolution for this instrument is 4 cm^{-1} and the spectral range is $800\text{--}4500\text{ cm}^{-1}$. OMNIC software (Version 8.3) was used for hardware configuration and data collection.

In order to analyze the elements in the solids, Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis was carried out using a JCM-6000PLUS instrument manufactured by JEOL (Tokyo, Japan).



Figure 14. Thermo-Nicolet Nexus 470 FT-IR

2.2.3.3 Fuel Specification Analysis

The fuel properties (according to ASTM D975) including density, viscosity, flash point, cloud point, and sulfur and nitrogen content were measured for HTP-oil samples and commercial diesel samples. An SVM 3001 Stabinger Viscometer (Anton Paar) (Figure 15(a)) was used to measure density and viscosity at $40\text{ }^{\circ}\text{C}$ via ASTM D4052⁴⁸ and ASTM D7042⁴⁹, respectively. Flash point was measured using a Tag 4 Flash Point Tester (Anton Paar) (Figure 15(b)) via ASTM D56⁵⁰. Cloud point was measured using a manually operated cloud point apparatus (Figure 15(c)) following the same operating procedures as listed in ASTM D2500⁵¹. Water content in oils was measured by a K20 Karl Fischer Coulometric Titrator (Figure 15(d)) via ASTM D6304⁵².

Sulfur and nitrogen content were measured using a TS-100 instrument (Mitsubishi Chemical Corporation). Sample was combusted under controlled oxygen in a pyrolysis furnace at $800\text{--}1000\text{ }^{\circ}\text{C}$ in argon atmosphere. The flue gas was then analyzed via sulfur detector (chemiluminescence detection) and nitrogen detector (fluorescence detection), following ASTM D1552⁵² and D5762⁵³, respectively.



Figure 15. (a) SVM 3001 Stabinger Viscometer, (b) TAG 4 - Tag Flash Point Tester, (c) Cloud Point Apparatus, and (d) K20 Karl Fischer Coulometric Titrator [Adapted from internet source⁵⁴]

2.3 Results

2.3.1 HDPE

2.3.1.1 Yields

In order to study how temperature and time affect HTP conversions, experiments were conducted at temperature 400-450 °C with reaction time 0.5-3 hr using 40 g model HDPE. No oil was obtained within 3 hr at 400 °C. At 425 °C (Figure 16(a)), solid wax was found at 40 minutes and oils were obtained at reaction time longer than that. The oil yield increases with longer time until 2.5 hr. Further extended time results in an increased gas generation and a reduced oil yield. Similar trends of oil and gas yields were found at reaction temperature 450 °C (Figure 16(b)). Higher reaction temperatures also accelerate the reactions. Experiments at 450 °C were carried out up to 1 hr of reaction time because of the reactor pressure limit. The highest oil yield (81%) was obtained at 425 °C with 2.5 hr. Among all conditions tested, little char was found.

The effects of polymer loading on product yields were also investigated. The increased polymer loading from 40 g to 80 g of model HDPE, results in a slightly higher oil yield. At reaction temperature of 425 °C with reaction time of 2.5 hr, 80 g model HDPE has an oil yield of 83%, compared to 81% using 40 g model HDPE.

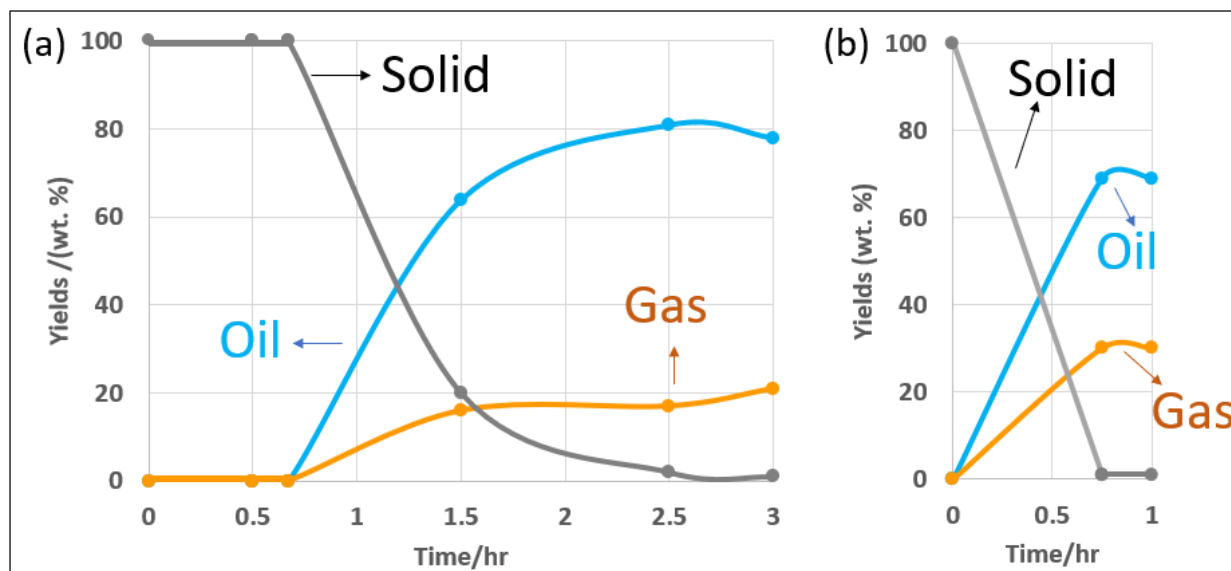


Figure 16. HTP product yields from model HDPE for reaction time of (a) 0-3 hr at 425 °C and (b) 0-1 hr at 450 °C

2.3.1.2 Carbon Numbers Distributions

In order to construct reaction pathways of HDPE under HTP, it is necessary to first understand the change of compositions of reaction intermediates along increased reaction time. Oil, as the major product under most conditions, was analyzed using GC $\times$ GC-FID. The results obtained were further lumped using two methods. One is to lump all hydrocarbons with the same carbon number (C#) regardless of their chemical categories. The other one is to divide all hydrocarbons into four groups: *n*-paraffins, iso-paraffins, olefins plus cyclics, and aromatics regardless of their C#.

In order to understand how the carbon numbers of reaction intermediates change with time, hydrocarbons with the same C# were grouped. In Figure 17(a), at 425 °C, the percentage of heavy hydrocarbons (C# ≥ 14) decreases with longer reaction time from 50 minutes to 3 hr, while the percentage of light hydrocarbons (C# < 14) increases. This indicates with extended reaction time, long chain hydrocarbons are cracked into shorter ones. A similar trend was found at 450 °C with reaction time from 30 minutes to 1 hr (Figure 17(b)). Different polymer loading from 40 g to 80 g of model HDPE was found posing little effects on product carbon number distribution (Figure 17(c)).

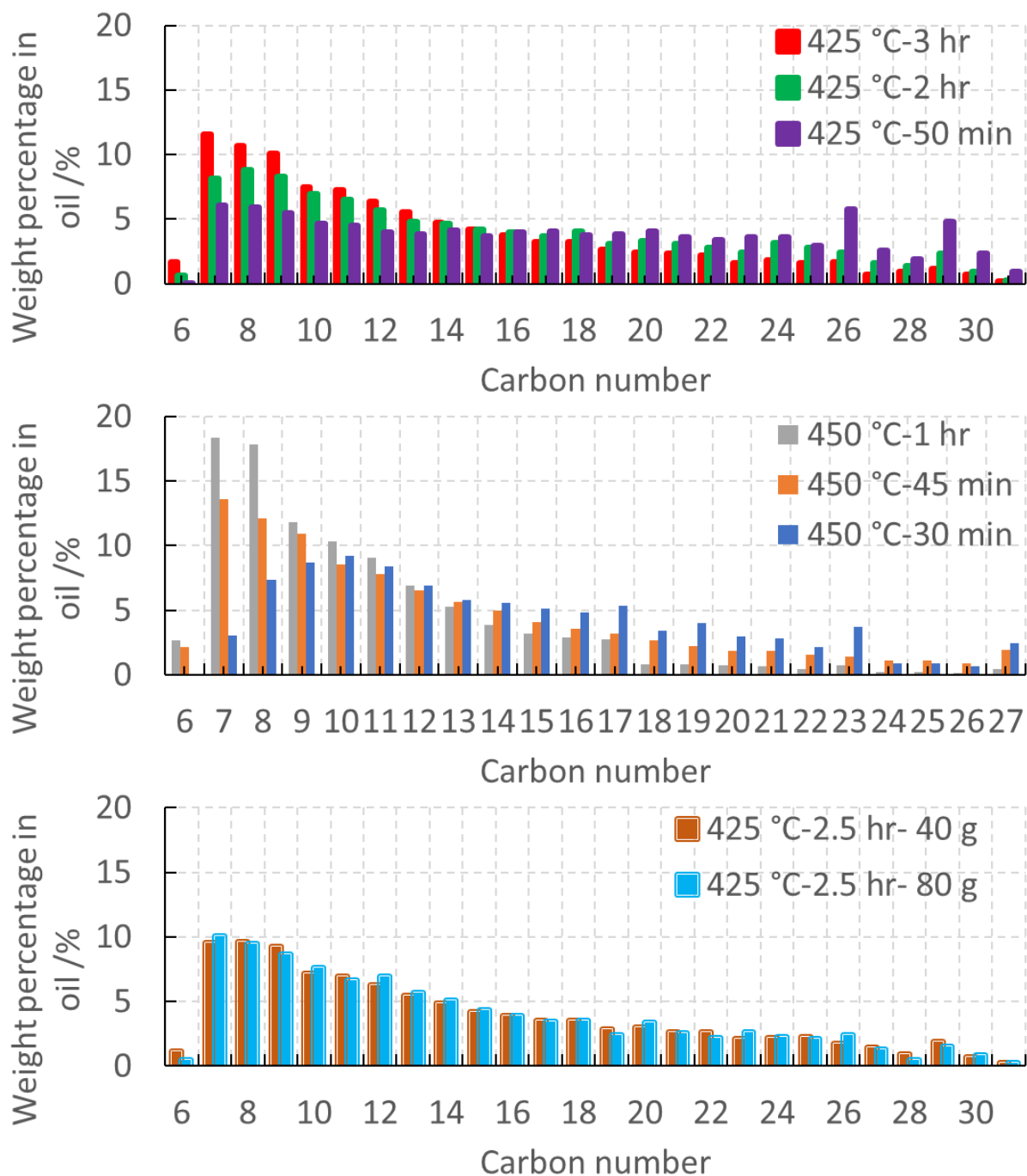


Figure 17. Carbon number distributions of oil produced at (a) 425 °C with reaction time of 50 minutes-3 hr (b) 450 °C with reaction time 30 minutes-1 hr and (c) 425 °C with reaction time of 2.5 hr using 40 and 80 g polymer loading

2.3.1.3 Chemical Categories

In order to study the change in chemical categories of reaction intermediates, chemical substances were grouped according to their chemical categories. The wax obtained at 425 °C with reaction time of 40 minutes was analyzed using FT-IR. The spectrum identifies only *n*-paraffins in the wax. The oil obtained at 425 °C with reaction time from 50 minutes to 3 hr were analyzed using GC × GC-FID (Figure 18). At 425 °C, as time increases from 40 minutes to 1 hr, there was a significant decrease of *n*-paraffin from 100 to 33.6% while olefins plus cyclics increased from 0 to 59.7%. This suggests a significant conversion from *n*-paraffins to olefins plus cyclics. Small fractions of iso-paraffins (4.3%) and aromatics (2.0%) were also found. When reaction time is further increased from 1 hr to 3 hr, the percentage of *n*-paraffins and iso-paraffins fluctuated slightly. The percentage of olefins plus cyclics is reduced to 52.3% at 3 hr while the percentage of aromatics increases to 10.3%. This indicates a generation of aromatics from olefins plus cyclics. A similar trend was found at 450 °C that olefins plus cyclics were generated from *n*-paraffins and converted into aromatics. Polymer loading has a minor effect on chemical categories of the oils. A 3% increase in the percentage of iso-paraffins was found in HTP using 80 g model HDPE than the one using 40 g model HDPE (Table 3).

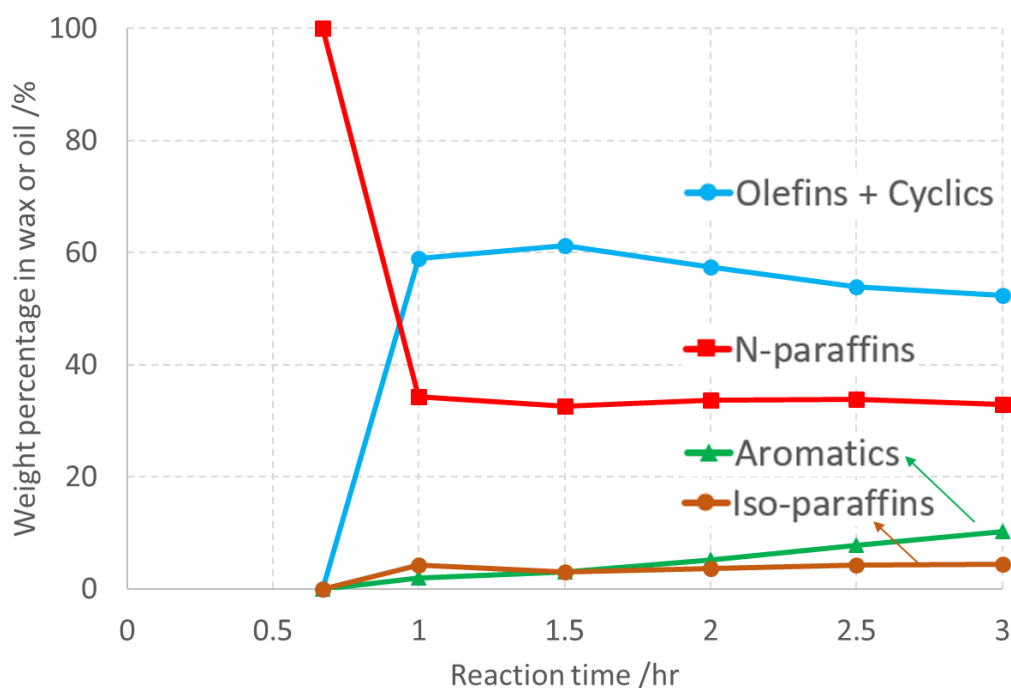


Figure 18. Chemical compositions of the wax or oils from model HDPE at reaction temperature 425 °C and time from 40 min to 3 hr

Table 3. Chemical categories of the oils from HTP with different polymer loading (40 g and 80 g)

Weight percentage in oil /%	40 g HDPE	80 g HDPE
N-paraffins	33.9	35.0
Iso-paraffins	4.2	7.2
Olefins + Cyclics	47.9	49.2
Aromatics	7.8	8.5

2.3.1.4 Potential Reaction Pathways of HDPE

Potential reaction pathways of HDPE in HTP were proposed based on the analyzes of reaction intermediates in different phases. Major reactions between intermediates are shown in Figure 19. At temperature no lower than 425 °C, reactions begin with the depolymerization of HDPE polymers into long chain *n*-paraffins (C₂₀-C₄₀) in wax. As time increases to 1 hr, long-chain *n*-paraffins in wax are converted into olefins and short chain *n*-paraffins in oil via β -scission and hydrogen abstraction, respectively. Olefins are then converted into cyclics via cyclization. As time further increases from 1 hr to 3 hr, cyclics undergo dehydrogenation to generate alkylbenzenes. Multi-ring aromatics are eventually generated from alkylbenzenes via further dehydrogenation. A small fraction of iso-paraffins can be generated from *n*-paraffins through isomerization. Gas was formed from olefins and *n*-paraffins. Reactions under a higher temperature follows the same reaction pathways but has a faster reaction rate.

The depolymerization of HDPE is initiated by free radical dissociation. In HDPE, C-C bond has a lower bond energy (348 kJ/mol) than C-H bond (413 kJ/mol). Thus, the dissociation breaks C-C bonds and generate free radicals (Equation 4). Representative hydrogen abstraction and β -scission are shown in Equation 5 and Equation 6. The produced α -olefins can generate free radicals by another dissociation and the radicals can cyclize as shown in Equation 7. Alkylbenzenes are generated from cyclics by dehydrogenation as shown in Equation 8. The small fraction of iso-paraffins is produced from *n*-paraffin radicals as stated in Equation 9. Gas is formed by recombination of short free radicals as shown in Equation 10. R1- R7 in Equations are

representing $(CH_2)_n$. Reactions of alkylbenzenes to multi-ring aromatics can be very complex and are not shown here.

