Chemical De-polymerization for reuse of Polyethylene Terephthalate (PET) towards a circular economy

by

Beza Moges

A thesis submitted to

The Faculty of Graduate Studies

of

Lakehead University

In partial fulfillment of the requirements

For the Degree of

Master of Science In

Environmental Engineering

April 2022

Supervisor:

Dr. Sudip Rakshit

Abstract

Sustainable and effective waste management is very important to address environmental pollution. This is especially the case for plastics as their inherent resistance to breakdown leads to their accumulation the environment. This is the case if the conventional linear economy is practised. The overall aim of this study is to breakdown Polyethylene Terephthalate (PET) bottle products to its monomers so that it can be re-polymerized and used in the same or similar applications. This will lead to reduced use of the virgin reactant, reduce accumulation in the environment and lead to a circular economy.

PET-based containers are one of the most commonly used plastics in food and beverage packaging. Even though PET is thermoplastic in nature, mechanical recycling of such material is hampered by thermo-oxidative, shear-induced chain scission and contamination by other plastic waste streams. Therefore, most such plastic products are downcycled into items of reduced value, such as textiles, toys, or fibers, and eventually end up in landfills and water resources, creating tremendous environmental problems. This study focuses on the chemical depolymerization of PET plastic to its monomers Terephthalate acid (TPA) and ethylene glycol (EG). The de-polymerization process was optimized to improve the TPA yield at low reaction temperatures. Pretreatments like ozone exposure of the polymer surface and ultrasound-assisted chemical hydrolysis increases the amount of TPA recovered. The optimization of the main hydrolysis factors (temperature, sodium hydroxide concentration, and time) was performed using the Central Composite Rotatable Design (CCRD) under the Response Surface Methodology (RSM) experimental design. Under the best conditions determined an average yield of 83.58% for the TPA was obtained and this value is higher than the value of 82.4% predicted by the model. However, the complete recovery of TPA was not possible. The results from analysis of the remaining product showed that there was a

i

formation of dimers mono (2- hydroxyethyl) terephthalate (MHET) and bis(2-hydroxyethyl) terephthalate (BHET) and short-chain polymers apart from TPA and EG. From HPLC Analysis 8.56% was quantified as BHET, MHET, and EG. Enzymatic hydrolysis of the remaining unconverted PET was investigated to improve the monomer recovery. A 5% increase in monomer recovery was observed due to the enzymatic hydrolysis. A combination of the chemical and enzymatic method monomer yields would be acceptable in scaled up processes.

Keywords: Chemical hydrolysis, Enzymatic hydrolysis, Polyethylene terephthalate (PET), Pretreatment, ozone, ultrasound, Optimization, Response surface methodology

Acknowledgments

Firstly, I would like to express my deep and sincere gratitude to my supervisor Prof. Dr. Sudip Rakshit, for his continuous support, motivation, immense knowledge, and encouragement during my research. His guidance, suggestions, and patience helped me in all the times of research and writing the thesis and gave me the chance to gain new experiences during my education. This thesis work would not have been possible without his guidance, advice, and invaluable support,

I would also give special thanks to my research group for giving me valuable suggestions, support, and helping me to complete the thesis.

Last but not the least, I would like to thank my family for their unstoppable caring and for giving me support throughout my life.

Table of contents

Contents

List of Figures

List of Tables

List of abbreviations

PET	Polyethylene Terephthalate
rPET	Recycled PET
TPA	Terephthalic Acid
EG	Ethylene Glycol
MHET	Mono(2-hydroxyethyl) Terephthalate
BHET	Bis(2-hydroxyethyl) Terephthalate
DMT	Dimethyl terephthalate
HiC	*Humicola insolens* Cutinase
LDPE	Low-Density Polyethylene
HDPE	High-density polyethylene
PVC	Polyvinyl Chloride
PP	Polypropylene
PS	Polystyrene
RSM	Response surface methodology
CCRD	Central composite rotatable design
PHAs	Polyhydroxyalkanoates
WL	Weight loss
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High-performance liquid chromatography
RC	Recycled content

CHAPTER 1: INTRODUCTION

Extensive use of plastic in everyday products has resulted in the accelerated change in many economies in the world. This is mainly because of the unique features of plastic materials, such as low cost, durability, transparency, chemical inertness, lightweight, and flexibility. Thus, in turn, has led to its use in a wide range of applications like automotive, packaging, and housing (Lintsen, Hollestelle, & Hölsgens, 2017; Vollmer et al., 2020). However, use and throw method followed, the so-called linear flow of plastics through the value chain creates critical environmental risks and pollution (Johansen, Christensen, Ramos, & Syberg, 2022).

The current global production of plastic is around 355 million tons. The rate is expected to rise four-fold by 2050 (Agenda, 2016; Eriksen, Christiansen, Daugaard, & Astrup, 2019; Young, 2019). Some of the plastics that are commonly used today are low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyhydroxyalkanoates (PHAs), polylactic acid (PLA), etc. Despite having many other uses, PET is largely used in the packaging industry, i.e., beverage and drinking water bottles. Figure 1 below shows different industrial Sectors where PET is used.
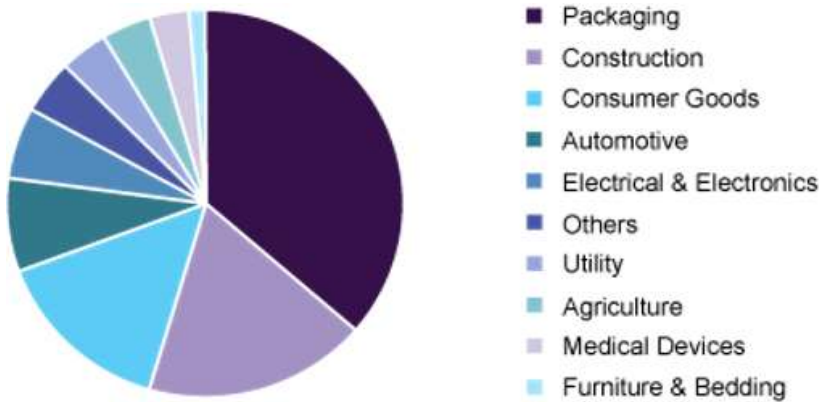
Figure 1.1: Global PET plastic share by end-use, 2020 (source: grandviewresearch.com, 2020).

PET production has been growing rapidly over the years. Global PET packaging consumption increased during 2015–19 at an annual average of 4.0% to 21.8 million tonnes. Global PET packaging consumption is projected to grow during 2020–25 at an annual average rate of 3.7% to 27.1 million tonnes (SMITHERS, 2020). PET is a thermoplastic polyester made from ethylene glycol (EG) and terephthalic acid (TPA) (PETRA, 2022; Wei & Zimmermann, 2017). A recent report by Statistica suggested that PET production in 2016 was 485 billion PET bottles, and the number was projected to reach 583.3 billion by 2021 (Petigny et al., 2019). However, the growth in production, especially in the packaging application, which is thrown away after a single-use, leads to a large accumulation of post-consumer end use waste in the environment. Therefore, these post-consumer PET wastes accumulate in terrestrial and marine environments. In landfills and wastewater plants they are broken down to micro-plastics which can enter the food chain. with more serious implications (Beaumont et al., 2019).

Polymer wastes have been managed using chemical and physical methods, such as landfill incineration, solvent extraction, etc. However, these methods have a lot of limitations that hinder their use. For instance, the incineration method presents problems like producing toxic gases and residual ash containing lead and cadmium. Additionally, the waste converts to other complex, harmful compounds like dioxins and furans (Grigore, 2017; Hopewell, Dvorak, & Kosior, 2009; Koshti, Mehta, & Samarth, 2018). Many studies on the biodegradation of plastics are ongoing because biodegradation is environmentally friendly and has less effect on the environment (Tiso et al., 2021). Biodegradation is when organic substances are broken down into smaller compounds by living microbial organisms. This can be done by either the microorganisms or by using the hydrolase enzymes produced by the microorganisms (Joutey, Bahafid, Sayel, & El Ghachtouli,

2013). During enzymatic hydrolysis, the ester bonds in the polymer chains are weakened and eventually break down, thus increasing the chances of recovering the monomers (Zimmermann, 2020). However, the efficiency of recovering the monomer using this method was very low (Mahal, 2021). Studies show that enzymatic hydrolysis of PET oligomers is way faster than a long-chain polymer. Hence, further incubation of chemically pretreated PET samples with enzymes gave the highest amount of TPA (Kim et al., 2021; Quartinello et al., 2017).

Although recycling has been considered the most promising way of reducing the environmental impacts of PET pollution (Bartolome, Imran, Cho, Al-Masry, & Kim, 2012; Thachnatharen, Shahabuddin, & Sridewi, 2021), the scenario is very poor in actual practice in most countries. In this regard, reports suggest that only 9% of plastic waste is recycled in Canada. A lot of effort has been dedicated to managing the packaging waste, and different studies report that 72% of the packaging waste is not recovered. 32% of this is reported to escape the collection stream, whereas 40% is believed to end up in landfills and the ocean (Agenda, 2016; Furukawa, Kawakami, Tomizawa, & Miyamoto, 2019; PETRA, 2022). Improved recycling of PET plastic would be the most appropriate way of reducing the environmental impact of PET plastics. Most collected end-of-use PET is currently being subjected to thermomechanical recycling: in which plastics are sorted, washed, melted, and remolded to make new plastic items (Ragaert, Delva, & Van Geem, 2017; Wei & Zimmermann, 2017). However, this recycling method implies a serious drawback: reduced optical and mechanical properties and migration of nonintentional added substances (NIAS) (Alvarado Chacon, Brouwer, & Thoden van Velzen, 2020; Badia, Vilaplana, Karlsson, & Ribes-Greus, 2009; Petigny et al., 2019). Thus, introducing virgin PET is common during PET bottle production to guarantee product performance. This implies a continuous need for oil-derived

virgin PET and a major break from a truly circular economy in which waste is designed out of the system, and materials are reused and recycled to return to production (Barnard, Arias, & Thielemans, 2021; CELC, 2019).

Chemical recycling is a process of breaking the bond between monomers and breaking down plastic at the molecular level. This means that the monomers can be recycled in a closed loop system. There is a growing interest in this method of recycling of plastic as it addresses mixed polymer and composite plastics that can only be recycled to lower quality products in the case of mechanical recycling (Bhogle & Pandit, 2018; Vollmer et al., 2020). Chemical recycling involves the complete or partial depolymerization of polymer chains to reclaim the original monomers and oligomers (Barnard et al., 2021; Bhogle & Pandit, 2018; Crippa & Morico, 2020). The depolymerization can be carried out either by Hydrolysis, Ammonolysis, Methanolysis, or Glycolysis, thereby forming different degradation products (A. Al-Sabagh, Yehia, Eshaq, Rabie, & ElMetwally, 2016; Crippa & Morico, 2020). Hydrolysis transforms post-consumer PET to TPA and EG. A growing interest in this method relates to developing PET synthesis directly from EG and TPA (A. Al-Sabagh et al., 2016). However, the energy barrier for depolymerization is normally high; thus, these reactions require high temperatures and pressures (Barnard et al., 2021). To make the polymer more susceptible to hydrolysis and make chemical recycling of PET feasible different pretreatment methods like ozone exposure of the polymer surface, ultrasound-assisted, microwave-assisted, UV irradiation, etc., have been studied (Bhogle & Pandit, 2018; H. Hu, Wu, & Zhu, 2018; Mahal, 2021). Partial depolymerization of PET leads to dimers and shorter chain polymers. This study focuses on the optimize the depolymerizing process of PET to improve the TPA yield while reducing the reaction time and temperature by incorporating ozone and ultrasound

treatments to the polymer surface to keep the energy consumption at a minimum and to convert the remaining hydrolysis product (dimer and short-chain polymers) completely to purified TPA using an enzyme. The overall aim of this study is recovering the monomers of PET for circular economy.

The specific objectives for this study include:

1) Optimization of PET depolymerization process using chemical methods

2) Enzymatic hydrolysis of the partially hydrolyzed products (dimer and short-chain polymers) to TPA

3) Estimate the recovery of the monomers (TPA and EG) and dimers (BHET and MHET) after hydrolysis of PET.

CHAPTER 2: LITERATURE REVIEW

2.1 Plastic pollution challenge

Plastics, tires, food, animal dung, woody biomass, and their combinations make up a significant portion of the world's solid waste. Because of the large amounts manufactured and its environmental impact, plastic attracts a lot of attention among these solid wastes (Zhao et al., 2022). The useful properties of plastics include their lightweight, low cost, processability, water, and electricity resistanc,e and great performance, plastics are frequently utilized for packaging (Miao, von Jouanne, & Yokochi, 2021; Welle, 2017). Polyethylene terephthalate (PET), Polyethylene (P,E) and polypropylene (PP) are typical plastics used in multilayer film packaging and other applications. Because most synthetic polymers are built for longevity and performance rather than recyclability and degradability, the great durability of plastics causes vast amounts of waste to accumulate in landfills and oceans (Webb, Arnott, Crawford, & Ivanova, 2012).

Most plastics in use today follow a linear economy strategy, in which plastics are manufactured, used once, and then discarded, resulting in single-use plastics. This consumption pattern play a significant role in its contribution to global waste and at the basis of the current plastic pollution crisis (CELC, 2019; Walker, McGuinty, Charlebois, & Music, 2021). Even though recycling is the most promising method of reducing plastic pollution, as mentioned earlier only 9% of plastic is currently recycled. This is due to the fact that post-consumer plastic waste typically consists of mixed polymers of variable composition. They also frequently contain numerous pollutants, both biological (e.g., food leftovers) and inorganic (e.g., inks) additives. This makes it challenging to recycle using traditional plastic waste recycling methods like Mechanical or physical processing which has difficulties and limitations (Zhao et al., 2022). As a result, the majority of this plastic

waste is either burnt at power plants or dumped in landfills or oceans, leaving it with little or no value. Replacement of plastics with alternative packaging materials, such as glass or metal containers, may result in more problems since these materials are much heavier, and there is increased carbon dioxide emissions during transport (Vollmer et al., 2020).

Current waste management system's in many countries are being transitioning their system to a circular economy. This aims towards circularity of resource flow while minimizing material loss out of the system, as an alternative to the current unsustainable linear economic model. Circular economy principles include retaining the highest value of products and materials in the system for as long as possible, reducing reliance on non-renewable resources, incorporating waste reduction into the system from the start, and avoiding and eliminating contamination, toxicity, and pollution (Bhuvaneswari. G, 2018). Recycling is one of the wastes reducing strategy to move towards circularity.

The overall aim of this work is to contribute to the selection of a sustainable and effective waste management method from the available options, as well as to develop a process that is feasible at low temperatures atmospheric pressures and uses environmentally friendly solvents for the de-polymerization of PET plastic, which is commonly used in single-use products.

