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Microwave Assisted Depolymerization of Waste Pet Bottles via Glycolysis

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MICROWAVE ASSISTED DEPOLYMERIZATION OF WASTE PET BOTTLES VIA GLYCOLYSIS

A Thesis
by
KINGSLEY BASSEY

Submitted in Partial Fulfillment of the

Requirements for the Degree of

MASTER OF SCIENCE

Major Subject: Chemistry

The University of Texas Rio Grande Valley
December 2021

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December 2021

ABSTRACT

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One of the most promising and sustainable chemical depolymerization methods for managing the complex environmental problem arising from waste poly(ethylene) terephthalate (PET) bottles is glycolysis. However key challenges such as longer reaction times, complex separation procedures for the depolymerized products, selectivity, thermally stable catalyst need to be addressed.

In this work, we investigated the glycolysis of waste PET under microwave conditions using 1,5,7-Triazabicyclo [4.4.0] dec5-ene (TBD) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) as catalyst. We evaluated the effect of reaction parameters such as temperature, catalyst concentration and time on PET depolymerization rate (%PET conversion) and product yield. The reaction was conducted using Anton Paar Monowave 400 microwave reactor at catalyst concentrations (0.5-10 wt./wt%), PET to ethylene glycol ratio of 1:10, temperature range 180-220°C. and time (2mins-120mins). PET was completely depolymerized within 25mins at 220°C using a catalyst concentration of 4.33wt/wt%, and the product was characterized using FTIR, NMR, TGA and DSC.

DEDICATION

I dedicate this thesis and all my academic progress made so far to my Parents for their unwavering support and prayers and to the Almighty God for wisdom, strength, and good health.

ACKNOWLEDGMENTS

My profound gratitude goes to my advisor and committee chair, Dr. Javier Macossay-Torres for his insightful and unparallel mentorship, patience, and guidance. It’s been a privilege and honor coming under your tutelage and I am grateful for providing the platform through which this project was successfully completed. To my research committee members Dr. Mohammed Uddin, Dr. Debasish Bandyopadhyay, and Dr. Shervin Fatehi, thanks for more than willing to help and your generous expertise whenever needed. To Thomas Eubanks, thanks for always responding to our equipment needs. To my colleagues in the lab- Diego, Fateema, Mayra and Dominique, thanks for the banters and valuable contributions

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CHAPTER I

INTRODUCTION

Globally, over 400 million tons of plastic materials is reportedly produced every year (UNEP, 2018). Plastics are an indispensable part of our everyday lives with useful applications in packaging, textile, building and construction, electrical, institutional and consumer products to mention a few. However, a large portion of this production usually ends up as waste after single use. Plastic waste constitutes one of the complex global environmental challenges due to its non-biodegradability in environmental components such as land and the ocean, causing a plethora of problems and health risks, most especially when they are broken down into microplastics.

Available estimates show that less than 10% of this waste is effectively recycled, hence the global push towards sustainable, and effective ways to recycle plastics without destroying their intrinsic material value (UNEP,2018; The new Plastic Economy, 2017; Eva et al., 2017) Plastics can be classified into different types such as polyethylene terephthalate (PET), polyethene (PE), polystyrene (PS), low- and high-density polyethylene (LHDE and HDPE), polyvinyl chloride (PVC), polypropylene (PP) among several others (UNEP, 2018).

PET is a thermoplastic polyester, with almost 70 million tons of global production per-annum, and it is used extensively in the packaging and textile industries. It represents one class of consumer plastic with widespread application on account of its outstanding clarity, low cost, lightweight, chemical resistance, durability, and excellent tensile strength (Neena & Thomas, 2014; Atta et al., 2006; IHS Markit, 2018).

PET can exist in a semi-crystalline or amorphous form depending on its thermal and processing history. It can be produced through a two-stage process as shown in Fig.1.1 (Sang & Seong, 2014; Di serio et al., 2004). In stage (1), the intermediate monomer, bis-2-hydroxylethyl terephthalate (BHET) is formed. This can be done using either the esterification of terephthalic acid with ethylene glycol (stage 1a) or through the transesterification of dimethyl terephthalate with ethylene glycol (stage 1b). Water formed in stage 1a is continuously removed via vacuum distillation. The need for methanol recovery and purifications arising from stage 1b makes the TPA approach a preferred option. In stage (2), polycondensation of the resulting intermediate BHET into PET is carried out at a temperature of 270-280°C, with continuous distillation of the ethylene glycol (Di serio et al., 2004).