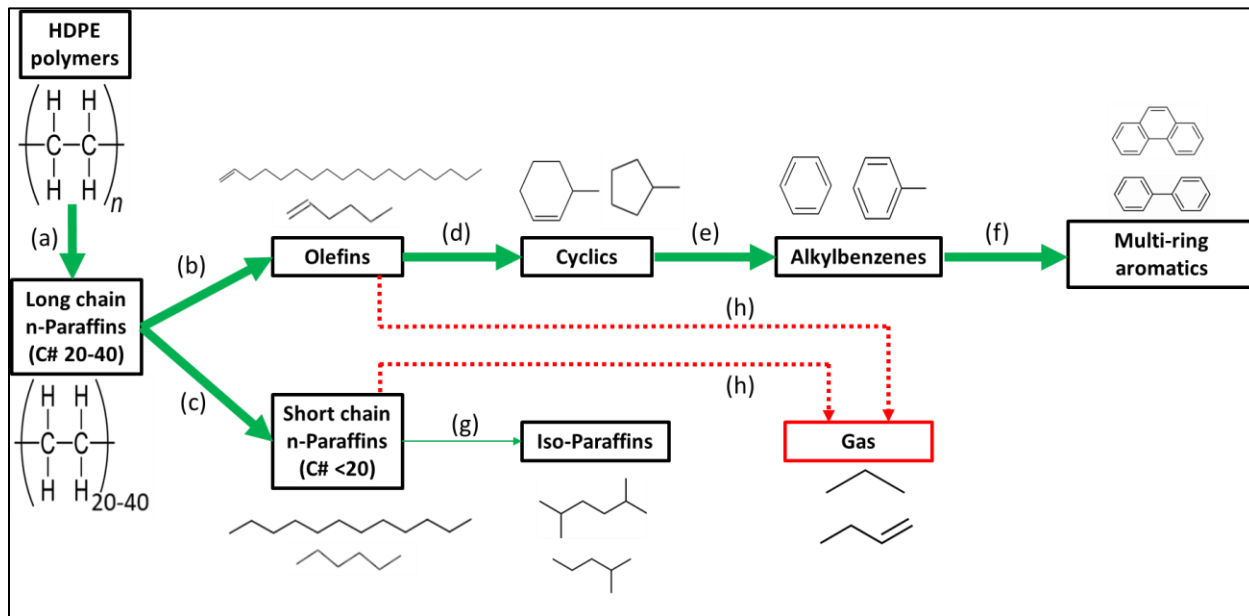
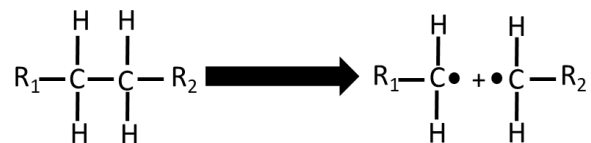
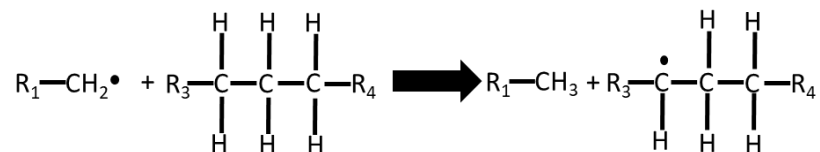


Figure 19. Potential reaction pathways for HDPE under HTP; (a) Depolymerization, (b) β -scission, (c) Hydrogen abstraction (d) Cyclization, (e) Dehydrogenation, (f) Further dehydrogenation to generate multi-ring aromatics, (g) Isomerization, and (h) gasification. The thickness of arrows indicates the relative amount of products.

Equation 4. Dissociation of HDPE Polymers



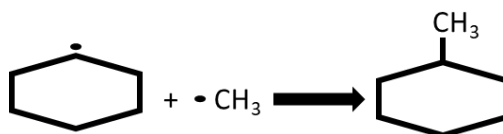
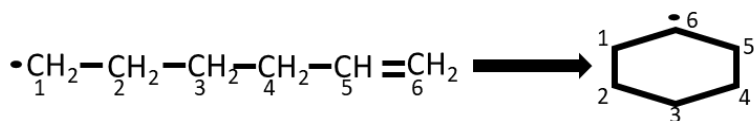
Equation 5. Hydrogen Abstraction



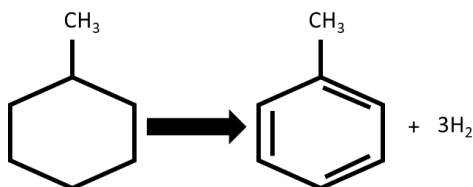
Equation 6. β -scission



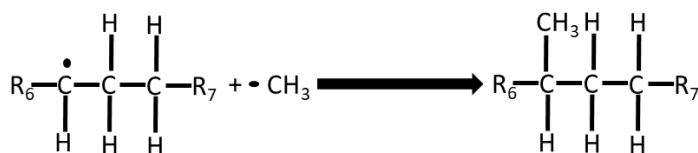
Equation 7. Three Steps of Cyclization



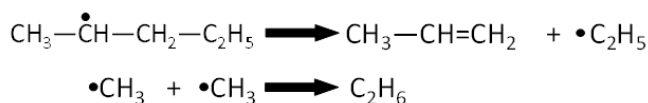
Equation 8. Dehydrogenation



Equation 9. Isomerization



Equation 10. Gas Formations



2.3.1.5 From Model HDPE to PE waste

Previous experiments were conducted using model HDPE to help understand the reaction mechanisms. PE waste pellets were tested under the same HTP conditions to verify the technical feasibility of converting plastic waste. PE waste were tested at 425 °C with 2.5 hr using 80 g feed. It has a lower oil yield (75%) and more solid residue (9%) than the ones of model HDPE. The difference resulted from the solid additives in the PE waste. SEM-EDS analysis was carried out for the solid residue and is discussed later in this Chapter.

The GC $\times$ GC-FID chromatogram for oils from model HDPE and PE waste were shown in Figure 20. They have similar peaks in 3-D view (Figure 20(a)) and also similar chromatograms (Figure 20(b)).

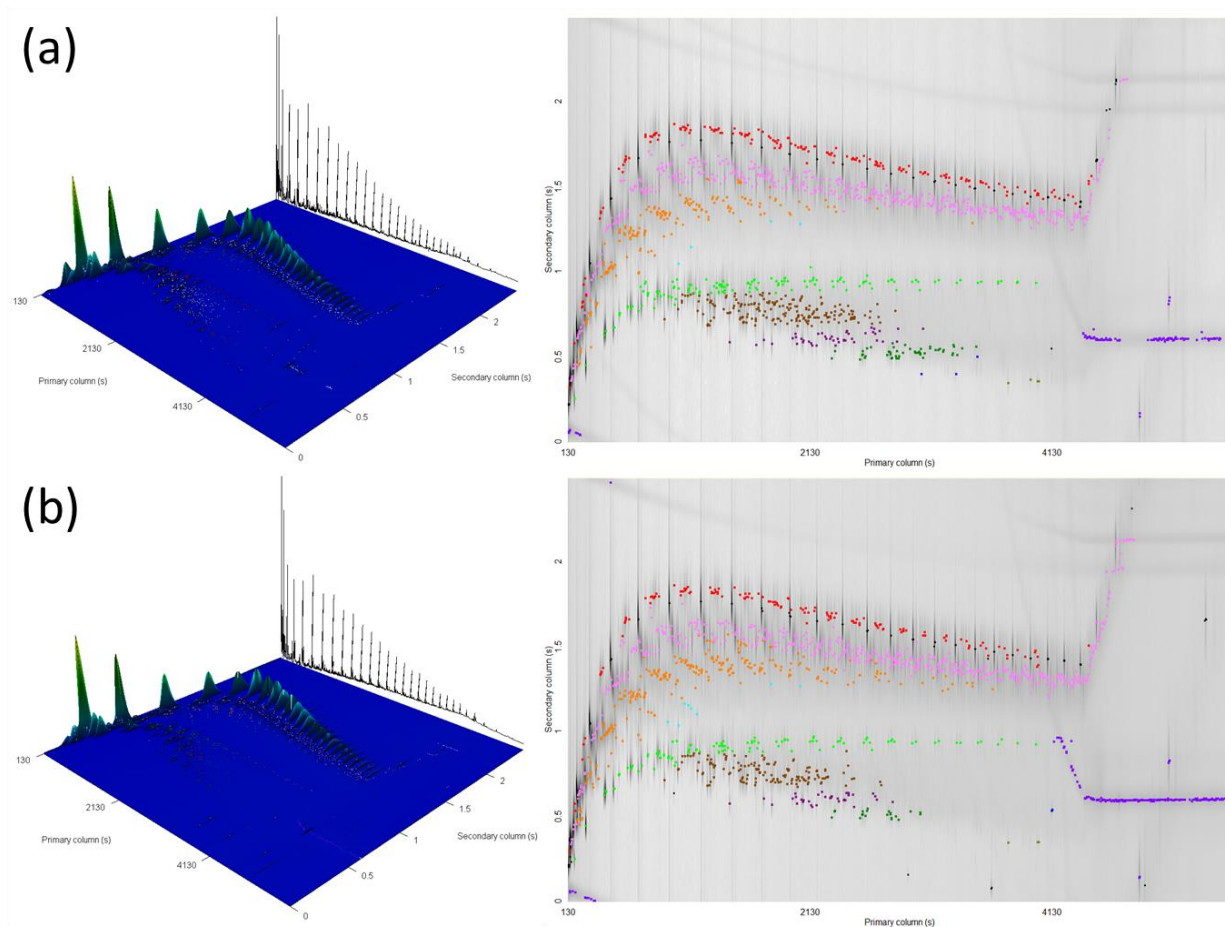


Figure 20. GC $\times$ GC-FID chromatogram in 3-D view and chromatogram with classification of oil produced at 425 °C with 2.5 hr from (a) PE waste and (b) model HDPE

The carbon number distribution was almost identical for model HDPE oil and PE waste oil (Figure 21). PE waste oil has the same amount of *n*-paraffins and iso-paraffins, less olefins plus cyclics, but more aromatics than model HDPE oil (Table 4). The slightly increased percentage of aromatics could result from low molecular weight PE in PE waste, which reacts faster and produces aromatics earlier.

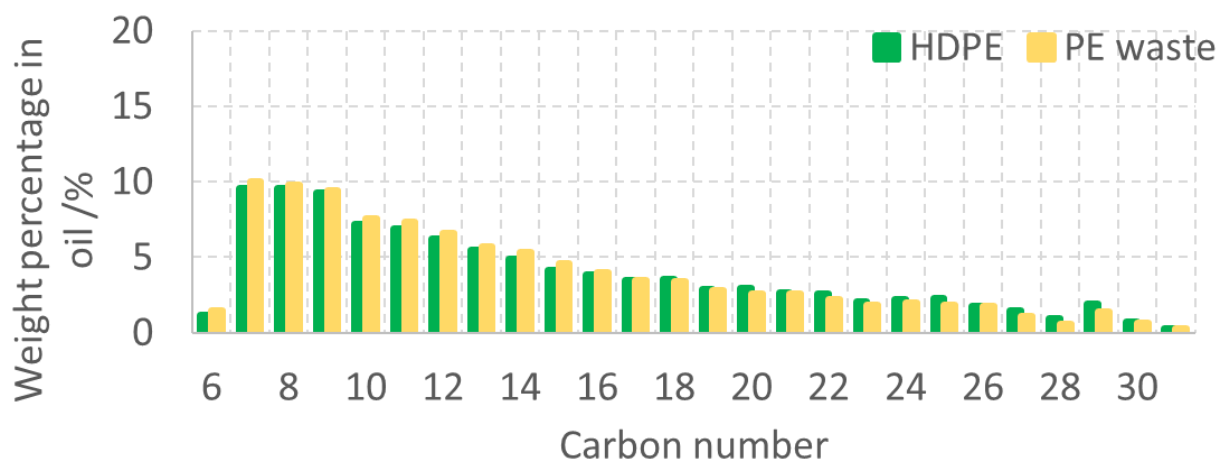


Figure 21. Carbon number distributions of oils produced at 425 °C and 2.5 hr from model HDPE and PE waste

Table 4. Chemical category information for oils produced at 425 °C and 2.5 hr from model HDPE and PE waste

Weight percentage in oil /%	HDPE	PE waste
<i>n</i> -paraffins	35.0	35.2
iso-paraffins	7.2	7.0
Olefins + Cyclics	49.2	44.9
Aromatics	8.5	12.8

SEM-EDS analysis was carried out to analyze the solid residue from PE waste after HTP. The results were shown in Figure 22 and Table 5. Carbon, oxygen, silicon, chlorine, calcium, and titanium were found in the solid residue. The majorities are oxygen (52.97%) and calcium (30.58%). These findings indicate the potential solid additives in PE waste, such as calcium carbonate, titanium dioxide, and silicon dioxide, which are used as dyes or fillers in polyolefins.

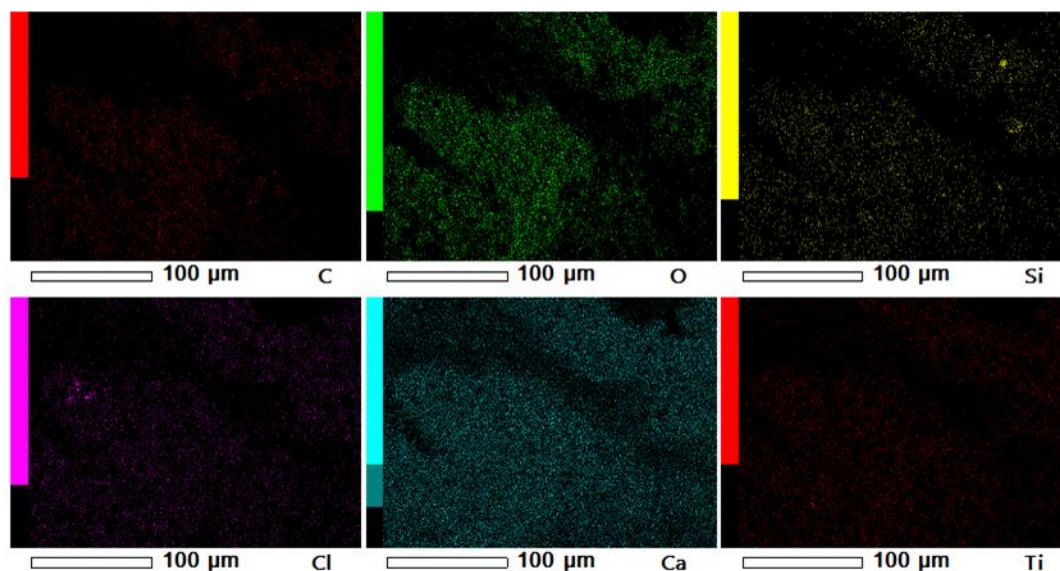


Figure 22. SEM-EDS mapping plots

Table 5. Elements identified by SEM-EDS and their mass percentages

Element	Mass%
C	9.60
O	52.97
Si	0.66
Cl	1.77
Ca	30.58
Ti	4.42
Total	100.00

In summary, PE waste behaves similar to model HDPE under the same HTP conditions. Solid additives in PE waste result in a lower oil yield and more solid residues. HTP is technically feasible to convert PE waste into products.

2.3.1.6 Product Applications

2.3.1.6.1 Paraffins wax

Wax-like product are obtained via HTP at a lower reaction temperature (not higher than 425 °C) and a shorter reaction time (no more than 40 minutes). Experiments at 425 °C with reaction time of 40 minutes using 80 g PE waste were conducted and crude wax product was obtained (Figure 23(a)). Further purifications were carried out. *n*-heptane was used to extract wax from the solids at 50 °C (Figure 23(b)). Activated carbon adsorption was conducted and wax was precipitated out at a low temperature (4 °C). The final clean wax product was shown in Figure 23(c).

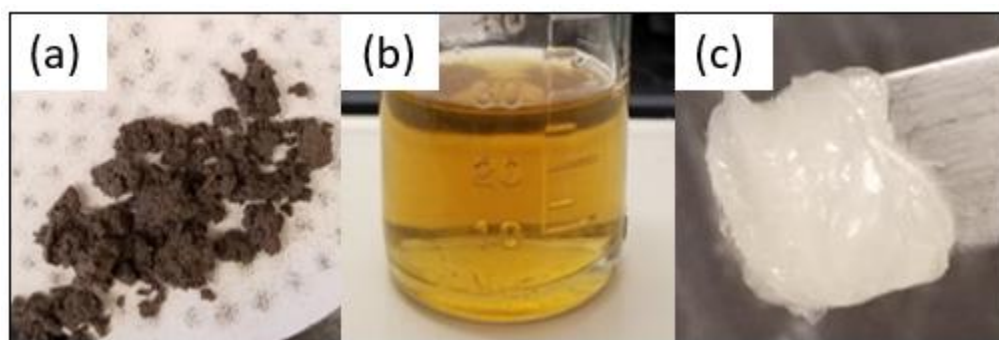


Figure 23 (a) Crude wax product (b) Dissolved wax in *n*-heptane (c) Final wax product

In order to investigate the chemical compositions of the obtained wax product from PE waste, FT-IR analysis was carried out. The spectrum was shown in Figure 24(a). The three valleys in the range of 4,000-2,500 cm^{-1} are because of the stretching vibration of C-H bonds. The two valleys in the range of 2,000-1,000 cm^{-1} are because of the formation vibration of C-H bonds. A tiny valley at 909.06 cm^{-1} is potentially because of the bending vibration of -C=CH_2 . The results show that the wax is composed of *n*-paraffins and potentially a small fraction of olefins. Commercial paraffin wax was also analyzed using FT-IR (Figure 24(b)). Apparently, the two spectra of wax from PE waste and commercial paraffin wax are very similar, which indicates the wax produced from PE waste via HTP can be of a high purity as commercial paraffin wax.

More properties including melting point range, oil content, and penetration resistance are needed for the wax from PE waste to be fully qualified as commercial wax product.