2.2 Polyethylene Terephthalate (TPA)

PET is a semi-crystalline thermoplastic polyester with high strength, transparency, and safety characteristics (Pudack, Stepanski, & Fässler, 2020). The intermediates used in the production of PET, pure terephthalic acid (TPA) and ethylene glycol (EG), are made from crude oil. The first product is a monomer bis(2-hydroxyethyl) terephthalate (BHET) combined with low molecular weight polymers when heated together (oligomers) (A. Al-Sabagh et al., 2016). The mixture then

reacts again, separating the excess ethylene glycol and forming the PET as described in Figure 2.1. The PET is a viscous molten liquid at this point. It's extruded and then quenched in water to create a glassy amorphous substance. Some PET is also made utilizing a dimethyl ester of terephthalic acid-based technique (DMT).
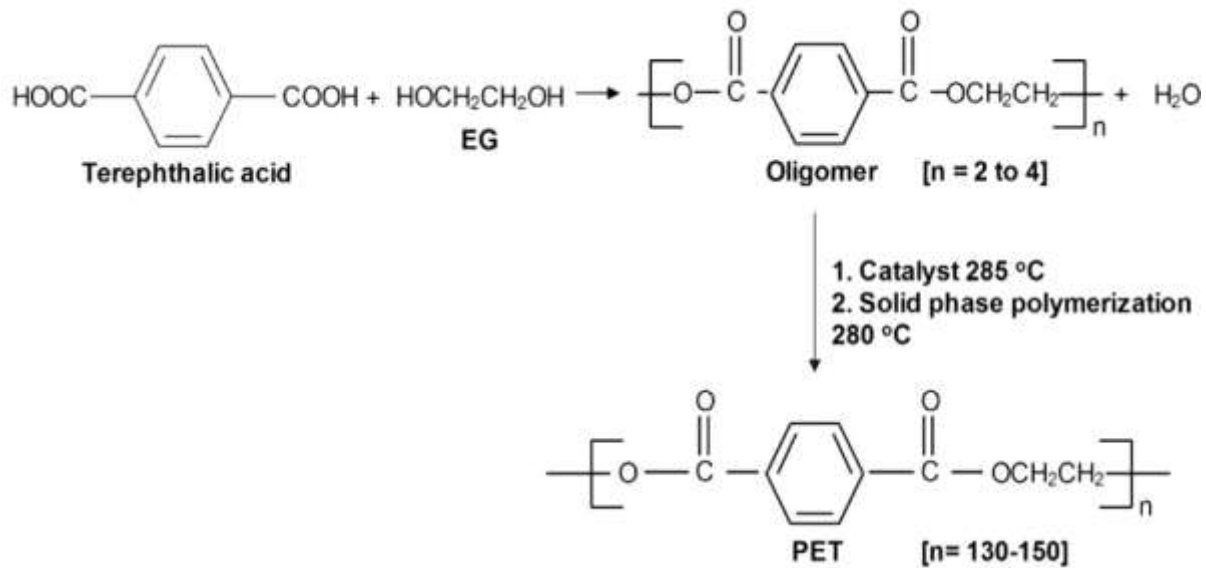
Figure 2.1: Reaction involved in the production of PET (Modified from A.-Sabagh et al.,)

PET is widely used for manufacturing textile and bottles. It mainly used in the food packaging industry, in the form of films trays, or bottles (Pudack et al., 2020). The chemical and physical stability of PET is the primary reason for its increased use. They're light, transparent, and durable. Furthermore, PET bottles provide an effective gas barrier against carbon dioxide, oxygen, and moisture, making them ideal for the packaging of liquid foods, such as water, juice, and particularly carbonated beverages (Ghoshal, 2019). Carbonated beverages, such as soda and soft drinks, contain carbonated water, which causes pressure to build up inside the package. Glass, metals, and PET bottles may all absorb this pressure. PET bottles, unlike glass and metal, are strong, light, inexpensive, and easy to transport, making them an excellent packaging material (Ghoshal, 2019).

As a result of their extensive use, PET bottles are produced in enormous quantities all over the world, resulting in an increase in waste output.

PET is a non-biodegradable material that can last hundreds of years. According to study published in "Environment and Climate Change Canada, 2019," the packaging sector accounts for around 43 percent of total plastic waste produced annually. The majority of waste is made up of post-consumer PET bottles. To manage this huge volume of PET waste, the Canadian Plastics Industry Association (CPIA) devised the 5Rs hierarchy. Reduce, reuse, recycle, recover, and retain are the 5Rs hierarchy.

2.3 Recycling methods of plastic waste

Plastic waste can be managed using the following three basic recycling methods: Thermo-mechanical, enzymatic, and chemical recycling. PET waste can also be incinerated for energy recovery. However, the latter runs the risk of releasing airborne pollutants.

2.3.1 Thermo Mechanical Recycling (simple re-melting)

Mechanical recycling, in which plastics are collected, sorted, washed, melted, and remolded to make new plastic items, is now the most used recycling method to combat plastic pollution (Ghosal & Nayak, 2022; Koshti et al., 2018). Thermoplastic polymers such as PET, PE and PP can be mechanically recycled, however thermoset polymer such as unsaturated polyester or epoxy resin cannot be mechanically recycled, since they cannot be remolded with heat. Even though thermoplastic polymers can be recycled in this method the waste stream's complex composition, makes mechanical recycling of contaminated plastic waste difficult (Hopewell et al., 2009).

Melt Extrusion is the most frequent process for producing regranulated material from typical waste polymers in mechanical recycling industries (Park & Kim, 2014; Schyns & Shaver, 2021). An extruder uses heat and rotating screws to induce thermal softening or plasticization. During extrusion thermo-oxidative and shear-induced chain scission, chain branching, and crosslinking of polymers within an extruder are introduced because of thermal conduction and viscous shearing applied to an extruder. This chain degradation reduces polymer chain length and in turn which affects its mechanical characteristics and processability. Because of this, the number of times a piece of plastic may be recycled is limited (Ragaert et al., 2017). In the case of PET because of the environmental advantages of using recycled PET (rPET) instead of virgin PET for bottles, the usage of recycled PET (rPET) in bottles has increased in recent years. However, several technical downsides, including reduced optical transparency, more yellow colors, decreased in intrinsic viscosity (IV), incidence of mechanical bottle failure, and migration of volatile compounds has observed (Alvarado Chacon et al., 2020; Thoden van Velzen, Brouwer, Stärker, & Welle, 2020). This is because of exposure of the polymer to high temperatures shear stresses, and pressures throughout the process. Alvarado et al. (2020) revealed that there was an increase in particle contamination as the recycling content of the PET and the type of rPET (PET from co-collection system). This particle contamination found to have a linear relationship to optical properties such as haze and color of the final product. A reduction in IV of around 9% to 14% is also observed for bottles made from virgin and rPET respectively. This is due to exposure of PET to high temperatures results in a reduction in molecular weight by thermomechanical degradation, resulting in a drop in IV. Migration of volatile compounds from PET bottle made with different types of rPET and at various levels of recycle content to mineral water was studied. In addition to well-known migrants (acetaldehyde, ethylene glycol, and 2-methyl-1,3-dioxolane) which are

derived from the ethylene glycol monomer, several migrated substances have a concern for the public health if exceed the acceptable limit were detected (Thoden van Velzen et al., 2020). Acetone, butanone, limonene furan, and benzene are some of the migrated substances detected. Even if the clear PET bottle is subjected to a mechanical recycling method repetitive PET sample has been reported to cause a decrease in mechanical properties such as tensile strength and elongation at break decreases and an increase in the yellowing drastically this is due to the degradation of the polymer backbone (Spinacé & De Paoli, 2001). As a result, repetitive thermal reprocessing of PET waste eventually leads to the material's downcycling into items of reduced value, such as textiles, toys, or fibers, and eventually end up in landfills and water resources, creating tremendous environmental problems

2.3.2 Enzymatic recycling

The enzymatic or biological recycling method has recently gotten a lot of interest because of its ability to combat plastic pollution in an environmentally acceptable way (Ghosal & Nayak, 2022; Koshti et al., 2018). Enzyme catalysts work at nearly ambient temperature and pressure and do not include the use of toxic solvents. The use of enzymes for recycling plastics entails the secretion of extracellular enzymes by microorganisms (including bacteria and fungi) and the subsequent reaction of the separated enzymes with polymers, resulting in the hydroperoxidation or hydrolysis of polymers and the formation of monomers and short polymer intermediates. Several elements influence the enzymatic biodegradation of plastics: hydrophobicity crystallinity of the polymer, surface topography, temperature, and molecular size of the polymer influence the degradation process (Kawai, Kawabata, & Oda, 2019).

Enzymatic degradation of most synthetic polymers is now being researched. According to recent studies, Polyethylene, Polystyrene, Polypropylene, Polyvinylchloride, and Polyethylene

terephthalate can be recycled enzymatically. Cutinase, Lipase, PETase, and Esterase are the four enzymes frequently studied in PET for enzymatic breakdown (Kawai et al., 2019; Maurya, Bhattacharya, & Khare, 2020). The enzymatic recycling process, however, is not widely used in industry due to several drawbacks, including low catalytic turnover due to insufficient access to active sites in polymers due to the substrate's high crystallinity, inhibition by intermediate metabolites, and kinetic instability and loss of enzymatic activity above a certain temperature. As a result of endogenous end products, the reaction media becomes acidic during enzymatic biodegradation or hydrolysis (Ghosal & Nayak, 2022).

2.3.3 Chemical recycling

Chemical recycling is a widely used recycling technology that adheres to the ideals of sustainable development. These technologies can degrade plastics and turn them into secondary raw materials, allowing new chemicals and plastics to be created of comparable quality to those manufactured from fossil fuels (CEFIC_Quantis, 2020). It is suited for a wide range of industrial and commercial applications, including food-contact applications, making it more appealing to researchers. By implementing these technologies, industries can increase resource efficiency and help to close the loop in the transition to a circular economy for plastics (Cefic, 2022). It entails turning waste plastic into component fragments via rupturing the hydrocarbon backbone through feedstock recycling, e.g. (pyrolysis or gasification), dissolution (purification) into a purified polymer, and depolymerization into monomers and oligomers (Lee & Liew, 2021; Raheem et al., 2019).

2.3.3.1 Feedstock recycling

Any thermal process that transforms polymers into simpler molecules to create feedstock for petrochemical-type processing is known as feedstock recycling. Pyrolysis and gasification are the two basic processes at work here (BPF, 2022). Pyrolysis, also known as thermal cracking, breaks

down a polymer chain into smaller intermediate products at different temperatures (300-900℃) (Miandad et al., 2019). This method has the advantage of treating co-mingled mixtures of different types of plastics while also reducing the detrimental impact of contamination from various organic, inorganic, or biological residues in the waste stream. Gasification is a process in which mixed waste materials are heated to a very high temperature (1000-1500℃) in the presence of a small amount of oxygen, breaking the molecules down to their simplest components to produce a syngas stream primarily composed of hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and nitrogen (N) (N_2). This gas can be burned to generate energy or used to create new hydrocarbons (BPF, 2022; Lopez et al., 2018). However, these two plastic recycling methods have some disadvantages because a phase transition is involved. It normally requires more energy than depolymerization. Additionally, the process generates poor oil and lower syngas yield without catalysts. The oil generated from pyrolysis requires upgrading for fuel uses, resulting in a high processing cost (Lopez et al., 2018; Miao et al., 2021). Also, as the end product is used as a fuel by combustion it results in further addition to greenhouse gas emissions.

2.3.3.2 Dissolution (purification)

Dissolution or precipitation can separate one polymer from a mixture of polymers in multilayer films, as well as remove colorants and other additives. It's a solvent-based purification method that includes dissolving plastic in either a single solvent or a solvent and anti-solvent combination (Vollmer et al., 2020). In the solvent/anti-solvent technique, a solvent selectively dissolves the polymer, followed by the addition of an anti-solvent to precipitate the polymer for recovery. The precipitated polymer is the end product, which is ideally unaffected by the process and can be reformulated into plastics (Poulakis & Papaspyrides, 2001). This study investigated the possibility of recycling PET by dissolution technique in the process *N*-Methyl-2-pyrrolidone (NMP) used as

a solvent while n-octan and n-hexane as anti-solvent, at a temperature of 165℃ and 90 mins stirring the yield in the polymer nearly attain the theoretical value. Some examples of a solvent/anti-solvent system include xylene, toluene, dichloromethane, and benzyl alcohol as a solvent, while n-hexane and methanol as anti-solvent. Selective dissolution is possible when a solvent can dissolve either the polymer of main interest or all other polymers save the target one. However, for solvents with a high boiling point, separating the combination obtained for re-use is energy and time expensive, and complete removal of solvents is another issue, as any leftover solvents influence polymer properties (Vollmer et al., 2020).

2.3.3.3 Depolymerization

Depolymerization is the reverse of polymerization, resulting in single-monomer molecules or shorter polymer fragments called oligomers. Because monomers are the same as those used to make polymers, depolymerized plastics have a similar quality to virgin monomers. Typical polymers that are suited for this technique include Polyethylene terephthalate (PET), Polystyrene (PS), Poly (methyl methacrylate) (PMMA), etc. The depolymerization of PET plastic waste can be carried out either by Glycolysis, Methanolysis, Ammonolysis, Aminolysis, and Hydrolysis, thereby forming different degradation products (A. Al-Sabagh et al., 2016; Crippa & Morico, 2020).

2.3.3.3.1 Glycolysis

One of the oldest methods for PET chemical recycling is PET glycolysis. This method involves the breakdown of PET's ester bonds under pressure and at a temperature in the range 180-240℃, with an excess glycol in the presence of a catalyst for 3-8 hours, resulting in the monomer bis (2-hydroxyethyl terephthalate) as shown in Figure 2.2. A low molecular mixture of oligomers with hydroxyl terminal groups also formed in this process. Ethylene glycol, diethylene glycol,

14

propylene glycol, and dipropylene glycol are the most commonly used solvents in PET breakdown (Crippa & Morico, 2020). The kinetics of PET glycolysis have revealed that without a catalyst, glycolysis is extremely slow and that complete depolymerization of PET to BHET is impossible (Pingale, Palekar, & Shukla, 2010; Troev, Grancharov, Tsevi, & Gitsov, 2003). Metal acetates (Zn, Co, Pb, and Mn), titanium phosphate, solid superacids, metal oxides, carbonates, and sulfates have all been developed in recent years for the glycolysis of PET. However, these catalysts have several drawbacks, including the need for high temperatures and pressures, difficult separation of the catalyst from the depolymerized products, the occurrence of side reactions, and the impurity of the products (A. M. Al-Sabagh et al., 2014). In addition to the BHET monomer, it produces an end product that comprises a considerable quantity of additional oligomers. As a result, recovering the BHET monomer when it is the intended product is difficult (A. M. Al-Sabagh et al., 2014).
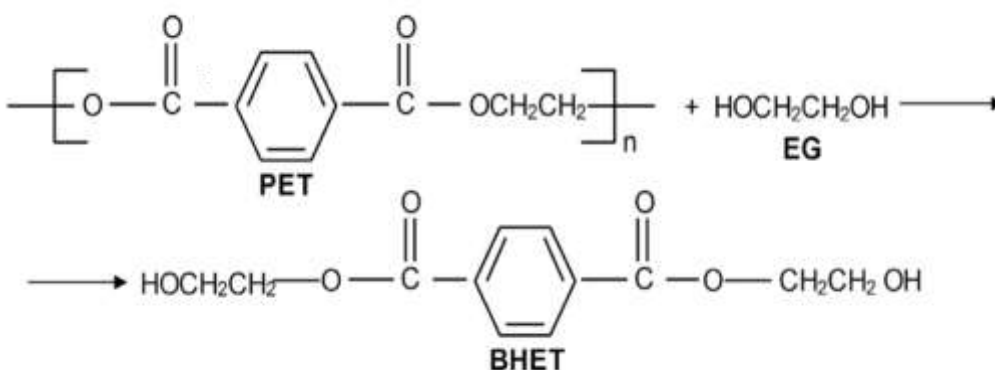
Figure 2.2: Glycolysis of PET (Modified from A.-Sabagh et al.,)

2.3.3.3.2 Methanolysis

Methanolysis is based on the treatment of PET with methanol at a relatively high temperature of 180-280°C and pressures 20-40atm that yields dimethyl terephthalate (DMT) and ethylene glycol as the main products as shown in figure 2.3. The process is commonly carried out in the presence of standard transesterification catalysts, the most common of which is zinc acetate. Magnesium

acetate, cobalt acetate, and lead dioxide are some of the other catalysts used in PET methanolysis. By treating molten PET with methanol at 210 °C in the absence of a catalyst PET was entirely depolymerized to DMT and EG (more than 99%) (Miandad et al., 2019). PET methanolysis has recently been performed using supercritical methanol at temperatures exceeding 300°C and pressures above 80 atm. PET decomposition was significantly faster under these conditions than when using liquid methanol, resulting in the synthesis of DMT and certain oligomers (Crippa & Morico, 2020).
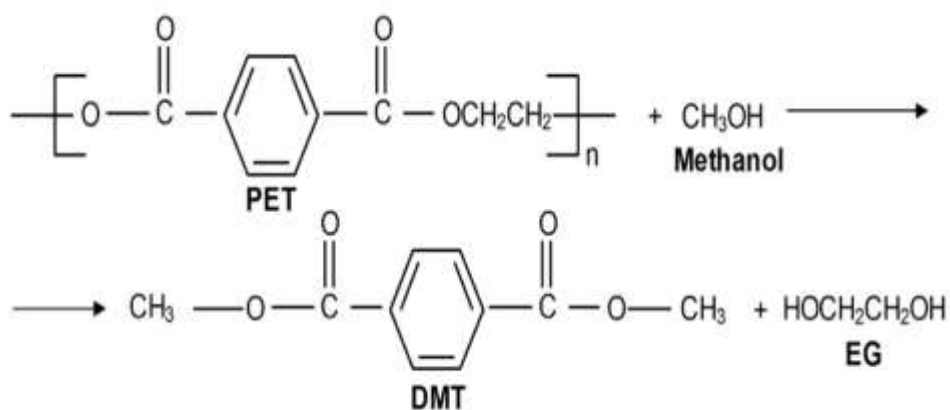
Figure 2.3: Methanolysis of PET (Modified from A.-Sabagh et al.,)

DMT is synthesized by methanolysis and has a higher purity in terms of physical pollutants than BHET, the monomer derived through PET glycolysis. Some organic contaminants, however, cannot be completely removed, resulting in a color mismatch (Crippa & Morico, 2020). The fundamental disadvantage of PET methanolysis is that, in addition to dimethyl terephthalate, the reaction products also include glycols, alcohols, and phthalate derivatives. Due to the isolation and purification of one product from the others, methanolysis is a somewhat costly technique. Since TPA is being used as the raw material in all new PET manufacturing methods, rather than DMT. In the methanolysis process, the conversion of DMT generated by hydrolysis to TPA adds a

substantial cost. As a result, methanolysis for PET recycling is not commonly employed in industry (Achilias & Karayannidis, 2004).