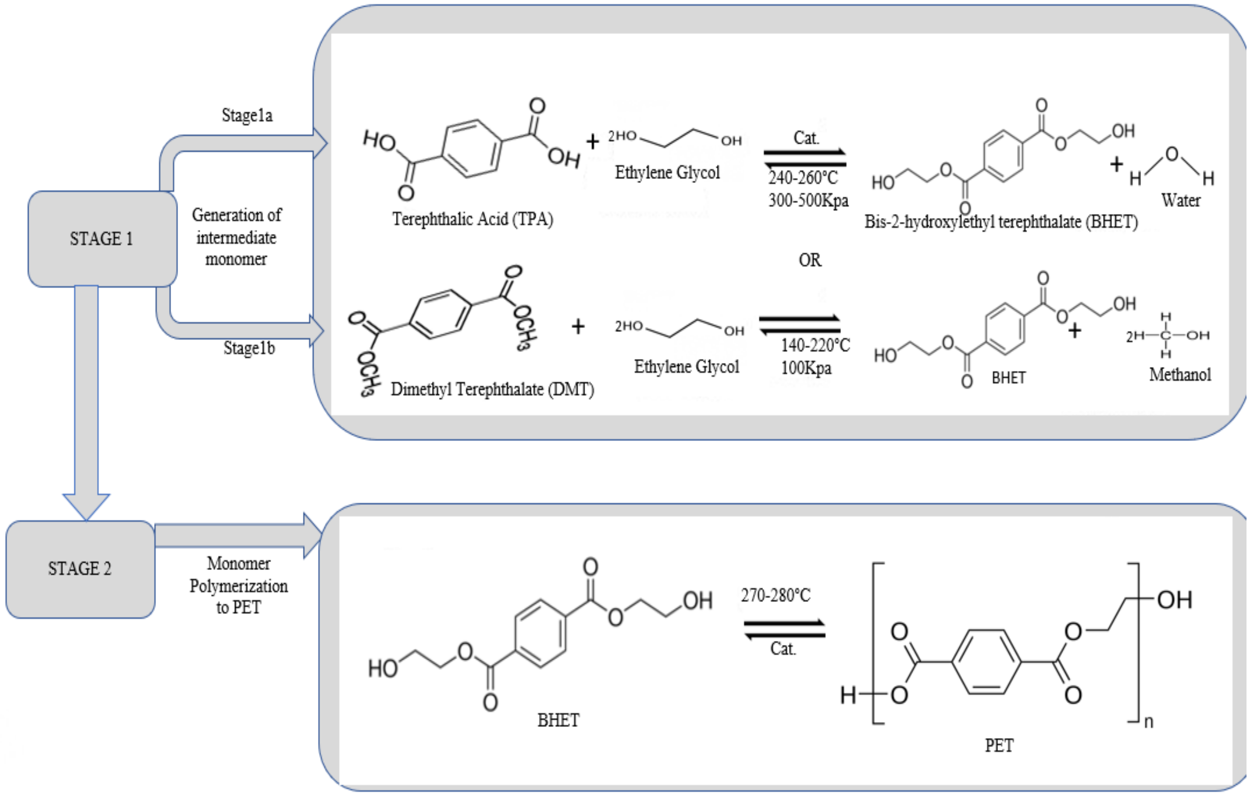

Figure 1.1: Reaction to produce PET

PET for most packaging applications is designed for single use, after which it turns into waste. PET waste accounts for 8% by weight and 12% by volume of the global solid waste (IHS Markit, 2018). In 2017, global PET bottle production was projected to reach 583.13 billion bottles per annum this 2021(Sandra & Mathew, 2017). With only 7% of that effectively recycled back into new bottles (Sandra & Mathew, 2017), the need for more effective ways of combating the deleterious impact of waste PET bottles in the environment while also promoting circularity cannot be overemphasized.

Recycling and Upcycling of PET

Several recycling approaches for waste PET are well documented in the literature (Neena & Thomas, 2017; Al-Sabagh, et al., 2016). PET recycling represents one of the most successful and widespread examples of polymer recycling (Mohammad et al., 2012). In recycling PET, minimizing the amount of contamination arising from contaminants like moisture, acetaldehyde, acetic acid from polyvinyl chloride degradation, rosin acid from adhesives and labels, coloring pigments and ink label, stabilizers such as diphenylamine and other additives leads to better recycled PET quality (Al-Sabagh, et al., 2016). PET recycling methods can be broadly classified into four, comprising of primary, secondary, tertiary and quaternary recycling methods (Al-Sabagh, et al., 2016). (Figure 1.2).

In primary recycling, clean uncontaminated industrial scrap and salvage are simply reprocessed and mixed with virgin PET or simply downcycled to second grade material. Secondary recycling entails physically reprocessing of waste PET. It is also known as mechanical recycling. Here, the waste PET is separated from its associated contaminants and readily reprocessed into granules by conventional melt extrusion (Al-Sabagh, et al., 2016; Mohammad et al., 2012). Although mechanical recycling is commonly used commercially to recycle waste PET, its operating conditions often results in the degradation of the polymer structure and loss of molecular weight. Furthermore, the presence of residual organometallic catalyst such as antimony and titanium from PET synthesis often results in major property deterioration during the secondary melt fabrication process (Fukushima, et al. 2011). Consequently, mechanically recycled PET generally downgrades the PET to secondary products such as fiber for clothing, carpeting, and engineering resins for reinforced automobile components (Fukushima, et al. 2011).