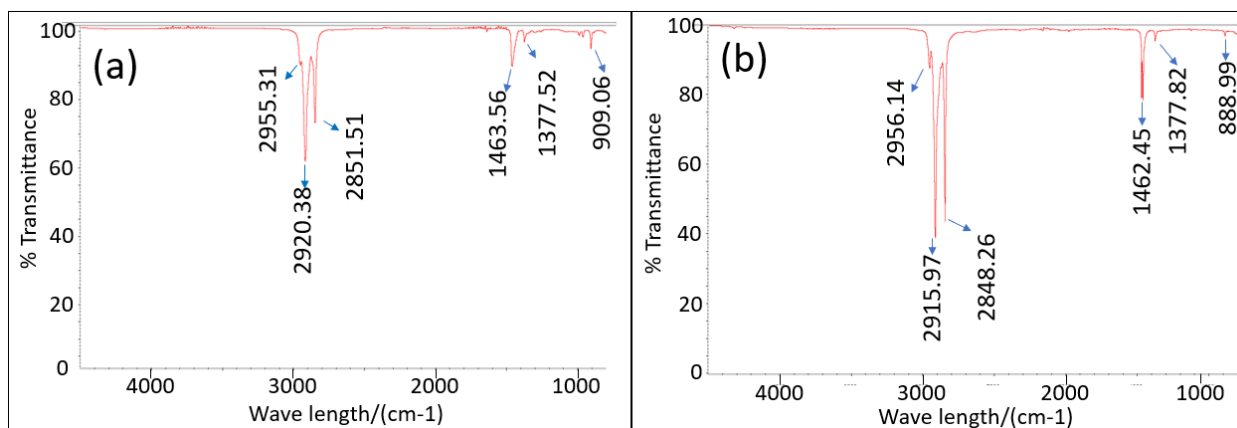


Figure 24. FT-IR spectra of (a) Final wax product (b) Standard paraffin wax

2.3.1.6.2 Diesel blendstock, naphtha and bunker fuel

Oil is the major product under most conditions. According to its chemical compositions, the oil product has the potential to be used as transportation fuels, especially diesel owing to its high percentage of *n*-paraffins. However, the oil product has a wide carbon number distribution from C6 to C31, which exceeds the range of diesel (C8-C25). Thus, distillation following ASTM D86 was conducted to separate the HTP oil into light oil (b.p. < 170 °C), diesel-like oil (170 °C ≤ b.p. < 300 °C), and heavy oil (b.p. ≥ 300 °C). The oil produced from PE waste (HTP oil) at 425 °C with a reaction time of 2.5 hr was distilled. 30% was recovered as light oil, 50% was recovered as diesel-like oil, and 20% was recovered as heavy oil (Figure 25).

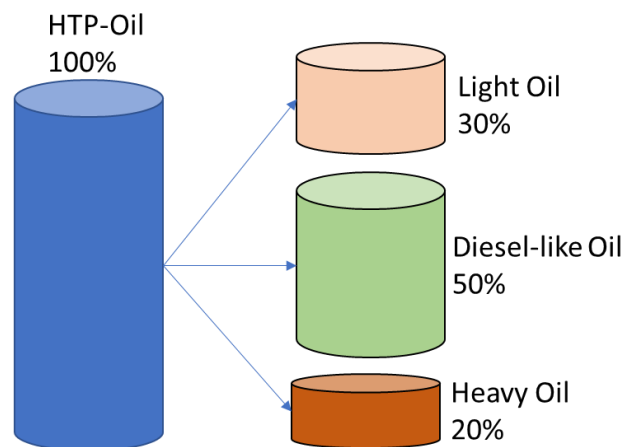


Figure 25. Distillation of oil produced from PE waste via HTP at 425 °C with a reaction time of 2.5 hr

GC × GC-FID analyses were carried out for HTP oil, the diesel-like fraction of the HTP oil (HTP-diesel), and commercial diesel (Figure 26). HTP oil (Figure 26(a)) has light fractions and a tailing of heavy hydrocarbons. However, the light and heavy fractions are removed after distillation. The HTP diesel (Figure 26(b)) is almost identical to commercial diesel (Figure 26(c)).

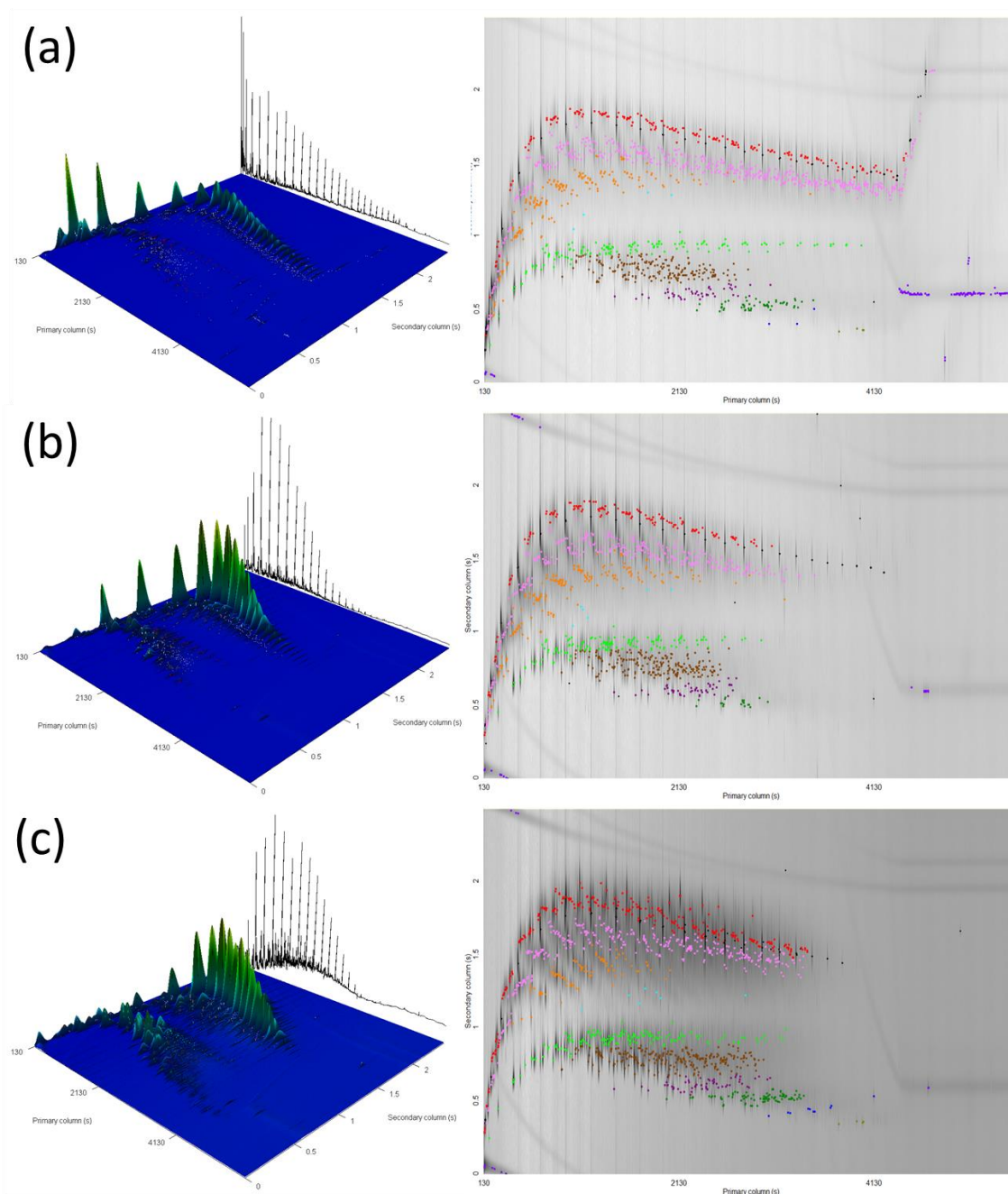


Figure 26. GC $\times$ GC-FID chromatogram in 3-D view and the projection of (a) HTP-oil, (b) HTP-diesel, and (c) commercial diesel

To test whether HTP diesel can be qualified as commercial diesel, fuel properties including flash point, water and sediment content, viscosity, sulfur content, cetane number, aromaticity, and cloud point were measured. Mixture of 10 vol.% HTP diesel and 90 vol.% local Speedway diesel (HTP-10), and 50 vol.% HTP diesel and 50 vol.% local Speedway diesel (HTP-50) were also tested. The results and ASTM requirements are shown in Table 6.

Flash point indicates at what temperature the sample will be ignited with a flame. It is significant to fuel storage safety as a higher flash point is preferred for safety. ASTM requires flash point to be at least 38 °C for No.1 diesel and at least 52 °C for No.2 diesel. Flash point of HTP-diesel was not measured because a large sample amount is needed. The flash points for HTP-10 and HTP-50 are 57 °C and 50 °C, respectively. It should be noticed that in this study flash point was measured using ASTM D56 method, which is slightly different from ASTM D93 method required by ASTM D975 for diesel. In general, D56 may give results up to 1-2 °C below the D93 results.^{50,55,56} Therefore, HTP-10 fits the requirement for both No.1 and No.2 diesel. HTP-50 meets the requirement for No.1 diesel and may also meet the requirement for No.2 diesel as well.

Water and sediment are impurities in diesel and they cause damages to engine. ASTM limits a maximum of 0.05 vol.% for water and sediment. Only 0.01 vol.% water was found in HTP-diesel, and no sediment was seen. Thus, HTP-diesel, HTP-10, and HTP-50 all meet the requirement.

A proper fuel kinematic viscosity is required for engine operations. A too high viscosity causes insufficient mixing of fuel with air and results in an uncompleted combustion. A too low viscosity results in insufficient lubrication for the oil supply system, which aggravates mechanically wearing. ASTM requires kinematic viscosity of 1.3- 2.4 mm²/s for No.1 diesel and 1.9- 4.1 mm²/s for No.2 diesel. HTP-diesel has a viscosity (1.650 mm²/s) in the range required for No.1 diesel. HTP-10 (2.549 mm²/s) and HTP-50 (2.070 mm²/s) meet the requirement for No.2 diesel.

Sulfur content needs to be lower than 15 ppm for diesel fuel to be quantified as ultra-low sulfur diesel. Too high sulfur raises environment concerns regarding acid rain and corrosions. Only 8 ppm sulfur was found in HTP-diesel. HTP-10 and HTP-50, as a blend of HTP-diesel and commercial diesel also meet the sulfur content requirement.

Cetane number is an indicator of the combustion speed of diesel fuel and the compression needed for ignition, as a higher cetane number indicating faster combustion and less compression needed. A cetane number between 40-60 is required for diesel fuel. ASTM D613⁵⁷ is an engine test method and requires at least 1 L of fuel which is beyond the productivity in this study. An alternative method was used to estimate cetane number based on the chemical compositions of the oils.⁵⁸ The estimated cetane number of the five kinds of local commercial diesel are in the range

of 41-52. And the estimated cetane numbers of HTP diesel, HTP-10, and HTP-50 are 41, 48, and 45, respectively, which all meet the minimum requirement, 40.

Another requirement for diesel is the maximum aromaticity (35 vol.%). A high percentage of aromatics in diesel reduces the cetane number and heating value. The percentages of aromatics in HTP diesel, HTP-10 and HTP-50 are 18, 19 and 20 wt.%, respectively. Different hydrocarbons with the same carbon number have a similar density to each other. Thus, HTP diesel, HTP-10 and HTP-50 are estimated to have less than or equal to 20 vol.% of aromatics, which is lower than the ASTM requirement.

Cloud point is a measurement of anti-freezing property as it is the temperature at which fuel begins to become cloudy. ASTM does not give a specific cloud point requirement since it varies from region to region and heavily depends on seasons. In summer, higher cloud point is allowed but in winter, lower cloud point is required to prevent fuel clogging. Cloud point of commercial diesels varies from -7 °C to -22 °C. The measured cloud point for HTP-diesel, HTP-10 and HTP-50 is -7, -10, -9 °C, respectively, which is similar to the cloud points of commercial diesel.

In summary, HTP-diesel meets all measured fuel property requirements for No.1 diesel, except for an unknown flash point and an unspecified cloud point requirement. HTP-10 meets all measured fuel property requirements for No.2 diesel. HTP-50 behaves similarly to commercial diesel except for a potentially lower flash point. HTP-diesel is promising to be used as No.1 ultra-low-sulfur diesel and can be used as No.2 ultra-low-sulfur diesel blendstock.

Table 6. Fuel properties for ASTM requirements, commercial diesel, HTP diesel, HTP-10 and HTP-50.

Property	ASTM Test Method	No.1-D S15	No. 2-D S15	Commercial Diesel	HTP Diesel	HTP-10	HTP-50
Flash Point, °C	D93	>38	>52	54-62 ^(a)	-	57 ^(a)	50 ^(a)
Water and Sediment, vol.%	D2709	<0.05	<0.05	-	0.01	<0.05	<0.05
Kinematic Viscosity, mm ² /s at 40 °C	D445	1.3-2.4	1.9-4.1	2.476-2.888	1.650	2.549	2.070
Sulfur, ppm (µg/g)	D5453	<15	<15	-	~8	-	-
One of the following properties must be met:							
(1) Cetane number	D613	>40	>40	41-52 ^(b)	41 ^(b)	48 ^(b)	45 ^(b)
(2) Aromaticity, percent volume	D1319	<35	<35	17-35 ^(c)	18 ^(c)	19 ^(c)	20 ^(c)
Cloud Point, °C	D2500	-	-	(-7)-(-22)	-7	-10	-9

(a) ASTM D56 is used instead of D93.

(b) Estimated based on chemical compositions.⁵⁸

(c) Weight fraction is used instead of volume fraction.

The HTP oil has two other fractions, the light oil and the heavy oil. The light oil cannot be used as gasoline directly because of its high percentage of *n*-paraffins which results in a low octane number. High octane number (≥ 87) is required by gasoline to avoid engine-knocking. However, the light oil can be used as naphtha, to produce gasoline via isomerization where *n*-paraffins are converted into iso-paraffins. The heavy oil has the potential to be used as bunker fuels for ships and power plants. Further analysis is needed.

The gas generated during HTP is mainly composed of short paraffins and olefins. It can be combusted for energy recovery.

2.3.1.6.3 Feedstock for specialty chemicals

Paraffins, olefins, cyclics, and aromatics are in the oil produced from PE waste via HTP. They are promising to be used as chemical feedstocks and specialty solvents if with proper separation methods.

2.3.2 PP

PP in HTP under supercritical water was previously studied using a 35 ml tubular reactor. The work was published on *ACS SUSTAIN CHEM ENG*.⁵⁹ The small scale reactor limits most characterizations of product. Experiments at a larger scale (500 ml) were carried out and the results were reported in this section.

2.3.2.1 Yields

Experiments using model PP were carried out at reaction temperature of 425 °C with a reaction time from 1 hr to 3 hr (Figure 27). At 1 hr, almost all PP feed are already converted into oil (75%) and gas (24%). When time increases to 3 hr, the oil yield decreases to 61% while gas yield increases to 38%. This indicates a conversion from oil to gas. At 425 °C, the highest oil yield (75%) was obtained at 1 hr for PP, while at 3 hr for HDPE (81%) (Figure 16(a)). This apparently is because PP reacts faster than HDPE under the same HTP conditions.

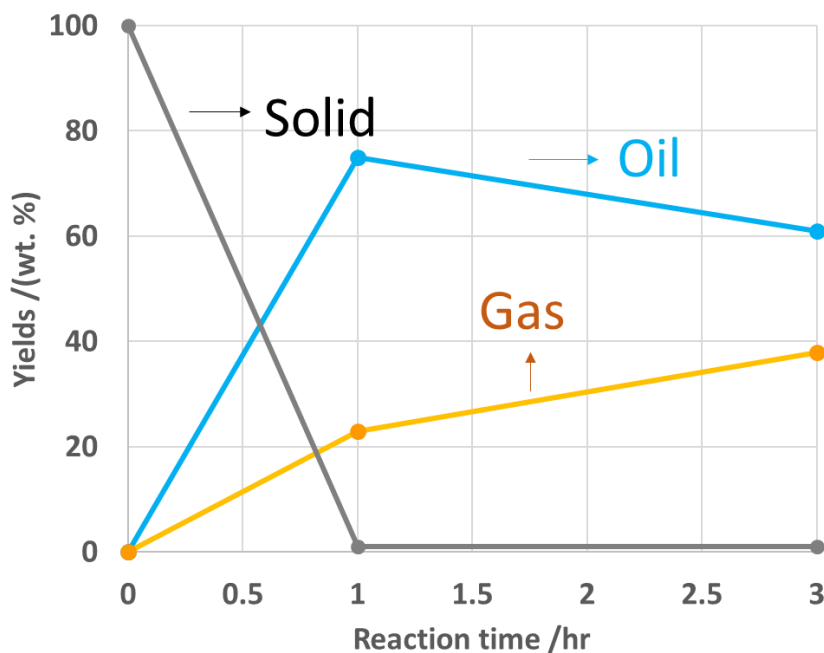


Figure 27. HTP product yields from model PP with a reaction time 0-3 hr at 425 °C

2.3.2.2 Chemical Categories

PP oils were analyzed using GC × GC-FID. Hydrocarbons identified were grouped according to their chemical categories. The result is shown in Figure 28. Olefins plus cyclics and iso-paraffins are first generated. Olefins plus cyclics reach 66.9% at 1 hr while iso-paraffins reach

26.2%. As reaction time increases to 3 hr, the percentage of olefins plus cyclics decreases to 40.4% while the percentage of aromatics increases from 6.9% to 29.4%. This indicates the generation of aromatics from olefins plus cyclics. The percentage of iso-paraffins fluctuates slightly. Less than 1% of *n*-paraffins was found under all conditions.