2.3.3.3.3 Ammonolysis

Ammonia reacts with PET in an ethylene glycol environment to form the major result of PET ammonolysis which is terephthalamide, as seen in Figure 2.4. The process is performed either with or without a catalyst, at temperatures ranging from 70 to 180 °C under pressure. In most cases, zinc acetate is used as a catalyst in the catalytic ammonolysis process. The product terephthalamide is used as a feedstock for the production of value-added products as it is not an economically important chemical in its natural state. Because of the economic application of the degradation products and the need of catalyst to increase the rate of reaction, Unlike the other PET recycling techniques, ammonolysis is not widely used for chemical recycling of PET waste now (Gupta & Bhandari, 2019).
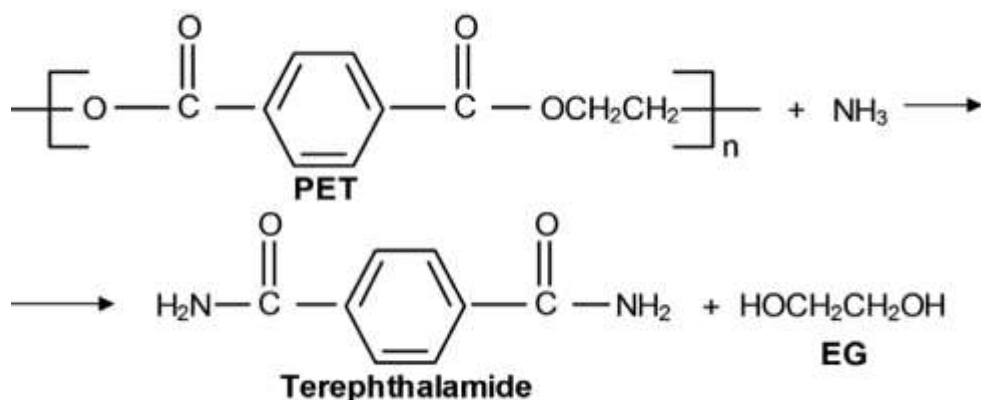
Figure 2.4: Ammonolysis of PET (Modified from A.-Sabagh et al.,)

2.3.3.3.4 Aminolysis

PET aminolysis produces corresponding TPA and EG diamines in the temperature range of 20–100°C, the reaction is mainly carried out using primary amine aqueous solutions, most often methylamine, ethylamine, and ethanolamine (A. Al-Sabagh et al., 2016). The effect of amines (aminolysis) which are organic bases over polymer degradation is faster than the effect of alcohols (i.e., glycolysis). However, this method has yet to be used on a large scale and is a disadvantage when the economy of the process is concerned.

2.3.3.3.5 Hydrolysis

PET hydrolysis converts PET waste into the monomers terephthalic acid (TPA) and ethylene glycol (EG). This approach is gaining popularity because it is the only method that yields reaction products TPA and EG (Mancini & Zanin, 2007; Sinha, Patel, & Patel, 2010). This is related to the trend in new PET synthesis factories to produce it directly from TPA and EG. Thus, DMT (the conventional monomer) is replaced, and eliminated methanol from the technological cycle. However, the utilization of high temperatures (200–250 °C) and pressures (1.4–2 MPa) and the considerable time required for complete depolymerization are the main drawbacks of this method (Sinha et al., 2010). PET can be hydrolyzed in three different ways: alkaline hydrolysis, acid hydrolysis, and neutral hydrolysis. Neutral hydrolysis of PET is carried out with water or steam, at a temperature close to the polymer boiling point, closer to 250°C, and in a pressurized system. On the other hand, acid hydrolysis produces fast reaction rates at atmospheric pressure by introducing more H+ ions into the process. The most common acids employed to catalyze PET hydrolysis are nitric and sulfuric acids (Mancini & Zanin, 2007). The generally utilized hydrolysis in industries is alkaline hydrolysis of PET using an aqueous alkaline solution of NaOH or KOH with a concentration of 4–20 weight % because it can tolerate highly polluted postconsumer PET

as magnetic recording tape, metalized PET film, or photographic film (X-ray film) and the procedure is simple and less expensive than neutral or acid hydrolysis (Štrukil, 2021). This thesis focuses on performing the alkaline hydrolysis process in a sustainable and cost-effective recycling approach by optimizing the reaction parameters (Time, Temperature, and alkali concentration) and applied pretreatments which will be explored in detail later.

Generally, the hydrolysis method is more applicable in the industries than the other depolymerization method like Aminolysis and ammonolysis, and TPA has become the main raw monomer in the case of hydrolysis rather than DMT and BHET, which are formed after methanolysis and glycolysis methods. However, as mentioned earlier, the energy barrier for depolymerization is normally high in the case of hydrolysis. Thus, these reactions require high temperatures and pressures. Advantages and disadvantages of the different PET depolymerization methods are shown in Table 2.1.

Table 2.1: Advantages and disadvantages of different PET depolymerization methods

Methods	Advantages	Disadvantages
Glycolysis	• The conversion of PET to BHET requires less glycol.	• High temperature and pressure are often required (180°C-240°C) • Low conversion in the absence of catalysts • Difficulty of BHET recovery due to the formation of significant number of oligomers in addition to the main product
Methanolysis	• The depolymerization product DMT can be polymerized to form PET • DMT with a higher purity in regard to physical contaminants compared to BHET	• Need of high temperature and pressure (2–4 MPa Temperature 180°C-280°C) • Costly due to the need of isolation and purification of glycols, alcohols, and phthalate derivatives produced during this process and conversion of the DMT to TPA.
Ammonolysis	• Products can be used in value-added polymers	• Pressure ≤ 2 MPa Temperature: 70°C-180°C • Toxic chemicals (Ammonium)
Aminolysis	• Easy purification of products • Products have wide application for production of value-added polymers • Can be carried out under mild condition 20°C-100°C	• Use of often toxic or expensive chemicals (Amines)
Hydrolysis	• The product TPA from depolymerization is the most used precursor the main raw material in the PET production industry • Works using alcohols as reaction medium, with higher energy efficiency	• High depolymerization Temperature 200-300°C and longer reaction time often required 200°C-300°C • Cost of purification of TPA

In order to make the polymer more susceptible to hydrolysis and make chemical recycling of PET feasible, different physiochemical pretreatment methods showed fast conversion and maximized the final product. Below are some of the pretreatments used in PET hydrolysis.

2.4 Pre-treatments of PET for hydrolysis process

Performing physicochemical pretreatments in different polymers before enzymatic and/or chemical hydrolysis has been found to be increase the reaction rate, decrease the reaction time, and increase the product's yield It can reach even though under milder reaction conditions (Bhogle & Pandit, 2018; Bhuvaneswari. G, 2018). In the case of PET hydrolysis, pretreatments showed increasing productivity reduced energy consumption by improve its susceptibility for hydrolysis by bringing oxygen to the surface of the PET in the case of ozone pretreatment and increasing the collision between PET molecules (mechanochemical impact of ultrasound on the reacting species) when ultrasound assistance during hydrolysis is applied (Bhogle & Pandit, 2018; Paliwal & Mungray, 2013). Some of the treatments are listed below.

2.4.1 Size reduction

In PET hydrolysis PET degradation increases as the size of PET is reduced. The surface area available for the reaction is greater in PET flakes with smaller particle sizes. As a result, the reaction rate is raised, and more conversions are possible. However, the process requires a lot of energy (Mahal, 2021). In the case of alkaline hydrolysis of PET, only the surface molecules were targeted by NaOH and hydrolyzed, therefore all of the PET molecules are unavailable for the process. As a result, PET particles with a high surface area (small particle size) have a higher possibility of interacting with NaOH, and hence the rate of reaction is faster for PET particles with lower particle size. High conversion of PET was recorded in alkaline hydrolysis of PET as the PET particle size decreases (Bhogle & Pandit, 2018; Mahal, 2021).

21

2.4.2 Polymer Swelling

Swelling of the polymer occurs when polymers are immersed in a solvent, and the solvent molecules penetrate the polymer and causing the polymer volume to expand. Swelling the polymer may reduce the complicated relationship in their structures, allowing them to dissolve more easily. The solvent molecules can permeate the polymer due to the size difference between the polymer and solvent molecules. In the case of PET, nonpolar solvents such as chloroform, dichloromethane, dichloromethane, and tetrahydrofuran are utilized for swelling since nonpolar solvents can break hydrogen bonds. This will make the PET more susceptible for hydrolysis (Chen et al., 2021).

PET bottles were hydrolyzed in an aqueous alkaline medium including potassium hydroxide (KOH), methanol, and a non-polar solvent for swelling the polymer at ambient temperature and atmospheric pressure, resulting in complete depolymerization of PET, according to a Loop Industries patent (Loop industries, 2017). Based on this, the experiment was performed on the reported conditions to test the reproducibility of the final results, and complete conversion of PET and 73% monomer recovery was obtained.

2.4.3 Ozone

Ozonation has been used in the treatment of water and wastewater and the remediation of polycyclic aromatic hydrocarbons (PAHs) in the soil (Nam & Kukor, 2000; Wu et al., 2021). The removal of naphthalene, fluorene, phenanthrene and anthracene from PAH-contaminated soil was achieved with ozone treatment followed by biodegradation (Nam & Kukor, 2000). Organic pollutants in wastewater can be successfully oxidized by ozone since it is such a potent oxidant. Ozone molecules are especially reactive because they include a highly unstable "nascent" oxygen atom. Ozone converts organic molecules to oxygenated intermediates by direct oxidation or the production of hydroxyl radicals. Ozone degrades polymeric materials by the formation of reactive

oxygen species. When polymers are exposed to ozone, it produces a variety of carbonyl and unsaturated carbonyl compounds. Intermediates (bipolar ions/peroxy radicals) are formed during these reactions, which are unstable and induce the degradation of large molecules or polymers. Figure 2.5 depicts the common response of ozone to aromatic structures (Zeenat, Elahi, Bukhari, Shamim, & Rehman, 2021).
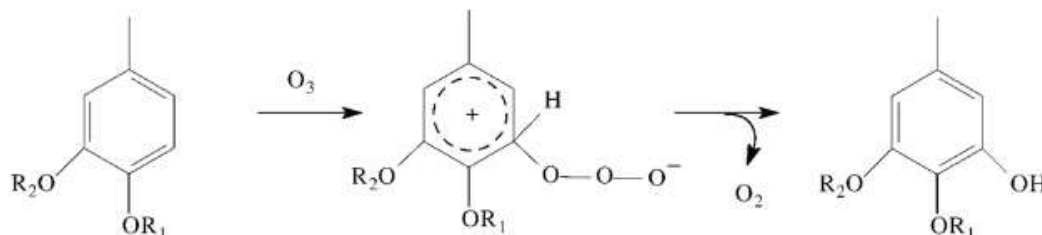
Figure 2.5: Reaction of ozone with Aromatic Structure.

Ozone treatment is also widely used in a surface modification technique to improve the hydrophilicity of the polymer surface, after ozone treatment of LDPE and PET film several polar groups such as carboxylic, anhydride, and hydroxylic groups were observed in the surface of the polymers through oxidation and chain scission resulted in increased (Ferreira et al., 2005; Gu, Wu, & Doan, 2009). Ozonation can take place in the gas or liquid phase. In the gas phase the ozone gas reacts with the substrate and in the liquid phase the substrate interacts either by direct oxidation or with hydroxyl radical (Tatyana, Chairez, & Poznyak, 2019). The efficiency of ozonation in the liquid and gas phase for polyethylene film was investigated by (Patel, 2008) resulted in the same efficiency in terms of peroxide generation and wettability of the surface. (Ferreira et al., 2005) studied ozone treatment of PET fiber for better adhesion to poly (hydroxyethyl methacrylate) hydrogels. The result was analyzed using contact angle measurement, the wettability of the PET surface increases as a result of ozone treatment this shows the formation of polar groups at the PET surface. However, changes in contact angle brought about by ozonation are partially reversed

following washing the sample with water after ozonation. This shows the removal of oxidized polymers that were generated during ozonation. Similarly, the XPS result showed a decrease in O=C values after washing procedures, confirms the removal of oxygen contain groups. This implies in the case of plastics liquid-phase oxidation might decrease the formation of polar and carbonyl groups on the PET surface because the residence time of ozone in liquid is much lower than in gas. (Mahal, 2021) observed the possibility of PET film degradation using ozone treatment followed by a hydrolysis process. In this study due to ozone treatment formation of hydroxyl groups and disappearance of the C-H bond observed which could enhance the hydrolysis process. However, not many reports have been found on the utilization of ozonation in the degradation of plastics. In our case gas-phase ozone treatment were used to enhance the hydrolysis process.

2.4.4 Ultrasound Treatment

Ultrasound is an elastic wave, similar to sound waves. Ultrasound waves, on the other hand, have a low wavelength and a higher frequency than sound waves (Vikulina & Vikulin, 2018). In order to purify wastewater and break down organic contaminants, ultrasonication has been utilized (Okitsu, Nanzai, Kawasaki, Takenaka, & Bandow, 2009). Microcavities in compounds are commonly caused by ultrasound. Shock waves in these cavities are caused by increased temperature and pressure inside the bubbles. Weak bonds, such as hydrogen bonds and van der Walls bonds, are disrupted as a result (Vikulina & Vikulin, 2018). Figure 2.6 depicts the general mechanism of ultrasonic cavitation on polymer.
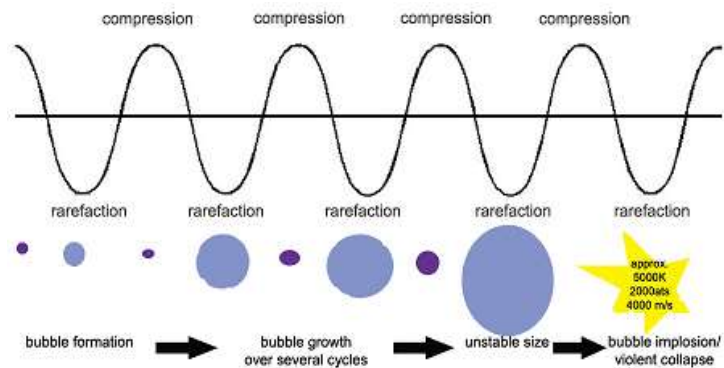
Figure 2.6: Ultrasonic Cavitation in polymer.

Figure 2. Under acoustic generated cavitation deterioration of polypropylene and low-density polyethylene was discovered (Okitsu et al., 2009). The ultrasonic degradation of carboxymethyl cellulose and polyvinyl alcohol was explored by (Mohod & Gogate, 2011). Ultrasonic breakdown of poly alkyl methacrylate also reported on the other study (Daraboina & Madras, 2009). Ultrasound can be utilized to depolymerize polymers in any of these studies. The efficiency of ultrasound in the chemical and enzymatic hydrolysis of PET also studied. (Bhogle & Pandit, 2018) reported 69% PET conversion with ultrasound and 46% without ultrasound using 10% NaOH concentration in methanol at 50°C in 60 mins of reaction time. Similarly, Mahal, (2021) observed the use of ultrasound during the hydrolysis process increased the weight loss from 6.6% to 9.5% in 10 mins of ultrasonication followed by 48h enzymatic hydrolysis (Mahal, 2021). Our study includes the ultrasound treatment together with ozone pretreatment and optimization of influencing factors of the hydrolysis. This will facilitate a complete conversion of PET and improve the TPA recovery. Additionally, enzymatic hydrolysis of short chain polymers formed during the hydrolysis process is carried out to further improve the monomer and dimer recovery.

Table 2.2: Advantages and disadvantages of different pretreatment method

Pretreatment methods	Mechanism	Advantages	Disadvantages	References
Size reduction	Increases effective surface area of reaction	Increases rate of reaction	Energy intensive	(Bhogle & Pandit, 2018; López-Fonseca, González-Velasco, & Gutiérrez-Ortiz, 2009; Yoshioka, Motoki, & Okuwaki, 2001)
Polymer swelling	Causes increase in volume of the & weaken the polymer bond	Reduces the reaction temperature and time	Hazardous chemicals	(Chen et al., 2021)
Ultraviolet (UV) irradiation	High-energy photons breaking the backbone of the molecule	Increases surface hydrophilicity of the polymer	Costly method, More maintenance cost	(Esmaeili, Pourbabaee, Alikhani, Shabani, & Esmaeili, 2013)
Ultrasound	Microbubbles cavity at the surface of solid particles of PET, Cause rupture of the bond	Reduce the expenditure on energy spent in agitation Increases product	Affected by Several factors the includes ultrasound frequency, sonication Time, sonication power and temperature	(Bhogle & Pandit, 2018; Paliwal & Mungray, 2013)
Ozone	The formation of active polar groups such as carboxyl group	Simple and inexpensive, Suitable for complicated shapes Facilitate the reaction by improving the hydrophilicity of the polymer surface	Long treatment time for effective oxidation	(Ferreira et al., 2005) (Gu et al., 2009)

2.5 Chemical hydrolysis of PET

As mentioned earlier the PET hydrolysis is carried out in an acidic, alkaline, or neutral (water) medium, resulting in the monomers TPA and EG. The acid-catalyzed hydrolysis of PET waste in the form of powder in 3 to 9 M sulfuric acid was carried out for 12 hours at temperatures ranging from 150C to 190C at atmospheric pressure. According to some reports, the degree of hydrolytic degradation was directly related to the acid concentration and reaction temperature, with complete degradation achieved at 3 M sulfuric acid, 190 C, and 1 hour, respectively (Yoshioka et al., 2001). Although high conversion of PET can be achieved by acidic hydrolysis, the reaction performed under harsh conditions and the need to recycle large volumes of acids makes the process very expensive and has a negative impact on the quality of recovered ethylene glycol (EG) (Shojaei, Abtahi, & Najafi, 2020). On the other hand, neutral hydrolysis is considered as more environmentally friendly, However, all mechanical impurities contained in the polymer stay in the TPA during neutral hydrolysis, compromising the purity of TPA (Aguado et al., 2014).

Several studies have investigated chemical hydrolysis of PET under alkaline condition since it is the only method that yields reaction products TPA and EG as mentioned earlier. It should be noted that high PET conversions and TPA yields are typically obtained only under extreme conditions such as high temperature, pressure, or the presence of catalysts (Štrukil, 2021). Similarly, most of the studies that reported high PET conversion and TPA yield did so under extreme conditions, as shown in table 1. Some reports that very high temperature and longer reaction time of chemical hydrolysis that makes the process expensive (López-Fonseca et al., 2009). However, this method can be carried out in both aqueous and non-aqueous solution. Using non aqueous solution like methanol, ethanol, butanol etc. instead of water in this hydrolysis process reduces reaction temperature and time (Bhogle & Pandit, 2018). Adding some ethereal solvents such as dioxane,

tetrahydrofuran, and dimethoxyethane to the solution resulted in speeding up the degradation rate of PET and lowers the reaction temperature (Shojaei et al., 2020). This is because adding ethereal solvents activate the nucleophilic power of hydroxide ion (Oku, Hu, & Yamada, 1997). PET was alkali depolymerized with a mixture of alcoholic(methanol) and ethereal solvents, A reaction period of 7 hours was required to convert more than 96 percent of PET with NaOH at 60°C in methanol, but this time was reduced to 40 minutes by replacing 10% of the methanol with dioxane as a co-solvent (L.-C. Hu, Oku, Yamada, & Tomari, 1997). However, tracking the volatile compounds that amities from using these solvents is another issue.

Paliwal and Mugary, (2013) conducted alkaline hydrolysis in the presence of ultrasonication and a phase transfer catalyst at 90°C and 10% w/w NaOH found that 100% PET conversion and TPA yield at a rate of 99%. This is because of the microbubble's formation on the PET surface because of ultrasound leads to accelerate the hydrolysis (Paliwal & Mungray, 2013). However, need of catalyst separation and catalyst cost make the process expensive. Recently another similar study was conducted in the presence of ultrasonication but without a phase transfer catalyst in both aqueous and non-aqueous solution (Bhogle & Pandit, 2018) . Because non-aqueous NaOH has a stronger affinity to the PET surface than aqueous NaOH, the weight loss of PET was 53% in non-aqueous media and 20% in aqueous medium. In this process firstly, sodium hydroxide (NaOH) cleaves the ester bond of PET, resulting in disodium terephthalate (Na_2TA) and EG. Second, disodium terephthalate (Na_2TA) is neutralized with concentrated sulphuric acid (H_2SO4), which precipitates TPA as a white solid. The mechanism of PET hydrolysis by NaOH and sulfuric acid is depicted in Figures 2.7 and 2.8.
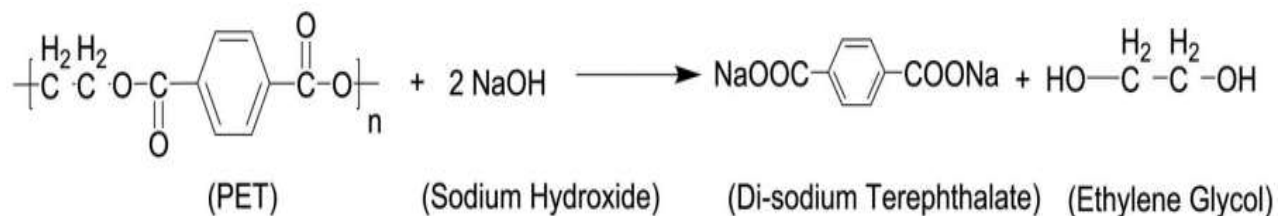
Figure 2.7: Step 1: formation of sodium salt of terephthalic acid and ethylene glycol.
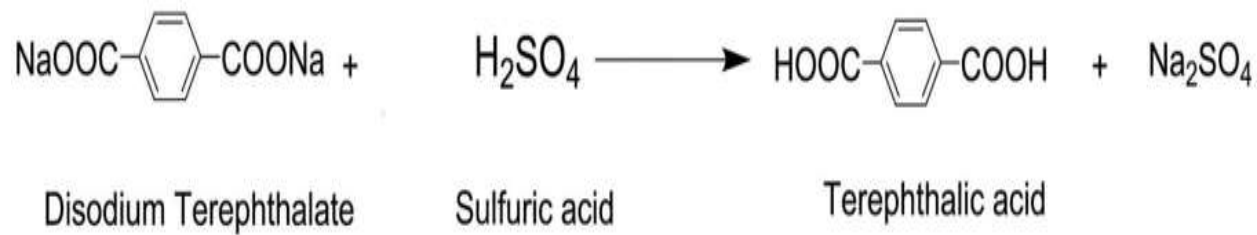
Figure 2.8: Step 2: formation of pure terephthalic acid (Bhogle and Pandit, 2018).

Bhogle and Pandit, (2018) found the highest PET conversion of 69% as the temperature rises from 40°C to 50°C.Thus, an increase in the temperature increases the hydrolysis reaction rate. However, the TPA yield was not reported. They also observed PET conversion drastically increase as PET particle size decreases. Since small particle size led to a higher probability of PET and NaOH interaction, the rate of reaction is higher for the smaller particle size of PET. We hypothesized that applying other pretreatments on the PET surface and optimizing the hydrolysis conditions, in combination with ultrasound, can improve the alkaline hydrolysis of PET improved for better conversion.

Table 2.3: Some recent studies on chemical depolymerization of PET

Sample	Pretreatments	Methods	Conditions	Results	Reference
PET flake	Microwave irradiation	Acid Hydrolysis	231 °C, under 2.6 MPa pressure	93% of TPA	(Ikenaga, Inoue, & Kusakabe, 2016)
PET flake	N/A	Alkaline hydrolysis	200°C	92 % of TPA	(Singh et al., 2018)
PET chips	N/A	Neutral hydrolysis	195 °C, 120 min, under pressure of 3 MPa & In the presence of catalyst	86% conversion & 92% of TPA yield	(Stanica-Ezeanu & Matei, 2021)
PET chips	Ball milling	Alkaline hydrolysis	1 mol L^{-1} NaOH, 125°C, 24 hr.	85% of TPA	(Štrukil, 2021)
PET flake	Swelling and dissolution	Alkaline hydrolysis	90°C	90 % TPA yield	(Chen et al., 2021)
PET powder	ultrasound assisted	Alkaline Hydrolysis	90°C 65 mins, In the presence of phase transfer catalyst10 % NaOH/	90% Yield of TPA	(Paliwal & Mungray, 2013)

Table 2.3: Some recent studies on chemical hydrolysis of PET (Continued).

PET type	Pretreatment	Breakdown method	Conditions	Yield and conversion	References
PET flake	Microwave irradiation	Alkaline hydrolysis	85°C 2.2 hr. In the presence of catalyst	97 % of TPA yield	(H. Hu et al., 2018)
PET granules	N/A	Alkaline hydrolysis	6.7 % NaOH/ quaternary phosphonium salt 80 C 1.5 hours	95 % conversion of PET; 23% w/o PTC after 10 hours	(López-Fonseca et al., 2009)
PET flake	N/A	Alkaline hydrolysis	80°C	90% TPA yield	(Ügdüler et al., 2020)
PET fibers	N/A	Alkaline hydrolysis	40 C 96 hour, 10% NaOH	25% weight loss	(Rahman & East, 2009)
PET powder	ultrasound assisted	Alkaline Hydrolysis	50 C 60 mins	69% conversion of PET	(Bhogle & Pandit, 2018)
PET film	ultrasound assisted plus ozone treatment	Alkaline Hydrolysis	8.5% NaOH,60 C, 2.9 hr under atmospheric pressure	100% weight loss and 83.58% yield of TPA	This work

CHAPTER 3: MATERIALS AND METHODS

The experiments carried out in this thesis were performed in four main steps. First, PET pretreatment studies were carried out to enhance the subsequent hydrolysis process. The second step was to use response surface methodology (RSM) to optimize the chemical hydrolysis process. Third, enzymatic hydrolysis of PET liquid oligomers using HiC enzyme. Finally, quantitative, and qualitative analysis were performed to determine the PET conversion rate and chemical yields of end products. The whole experimental process of PET depolymerization is depicted in Figure 3.1.
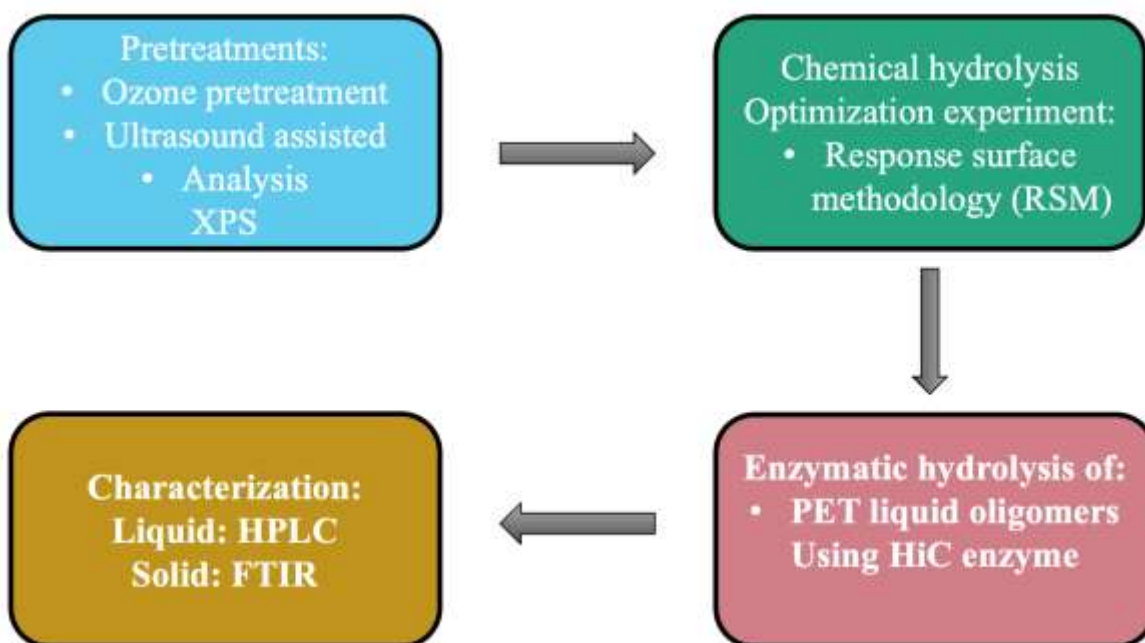
Figure 3.1: Experiment procedures for PET hydrolysis.

3.1 Materials

The next section lists the materials used in this study as well as the sources from which they were obtained.

3.1.1 Polyethylene terephthalate (PET) plastic samples

Transparent, amorphous polyethylene terephthalate (PET) film with thickness of 0.25 mm obtained from Goodfellow (Goodfellow Cambridge Limited, England) was used in all experiments carried out in this study.

3.1.2 Chemicals

Sulphuric acid (purity: 98%) sodium hydroxide pellets (purity: 98%), methanol, analytical grade Bis-2-hydroxyethyl terephthalate (BHET), ethylene glycol (EG) and terephthalic acid (TPA) used in this study was obtained from Sigma-Aldrich.

3.1.3 Enzymes

Immobilized HiC (cutinase, NZ51032, Novozymes, labelled as Lipase by the supplier) obtained from Cedarlane, Canada available lab was used in this study. According to the company specifications, *Humicola insolens* was the source organism for the cutinase enzyme. The enzyme was absorbed into polymethacrylate divinylbenzene copolymer beads, which range in size from 250 to 700 microns.

3.1.4 Ozone Generator

The Titan Glass Ozone Generator (WD8) from Longevity Ozone Resources Inc available in our lab was employed for ozone treatment. Compressed Oxygen (UN 1072, class 2) obtained from Praxair was used as an input gas for the ozone generator.