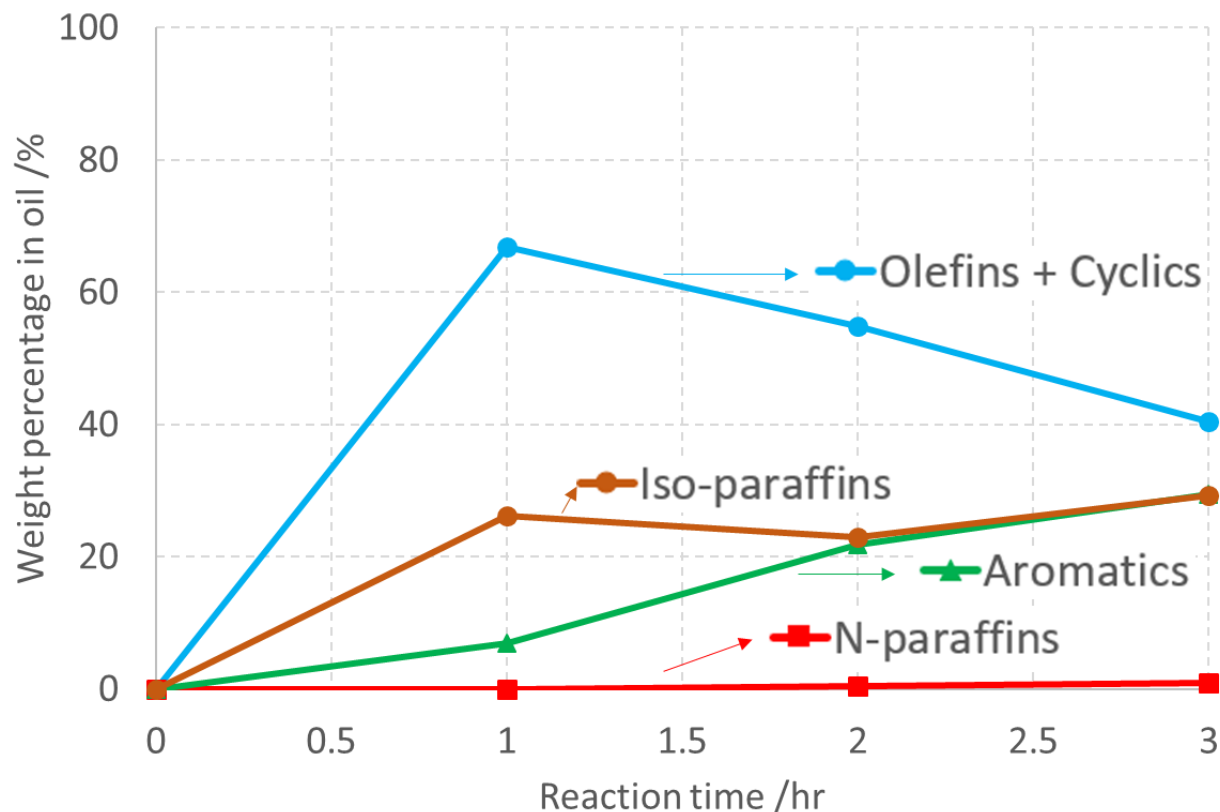


Figure 28. Chemical compositions of the oils from model PP at reaction temperature 425 °C with reaction time up to 3 hr.

2.3.2.3 Potential Reaction Pathways of PP

Potential reaction pathways for PP under HTP were proposed based on the analysis of reaction intermediates. The scheme is shown as Figure 29. Reactions starts with the depolymerization of PP polymers into oligomers. The oligomers are mainly converted into olefins while a fraction is converted into iso-paraffins. With extended time, cyclics are generated from olefins, and the formed cylics are converted into alkylbenzenes via dehydrogenation. As reaction time further increases, alkylbenzenes are converted into multi-ring aromatics. Gas is formed from

short chain free radical recombination. Representative reaction formulas were shown as Equation 11-15.

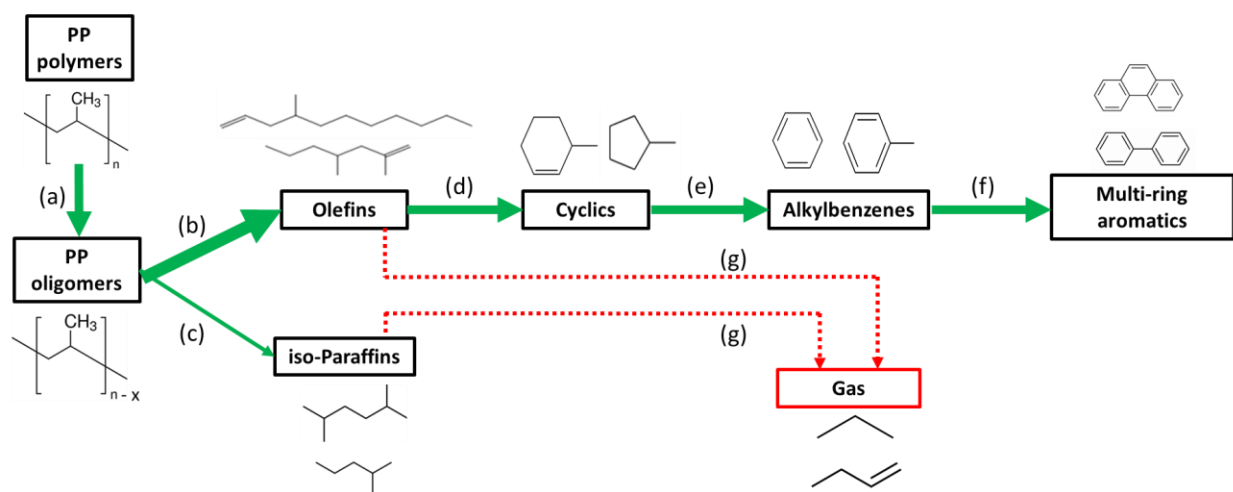
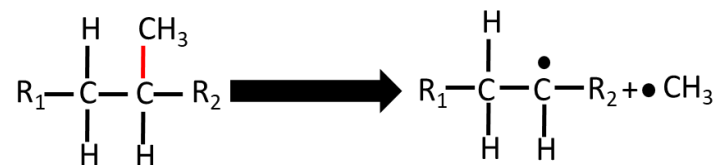
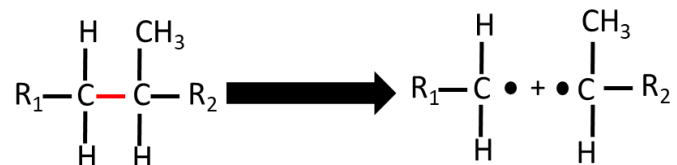


Figure 29. Potential reaction pathways for PP under HTP; (a) Depolymerization, (b) β -scission, (c) Hydrogen abstraction (d) Cyclization, (e) Dehydrogenation to generate single-ring aromatics, (f) Further dehydrogenation to generate multi-ring aromatics, and (g) gasification. The thickness of arrows indicates the relative amount of products.

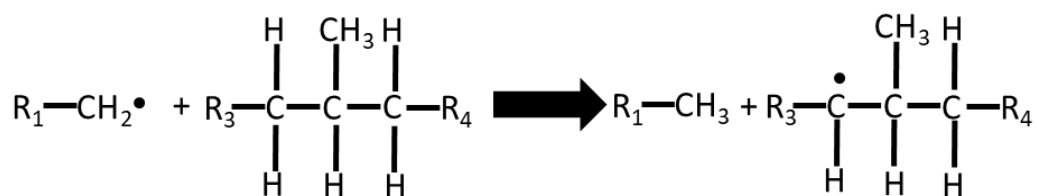
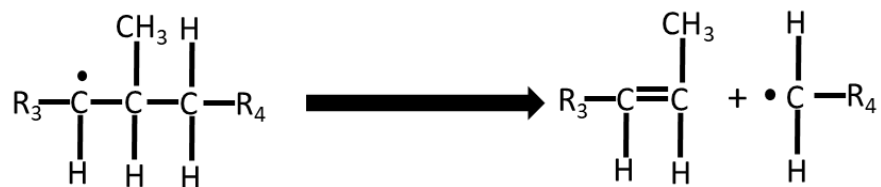
The depolymerization of PP starts from free radical dissociation. PP has two different kinds of C-C bonds, one is C-CH₃ bonds, and the other is C-C bonds on the backbone. The two kinds of C-C bond both can break and generate different free radicals (Equation 11 and Equation 12). The radicals generated from C-CH₃ bond breaking, can go through β -scission directly and generate olefins (Equation 13). Radicals generated from breaking C-C bonds on backbone, goes through hydrogen abstraction where paraffins are produced, and then β -scission where olefins are produced (Equation 14 and Equation 15). The formed olefins then go through cyclization to generate cyclics (Equation 16), which is then converted into aromatics (Equation 17). Gas is formed from small radical recombination (Equation 18). R1-R4 represent unit structure in PP polymers. Multi-ring aromatics are converted from single-ring aromatics, and the reactions are not shown here.

Equation 11. Dissociation of PP polymers by breaking C-CH₃ bonds

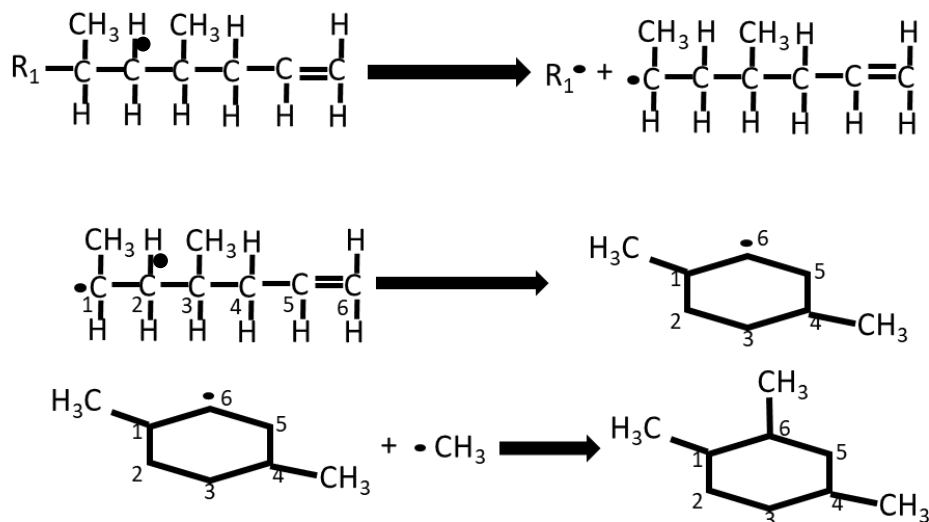
Equation 12. Dissociation of PP polymers by breaking C-C bonds on backbone

Equation 13. β -scission after breaking C-CH₃ bonds

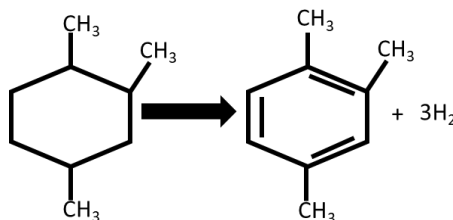
Equation 14. Hydrogen abstraction after breaking C-C bonds on backbone

Equation 15. β -scission after breaking C-C bonds on backbone

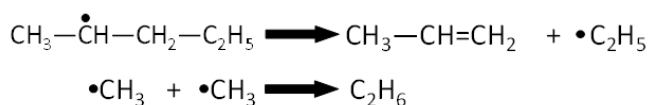
Equation 16. Cyclization



Equation 17. Dehydrogenation



Equation 18. Gas formations



2.3.2.4 Product Applications

Oil is the major product of PP under most HTP conditions tested. About 75% of the oil is gasoline-like (C4-C12). The oil is rich in iso-paraffins, which are favored by gasoline because of their high octane number. A higher octane number indicates more compression the fuel can withstand before ignited. The PP oil is promising to be used as gasoline after removing the heavy hydrocarbons via distillation. Engine test is needed in the future to identify the octane number of PP-oil.

The PP oil also has the potential to be sold as naphtha, which is the feedstock for gasoline, and other kinds of valuable specialty solvents such as iso-paraffin based solvents. The solvents are

widely used in fields such as cleaning and degreasing⁶⁰, inkjet printing⁶¹, paints and coating⁶², and metal working⁶³. The gas generated under HTP for PP can be combusted for energy recovery.

2.4 Discussions

2.4.1 Different Pathways of HDPE and PP

HDPE and PP have different reaction pathways (Figure 19 and Figure 29) because of their polymer structures. As described in section 2.3.1.4 and section 2.3.2.3, C-C bonds break in HTP reactions of polyolefins rather than C-H bonds because of the lower bond energy in C-C bonds. HDPE only has C-C bonds on the backbone. But PP has two kinds of C-C bond. One is on the backbone, and the other is the C-CH₃ bond, which has an even lower bond energy (335 kJ/mol) than C-C bonds on the backbone (347-377 kJ/mol) and tends to break first.^{64,65} This is the key reason that PP is converted to oils and gases earlier than HDPE under the same HTP conditions.

In HTP conversion of PP, two kinds of C-C bonds both can break to generate free radicals via dissociation. After the breaking of C-CH₃ bonds, only olefins are generated by following β -scission (Equation 13). Instead, after the breaking of C-C bonds on backbone, both paraffins and olefins are generated in the following hydrogen abstraction and β -scission (Equation 14 and Equation 15). The extra dissociation reaction of PP results in more olefins plus cyclics and less paraffins than the ones in HDPE oil.

HDPE-oil is rich in *n*-paraffin which is similar to its polymer structure. A small fraction of iso-paraffins was isomerized from *n*-paraffins. PP-oil is rich in iso-paraffins and has neglectable amount of *n*-paraffins. The difference of paraffin category is also because of the polymer structure of HDPE and PP.

2.4.2 Roles of Water

Reactions of thermal pyrolysis occur in a viscous polymer phase, and polymers are relatively concentrated. Secondary and higher order reactions are favored, such as polycondensate formation which eventually generates char. Supercritical water used in HTP reduces the polymer concentration by a partial dissolution of the molten polymer phase. The reduced polymer concentration favors reactions of lower order such as β -scission (unimolecular reaction). Reactions with higher order are suppressed. Supercritical water serves as an effective solvent and reaction medium in HTP for polyolefins. This is the reason why no or little char (< 1%) was found under

all conditions tested in this study. Relatively high oil yields (70-90%) and low gas yields (10-30%) were also achieved owing to the use of supercritical water as a good solvent.

In addition, water is not a reactant or a product in this study. No significant amount of oxygenated compounds was found in wax or oil products under all conditions and the weight of water remains the same before and after HTP experiments.

It is still unclear whether water functions as a catalyst in this study. In principle, supercritical water itself, the H^+ and OH^- ions, and the $H\cdot$ and $OH\cdot$ radicals in supercritical water can catalyze a wide variety of reactions, including hydrogenation/dehydrogenation.²⁹ Research is needed in the future to specifically identify which reaction is catalyzed by supercritical water.

2.4.3 Cost Analyzes

Preliminary cost analyzes were carried out to test the economic feasibility of HTP. An industrial scale plant treating 2,000 metric ton PE waste per day was assumed. One can find a great profit margin for wax production (\$0.54/kg plastic processed) from PE waste (Table 7). This plant is estimated to produce 0.48 million tons of wax annually, which will not oversaturate the global wax market (about 6 million per year).

Table 7. Cost analysis for wax production from PE waste via HTP

	Price (\$/kg plastic processed)
Feedstock ^(a)	0.1764
HTP Equipment ^(b)	0.0641
Waste treatment ^(c)	0.0042
Electricity and other utilities ^(c)	0.0125
Distillation for solvent recovery ^(d)	0.0083
Activated carbon regeneration ^(e)	0.0006
Total processing cost	0.0868
Paraffin wax selling price	0.80
Net profit	0.54

a) Using PE waste from EREMA as feedstock

b) Updated from Zhu et al., 2013²⁵. Assuming a plant processing 2,000 metric ton/day and assuming 20 years for depreciation. An inflation factor of 1.2351 from 2007 to 2019 was applied.

- c) Updated from Zhu et al., 2013.²⁵ Plastic HTP has less waste in water compared to biomass HTP. This includes solid waste treatment and minor wastewater treatment.
- d) Distillation for separating binary liquid mixture. Data obtained from Hinchliffe et al., 2000⁶⁶
- e) Assuming activated carbon regenerated by hot nitrogen. Data obtained from Sabio et al., 2004⁶⁷

The cost analysis for oil production from PE waste (Table 8) also indicates a profit margin. Oil yield and diesel fraction in oil are assumed to be 80 and 50% respectively. As a result, \$0.149 can be earned for every kilogram of PE waste treated. A higher profit can be achieved by increasing the oil yield and diesel fraction in oil. The fuel production from PE waste via HTP will not disturb current fuel market. Even all PE waste is converted into diesel at a 100% yield, that only meets 5.7% of global annual diesel demand.

Table 8. Cost analysis for fuel production from PE waste via HTP

	Price (\$/kg plastic processed)
Feedstock ^(a)	0.1764
HTP Equipment ^(b)	0.0641
Waste treatment ^(c)	0.0042
Electricity and other utilities ^(c)	0.0125
Distillation ^(d)	0.0165
Total processing cost	0.0968
Diesel ^(e)	0.32 ^(g)
Light and heavy oil ^(f)	0.10 ^(g)
Net profit	0.15

- (a) Using PE waste from EREMA as feedstock
- (b) Updated from Zhu et al., 2013.²⁵ Assuming a plant processing 2,000 metric ton/day and assuming 20 years for depreciation. An inflation factor of 1.2351 from 2007 to 2019 was applied.
- (c) Updated from Zhu et al., 2013.²⁵ Plastic HTP has less waste in water compared to biomass HTP. This includes solid waste treatment and minor wastewater treatment.
- (d) Assuming distillation capable for processing 71.9 m³/hr. The capital cost of the column was \$10.3 million while the operational cost is 200,000\$/year. A security factor of 10 was applied.
- (e) Using \$0.644/kg as diesel price which is the price including crude oil, refining cost and profits for producing diesel from crude petroleum.⁶⁸

- (f) Using \$0.2/kg as the selling price for light and heavy oil.⁶⁹
- (g) Assuming after distillation, 50% of oil is recovered as diesel fraction and 50% is as light and heavy oil fraction.