3.1.5 Ultrasonic Bath

For ultrasonic treatment CPX Series Digital Ultrasonic Bath (40 Hz, CAT: 15-337-419, Fisher Scientific TM) available in our lab was used

3.2 Experimental methods

3.2.1 Ozone pre-treatment of PET samples and characterization

PET samples were pretreated by ozone, which has the ability to modify polymer surface by incorporating reactive O_2 species to the polymer surface and leads to an increase in the oxygenated carbonyl groups on the polymer surface. X-Ray Photoelectron Spectroscopy (XPS) analysis methods were applied to quantify the amount of oxygen content and chemical change introduced by ozone treatment.

3.2.1.1 Ozone pre-treatment

This procedure was adapted from (Tian et al., 2017). 1x3 inch polyethylene terephthalate (PET) films were pre-treated by being washed with dilute soap water, rinsed three times with Milli-Q water, and then air-dried overnight. Four strips in a row were hung vertically using clips and placed inside a glass ozonation chamber, which was connected to the ozone generator and was located within a fume hood. Oxygen from a cylinder was delivered at 8 L/min flow rate to the ozone generator for 1.5 hours. This amounted to about 18 grams of ozone in total as per the ozone generator specification sheet and confirmed by chemical analysis. The optimum amount of ozone (1.5 grams per sample) that leads to higher monomer recovery was adapted from previous research conducted in our lab (Mahal, 2021). The samples were removed after the reaction was complete and prepared for analysis and subsequent hydrolysis procedures.

3.2.1.2 X-ray photoelectron spectroscopy (XPS)

In order to determine the changes that occurred on ozone treated PET, X-ray photoelectron spectroscopy (XPS) measurements were performed. The characterization of both unpretreated PET and ozonated PET samples was performed on a Kratos Supra spectrometer using a monochromatic Al Kα source available at Lakehead University Center for Analytical Services (LUCAS).

3.2.2 Chemical Hydrolysis of PET films

Three experiments for the chemical hydrolysis of the PET film were perform in order to analyze the effects of ozone and ultrasound treatments on the hydrolysis process. First, the hydrolysis process of PET film (untreated) is carried out in a magnetic stirrer. A second sample for hydrolysis of PET film was carried out in an ultrasound-assisted system as described in a following section. The third sample used was the ozone pretreated PET film followed by ultrasound assisted. The procedure for the three sets of experiments are as follows.

3.2.2.1 Chemical hydrolysis of untreated PET film

20 ml of 2.5 M methanolic NaOH solution and 1x1 inch (198 mg) virgin PET films were put into 3x125 mL Erlenmeyer flasks. The flasks were placed in the magnetic stirrer for 1 hour at 45°C with 100 rpm agitation. After 1 hour, 20 mL of chilled distilled water was added to each flask in order to stop the reaction. This method was adapted from (Bhogle & Pandit, 2018). Vacuum filtration was used to extract unreacted PET, which was then washed with distilled water and placed in a hot air oven at 80°C for 45 minutes to remove the methanol, then placed in a freezer at -80°C overnight, followed by freeze-drying for 3 hours. The final weight of the samples was measured, and the gravimetric weight loss was computed. In order to precipitate TPA, the pH of the liquid solution was reduced to 2.5 by adding pure H_2SO_4. The white precipitate was vacuum filtered and rinsed with distilled water to remove the salt which forms alongside TPA precipitate.

The residue is then placed in a hot air oven at 80°C for 45 minutes to remove the methanol, then put in a freezer at -80°C overnight, and finally freeze-dried for 3 hours. In order to prepare the filtrate for the HPLC analysis, the pH was increased to 7, and the solution was stored in a freezer. Finally, the total recovery of monomers and dimers was calculated by adding the weight of the recovered TPA (obtained by precipitation) to the HPLC recovery portion (measured from the liquid filtrate remaining after precipitate filtered out.

In this study, PET conversions and TPA yield were calculated by equation (1) and equation (2)

$$\%PET\ Conversion = \left(\frac{W_{PET,i} - W_{PET,f}}{W_{PET,i}}\right) \times 100 \dots\dots\dots\dots\dots (1)$$

Where:

$W_{PET,i}$ = initial weight of PET

$W_{PET,f}$ = is the final weight of PET which remains on filter paper after filtration

$$\%TPA\ Yield = \frac{N_{TA}}{N_{TA,o}} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots (2)$$

Where:

N_{TA} = number of moles of TPA precipitated

N_{TAo} = number of moles of TA that could have theoretically been precipitated based on 100% PET conversion

3.2.2.2 Ultrasound Assisted and ozone pretreated PET hydrolysis procedures

This procedure used in these experiments were similar to the chemical hydrolysis of untreated PET film described in the previous section. The difference here was ultrasonic energy was incorporated during the chemical hydrolysis reaction for both untreated PET and ozone pretreated PET in separate experiments. The samples that had ozone pretreated followed by ultrasound aided hydrolysis yielded a greater PET conversion and TPA production in this experiment. This method confirmed earlier experiments carried out in our lab by Mahal, (2020) and was carried out chosen as a prescreening experiment for the further studies in this thesis.

3.2.3 Experimental Design using RSM

In order to improve the effectiveness of the hydrolysis process (high weight loss and TPA yield), optimization of experimental conditions for PET depolymerization was conducted to find the best conditions for PET hydrolysis. The experimental design was carried out using the Central composite design (CCD) technique under Response surface methodology (RSM). Minitab version 17 was used for the experimental design, statistical analysis, quadratic model buildings, and graph plotting. Data were analyzed using the Analysis of variance (ANOVA). The three parameters, temperature, NaOH concentration, and time were chosen as independent variables, while PET conversion and the TPA yield are the output response variable. The experimental ranges are chosen to be temperature (30-60°C), sodium hydroxide (5-15% w/w) and time (1-4 hours). Ranges and levels, together with the actual and the coded values of independent variables are listed in Table 3.1. The lower and higher values were based on the previous research carried out by (Hu et al., 2017) and obtained from experiments conducted in our laboratory.

Table 3.1: Experimental range and level of independent variables.

Variables	Coded factor levels				
	$-\alpha$	-1	0	1	α
X1: Temperature (℃)	30	36	45	54	60
X2: NaOH amount (%)	5	7	10	13	15
X3: Time (hr.)	1	1.6	2.5	2.9	4

3.2.4 Enzymatic hydrolysis of partially hydrolyzed products

The filtrate obtained after precipitation and filtration of chemical hydrolysis sample was used in enzymatic hydrolysis. As it is reported that the enzymatic hydrolysis of PET oligomers is faster than for long-chain polymers (Quartinello et al., 2017). Initially the methanol present in the filtrate after chemical hydrolysis was removed from the solution by rotary vapor. The PH was brought back to neutral so that the enzyme works optimally. Then 15mg/ml of HiC enzyme is added to the solution after the solution reaches the desired temperature and placed in the rotary shaker for 3 hours at a temperature of 60℃ and 150 rpm rotation. After the reaction is completed, the liquid sample is filtered out and subjected to HPLC analysis in order to analyze and quantify the concentration of its component.

3.2.5 Analysis of end products of chemical hydrolysis

Characterization of recovered solid products was performed using Fourier transform-infrared spectroscopy (FT-IR). Analysis of liquid products was carried out by using High-Performance Liquid Chromatography (HPLC).

3.2.5.1 FT-IR Analysis

Analysis of chemical functional groups was carried out by using Fourier transform-infrared spectroscopy (FT-IR). Around 10-20 mg commercial standard TPA and TPA samples recovered after chemical hydrolysis were pressed into the crystal head and characterized over a range of $4000\text{-}500\text{cm}^{-1}$ using the FT-IR spectrophotometer (a Bruker Tensor 37 Fourier Transform Infrared) available at Lakehead University Center for Analytical Services (LUCAS).

3.2.5.2 HPLC Analysis

The filtrate obtained after separation of the solid precipitate obtained after chemical hydrolysis were analyzed using High performance liquid chromatography (HPLC) system. An Agilent HPLC system available in our lab was used. The column used was Agilent Poroshell 120, EC-C18 (2.7 μm, 4.6x100 mm) with a guard column. A gradient mixture of 0.1% (v/v) formic acid, methanol and water was used as mobile phase at a ratio from 1:5:94 to 1:90:9. Injection volume was 1 μL at a flow rate of 0.75 mL/min and temperature was 40±0.8 C. Total elution time was 18 minutes including 7 minutes' post time. Detection was done using an UV detector at 299 nm. Standard solutions for TPA (0.1, 0.2, 0.4, 0.6, 0.8,1 mM) and MHET, BHET, and EG (2, 4, 6, 8, 10 mM) were prepared in tris-HCl buffer (pH 8).

The MHET solutions were obtained by BHET hydrolysis by HiC. BHET (10mM) in 10 ml solution of Tris-HCl PH of 8 added in a beaker and placed into the water bath when a temperature of the solution reaches 60°C then (6genzyme/gBHET enzyme) was added and the agitation was 180 rpm for 30 minutes. Then enzymes were separated, and solution was diluted as the concertation range indicated above. Then all the standard solutions run through HPLC. TPA, MHET, and BHET calibration curves were constructed based on the HPLC peak area of the compound at each

concentration. The retention time of TPA, MHET, BHET and EG was 8.8,7.9,10.9 and 11.5 min, respectively.

CHAPTER: 4 RESULTS AND DISCUSSIONS

The pretreatment of PET before hydrolysis has been found to improve yields. In this chapter, all the experiments carried out in the course of this study will be discussed. This will include ozone pretreatment, combined ultra-sonication and hydrolysis, rigorous optimization of the hydrolysis process and enzymatic hydrolysis of the oligomers left after chemical hydrolysis with the aim of complete hydrolysis of the polymer to its constituent monomers.

4.1 Ozone Pre-treatment of PET film and its characterization

The aim of performing an ozone treatment was to enhance the hydrolysis process before the influencing factors for the hydrolysis are optimized. Then followed by optimizing the conditions to study whether this pretreatment in combination with the optimum conditions for the hydrolysis improve the main products conversion rate and chemical yields. Ozone pretreatment was carried out by exposing the strips of PET films to ozone in a chamber for 90 minutes at an ozone flow rate of 8L/m. Details of this experiment are given in methods section in chapter 3.

4.1.1 XPS Analysis

The PET films that were pretreated with zone were studied using an XPS system. The results are given in figure 4.1. Analyzing the high-resolution XPS spectra revealed the chemical composition of the PET surface. Figure 4.1 (a) and (b) show the C1s spectra of PET Film before and after 1.5h ozone treatment. The components of the C1s high resolution were fitted with peaks at 284.5, 285.5, 286.6, and 289 eV, which correspond to benzene ring (C– (C, H), methylene carbon bonded to one oxygen (C–O), carbonyl group (C=O) and ester functional groups (COOH), respectively (Endo et al., 2017; Ferreira et al., 2005). Following the ozone treatment, the peak at 287.7 (C=O), 289 (COOH) increases significantly, However the peak at 285.9 (C-O) does not show significant

changes. The XPS indicates the peak C1s (C-C or C-H) groups decreased by 34%, this means that the ozone treatment breaks the (C-C or C-H) and increases the carbonyl (CO) and ester functional (COOH) groups on PET surface. Hence, the increase of such functional groups will enhance the hydrolysis process.

(a)

(b)
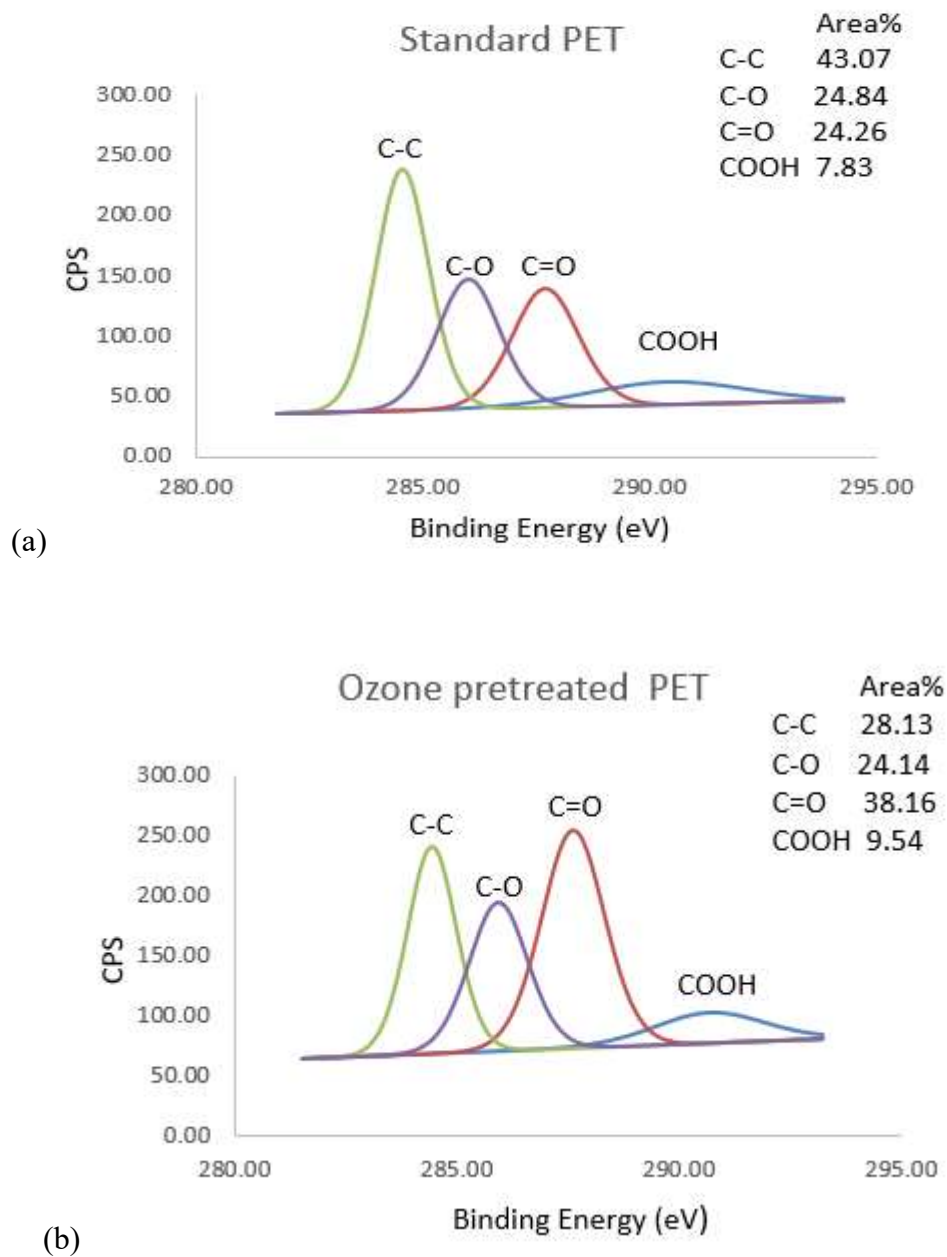
Figure 4.1: XPS C1s spectrum of untreated (a) and ozone treated PET (b)

4.2 Chemical Hydrolysis of Untreated PET film

Chemical hydrolysis was carried out using a methanolic NaOH solution in this approach. PET has poor resistance against non-aqueous alkaline solutions (like NaOH) as compared to aqueous solutions (Bhogle & Pandit, 2018; Kamaruzamal, 2014). This is because of PET is hydrophobic and repels strongly polar water molecules (such as those coupled with sodium hydroxide to form a hydrate). Alcohols, like methanol and ethanol, on the other hand, are less polar than water and hence experience less repulsion from the PET material. Among the alcohols the one with smaller molecular size has better access to the PET material than the larger size of the solvent molecules. Alkaline hydrolysis of PET found to be faster in methanol than ethanol (Shukla & Mathur, 2000). Hence the solvent methanol is used in this work. The following sections present the results of chemical hydrolysis of virgin PET films as well as a discussion of the topic.

One hour of chemical hydrolysis by methanolic NaOH solution resulted in 40% WL of PET films. This is similar to results obtained by Bhogle and Pandit, (2018) who reported 42% weight loss. The yield of TPA was found to be 25.69%. After the hydrolysis the liquid potion of the sample was acid treated to a pH of 2.5 to precipitate out the TPA. However, there was 14.3% difference between TPA precipitated and weight loss which implies that some of the PET polymer was not turned into TPA but solubilized in the liquid solution. HPLC analysis of the filtrate was thus carried out.

As observed from HPLC analysis (Figure 4.2), except for TPA, peaks of all the monomers and dimers were found This is because all the TPA that was formed during the hydrolysis process precipitated out after the acid-neutralization step. The quantities obtained was 4.4% BHET, 0.47% MHET, and 0.88% EG was obtained on HPLC analysis. The HPLC based recovery was 5.7% and

the total recovery was 31.38% including TPA precipitated by adding H_2SO_4. There was still a difference of 8.73% between the WL and total recovery. The possible explanation could be PET underwent partial hydrolysis during chemical hydrolysis process. The partially hydrolyzed molecules were solubilized in the chemical solution thus did not break down to monomers and dimers completely.
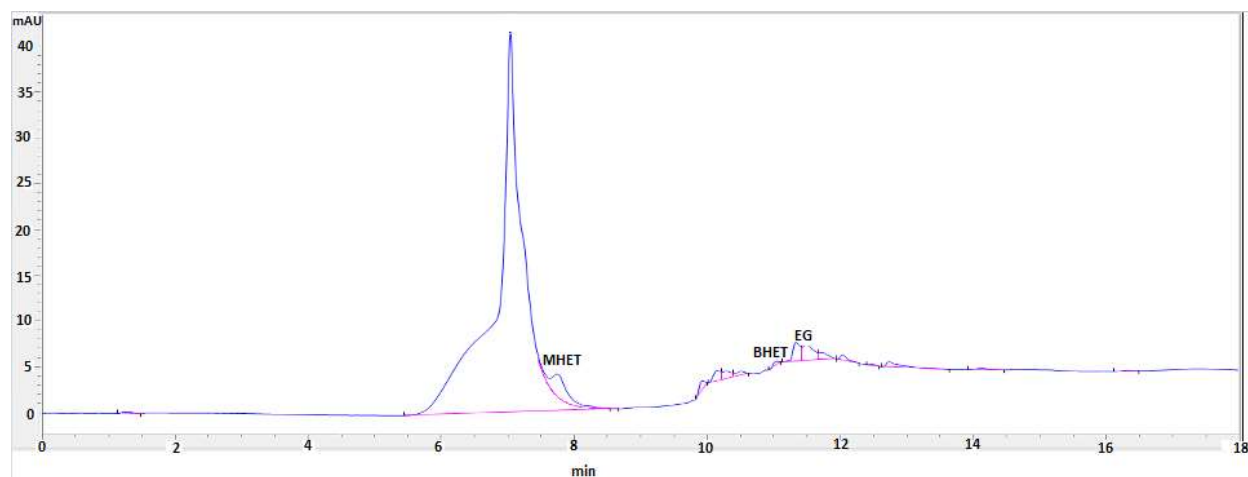
Figure 4.2: HPLC analysis peaks for MHET, BHET, EG and other short chain polymers.

4.3 Ultrasound Assisted Chemical Hydrolysis of PET film

Sonication was used to accelerate the breakdown of PET. The term ultrasound assisted used in this thesis implies that sonication and hydrolysis were carried out at the same time. This was done for ozone pretreated and samples with no pretreatment. The results of this experiment will be discussed in the following section.

Without pretreatment, the ultrasound assisted chemical hydrolysis of PET film resulted in 64% WL and 46.33% of TPA precipitated after acid neutralization. The result showed a 24% and 20.64% increase of WL and amount TPA precipitated respectively when the process performed in ultrasound compared to the process performed without ultrasound treatment. This was due to

micro-cavity formed during ultra-sonication that facilitate breakdown. The weight loss and amount of TPA yield increased to 88% and 64.3% respectively in ozone pretreatment followed by ultrasound assisted chemical hydrolysis. This implies the oxidation of PET by ozone enhanced chemical hydrolysis in all cases.

Combination of ultrasound energy during chemical hydrolysis and ozone pretreated PET increased the monomer and dimer recovery compared to ultrasound aided chemical hydrolysis with no ozone pretreatment untreated PET. The monomer recovery in HPLC increases from 6.03% to 9.38% when ozone pretreatment is applied. The total recovery for virgin PET and ozone pretreated PET film after the ultrasound assisted hydrolysis was 52.07% and 73.68% respectively including TPA precipitation using H_2SO_4. Table 4.1 summarizes the HPLC recovery of monomers and dimers from chemical hydrolysis.

Table 4.1: Weight loss and HPLC analysis of monomers and dimers on pretreatment and chemical hydrolysis of PET.

Chemical hydrolysis process	% TP A	% BHET	% MHET	% EG	% HPLC	% Weight of washed filtrate after neutralization	% Total Recovery	% Weight Loss
No pretreatments	0	4.4	0.43	1.13	5.7	25.69	31.38	40
Ultrasound assisted	0	3.59	1.48	0.63	6.03	46.33	52.07	64.45
Ozone pretreated during chemical hydrolysis	0	5.96	2.09	0.97	9.38	64.3	73.68	87.68

4.4 Experimental design for the rigorous optimization of chemical hydrolysis of PET

The aim of performing this optimization process is to get the higher yield of monomers from PET hydrolysis by optimizing the main factors in alkaline hydrolysis of PET which are Temperature, time and NaOH concentration. The range of these three parameters studied are given in Table 3.1. These ranges were chosen based on literature review and our own set of preliminary experiments. A set of 20 experiments based on CCD were carried out for the optimization.

The full factorial rotatable central composite design (CCD) with three factors in five levels, as well as the results of PET conversion percentage TPA yield, are presented in Table 4.2.

Table 4.2: Design and results of central composite.

Run	Block	Temperature (°C)	NaOH con (%)	Time (hr.)	Weight loss (%)	TPA (%)
		Design and experimental values of central composite				
1	1	36.00	7.00	1.60	49.5	33.06
2	1	54.00	13.00	1.60	100.0	43.23
3	1	54.00	7.00	3.40	100.0	80.00
4	1	36.00	13.00	3.40	100.0	26.32
5	1	45.00	10.00	2.50	100.0	66.31
6	1	45.00	10.00	2.50	100.0	70.26
7	2	54.00	7.00	1.60	97.0	72.60
8	2	36.00	13.00	1.60	95.7	23.79
9	2	36.00	7.00	3.40	100.0	76.57
10	2	54.00	13.00	3.40	100.0	43.00
11	2	45.00	10.00	2.50	100.0	79.37
12	2	45.00	10.00	2.50	100.0	76.00
13	3	30.00	10.00	2.50	59.0	44.10
14	3	60.00	10.00	2.50	100.0	79.75
15	3	45.00	5.00	2.50	52.8	37.28
16	3	45.00	15.00	2.50	100.0	25.64
17	3	45.00	10.00	1.00	88.3	50.00
18	3	45.00	10.00	4.00	100.0	78.80
19	3	45.00	10.00	2.50	100.0	79.98
20	3	45.00	10.00	2.50	100.0	72.00

4.4.1 Optimization of Influencing Factors

The objective of the optimization is to get the best value for variables from a model obtained via experimental design and analysis. The numerical optimization of the model was carried out with the help of the software Minitab, considering each value of response (weight loss and TPA yield). The empirical quadratic model of the ANOVA indicates that the model is highly significant, as the *p*-value of the model is less than 0.05, and the R^2 values for the conversion of PET and TPA yield are 0.89 and 0.93 respectively. This suggests that most of the variations are explained by the model. In the present study, the independent variables of the quadratic model including the first order X_1, X_2 and X_3, the second order X_2^2 are highly significant because p-value is less than 0.05, but the other interactions are insignificant at p-value greater than 0.05

An approximate regression model of the weight loss and TPA yield based on the experimental results was evaluated and expressed by the following quadratic equations.

$$Y_1 = -401.4 + 10.18X_1 + 30.42X_2 + 60.0X_3 - 0.661X_2^2 \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$Y_2 = -399.9 + 7.71X_1 + 37.28X_2 + 77.0X_3 - 1.703X_2^2 \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where, Y_1 represents response variable Weight loss (%) and Y_2 represents TPA yield (%) X_1, X_2 X_3 are depolymerization temperature, NaOH amount and depolymerization time.

Table 4.3 and table 4.4 shows the statistical testing of the model performed by the ANOVA.

Table 4.3: Results of analysis of variance of weight loss.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	11	4813.29	437.57	6.17	0.008
X_1	1	1057.85	1057.85	14.91	0.005
X_2	1	1196.14	1196.14	16.86	0.003
X_3	1	443.70	443.70	6.25	0.037
X_1^2	1	334.47	334.47	4.71	0.062
X_2^2	1	506.84	506.84	7.14	0.028
X_3^2	1	2.81	2.81	0.04	0.847
X_1*X_2	1	233.39	233.39	3.29	0.107
X_1*X_3	1	335.53	335.53	4.73	0.061
X_2*X_3	1	302.70	302.70	4.27	0.073
Error	8	567.57	70.95		
Lack-of-Fit	5	567.57	113.51	*	*
Pure Error	3	0.00	0.00		
Total	19	5380.86			
R^2		0.894			p-value

Table 4.4: Results of analysis of variance of TPA yield.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	11	8053.23	732.11	10.71	0.001
X_1	1	1415.00	1415.00	20.71	0.002
X_2	1	1573.57	1573.57	23.03	0.001
X_3	1	756.33	756.33	11.07	0.010
X_1^2	1	272.84	272.84	3.99	0.081
X_2^2	1	3368.02	3368.02	49.28	0.000
X_3^2	1	171.36	171.36	2.51	0.152
X_1*X_2	1	5.78	5.78	0.08	0.779
X_1*X_3	1	188.37	188.37	2.76	0.135
X_2*X_3	1	294.76	294.76	4.31	0.071
Error	8	546.70	68.34		
Lack-of-Fit	5	500.98	100.20	6.57	0.076
Pure Error	3	45.72	15.24		
Total	19	8599.94			
R^2		0.93			p-value

4.4.2 Response Surface Analysis

Three-dimensional (3D) surfaces are a graphical representation of a regression equation for optimizing reaction conditions, and they are the most useful method for revealing reaction system conditions. The interaction effects of depolymerization temperature, NaOH amount and time on the TPA yield are illustrated in Fig 4.1 which clearly illustrates the interaction effects of depolymerization temperature, NaOH amount and time, respectively.
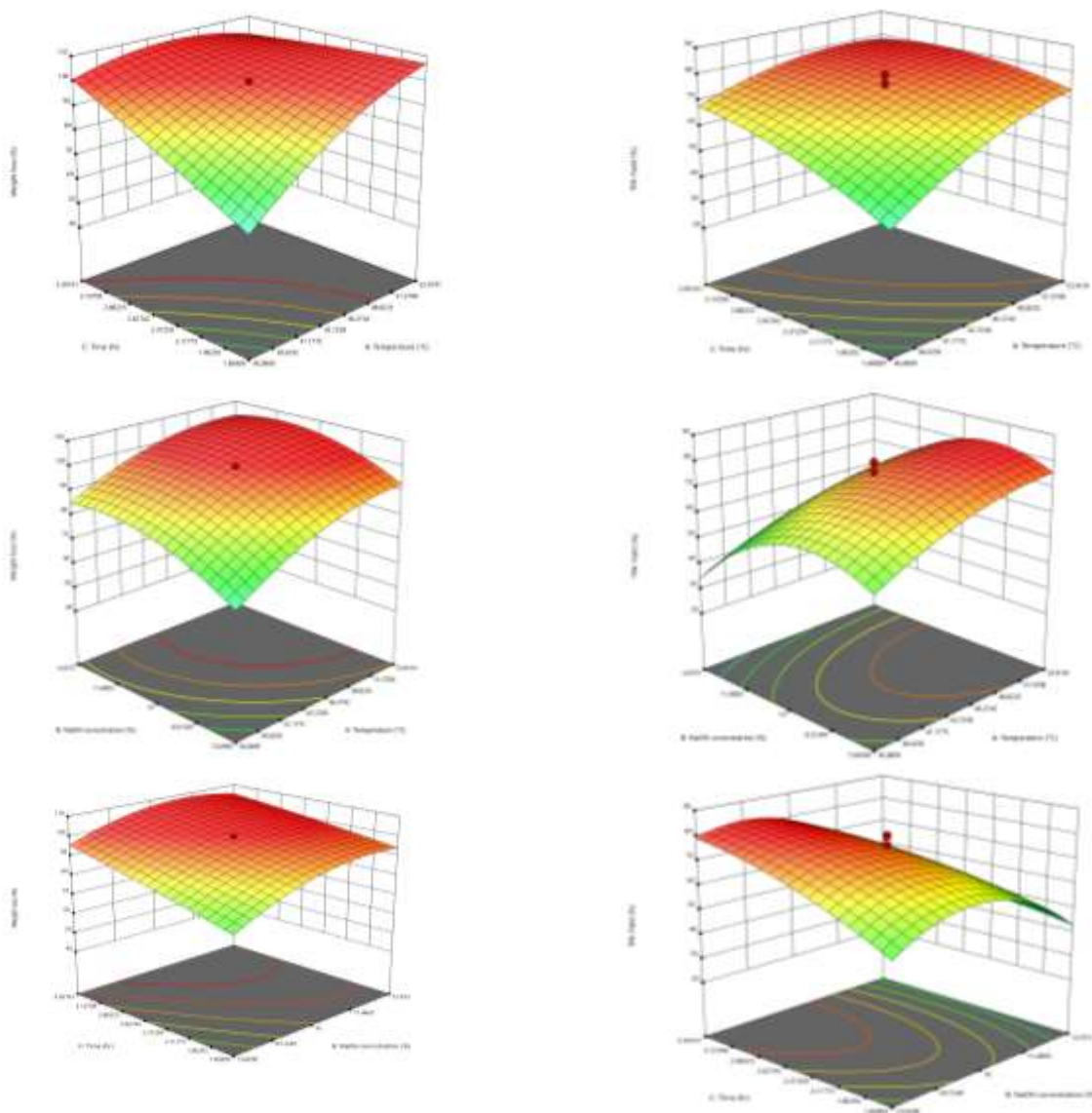

Figure 4.3: Graphical illustration interactions between the various factors for weight loss (left) and TPA yield (right).

It is observed that the weight loss (graphs on the left-hand side) increases with an increase in all the depolymerization factors. However, the TPA yield (graphs on the right-hand side) is highly affected by the NaOH concentration and the interaction of the NaOH amount with the other two factors. The yield increases with time and temperature at a fixed value of NaOH amount. As NaOH concentration decreases, the TPA yield also decreases due to very low concentration of NaOH sufficient nuclei might not have formed to generate intense cavitation. The TPA yield also decreases when the NaOH concentration is above 10%. This can be explained by the fact that strong alkalis like NaOH may not only hydrolyze esters, but also, they may serve as catalyst to esterification reaction at higher concentrations (Paliwal & Mungray, 2013). Thus, the cause of reduction in TA yield at 15% NaOH may be because of shifting of reaction towards ester formation. Many studies confirm that optimum concentration for NaOH is 10% (w/w) since if the concentration is lower or higher, the yield of TPA decreases. However, our result shows that the maximum amount of TPA generation is between the range of (7-10) % which makes the process more energy efficient by reducing the amount of salt generated when a higher amount of NaOH is used and hence the process economically feasible.

Optimization of the responses for determining optimized points for operational conditions and achieving the maximum weight loss and TPA yield percentage was performed by estimation model 3 and 4. Table 4.5 shows the best conditions for maximum weight loss and TPA yield, as well as the predicted values for each response.

Table 4.5: Predicted values of weight loss and TPA yield.

Solution	Temperature (°C)	NaOH con. (%)	Hydrolysis Time(hr.)	Weight loss (%) Fit	TPA Yield (%) Fit
1	57.8788	8.53535	2.90909	100.000	82.4483

Considering the product performance and the limitations of practical operation, the above conditions were rounded off to a depolymerization temperature of 60°C, 8.5% NaOH and depolymerization time of 3 hours.