In summary, both wax and oil production from PE waste via HTP are estimated to be an economically feasible process.

2.4.4 Product Competitions

Potential competitors for HTP fuel products include pyrolysis fuels, and biodiesels. Thermal pyrolysis has a relative low oil yield if catalysts are not used. Pyrolysis processes mixed plastic waste which results in a poor fuel quality. Thus, further costly upgrades are needed.

Biomass HTP produces oils with a low yield about 30% while 50% of feed is dispersed in water phase.²⁵ Further treatments are also needed for upgrading the oils produced from biomass to biodiesels. In addition, biodiesel has a lower heating value (39-43 MJ/kg) because of the oxygenated compounds in it. As a result, the state of technology for producing biodiesel at 2018 is \$3.50 per gallon gasoline equivalent(GGE),⁷⁰ which is not competitive to commercial diesel price (\$2.08/gallon or \$2.36/GGE)^{71,72}.

Few competitors were found for HTP wax products. Few researches were reported for wax production from plastic waste via pyrolysis. Currently paraffin wax is mainly produced by the fractionation of crude petroleum. HTP wax from PE waste is estimated to be a technically and economically feasible process. However, HTP wax production can only be a partial solution for reducing polyolefin waste because of the relatively small global wax demand.

2.4.5 Summary

In this chapter, HTP of polyolefins was introduced. HTP can effectively convert HDPE into wax and oil and convert PP into oil. Reaction temperature of 400- 450 °C and reaction time of 0.5 -3 hr were explored. Highest oil yield was obtained at 425 °C with 2.5 hr for HDPE (83%), and at 425 °C with 1 hr for PP (75%). Higher temperature and longer reaction time reduce oil yields because of increased gas generation. Based on results from GC × GC-FID, effects of temperature, time and feed loading on product composition were investigated. Higher temperature and extended reaction time favor shorter carbon chain hydrocarbons and aromatics. Polymer loading tested had little impact on the product compositions. Potential reaction pathways were

proposed for HDPE and PP, respectively. PP was found reacting faster than HDPE under the same conditions. HTP can be a both technically and economically feasible process for converting PE waste. In summary, HTP is a versatile process (Figure 30) that can help reduce polyolefin waste accumulation by converting it into useful and profitable products.

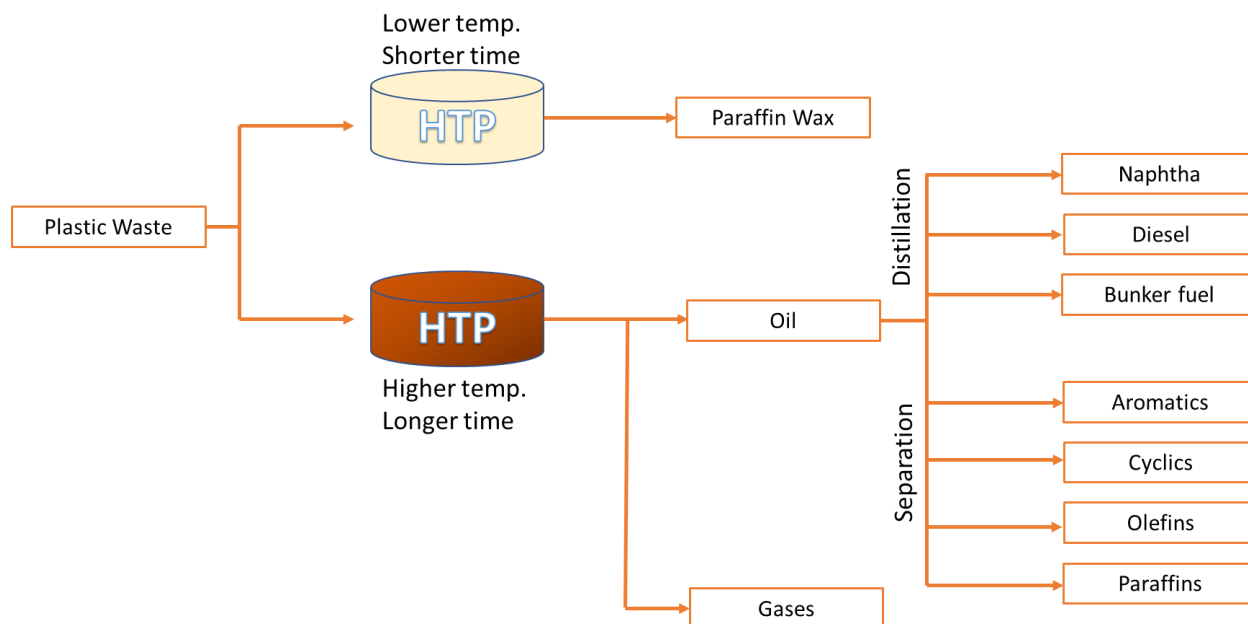


Figure 30. Converting plastic waste into useful products via HTP

CHAPTER 3. SEQUENTIAL SELECTIVE EXTRACTION & ADSORPTION (SSEA)

3.1 Introduction

Solvent extraction is a recycling method that aims to recover pristine polymers from plastic waste by dissolution and reprecipitation techniques.⁷³⁻⁷⁵ Polymers in plastic waste are dissolved and separated from the insoluble in waste. The dissolved polymers are then precipitated and recovered by the use of anti-solvent.⁷³ Solvent and anti-solvent are recovered by distillation and then be reused. Because polymer structures are preserved during solvent extraction, the recovered polymers are estimated to function the same as virgin polymers.^{73,76} Solvent extraction is a promising method to reduce plastic waste accumulation by recovering them for reuse. In addition, solvent extraction is a more sustainable process, by reducing the crude oil consumption for virgin polymer synthesis.

Plastic polymers have either amorphous or semi-crystalline polymer structures. Common amorphous polymers are polystyrene and polycarbonate, while polyolefins are all semi-crystalline ones. Polymer structure of amorphous ones is irregular and disordered, allowing a high mobility of the molecules and making the polymers easier to dissolve in organic solvents. However, semi-crystalline polymers have a more restrained structure, which increases the difficulty of their dissolution in organic solvents. High temperature is usually needed to decrease the crystallinity and help the dissolution of semi-crystalline polymers.

Solvation power is an indicator of the ability of a solvent to disperse and dissolve polymers.⁷⁷ It can be predicted from solubility parameters including dispersion, polarity, and hydrogen bonding.⁷⁸ Previous studies found that polyolefins can be dissolved at temperature 100-140 °C in aromatic solvents such as toluene and xylene.⁷³⁻⁷⁵ These aromatic solvents can provide sufficient solvation power to dissolve polyolefins. However, the intense use of aromatic solvents raises concerns regarding toxicity. Toluene is rated as Class 2 by NFPA 704 Standard, indicating potential temporary incapacitation or possible residual injury caused by intense or continued exposure.⁷⁹ In addition, solvent cost contributes significantly to the overall cost, as a lower solvent cost allows higher profits. The price of toluene is \$0.93/kg according to ICIS, which is higher than common hydrocarbon solvents, for example \$0.40/kg of heptane.^{79,80} Reduced use of aromatic solvents is beneficial to mitigate safety risks and decrease process costs.

Researchers were also seeking alternative solvents. Paraffin hydrocarbon solvents are less toxic with a lower cost. For example, *n*-heptane is rated as Class 1 by NFPA 704 for only potentially causing minor residual injury, and the price of *n*-heptane is only \$0.40/kg according to ICIS.^{79,80} The low toxicity and low solvent cost are preferred for large scale production. However, the solvation power of paraffin hydrocarbon solvents is insufficient to dissolve polyolefins.

Hereby, the idea is proposed to mix one strong solvent (like toluene and xylene) and one weak solvent (like hexane and heptane). The mixed solvents are expected to have an adjustable solvation power, a reduced health hazard and a lower solvent cost. Solvent component and mixing ratio can manipulate the solvation power of mixed solvent, which allows selective extractions between different polymers. A selective extraction process can be applied to separate mixture of different polymers in a sequential order. A previous study extracted polycarbonate from waste electrical and electronic equipment using mixed acetone and dichloromethane.⁸¹

It is impossible to experimentally test all potential solvents with various mixing ratios because of the almost infinite combinations. Hansen Solubility Parameters (HSP) was thus used to determine potential solvent pairs and mixing ratio for target type of polymer. HSP predicts the solubility of polymers in solvents based on their dispersion, polar and hydrogen bonding parameters (δ_D , δ_P , δ_H).^{78,82} A spatial rectangular coordinate system (Hansen sphere) is established using these three parameters as axes. Each kind of polymer has an experimentally determined R_0 as the radius for a “solubility sphere”. Each solvent is a point in Hansen sphere. The solvents, which can dissolve the polymer are included in the sphere. Information of δ_D , δ_P , δ_H and R_0 for solvents and polymers are available in handbooks.⁸² The distance between the polymer sphere center and the solvent point (R_a) is calculated using Equation 19:

$$R_a^2 = 4 * (\delta_{D,solvent} - \delta_{D,polymer})^2 + (\delta_{P,solvent} - \delta_{P,polymer})^2 + (\delta_{H,solvent} - \delta_{H,polymer})^2$$

Relative Energy Difference (RED) is defined as R_a/R_0 , which indicates the solvent can dissolve the polymer when RED is < 1 . If RED is > 1 , the solvent should not dissolve the polymer. The smaller the RED, the better predicted dissolution performance. The solubility parameters for the mixed solvents are estimated as the average of the parameters of component solvents. An example for the Hansen sphere of LDPE is shown in Figure 31. Toluene and xylene are in the sphere indicating they are good solvent for dissolving LDPE, while hexane and heptane are on the edge indicating they are poor solvents. The mixture of 50:50 vol.% toluene and heptane is also in the sphere, which is estimated to be able to dissolve LDPE as well.

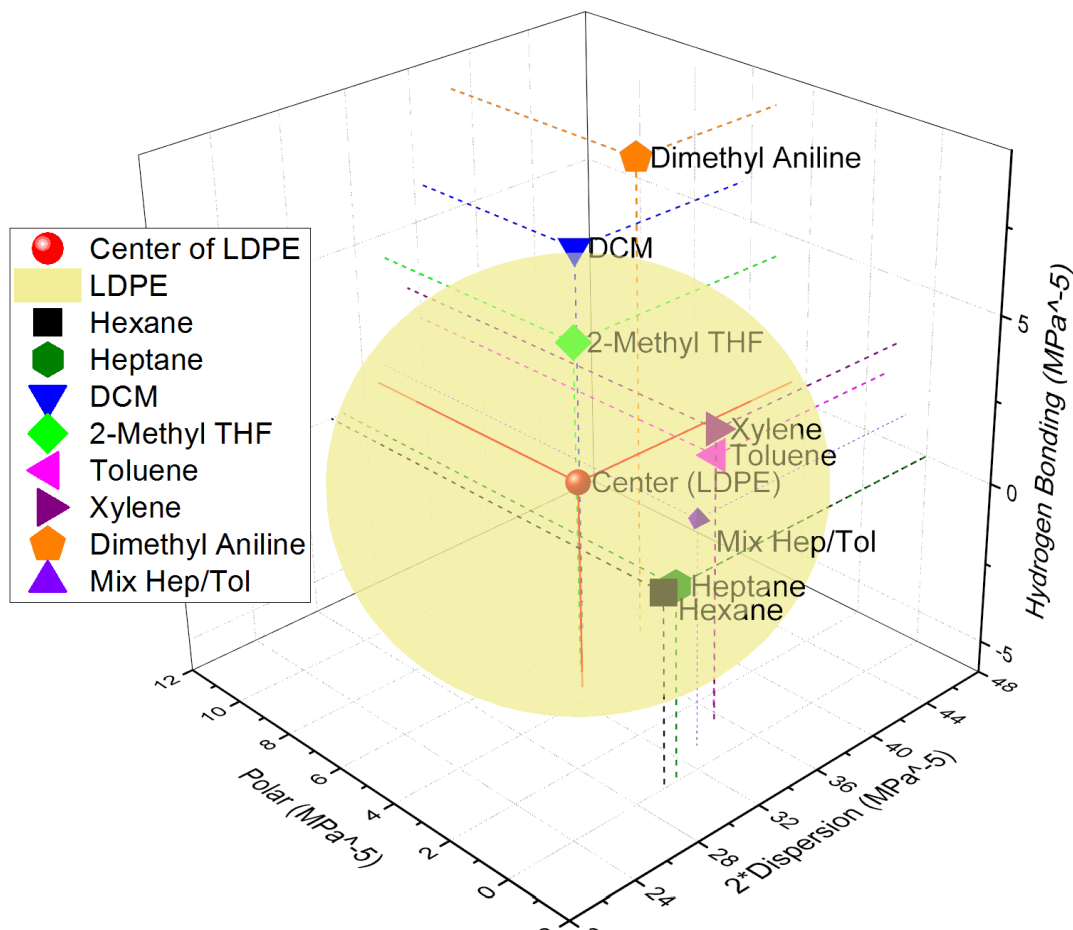


Figure 31. Hansen sphere for LDPE

Plastic products contain not only polymers. Various chemical substances, known as additives, are added into plastics to improve their physical properties and extend the service life. Common additives include but are not limited to dyes, antioxidants, heat stabilizers, UV light stabilizers, flame retardants, electrical property modifier, fillers, reinforcing fibers, processing aid additives, cross-linking additives, and sterilization and radiation resistance additives.⁸³ A proper fraction of additives in plastic is necessary to control their behavior and prevent from harming physical properties of plastic.⁸³ But the presence of those residual additives in recovered polymers results in an awkward color, damage their properties and reduce their value. Therefore, it is necessary to remove those additives from the recovered polymers, especially the dyes. Recovered polymers from mixed colored plastic waste via only extraction is of dirty-looking and only have very limited applications. Few studies on additive removal from polyolefins were reported and no successful removal was claimed. A previous study tested o-dichlorobenzene to separate titanium

dioxide, a common white dye, from PE polymers. However, only partial removal was achieved, as the recovered PE still contained a fraction of titanium dioxide. Those additives are usually of low molecular weight and thus adsorption was proposed in this study. Activated carbon is one of the most affordable adsorbents owing to its low cost and easy regeneration process. It was used to remove methylene blue, an organic dye, from textile wastewaters.⁸⁴ Enlightened by this, activated carbon is used in this study to adsorb dyes and other additives from recovered polymers. In some cases, water is also used as a hydrophilic additive extractor.

Sequential Selective Extraction and Adsorption (SSEA) process was developed in this study to recover pristine polymers from polyolefin waste using mixed solvent for extraction and activated carbon for adsorption. Model polyolefins were first studied to help understand fundamental principles. The technical feasibility of SSEA was tested using polyolefin waste. Preliminary cost analysis was also carried out to test the economic feasibility.

This is the first study to apply mixed solvents to recover polyolefin polymers. The mixed solvents can extract different polymers selectively with a reduced toxicity and solvent cost. Optimal extraction conditions were obtained from experiments using model LDPE, LLDPE, and HDPE. LLDPE was selectively extracted by mixed solvents from a blend of LLDPE and PP. The DSC results indicate the high purity of recovered LLDPE. Pristine PE polymers was obtained from dirty-looking PE waste after SSEA, which was never achieved in any previous study. The preliminary cost analysis indicates SSEA to be a cost-effective recycling method for polyolefins. SSEA has the potential to reduce polyolefin waste accumulation by recovering them as pristine polymers to be reused.

3.2 Methodology

3.2.1 Materials

Four types of model polymer (LDPE, LLDPE, HDPE, PP) pellets with a weight averaged molecular weight ($\overline{M}_w$) as 50,000, 100,000, 180,000, and 250,000 and their mixture (a 50:50 wt.% blend of LLDPE/PP) were used in this study. PE waste (EREMA, the same as described in section 2.3.1) was also used in this study as a representative of available PE waste. All organic solvents (*n*-heptane, toluene, and cyclohexane) were purchased from Thermo Fisher Scientific and used as

received. Activated carbon was purchased from Calgon Carbon Corporation (Pittsburgh, PA). Water used was deionized using a Milli-Q water purification system.

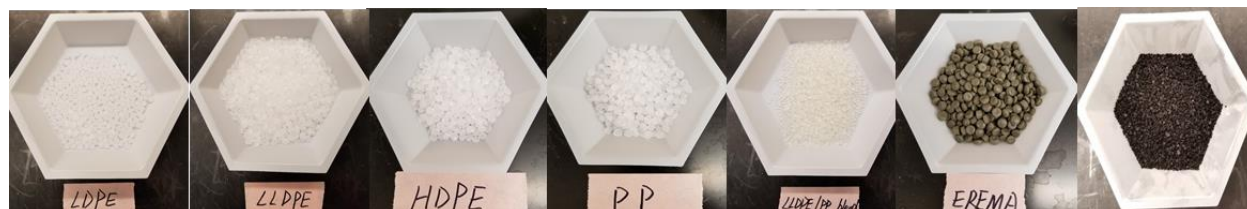


Figure 32. From left to right are model LDPE, LLDPE, LLDPE/PP blend, HDPE, PP, PE waste (EREMA) and activated carbon.