4.4.4 Validation of the optimization results

Using the optimum conditions obtained, the experiments were performed in triplicate to confirm the model adequacy for predicting the maximum yield of TPA that can be recovered. The average yield of TPA was 83.58 % which is slightly more than the predicted value 82.4%, The good agreement between the predictive results and experimental results verified the validity of an optimal point indicating that the strategy to optimize the depolymerization conditions of PET and to obtain the maximal TPA yield with RSM is feasible.

However, the difference of the weight loss and the recovery of the TPA is about 16.42%. HPLC analysis was employed to quantify the rest of the liquid components and we observed BHET (6.04%), MHET (1.8%), and EG (0.72%), the total HPLC recovery was 8.56% and the total recovery of the monomer and dimers was 92.14% including TPA precipitated using acid. The difference of the weight loss (100%) between total recovery of the hydrolysis (92.14%) is 7.86%. The difference in the recovery might be attributed to the PET oligomers which result from the partially hydrolyzed products of the hydrolysis process and are neither converted to monomer or dimers. As the oligomers are in solution (not solid phase), it was decided to try and break these

down to its monomers using enzymatic hydrolysis. Earlier enzyme-based experiments had indicated that enzyme-based hydrolysis was limited by the sloid nature of the Pet films.

4.5 Enzymatic hydrolysis of partially hydrolyzed products

As mentioned earlier, in addition to BHET and MHET, there was a formation of partially hydrolyzed products from the hydrolysis process. In order to convert PET oligomers to monomers or dimers enzymatic hydrolysis was carried out.

The enzymatic reaction involved PET liquid phase oligomers along with BHET, MHET, and EG and the reaction product was analyzed using HPLC. Although Quartinello et al., (2017) reported that there is a possibility of converting PET oligomers to TPA, our HPLC analysis did not find any peaks for the TPA after carrying out enzymatic hydrolysis for three hours. However, the total HPLC recovery increases from 8.56% to 13.72%, BHET increases from 6.04% to 13.72% and MHET from 1.8% to 2.2 %. This suggests that there was a better of conversion of short chain polymers to BHET and slow conversion of BHET to MHET. Carniel et al., (2016) observed similar fast conversion of PET to BHET. However, the conversion of BHET to MHET, and subsequently to TPA was slow using HiC enzyme. The total recovery of the monomers and dimers, including TPA precipitate increases from 92.14 to 97.3 % due to the further enzymatic hydrolysis.

Table 4.6: Overall material balance for PET hydrolysis

	Reactant			Products (monomer and dimers)				
Material	NaOH (pellets)	H_2SO_4	TPA	EG		MHET	BHET	Byproduct Na_2SO_4
Theoretical yield based on 100% conversion	gr/0.1932gr PET	1.7	0.5	0.167	0.06		-	-	2.166
Experimental yield chemical hydrolysis				0.1615	0.0014	0.0035	0.012	
Chemical + enzymatic hydrolysis				0.1615	0.00197	0.0038	0.02	

4.6 Characterization of Terephthalic Acid (TPA) precipitate obtained on precipitation of chemical hydrolysates

After chemical hydrolysis of PET films, the weight loss was calculated based on the difference of weight of the original film and the remaining film. The solution obtained was then separated and neutralized using 0.5M H_2SO_4 acid solution. In our previous discussions we have assumed that the precipitate obtained were all TPA. In order to confirm this FTIR analysis were carried out. FT-IR spectra of TPA recovered by precipitation and standard TPA showed the similarities of the functional groups in Figure 4.3. It directly demonstrates a high level of correlations of FTIR spectra for both samples. The characteristics peaks of the functional group, 1278 cm^{-1} due to C–O stretching, the peak at C=C aromatic stretch at around 1573cm^{-1}, and the strong absorption peak at 1674 cm^{-1} was due to C=O stretching; it strongly indicated that the terephthalic acid recovered after PET hydrolysis was pure.
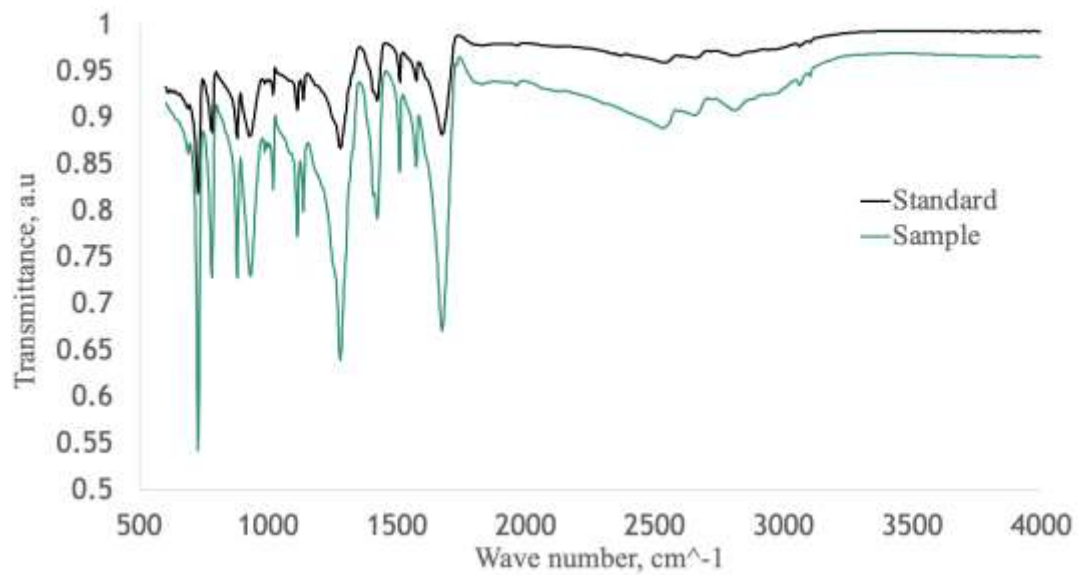
Figure 4.4: FT-IR spectra of recovered TPA from hydrolyzed PET film and standard TPA.

CHAPTER 5: Conclusion &Recommendations for future work

5.1 Conclusions

Chemical depolymerization of untreated PET film using 2.5 M NaOH solution after 1 hour gave 40% WL. This result agrees with Bhogle and Pandit, (2018), who reported 42% WL of PET in non-aqueous alkaline hydrolysis. The total recovery from the conversion is 31.38% including 5.7% from HPLC recovery and 25.69 % monomers (from precipitated TPA after acid neutralization). WL increased to 64.45% when ultrasound energy is incorporated during chemical hydrolysis and the total recovery of the monomers increased to 52.07% including TPA precipitation. The weight loss and total monomer recovery was further increased to 88% and 73.68% respectively when ozone pretreatments were incorporated with ultrasound-assisted during chemical hydrolysis. This result agrees with experiments carried out in our lab by Mahal, (2020) who reported the WL is increased from 60% to 80 % when ozone is incorporated with Ultrasound-assisted chemical hydrolysis. This result again proved that ultrasound and ozone pretreatments increased the functional groups, and weakened the bonds of the PET films, thus increasing the hydrolysis.

In increase PET conversion and obtain higher monomer recovery while carrying out the reaction under mild conditions, the influencing factors (temperature, NaOH amount and time) of the depolymerization process were rigorously optimized using RSM. It was found out that the weight loss was increased as all operational parameters are increased. In the present study, the RSM was successfully employed to find out the significance of factors at different levels during PET depolymerization process. The optimal values of process parameters were as follows: 58°C, 2.9 hours reaction time, and 8.5% (w/w) of NaOH. Under these conditions, the predicted results included a weight loss of 100%, and a TPA yield of 82.4%. The hydrolysis condition values by optimization were validated by experiments and an average yield of 83.6 % was obtained for the

TPA after an acid neutralization. The yield is slightly higher than the predicted value and confirms the validity of the model. However, the remaining 16.4% that was not converted to TPA remains and needed to be explored further.

The HPLC analysis of the filtrate monomer was found to be 8.56% and it consists of 6.04% BHET, 1.8% MHET, and 0.72% EG. The total recovery was 92.14% including 83.6% TPA precipitation. The other 8.54% was assumed to be short chain polyolefins which were dissolved in the solution. In order to convert this short chain polymer and dimers /monomer, the solutions were enzymatic hydrolyzed by incubation for 3 hours with a temperature of 60°C and pH of 8 using 15mg/ml of Humicola insolens cutinase (HiC). The solutions were analyzed and HPLC recovery increases from 8.56% to 13.72% (difference of 5.16%), BHET increases from 6.04% to 13.72% and MHET from 1.8% to 2.2 %. This suggests that there was a better of conversion of short chain polymers to BHET and also, a slow conversion of BHET to MHET. The total conversion of the monomers from chemical and enzymatic hydrolysis process was 97.3%. Considering the scale and potential variability of the samples, this high level of breakdown is considered sufficient for the breakdown and re-use of PET.

5.2 Recommendations for future work

In order to implement efficient and green route for PET degradation, more works need to focus on improving the chemoenzymatic hydrolysis process using one pot reaction. Using a combination of enzyme like HiC and *Lipase from Candida antarctica (*CALB) to convert all the dimers and short chain into TPA. Besides, recovering the monomer further studies are required for the separation of the monomers obtained after hydrolysis and remaking PET using the recovered monomers in order to a circular economy.

References

Achilias, D. S., & Karayannidis, G. P. (2004). The Chemical Recycling of PET in the Framework of Sustainable Development. *Water, Air and Soil Pollution: Focus, 4*(4), 385-396. doi:10.1023/B:WAFO.0000044812.47185.0f

Agenda, I. (2016). *The New Plastics Economy Rethinking the future of plastics.* Paper presented at the World Economic Forum.

Aguado, A., Martínez, L., Becerra, L., Arieta-araunabeña, M., Arnaiz, S., Asueta, A., & Robertson, I. (2014). Chemical depolymerisation of PET complex waste: hydrolysis vs. glycolysis. *Journal of Material Cycles and Waste Management, 16*(2), 201-210. doi:10.1007/s10163-013-0177-y

Al-Sabagh, A., Yehia, F., Eshaq, G., Rabie, A., & ElMetwally, A. (2016). Greener routes for recycling of polyethylene terephthalate. *Egyptian Journal of Petroleum, 25*(1), 53-64.

Al-Sabagh, A. M., Yehia, F. Z., Eissa, A.-M. M. F., Moustafa, M. E., Eshaq, G., Rabie, A.-R. M., & ElMetwally, A. E. (2014). Glycolysis of Poly(ethylene terephthalate) Catalyzed by the Lewis Base Ionic Liquid [Bmim][OAc]. *Industrial & Engineering Chemistry Research, 53*(48), 18443-18451. doi:10.1021/ie503677w

Alvarado Chacon, F., Brouwer, M. T., & Thoden van Velzen, E. U. (2020). Effect of recycled content and rPET quality on the properties of PET bottles, part I: Optical and mechanical properties. *Packaging Technology and Science, 33*(9), 347-357.

Badia, J., Vilaplana, F., Karlsson, S., & Ribes-Greus, A. (2009). Thermal analysis as a quality tool for assessing the influence of thermo-mechanical degradation on recycled poly (ethylene terephthalate). *Polymer Testing, 28*(2), 169-175.

Barnard, E., Arias, J. J. R., & Thielemans, W. (2021). Chemolytic depolymerisation of PET: a review. *Green Chemistry, 23*(11), 3765-3789.

Bartolome, L., Imran, M., Cho, B. G., Al-Masry, W. A., & Kim, D. H. (2012). Recent developments in the chemical recycling of PET. *Material recycling-trends and perspectives, 406*, 576-596.

Beaumont, N. J., Aanesen, M., Austen, M. C., Börger, T., Clark, J. R., Cole, M., . . . Wyles, K. J. (2019). Global ecological, social and economic impacts of marine plastic. *Marine pollution bulletin, 142*, 189-195.

Bhogle, C. S., & Pandit, A. B. (2018). Ultrasound-assisted alkaline hydrolysis of waste poly (ethylene terephthalate) in aqueous and non-aqueous media at low temperature. *Indian Chemical Engineer, 60*(2), 122-140.

Bhuvaneswari. G, H. (2018). 3 - Degradability of Polymers. In S. Thomas, A. V. Rane, K. Kanny, A. V.K, & M. G. Thomas (Eds.), *Recycling of Polyurethane Foams* (pp. 29-44): William Andrew Publishing.

BPF. (2022). Chemical Recycling 101. *British Plastic Federation*.

Cefic. (2022). Chemical Recycling: Making Plastics Circular. *The European Chemical Industry Council*.

CEFIC_Quantis. (2020). Chemical Recycling: Greenhouse gas emission reduction potential of an emerging waste management route. *The European Chemical Industry Council*, 1-24.

CELC. (2019). A CIRCULAR ECONOMY FOR PLASTICS IN CANADA A bold vision for less waste and more value *Circular Economy Leadership Coalition*, 1-14.

Chen, W., Yang, Y., Lan, X., Zhang, B., Zhang, X., & Mu, T. (2021). Biomass-derived γ-valerolactone: efficient dissolution and accelerated alkaline hydrolysis of polyethylene terephthalate. *Green Chemistry, 23*(11), 4065-4073. doi:10.1039/D1GC00665G

Crippa, M., & Morico, B. (2020). PET depolymerization: a novel process for plastic waste chemical recycling *Studies in Surface Science and Catalysis* (Vol. 179, pp. 215-229): Elsevier.

Daraboina, N., & Madras, G. (2009). Kinetics of the ultrasonic degradation of poly (alkyl methacrylates). *Ultrasonics Sonochemistry, 16*(2), 273-279. doi:https://doi.org/10.1016/j.ultsonch.2008.08.007

Endo, T., Reddy, L., Nishikawa, H., Kaneko, S., Nakamura, Y., & Endo, K. (2017). Composite engineering–direct bonding of plastic PET films by plasma irradiation. *Procedia Engineering, 171*, 88-103.

Eriksen, M. K., Christiansen, J., Daugaard, A. E., & Astrup, T. F. (2019). Closing the loop for PET, PE and PP waste from households: Influence of material properties and product design for plastic recycling. *Waste management, 96*, 75-85.

Esmaeili, A., Pourbabaee, A. A., Alikhani, H. A., Shabani, F., & Esmaeili, E. (2013). Biodegradation of low-density polyethylene (LDPE) by mixed culture of Lysinibacillus xylanilyticus and Aspergillus niger in soil. *Plos one, 8*(9), e71720.

Ferreira, L., Evangelista, M. B., Martins, M. C. L., Granja, P. L., Esteves, J. L., & Barbosa, M. A. (2005). Improving the adhesion of poly(ethylene terephthalate) fibers to poly(hydroxyethyl methacrylate) hydrogels by ozone treatment: Surface characterization and pull-out tests. *Polymer, 46*(23), 9840-9850. doi:https://doi.org/10.1016/j.polymer.2005.08.033

Furukawa, M., Kawakami, N., Tomizawa, A., & Miyamoto, K. (2019). Efficient degradation of poly (ethylene terephthalate) with Thermobifida fusca cutinase exhibiting improved catalytic activity generated using mutagenesis and additive-based approaches. *Scientific reports, 9*(1), 1-9.

Ghosal, K., & Nayak, C. (2022). Recent Advances in Chemical Recycling of Polyethylene Terephthalate Waste into Value Added Products for Sustainable Coating Solutions- Hope Vs Hype. *Materials Advances*. doi:10.1039/D1MA01112J

Ghoshal, G. (2019). 2 - Recent Development in Beverage Packaging Material and its Adaptation Strategy. In A. M. Grumezescu & A. M. Holban (Eds.), *Trends in Beverage Packaging* (pp. 21-50): Academic Press.

Grigore, M. E. (2017). Methods of recycling, properties and applications of recycled thermoplastic polymers. *Recycling, 2*(4), 24.