3.2.2 Experiment Descriptions

Extraction started with weighing out 1-5 g polymer and collecting it in a 200 ml round bottom flask. Then 20-100 ml binary mixed solvents (50:50 vol.% mixture of two solvents predicted by Hansen sphere) were decanted into the flask. A stir bar was placed in the flask for stirring. A desired temperature (70-100 °C) was reached by heating with water bath or oil bath. A condenser was attached to the flask if the temperature is above boiling points of solvents being used. A schematic is shown in Figure 33. The extraction usually takes 0.5-6 hr.

After extraction, 0.5-5 g activated carbon is added into the flask for adsorption. The temperature and stirring rate are kept the same as the ones in extraction. Adsorption usually takes 3-6 hr. Water is added into the flask to extract hydrophilic additives. The mixture of polymers, activated carbon and solvents are then separated using an Eppendorf centrifuge at 9000 RPM for 15 minutes.

If no adsorption is conducted after extraction, the mixture of solution and undissolved polymers are transferred on to a petri dish and undissolved polymers are separated out by manually picking up. The dissolved polymers are dried and weighted. The yield of polymer recovery is calculated as Equation 20:

$$\text{Polymer Recovery Yield (d.w \%)} = W_{\text{recovered polymer}} / W_{\text{feedstock}} \times 100$$

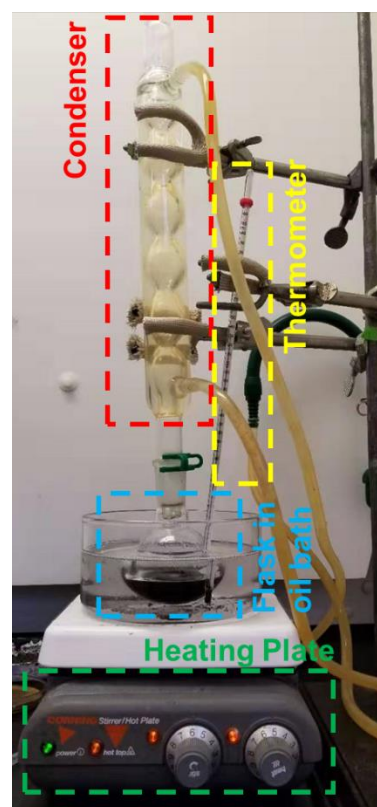


Figure 33. Apparatus for extraction and adsorption

3.2.3 Characterizations

In order to characterize the recovered polymers, differential scanning calorimetry (DSC) is used. It measures the difference of heat needed to increase unit temperature between sample and reference. A Perkin Elmer differential scanning calorimeter is used in this study (Figure 34). Each time 10-20 mg sample is tested. The sample and the reference was heated from 0 °C to 200 °C at 10 °C/min under nitrogen atmosphere. They were then kept at 200 °C for 5-10 min, followed by a cooling process to 0 °C at -10 °C/min. Pyris software is used to collect and analyze data.



Figure 34. Perkin Elmer Differential Scanning Calorimetry

3.3 Results

3.3.1 Extraction

3.3.1.1 Model Polyolefins

Model polyolefins were first tested for condition screening. HSP predicts a 50:50 vol.% mixture of toluene and heptane as proper mixed solvents (RED 0.64) for LDPE. Experiments using mixed solvents, single toluene solvent, and single heptane solvent were conducted at 70 °C for 1 hr ((a)). The mixed solvents can dissolve 93% model LDPE which is similar to 97% using single toluene solvent. Single heptane solvent cannot dissolve any LDPE.

Linear Low-Density Polyethylene (LLDPE) is one subcategory of LDPE. It has a higher crystallinity than LDPE. However, its main chemical structure is the same as LDPE. HSP predicts a 50:50 vol.% mixture of toluene and heptane as a good solvent for LLDPE. Model LLDPE dissolution experiments were conducted at 80 °C for 2 hr ((b)). Single toluene and the mixture of toluene and heptane can both dissolve 100% for LLDPE while single heptane cannot dissolve any LLDPE.

However, HSP predicted the 50:50 vol.% mixture of toluene and heptane as a poor solvent (RED 1.48) for HDPE. This is confirmed by dissolution experiments at 95 °C for 3 hr ((c)). Single

toluene solvent can dissolve 92% while the mixed solvent only dissolved 2%. Instead, HSP suggested a 50:50 vol.% mixture of toluene and cyclohexane to be a good solvent (RED 0.83) for HDPE. It dissolved 93% HDPE at 95 °C in 3 hr.

Although HSP predicates the mixture of toluene and heptane to be a good solvent for PP (RED 0.46). No PP was dissolved in the mixed solvents, single toluene or single heptane at 100 °C for 3 hr. A potential reason is that PP has a higher crystallinity and requires a higher temperature above 100 °C. Previous study identified model PP can dissolve in single toluene solvent at 140 °C.⁷⁵

3.3.1.2 Separation of Polyolefin Blends

The selectivity of mixed solvents for different polyolefins was tested using a blend of LLDPE and PP. Experiments were carried out at 80 °C for 6 hr. 92% of LLDPE dissolved while no PP dissolved. The recovered LLDPE and the initial LLDPE/PP blend were analyzed using DSC. LLDPE/PP blend has two peaks in the DSC plot (Figure 36). The peak at about 120 °C is the melting peak of LLDPE while the one at around 170 °C is the melting peak of PP. Only one peak at around 120 °C was found for recovered LLDPE indicating no PP was extracted together with LLDPE. This result showed the selectivity of mixed solvents against polyolefin mixture.

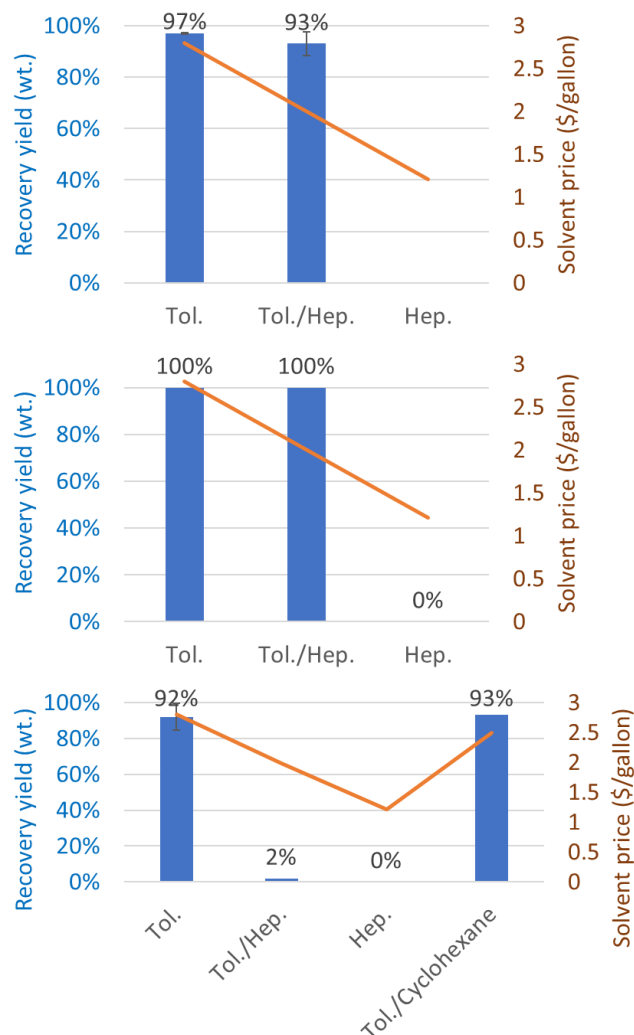


Figure 35. Recoveries and solvent costs for model (a) LDPE at 70 °C (b) LLDPE at 80 °C (c) HDPE at 95 °C using single toluene, heptane and 50:50 vol.% mixture of toluene and heptane and 50:50 vol.% mixture of toluene and cyclohexane, with a 1 g: 20 ml polymer to solvent ratio

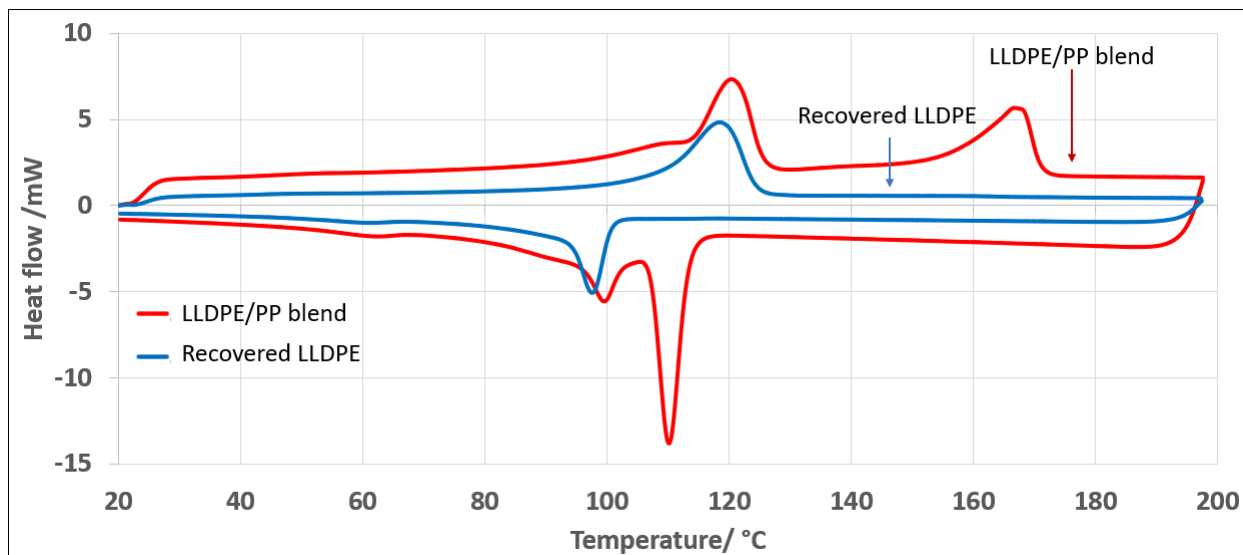


Figure 36. DSC plots for LLDPE/PP blend (red) and recovered LLDPE (blue)

3.3.1.3 From Model Polymers to Waste

Model polyolefins were used to screen conditions and test the selectivity of mixed solvents. In order to investigate the technical feasibility of SSEA, experiments using PE waste were conducted. Two conditions were tested, and the results are shown in Figure 37. 11% polymer was dissolved at 80 °C in 4 hr using 50:50 vol.% mixed toluene and heptane, indicating the PE waste can have about 11% LDPE or LLDPE. The other condition, using mixed toluene and cyclohexane at 95 °C for 3 hr reached a 100% dissolution ratio of LDPE, LLDPE and HDPE. This result indicates SSEA can dissolve PE waste as well.

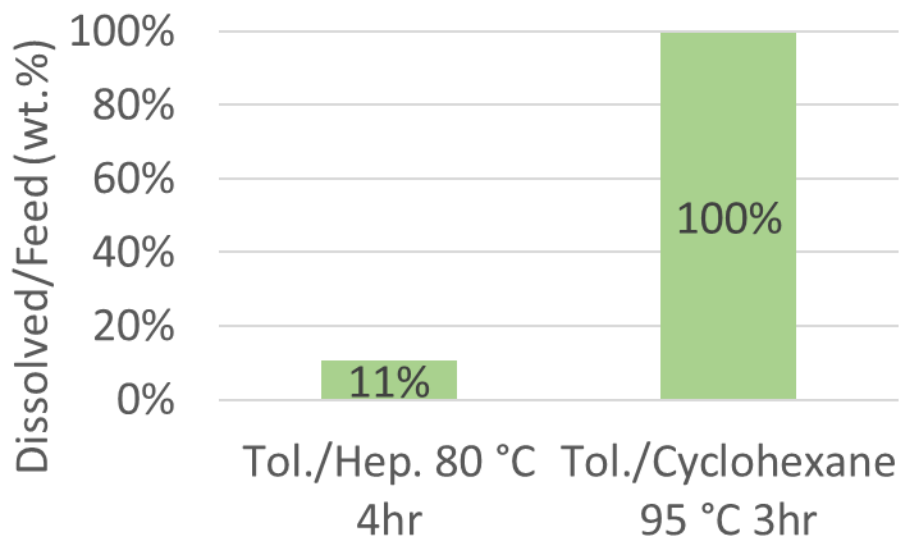


Figure 37. Dissolution ratios for PE waste using 50:50 vol.% mixture of toluene and heptane at 80 °C for 4 hr, and toluene and cyclohexane at 95 °C for 3 hr.

3.3.2 Adsorption

As introduced in section 3.3.1.3, PE polymers (Figure 38(a)) were dissolved using mixed solvents. But the extracted polymers are still with color, indicating dyes were also extracted. Therefore, adsorption was carried out to remove the dyes. The recovered polymers are white (Figure 38(b)), while no other color was observed. This color change from yellow green to white suggested dyes were removed and pristine polymers were obtained via SSEA. More characterization methods are needed in the future to investigate the removal of other kinds of additives besides dyes.

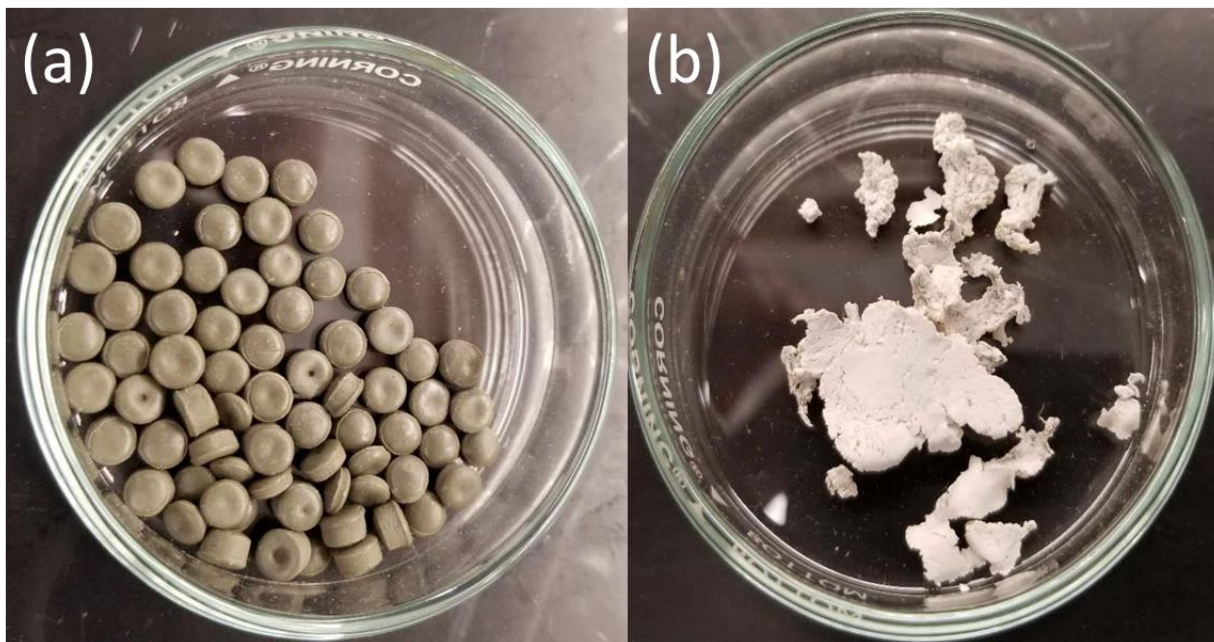


Figure 38. (a) PE waste (yellow green) and (b) Recovered LLDPE (white) via SSEA.

3.4 Discussions

3.4.1 Cost Analysis

A preliminary cost analysis was conducted to investigate the economic feasibility of SSEA. A plant size of processing 2,000 metric tons of PE waste per day is assumed. The PE polymers are assumed to be 100% recovered. A 5% solvent lost during distillation is estimated. As shown in Table 9, the feedstock and total processing cost are \$0.1764 and \$0.3558/kg plastic feedstock, respectively. The selling price for recovered pristine PE is \$1.20/kg and as a result, the profit margin for SSEA is estimated to be \$0.67/kg, which indicates SSEA to be a cost-effective recycling method for PE waste.

Table 9. Cost analysis for pristine polymer recovery from polyolefin waste via SSEA

	Price (\$/kg plastic processed)
Feedstock ^(a)	0.1764
Extraction and adsorption equipment ^(b)	0.0144
Distillation ^(c)	0.0083
Make-up solvents ^(d)	0.3325
Activated carbon ^(e)	0.0006
Total processing cost	0.3558
Selling price (virgin LDPE, HDPE)	1.20
Net profit	0.67

(a) Using PE waste (EREMA) as feedstock

(b) Assuming a 2000 metric ton/day plant scaled up from Weeden Jr, George S et al., 2015⁸⁵

(c) Distillation for separating binary liquid mixture. Data obtained from Hinchliffe et al., 2000⁶⁶

(d) Assuming 1:10 plastic: solvent ratio for extraction and 5% solvent lost during distillation. Price of toluene and heptene obtained from ICIS⁸⁰

(e) Assuming activated carbon regenerated by hot nitrogen. Data obtained from Sabio et al., 2004⁶⁷

3.4.2 Product Competitions

Virgin polymers are the major competitor of recovered pristine polymers. SSEA preserves the polymer structures and has a lower cost than virgin polymer synthesis. Thus SSEA is more competitive. However, it should be noted that more product analysis is needed to test the physical properties of the recovered polymers.

Biodegradable polymers are another potential competitor. However, the high cost of biodegradable polymers makes them not competitive.⁸⁶ Their physical properties like stretching and bending resistance can be inferior to conventional petroleum-based polymers as well.²⁰ In addition, their degradation time heavily depend on weather, humidity, and sunlight, which is hardly controllable.²¹ All of these problems need to be addressed before biodegradable polymers can replace petroleum-based polymers.

3.4.3 Summary

In this chapter, SSEA is introduced as a promising solution to recover pristine polymers from polyolefin waste. Mixed solvents have a tunable selectivity with reduced toxicity and solvent cost. Optimal extraction conditions were obtained from experiments using model LDPE, LLDPE and HDPE. The selectivity of mixed solvents was tested by the separation of LLDPE from a LLDPE/PP blend. Dyes were successfully removed by adsorption. It is the first time to recover pristine polymers from PE waste via SSEA, which shows the potential of SSEA to reduce the polyolefin waste accumulation. Crude cost analysis also indicates SSEA to be a cost-effective process.

CHAPTER 4. FURTHER DISCUSSIONS AND RECOMMENDATIONS

4.1 Energy and Greenhouse Emissions

Process energy demand, energy efficiency, and greenhouse gas (GHG) emissions are essential parameters in determining whether a process is energy efficient and estimating its environment impacts. Those parameters are estimated for SSEA and HTP and are compared to virgin polymer synthesis, conventional fuel production, and other plastic recycling methods including incineration, mechanical recycling and pyrolysis. The results are shown in Table 10. Energy efficiency is calculated as the energy embedded in the products divided by the process energy input. Data for diesel production was modified from the data for gasoline production because of the similar process for producing gasoline and diesel from crude oil. No data for pilot scale plastic HTP are available. Thus, data for pilot scale biomass HTP was used for plastic HTP because of similar conditions.

SSEA has 10 times lower process energy input, and more than 20 times higher energy efficiency compared to virgin polymer production, which strongly indicate SSEA to be an energy efficient process. SSEA also emits less GHG than virgin polymer production. Mechanical recycling required a higher process energy input than SSEA, mainly because of the energy intensive washing and drying processes for feedstock. Fuel production via HTP has a lower process energy demand and less GHG emissions but a higher energy efficiency than conventional diesel production. Although incineration has the lowest process energy demand, its energy efficiency is much lower than fuel production via HTP and its GHG emissions are much higher. Pyrolysis has similar parameters as fuel production via HTP. To sum, SSEA and HTP are energy efficient process for recycling plastic waste, and they are estimated to have less GHG emissions than virgin polymer synthesis, conventional fuel production, and other plastic recycling methods.

Table 10. Estimates of process energy demand, energy efficiency (E_{out}/E_{in}), greenhouse gas (GHG) emissions for production of virgin polymer, diesel, and different plastic recycling methods^{12,26,87,88}

	Process energy input (MJ/kg)	Energy efficiency	GHG (kg CO ₂ /kg product)	Products
Virgin polymer	40	1.2	1.8	Polymer
Diesel production	4.6	10	1.9	Fuel
Incineration	0.02-0.03	3.7	3.2	Energy
Mechanical recycling	9	5.3	0.6	Polymer
SSEA	1.8	26.7	0.5	Polymer
Pyrolysis	3.6	11.7	-	Oil
HTP for fuel	2.8	12.0	0.2-0.6	Naphtha, Diesel, and Bunker fuel

4.2 Sherwood Plots

The Sherwood plot is well-known for its prediction of sale price or processing cost of a chemical substance based on its concentration in feedstocks. The cost predication is within an order of magnitude to the real cost.⁸⁹ A linear relationship was established between the log value of the product price and the log value of its concentration (weight fraction) in feeds. A lower concentration results in a higher predicted cost. A Sherwood plot for common chemicals is shown in Figure 39. Based on preliminary cost analyzes of HTP and SSEA introduced in sections 2.4.3 and 3.4.1, specific Sherwood plots for HTP producing fuel and SSEA are established and shown in Figure 40 and Figure 41, respectively.

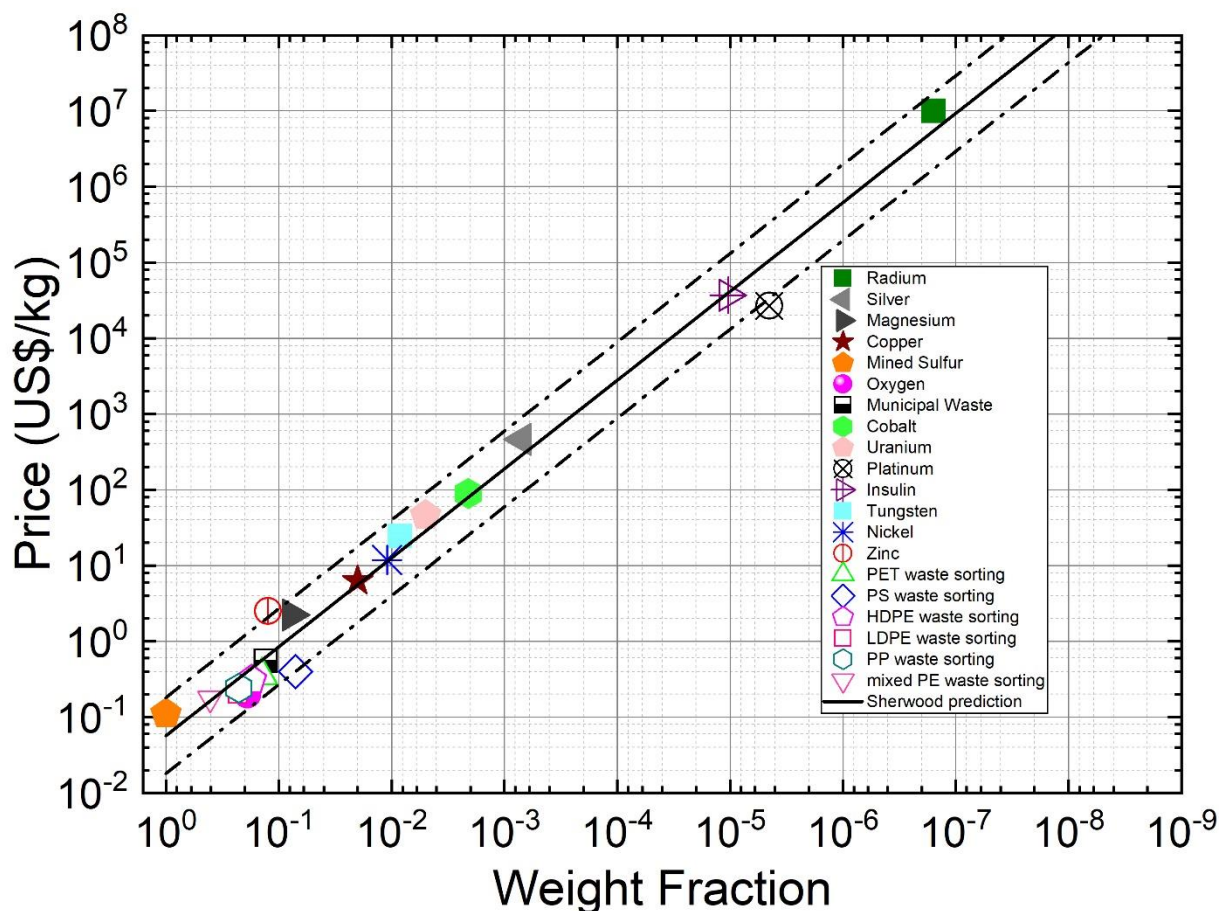


Figure 39. A general Sherwood plot

In Figure 40, sorted polyolefin waste cost and total cost for producing fuels from sorted polyolefin waste via HTP are presented. The HTP cost include both feedstock cost and processing cost. A horizontal line is drawn to indicate the selling price of HTP oils as diesel, naphtha and bunker fuel. A potential profit margin for HTP is indicated if diesel price line is above the point for total HTP cost. Fuel production from sorted LDPE, and the mixture of LDPE and HDPE are estimated to be economically feasible. Sorted HDPE has a too high feedstock cost which allows no margin for profit. Potential improvements can be achieved by the reduction of feedstock cost.

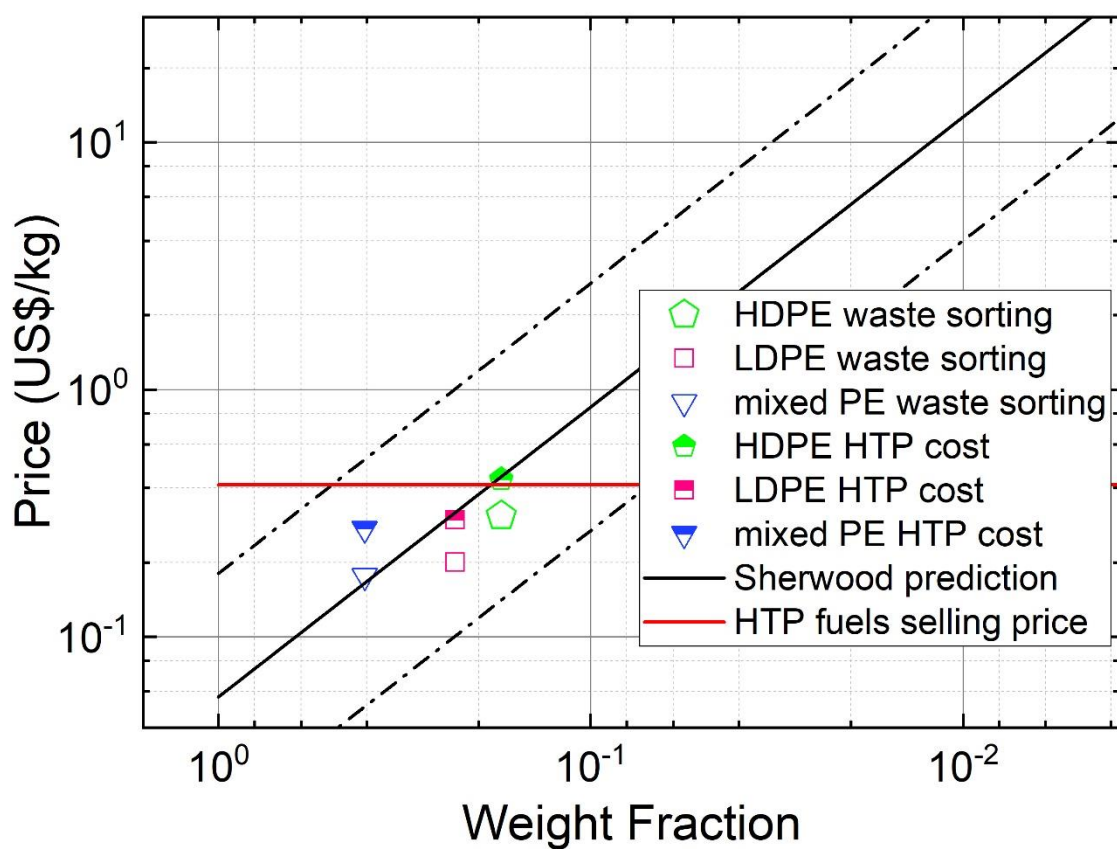


Figure 40. Sherwood plot for polyolefin HTP

In Figure 41, one can find points indicating sorted polyolefin feedstock cost, total SSEA cost (feedstock and processing cost), and polyolefin polymer price. The space between the total SSEA cost and polyolefin polymer price indicate the profit margin for SSEA. Recovering sorted LDPE and HDPE via HTP are both estimated to be economically feasible.

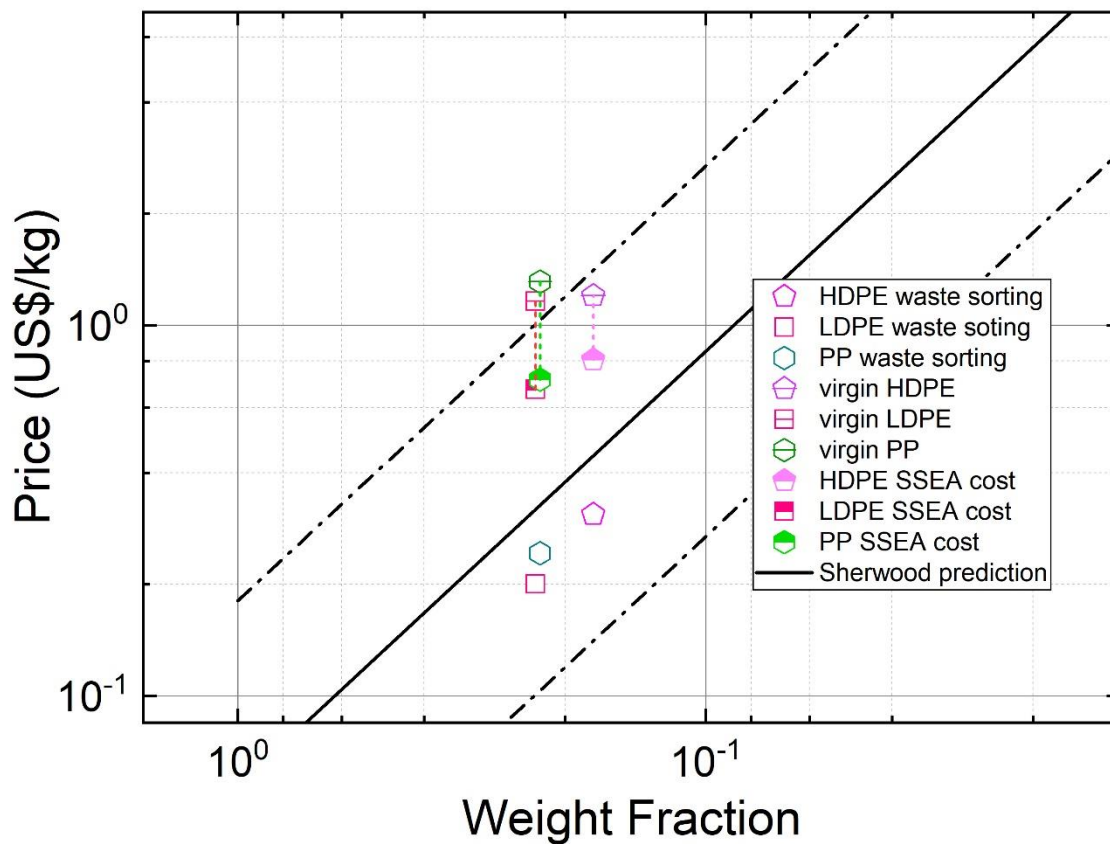


Figure 41. Sherwood plot for polyolefin SSEA

4.3 The Combination of SSEA and HTP

SSEA and HTP can be combined to form a more flexible method for polyolefin waste. Mixed polyolefin waste can be processed when sorted ones are not available. An example of this combination to treat mixed polyolefin waste is to first recover LDPE, and HDPE as pristine polymers via SSEA, followed by fuel production using PP via HTP. HDPE can also be converted into wax or oils via HTP if it has more profits than SSEA. The flexibility of this combination allows better and faster correspond to market change.

4.4 Future Work

Future work can be divided into two parts. For HTP, no comprehensive analysis of the gas products has been conducted, which is critical in developing the full reaction mechanisms. Thus,

detailed gas analysis is needed in the future. GC $\times$ GC-FID cannot distinguish between olefins and cyclics. Other analytical methods are needed in the future, for example the co-analysis using FID and mass spectrometry (MS) at the same time. More properties for wax product need to be measured such as melting point and penetration resistance. For fuels, the cetane number are estimated based on chemical compositions. Experimentally measured cetane numbers via engine tests are needed to verify the estimation. HTP experiments using PP waste are needed in the future to verify the technical feasibility of HTP against PP waste.

In SSEA, recovered polymers are assumed to perform the same as virgin polymers. More analysis is needed to verify the performance of recovered polymers. High temperature gel permeation chromatography (GPC) are needed to obtain the molecular weight distribution of the recovered polymers. Physical property measurements are required to test properties including but not limited to strength, toughness and viscoelasticity. Also, efficient separation of LDPE from HDPE needs to be developed, and effective characterization methods are required to distinguish them. More experiments targeting additive removal from recovered polymers are critical and proper analytical methods are also needed to detect the small amounts of additives.

Up to now, HTP and SSEA are tested in lab scale. A mini-pilot or pilot scale will be beneficial to demonstrate the technical feasibility of the two methods. In addition, Techno-Economic Analysis (TEA) and Life-Cycle Assessment (LCA) should be carried out along the development of SSEA and HTP, as they provide important information for optimizing product portfolios, processing energy, and processing cost, and for evaluating the environmental impacts.

4.5 Summary

The goal of this study is to develop HTP and SSEA as effective recycling methods for polyolefin waste. The achievements on HTP were discussed in CHAPTER 2. Potential reaction pathways for HDPE and PP have been proposed. Useful products including wax and fuels were obtained and compared to commercial products. SSEA was introduced in CHAPTER 3. Mixed solvents have been used and compared to single solvents. Pristine PE polymers were recovered from PE waste. Process energy demand, energy efficiency, and GHG emissions were estimated for SSEA and HTP, and compared to virgin polymer synthesis, diesel production as well as other plastic recycling methods, in Section 4.1. Specific Sherwood plot indicating economic feasibility

were introduced in Section 4.2. An integrated system combining SSEA and HTP was proposed in Section 4.3. Proposed future work for this study was discussed in Section 4.4.