Gu, H., Wu, J., & Doan, H. (2009). Hydrophilicity Enhancement of High-Density Polyethylene Film by Ozonation. *Chemical Engineering & Technology, 32*(5), 726-731. doi:https://doi.org/10.1002/ceat.200800433

Gupta, P., & Bhandari, S. (2019). 6 - Chemical Depolymerization of PET Bottles via Ammonolysis and Aminolysis. In S. Thomas, A. Rane, K. Kanny, A. V.K, & M. G. Thomas (Eds.), *Recycling of Polyethylene Terephthalate Bottles* (pp. 109-134): William Andrew Publishing.

Hopewell, J., Dvorak, R., & Kosior, E. (2009). Plastics recycling: challenges and opportunities. *Philosophical Transactions of the Royal Society B: Biological Sciences, 364*(1526), 2115-2126.

Hu, H., Wu, Y., & Zhu, Z. (2018). Optimization of microwave-assisted preparation of TPA from waste PET using response surface methodology. *Journal of Polymers and the Environment, 26*(1), 375-382.

Hu, L.-C., Oku, A., Yamada, E., & Tomari, K. (1997). Alkali-Decomposition of Poly(ethylene terephthalate) in Mixed Media of Nonaqueous Alcohol and Ether. Study on Recycling of Poly(ethylene terephthalate). *Polymer Journal, 29*(9), 708-712. doi:10.1295/polymj.29.708

Ikenaga, K., Inoue, T., & Kusakabe, K. (2016). Hydrolysis of PET by combining direct microwave heating with high pressure. *Procedia Engineering, 148*, 314-318.

Johansen, M. R., Christensen, T. B., Ramos, T. M., & Syberg, K. (2022). A review of the plastic value chain from a circular economy perspective. *Journal of Environmental Management, 302*, 113975.

Joutey, N. T., Bahafid, W., Sayel, H., & El Ghachtouli, N. (2013). Biodegradation: involved microorganisms and genetically engineered microorganisms. *Biodegradation-life of science, 1*, 289-320.

Kamaruzamal, N. S. A. (2014). *Development of Solvent-Based Recycling Technique for Polyethylene Terephthalate from Waste Plastic*: UNIVERSITI TEKNOLOGI PETRONAS.

Kawai, F., Kawabata, T., & Oda, M. (2019). Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields. *Applied Microbiology and Biotechnology, 103*(11), 4253-4268. doi:10.1007/s00253-019-09717-y

Kim, H. T., Hee Ryu, M., Jung, Y. J., Lim, S., Song, H. M., Park, J., . . . Sung, B. H. (2021). Chemo-Biological Upcycling of Poly (ethylene terephthalate) to Multifunctional Coating Materials. *ChemSusChem, 14*(19), 4251-4259.

Koshti, R., Mehta, L., & Samarth, N. (2018). Biological recycling of polyethylene terephthalate: a mini-review. *Journal of Polymers and the Environment, 26*(8), 3520-3529.

Lee, A., & Liew, M. S. (2021). Tertiary recycling of plastics waste: an analysis of feedstock, chemical and biological degradation methods. *Journal of Material Cycles and Waste Management, 23*(1), 32-43. doi:10.1007/s10163-020-01106-2

Lintsen, H. W., Hollestelle, M. J., & Hölsgens, H. (2017). *The plastics revolution: how the Netherlands became a global player in plastics*: Foundation for the History of Technology.

Loop industries. (2017). Polyethyelen Terephthalate Depolymerization *Innovation sciences, et*.

López-Fonseca, R., González-Velasco, J. R., & Gutiérrez-Ortiz, J. I. (2009). A shrinking core model for the alkaline hydrolysis of PET assisted by tributylhexadecylphosphonium bromide. *Chemical Engineering Journal, 146*(2), 287-294. doi:https://doi.org/10.1016/j.cej.2008.09.039

Lopez, G., Artetxe, M., Amutio, M., Alvarez, J., Bilbao, J., & Olazar, M. (2018). Recent advances in the gasification of waste plastics. A critical overview. *Renewable and Sustainable Energy Reviews, 82*, 576-596. doi:https://doi.org/10.1016/j.rser.2017.09.032

Mahal, Z. (2021). *Enhanced hydrolysis of polyethylene terephthalate (PET) plastics by ozone and ultrasound pretreatment.*

Mancini, S. D., & Zanin, M. (2007). Post Consumer Pet Depolymerization by Acid Hydrolysis. *Polymer-Plastics Technology and Engineering, 46*(2), 135-144. doi:10.1080/03602550601152945

Maurya, A., Bhattacharya, A., & Khare, S. K. (2020). Enzymatic Remediation of Polyethylene Terephthalate (PET)–Based Polymers for Effective Management of Plastic Wastes: An Overview. *Frontiers in Bioengineering and Biotechnology, 8*. doi:10.3389/fbioe.2020.602325

Miandad, R., Rehan, M., Barakat, M. A., Aburiazaiza, A. S., Khan, H., Ismail, I. M. I., . . . Nizami, A.-S. (2019). Catalytic Pyrolysis of Plastic Waste: Moving Toward Pyrolysis Based Biorefineries. *Frontiers in Energy Research, 7*. doi:10.3389/fenrg.2019.00027

Miao, Y., von Jouanne, A., & Yokochi, A. (2021). Current Technologies in Depolymerization Process and the Road Ahead. *Polymers, 13*(3), 449.

Mohod, A. V., & Gogate, P. R. (2011). Ultrasonic degradation of polymers: Effect of operating parameters and intensification using additives for carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA). *Ultrasonics Sonochemistry, 18*(3), 727-734. doi:https://doi.org/10.1016/j.ultsonch.2010.11.002

Nam, K., & Kukor, J. J. (2000). Combined ozonation and biodegradation for remediationof mixtures of polycyclic aromatic hydrocarbons in soil. *Biodegradation, 11*(1), 1-9. doi:10.1023/A:1026592324693

Okitsu, K., Nanzai, B., Kawasaki, K., Takenaka, N., & Bandow, H. (2009). Sonochemical decomposition of organic acids in aqueous solution: Understanding of molecular behavior during cavitation by the analysis of a heterogeneous reaction kinetics model. *Ultrasonics Sonochemistry, 16*(1), 155-162. doi:https://doi.org/10.1016/j.ultsonch.2008.06.006

Oku, A., Hu, L. C., & Yamada, E. (1997). Alkali decomposition of poly (ethylene terephthalate) with sodium hydroxide in nonaqueous ethylene glycol: a study on recycling of terephthalic acid and ethylene glycol. *Journal of Applied Polymer Science, 63*(5), 595-601.

Paliwal, N. R., & Mungray, A. K. (2013). Ultrasound assisted alkaline hydrolysis of poly(ethylene terephthalate) in presence of phase transfer catalyst. *Polymer degradation and stability, 98*(10), 2094-2101. doi:https://doi.org/10.1016/j.polymdegradstab.2013.06.030

Park, S. H., & Kim, S. H. (2014). Poly (ethylene terephthalate) recycling for high value added textiles. *Fashion and Textiles, 1*(1), 1. doi:10.1186/s40691-014-0001-x

Patel, D. P. (2008). *An Investigation Into Surface Modificatin Of Polyethylene Film By Ozonation.* Ryerson University. Retrieved from https://rshare.library.ryerson.ca/articles/thesis/An_Investigation_Into_Surface_Modificati n_Of_Polyethylene_Film_By_Ozonation/14655726

Petigny, J., Ménigault, C., Luisce, T., Harscoët, E., David, A., Mitsios, A., . . . Lysenko, D. (2019). Economic study of the canadian plastic industry, markets and waste. *Environment and Climate Change Canada. En4–366/1–2019E-PDF*.

PETRA. (2022). PET – WHAT IS IT AND WHERE DOES IT COME FROM? *PET Resin Association*, 1-4.

Pingale, N. D., Palekar, V. S., & Shukla, S. R. (2010). Glycolysis of postconsumer polyethylene terephthalate waste. *Journal of Applied Polymer Science, 115*(1), 249-254. doi:https://doi.org/10.1002/app.31092

Poulakis, J. G., & Papaspyrides, C. D. (2001). Dissolution/reprecipitation: A model process for PET bottle recycling. *Journal of Applied Polymer Science, 81*(1), 91-95. doi:https://doi.org/10.1002/app.1417

Pudack, C., Stepanski, M., & Fässler, P. (2020). PET Recycling – Contributions of Crystallization to Sustainability. *Chemie Ingenieur Technik, 92*(4), 452-458. doi:https://doi.org/10.1002/cite.201900085

Quartinello, F., Vajnhandl, S., Volmajer Valh, J., Farmer, T. J., Vončina, B., Lobnik, A., . . . Guebitz, G. M. (2017). Synergistic chemo-enzymatic hydrolysis of poly (ethylene terephthalate) from textile waste. *Microbial biotechnology, 10*(6), 1376-1383.

Ragaert, K., Delva, L., & Van Geem, K. (2017). Mechanical and chemical recycling of solid plastic waste. *Waste management, 69*, 24-58.

Raheem, A. B., Noor, Z. Z., Hassan, A., Abd Hamid, M. K., Samsudin, S. A., & Sabeen, A. H. (2019). Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review. *Journal of cleaner production, 225*, 1052-1064.

Rahman, M., & East, G. C. (2009). Titanium Dioxide Particle-induced Alkaline Degradation of Poly(ethylene Terephthalate): Application to Medical Textiles. *Textile Research Journal, 79*(8), 728-736. doi:10.1177/0040517507081916

Schyns, Z. O., & Shaver, M. P. (2021). Mechanical recycling of packaging plastics: A review. *Macromolecular rapid communications, 42*(3), 2000415.

Shojaei, B., Abtahi, M., & Najafi, M. (2020). Chemical recycling of PET: A stepping-stone toward sustainability. *Polymers for Advanced Technologies, 31*(12), 2912-2938. doi:https://doi.org/10.1002/pat.5023

Shukla, S. R., & Mathur, M. R. (2000). Action of alkali on polybutylene terephthalate and polyethylene terephthalate polyesters. *Journal of Applied Polymer Science, 75*(9), 1097-1102. doi:https://doi.org/10.1002/(SICI)1097-4628(20000228)75:9<1097::AID-APP2>3.0.CO;2-7

Singh, S., Sharma, S., Umar, A., Mehta, S. K., Bhatti, M. S., & Kansal, S. K. (2018). Recycling of waste poly (ethylene terephthalate) bottles by alkaline hydrolysis and recovery of pure

nanospindle-shaped terephthalic acid. *Journal of nanoscience and nanotechnology, 18*(8), 5804-5809.

Sinha, V., Patel, M. R., & Patel, J. V. (2010). Pet Waste Management by Chemical Recycling: A Review. *Journal of Polymers and the Environment, 18*(1), 8-25. doi:10.1007/s10924-008-0106-7

SMITHERS. (2020). The Future of PET Packaging to 2025. *ASMITHERS INNOVATE WITH CONFIDENCE*, 1-4.

Spinacé, M. A. S., & De Paoli, M. A. (2001). Characterization of poly(ethylene terephtalate) after multiple processing cycles. *Journal of Applied Polymer Science, 80*(1), 20-25. doi:https://doi.org/10.1002/1097-4628(20010404)80:1<20::AID-APP1069>3.0.CO;2-S

Stanica-Ezeanu, D., & Matei, D. (2021). Natural depolymerization of waste poly(ethylene terephthalate) by neutral hydrolysis in marine water. *Scientific reports, 11*(1), 4431. doi:10.1038/s41598-021-83659-2

Štrukil, V. (2021). Highly Efficient Solid-State Hydrolysis of Waste Polyethylene Terephthalate by Mechanochemical Milling and Vapor-Assisted Aging. *ChemSusChem, 14*(1), 330-338. doi:https://doi.org/10.1002/cssc.202002124

Tatyana, P., Chairez, I., & Poznyak, A. (2019). Ozonation as main method for organic contaminants degradation in three different phases: liquid, solid, and gaseous (pp. 3-23).

Thachnatharen, N., Shahabuddin, S., & Sridewi, N. (2021). *The waste management of polyethylene terephthalate (PET) plastic waste: A review.* Paper presented at the IOP Conference Series: Materials Science and Engineering.

Thoden van Velzen, E. U., Brouwer, M. T., Stärker, C., & Welle, F. (2020). Effect of recycled content and rPET quality on the properties of PET bottles, part II: Migration. *Packaging Technology and Science, 33*(9), 359-371.

Tian, L., Kolvenbach, B., Corvini, N., Wang, S., Tavanaie, N., Wang, L., . . . Ji, R. (2017). Mineralisation of 14C-labelled polystyrene plastics by Penicillium variabile after ozonation pre-treatment. *New Biotechnology, 38*, 101-105. doi:https://doi.org/10.1016/j.nbt.2016.07.008

Tiso, T., Narancic, T., Wei, R., Pollet, E., Beagan, N., Schröder, K., . . . Wierckx, N. (2021). Towards bio-upcycling of polyethylene terephthalate. *Metabolic engineering, 66*, 167-178.

Troev, K., Grancharov, G., Tsevi, R., & Gitsov, I. (2003). A novel catalyst for the glycolysis of poly(ethylene terephthalate). *Journal of Applied Polymer Science, 90*(4), 1148-1152. doi:https://doi.org/10.1002/app.12711

Ügdüler, S., Van Geem, K. M., Denolf, R., Roosen, M., Mys, N., Ragaert, K., & De Meester, S. (2020). Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis. *Green Chemistry, 22*(16), 5376-5394. doi:10.1039/D0GC00894J

Vikulina, V., & Vikulin, P. (2018). The effect of ultrasound on the process of water softening. *MATEC Web Conf., 251*, 03003.

Vollmer, I., Jenks, M. J., Roelands, M. C., White, R. J., van Harmelen, T., de Wild, P., . . . Weckhuysen, B. M. (2020). Beyond mechanical recycling: Giving new life to plastic waste. *Angewandte Chemie International Edition, 59*(36), 15402-15423.

Walker, T. R., McGuinty, E., Charlebois, S., & Music, J. (2021). Single-use plastic packaging in the Canadian food industry: consumer behavior and perceptions. *Humanities and Social Sciences Communications, 8*(1), 80. doi:10.1057/s41599-021-00747-4

Webb, H. K., Arnott, J., Crawford, R. J., & Ivanova, E. P. (2012). Plastic degradation and its environmental implications with special reference to poly (ethylene terephthalate). *Polymers, 5*(1), 1-18.

Wei, R., & Zimmermann, W. (2017). Biocatalysis as a green route for recycling the recalcitrant plastic polyethylene terephthalate. *Microbial biotechnology, 10*(6), 1302-1307. doi:10.1111/1751-7915.12714

Welle, F. (2017). The Facts about PET. 1-5.

Wu, B., Majumdar, R. D., Lysak, D. H., Ghosh Biswas, R., Tabatabaei-Anaraki, M., Jenne, A., . . . Simpson, A. J. (2021). Towards real-time kinetic monitoring of wastewater treatment: A case study of sunlight and ozone treatment of unconcentrated wastewater using flow NMR. *Chemical Engineering Journal, 405*, 126696. doi:https://doi.org/10.1016/j.cej.2020.126696

Yoshioka, T., Motoki, T., & Okuwaki, A. (2001). Kinetics of Hydrolysis of Poly(ethylene terephthalate) Powder in Sulfuric Acid by a Modified Shrinking-Core Model. *Industrial & Engineering Chemistry Research, 40*(1), 75-79. doi:10.1021/ie000592u

Young, R. (2019). Canada's plastic problem: Sorting fact from fiction. *Oceana*.

Zeenat, Elahi, A., Bukhari, D. A., Shamim, S., & Rehman, A. (2021). Plastics degradation by microbes: A sustainable approach. *Journal of King Saud University - Science, 33*(6), 101538. doi:https://doi.org/10.1016/j.jksus.2021.101538

Zhao, X., Korey, M., Li, K., Copenhaver, K., Tekinalp, H., Celik, S., Ozcan, S. (2022). Plastic waste upcycling toward a circular economy. *Chemical Engineering Journal, 428*, 131928.

Zimmermann, W. (2020). Biocatalytic recycling of polyethylene terephthalate plastic. *Philosophical Transactions of the Royal Society A, 378*(2176), 20190273.