REFERENCES

1. Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Sci Adv.* 2017;3(7):e1700782. doi:10.1126/sciadv.1700782
2. Jambeck JR, Geyer R, Wilcox C, et al. the ocean. 2015;347(6223).
3. Rochman CM. Microplastics research - from sink to source. *Science* (80-). 2018;360(6384):28-29. doi:10.1126/science.aar7734
4. Lavers JL, Bond AL. Exceptional and rapid accumulation of anthropogenic debris on one of the world's most remote and pristine islands. *Proc Natl Acad Sci.* 2017;114(23):6052-6055. doi:10.1073/pnas.1619818114
5. Laville S, Taylor M. *A Million Bottles a Minute: World's Plastic Binge "as Dangerous as Climate Change."*; 2017. <http://www.ecologiapolitica.org/wordpress/wp-content/uploads/2017/08/04-Guardian.pdf>.
6. Horton AA, Walton A, Spurgeon DJ, Lahive E, Svendsen C. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci Total Environ.* 2017;586:127-141. doi:10.1016/j.scitotenv.2017.01.190
7. Guern C Le. WHEN THE MERMAIDS CRY: THE GREAT PLASTIC TIDE. <http://coastalcare.org/2009/11/plastic-pollution/>. Published 2018.
8. Cole M, Lindeque P, Halsband C, Galloway TS. Microplastics as contaminants in the marine environment: A review. *Mar Pollut Bull.* 2011;62(12):2588-2597. doi:10.1016/j.marpolbul.2011.09.025
9. *Bisphenol A Action Plan.*; 2010.
10. Hopewell J, Dvorak R, Kosior E. Plastics recycling: Challenges and opportunities. *Philos Trans R Soc B Biol Sci.* 2009;364(1526):2115-2126. doi:10.1098/rstb.2008.0311
11. Anuar Sharuddin SD, Abnisa F, Wan Daud WMA, Aroua MK. A review on pyrolysis of plastic wastes. *Energy Convers Manag.* 2016;115:308-326. doi:10.1016/j.enconman.2016.02.037

12. Nabavi-Pelesaraei A, Bayat R, Hosseinzadeh-Bandbafha H, Afrasyabi H, Chau K wing. Modeling of energy consumption and environmental life cycle assessment for incineration and landfill systems of municipal solid waste management - A case study in Tehran Metropolis of Iran. *J Clean Prod.* 2017;148:427-440. doi:10.1016/j.jclepro.2017.01.172
13. Harrabin R. Should we burn or bury waste plastic? <https://www.bbc.com/news/science-environment-43120041>. Published 2018.
14. Baytekin B, Baytekin HT, Grzybowski BA. Retrieving and converting energy from polymers: Deployable technologies and emerging concepts. *Energy Environ Sci.* 2013;6(12):3467-3482. doi:10.1039/c3ee41360h
15. Should plastics be a source of energy? *C&EN Glob Enterp.* 2018. doi:10.1021/cen-09638-cover
16. Garcia JM, Robertson ML. The future of plastics recycling. *Science (80-).* 2017;358(6365):870-872. doi:10.1126/science.aag0324
17. Ragaert K, Delva L, Van Geem K. Mechanical and chemical recycling of solid plastic waste. *Waste Manag.* 2017;69:24-58. doi:10.1016/j.wasman.2017.07.044
18. Kunwar B, Cheng HN, Chandrashekar SR, Sharma BK. Plastics to fuel: a review. *Renew Sustain Energy Rev.* 2016;54:421-428. doi:10.1016/j.rser.2015.10.015
19. Sudesh K, Iwata T. Sustainability of biobased and biodegradable plastics. *Clean - Soil, Air, Water.* 2008. doi:10.1002/clen.200700183
20. Madhavan Nampoothiri K, Nair NR, John RP. An overview of the recent developments in polylactide (PLA) research. *Bioresour Technol.* 2010. doi:10.1016/j.biortech.2010.05.092
21. Napper IE, Thompson RC. Environmental Deterioration of Biodegradable, Oxo-biodegradable, Compostable, and Conventional Plastic Carrier Bags in the Sea, Soil, and Open-Air Over a 3-Year Period. *Environ Sci Technol.* 2019;53(9):4775-4783. doi:10.1021/acs.est.8b06984
22. Geyer R, Jambeck JR, Law KL. Production, uses, and fate of all plastics ever made. *Sci Adv.* 2017;3(7):5. doi:10.1126/sciadv.1700782
23. Peterson AA, Vogel F, Lachance RP, Fröling M, Antal MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ Sci.* 2008;1(1):32-65. doi:10.1039/b810100k

24. Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresour Technol.* 2015;178:147-156. doi:10.1016/j.biortech.2014.09.132
25. Zhu Y, Biddy MJ, Jones SB, Elliott DC, Schmidt AJ. Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. *Appl Energy.* 2014;129:384-394. doi:10.1016/j.apenergy.2014.03.053
26. Chen WT, Zhang Y, Zhang J, et al. Co-liquefaction of swine manure and mixed-culture algal biomass from a wastewater treatment system to produce bio-crude oil. *Appl Energy.* 2014;128:209-216. doi:10.1016/j.apenergy.2014.04.068
27. Chen WT, Tang L, Qian W, et al. Extract Nitrogen-Containing Compounds in Biocrude Oil Converted from Wet Biowaste via Hydrothermal Liquefaction. *ACS Sustain Chem Eng.* 2016;4(4):2182-2190. doi:10.1021/acssuschemeng.5b01645
28. Caniaz RO, Erkey C. Process intensification for heavy oil upgrading using supercritical water. *Chem Eng Res Des.* 2014;92(10):1845-1863. doi:10.1016/j.cherd.2014.06.007
29. Savage PE. A perspective on catalysis in sub- and supercritical water. *J Supercrit Fluids.* 2009;47(3):407-414. doi:10.1016/j.supflu.2008.09.007
30. Savage PE. Organic Chemical Reactions in Supercritical Water. *Chem Rev.* 2002;99(2):603-622. doi:10.1021/cr9700989
31. Gai C, Li Y, Peng N, Fan A, Liu Z. Co-liquefaction of microalgae and lignocellulosic biomass in subcritical water. *Bioresour Technol.* 2015. doi:10.1016/j.biortech.2015.03.015
32. Lemmon EW, McLinden MO, Friend DG. No Title. In: *Thermophysical Properties of Fluid Systems.*
33. Pedersen TH, Grigoras IF, Hoffmann J, et al. Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation. *Appl Energy.* 2016;162:1034-1041. doi:10.1016/j.apenergy.2015.10.165
34. Funazukuri T. Hydrothermal Depolymerization of Polyesters and Polycarbonate in the Presence of Ammonia and Amines. In: *Recycling Materials Based on Environmentally Friendly Techniques.* ; 2015. doi:10.5772/59198
35. Pei X, Yuan X, Zeng G, et al. Co-liquefaction of microalgae and synthetic polymer mixture in sub- and supercritical ethanol. *Fuel Process Technol.* 2012;93(1):35-44. doi:10.1016/j.fuproc.2011.09.010

36. Watanabe M, Hirakoso H, Sawamoto S, Tadafumi Adschiri, Arai K. Polyethylene conversion in supercritical water. *J Supercrit Fluids*. 1998;13(1-3):247-252. doi:10.1016/S0896-8446(98)00058-8
37. Moriya T, Enomoto H. Characteristics of polyethylene cracking in supercritical water compared to thermal cracking. *Polym Degrad Stab*. 1999;65(3):373-386. doi:10.1016/S0141-3910(99)00026-9
38. Zhang R, Su X, Zhao Y, Bi J. Investigation on Degradation of Waste Plastic in Supercritical Water. 2007;35(4).
39. Williams PT, Slaney E. Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures. *Resour Conserv Recycl*. 2007;51(4):754-769. doi:10.1016/j.resconrec.2006.12.002
40. Williams PT, Slaney E. Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures. *Resour Conserv Recycl*. 2007;51(4):754-769. doi:10.1016/j.resconrec.2006.12.002
41. Zhao X, Zhan L, Xie B, Gao B. Products derived from waste plastics (PC, HIPS, ABS, PP and PA6) via hydrothermal treatment: Characterization and potential applications. *Chemosphere*. 2018;207:742-752. doi:10.1016/j.chemosphere.2018.05.156
42. Su X, Zhao Y, Zhang R, Bi J. Investigation on degradation of polyethylene to oils in supercritical water. *Fuel Process Technol*. 2004;85(8-10):1249-1258. doi:10.1016/j.fuproc.2003.11.044
43. Drews A. Standard Test Method for Distillation of Petroleum Products at Reduced Pressure. *Man Hydrocarb Anal 6th Ed*. 2008:222-222-18. doi:10.1520/mnl10861m
44. GC column. <https://blog.restek.com/?p=10091>.
45. GC columns. <https://www.thetruthaboutforensicscience.com/the-top-2-problems-seen-with-gas-chromatography-bac-results/>.
46. Vozka P, Kilaz G. How to obtain a detailed chemical composition for middle distillates via GC × GC-FID without the need of GC × GC-TOF/MS. *Fuel*. 2019. doi:10.1016/j.fuel.2019.03.009
47. Flame ionization detector. https://en.wikipedia.org/wiki/Flame_ionization_detector.
48. D40052-15. Standard Test Method for Density , Relative Density , and API Gravity of Liquids by Digital Density Meter. *ASTM Int*. 2013:1-8. doi:10.1520/D4052-18A.2

49. ASTM-D7042. Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity). 2008:1-7.
doi:10.1520/D7042-12A.2
50. American Society for Testing and Materials. Standard Test Method for Flash Point by Tag Closed Cup Tester ASTM D-56. *Stand Test Methods Pet Prod Lubr.* 1998:1-12.
doi:10.1520/D0056-16A.2
51. ASTM D2500-17. American Society for Testing and Materials - Standard test method for cloud point of petroleum products and liquid fuels. *Astm D2500.* 2017:1-6.
doi:10.1520/D2500-17A.2
52. Products P. Standard Test Method for Determination of Water in Petroleum Products , Lubricating Oils , and Additives by Coulometric Karl Fischer Titration 1. *Annu B ASTM Stand.* 2005:1-6. doi:10.1520/D6304-16.2
53. Products P, Products P, Detection C. Standard Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet. 1999;05(February):3-8. doi:10.1520/D5762-12.2
54. Laboratories and Equipment. <https://engineering.purdue.edu/FLORE/research/facilities>.
55. Products P. Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester 1. *Annu B ASTM Stand.* 2007;i(Reapproved 2006):1-5. doi:10.1520/D0093-18
56. MIL-DTL-5624W, 28 Mar 2016, Detail Specification: Turbine Fuel, Aviation, Grades JP-4 and JP-5.
<https://quicksearch.dla.mil/Analyse/ImageRedirector.aspx?token=5739769.5558>.
57. Products P. Standard Test Method for Cetane Number of Diesel Fuel Oil 1. *Annu B ASTM Stand.* 2003;i(Reapproved):1-4. doi:10.1520/D0613-18A.
58. Ghosh P, Jaffe SB. Detailed composition-based model for predicting the cetane number of diesel fuels. *Ind Eng Chem Res.* 2006;45(1):346-351. doi:10.1021/ie0508132
59. Chen, W., Jin, K., & Wang, N. (2018). The Use of Supercritical Water for the Liquefaction of Polypropylene into Oil. Manuscript submitted for publication.
60. HYDROCARBON SOLVENTS FOR PARTS CLEANING.
http://english.metiz.com.tw/aqua_solvent.htm.
61. *Europäisches Patentamt European Patent Office *EP001314767A1*.*
62. Isoparaffin Solvents - IP SOLVENT and IP CLEAN.
<https://www.idemitsu.com/products/petrochemicals/chemicals/solvent.html>.

63. ISANE® for paints, resins and metal working, etc.
<http://www.totalspecialfluids.com/en/Hydrocarbon-fluids/isoparaffins-solvents-isane.html>.
64. Brill TB, Savage PE. Kinetics and mechanisms of hydrothermal organic reactions.
Aqueous Syst Elev Temp Press Phys Chem Water, Steam Hydrothermal Solut. 2004;643-675. doi:10.1016/B978-012544461-3/50017-X
65. Stephen J. Blanksby, G. Barney Ellison. Bond Dissociation Energies of Organic Molecules. *Acc Chem Res.* 2003. doi:10.1021/AR020230D
66. Hinchliffe AB, Porter KE. A comparison of membrane separation and distillation. *Chem Eng Res Des.* 2000;78(2):255-268. doi:10.1205/026387600527121
67. Sabio E, González E, González JF, González-García CM, Ramiro A, Gañan J. Thermal regeneration of activated carbon saturated with p-nitrophenol. *Carbon N Y.* 2004;42(11):2285-2293. doi:10.1016/j.carbon.2004.05.007
68. Diesel Prices and Outlook.
https://www.eia.gov/energyexplained/index.php?page=diesel_prices.
69. Naphtha. <https://tradingeconomics.com/commodity/naphtha>.
70. Energy B, Frontiers E, Benefit IT. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Funding Opportunity Announcement (FOA) Number : DE-FOA-0001647 FOA Type : Initial Table of Contents. 2017.
71. 114000 BTU per Gallon to Calories per Litre. Wolfram-Alpha
<http://www.wolframalpha.com/input/?i=114000+BTU+per+gallon+to+calories+per+litre>. Accessed July 14, 2019.
72. Gable C, Gable S. Fuel Energy Comparisons: Gasoline Gallon Equivalents. *About.com*.
<http://alternativefuels.about.com/od/resources/a/gge.htm>. Accessed July 14, 2019.
73. Achilias DS, Giannoulis A, Papageorgiou GZ. Recycling of polymers from plastic packaging materials using the dissolution-precipitation technique. *Polym Bull.* 2009;63(3):449-465. doi:10.1007/s00289-009-0104-5
74. Achilias DS, Roupakias C, Megalokonomos P, Lappas AA, Antonakou V. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *J Hazard Mater.* 2007;149(3):536-542. doi:10.1016/j.jhazmat.2007.06.076
75. Achilias DS, Roupakias C, Megalokonomos P, Lappas A, ANTONAKOU E. Recycling techniques of polyolefins from plastic wastes. *Glob NEST J.* 2008;10(1):114-122.

76. Achilias DS, Giannoulis A, Papageorgiou GZ. Recycling of polymers from plastic packaging materials using the dissolution-precipitation technique. *Polym Bull.* 2009;63(3):449-465. doi:10.1007/s00289-009-0104-5
77. Gutmann V. Solvent effects on the reactivities of organometallic compounds. *Coord Chem Rev.* 1976. doi:10.1016/S0010-8545(00)82045-7
78. Hansen Solubility Parameters. <https://www.hansen-solubility.com/>.
79. NFPA Chemicals. https://www.newenv.com/resources/nfpa_chemicals/.
80. Indicative Chemical Prices A-Z.
<https://www.icis.com/explore/commodities/chemicals/channel-info-chemicals-a-z/>.
81. Weeden GS, Soepriatna NH, Wang NHL. Method for efficient recovery of high-purity polycarbonates from electronic waste. *Environ Sci Technol.* 2015;49(4):2425-2433. doi:10.1021/es5055786
82. Hansen C. *Tables A.1–A.2. In Hansen Solubility Parameters: A User's Handbook.*; 2007.
83. Tolinski M. Colorants. *Addit Polyolefins.* 2015:103-116. doi:10.1016/B978-0-323-35884-2.00009-0
84. Hameed BH, Din ATM, Ahmad AL. Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *J Hazard Mater.* 2007. doi:10.1016/j.jhazmat.2006.07.049
85. Weeden GS, Soepriatna NH, Wang NHL. Method for efficient recovery of high-purity polycarbonates from electronic waste. *Environ Sci Technol.* 2015;49(4):2425-2433. doi:10.1021/es5055786
86. Dabiri S, Wu G, Timko MT, Ghoniem AF. Mixing of single-component hydrocarbon droplets and water at supercritical or near-critical conditions. *J Supercrit Fluids.* 2012;67:29-40. doi:10.1016/j.supflu.2012.02.014
87. Chen WT, Jin K, Linda Wang NH. Use of Supercritical Water for the Liquefaction of Polypropylene into Oil. *ACS Sustain Chem Eng.* 2019;7(4):3749-3758. doi:10.1021/acssuschemeng.8b03841
88. Gai, C.; Zhang, Y.; Chen, W.-T.; Zhang, P.; Dong, Y., Energy and nutrient recovery efficiencies in biocrude oil produced via hydrothermal liquefaction of *Chlorella pyrenoidosa*. *RSC Advances* 2014, 4, (33), 16958-16967.

89. Grübler A. *Technology and Global Change*. Cambridge University Press; 1998.
[https://books.google.com/books?hl=en&lr=&id=MqIQUV3nJrAC&oi=fnd&pg=PR9&dq=Grübler+A.+Technology+and+Global+Change.+Cambridge+University+Press%3B+1998&ots=qmqsjBi0QI&sig=6bCg8JESbND8LSwJMIgoyET2jTw#v=onepage&q=Grübler A. Technology and Global Change. Cam.](https://books.google.com/books?hl=en&lr=&id=MqIQUV3nJrAC&oi=fnd&pg=PR9&dq=Grübler+A.+Technology+and+Global+Change.+Cambridge+University+Press%3B+1998&ots=qmqsjBi0QI&sig=6bCg8JESbND8LSwJMIgoyET2jTw#v=onepage&q=Grübler+A.+Technology+and+Global+Change.+Cam)

PUBLICATIONS

Journal

Chen, W. T., Jin, K., & Linda Wang, N. H. (2019). Use of Supercritical Water for the Liquefaction of Polypropylene into Oil. *ACS Sustainable Chemistry & Engineering*, 7(4), 3749-3758.

Patent

Chen, W., Jin, K., & Wang, N. (2019). Method of Converting Plastic Waste into Useful Stock *U.S. Patent Application, No. 16/389,855*. Washington, DC: U.S. Patent and Trademark Office. Patent Pending