Tertiary recycling involves the transformation of the polymer chain into its constituent monomers using solvent or by using heat (pyrolysis) to degrade the waste PET in the absence of air (Fukushima, et al. 2011). Quaternary recycling simply recovers the energy content in waste PET via incineration. This approach is completely destructive as the byproduct from the incineration plants is mostly disposed in landfills. In recent times, growing interest have been on not just recycling waste PET, but rather upcycling plastic wastes (Basic energy science roundtable, 2019).

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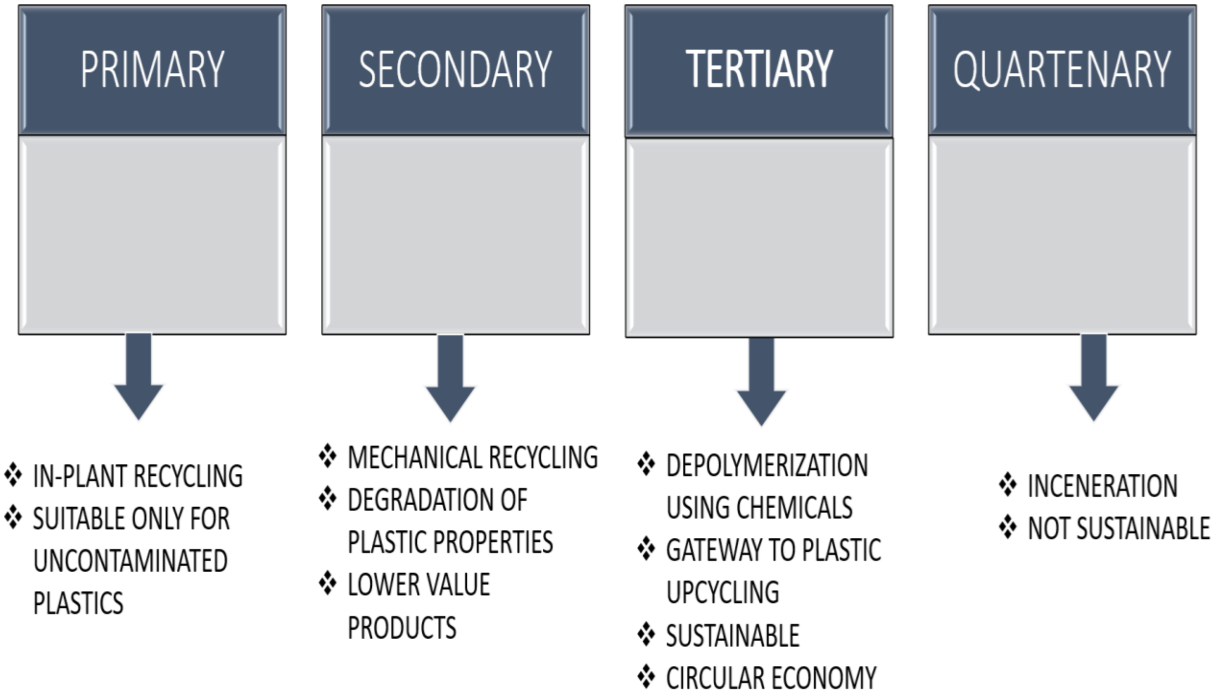


Figure 1.2: PET recycling methods

In upcycling, waste plastic is selectively converted into new plastics with same or higher functionality, chemicals, fuels, or higher-value products. This approach significantly reduces the use of fossil fuels, save energy, expands the types of plastics that could be recycled (i.e., mixtures of plastics), and reduces the amount of plastics in the environment (Basic energy science roundtable, 2019). Despite these merits, key challenges such as slow reaction rates, low selectivity, severe reaction conditions and expensive/complex purification processes still need to be overcome to optimize the process, and make them less expensive with enhanced technical, environmental, and economic feasibility and sustainability (Basic energy science roundtable, 2019). To upcycle waste PET, we first need to break it down via depolymerization using chemicals, heat and in more recent studies, microorganisms/enzymes (Tournier et al. 2020).

Chemical Depolymerization of PET

Chemical depolymerization is a tertiary recycling approach that uses solvents to breakdown waste PET into its constituent monomers such as terephthalic acid (TPA), dimethyl terephthalate (DMT), bis-hydroxylethyl terephthalate (BHET), and ethylene glycol (EG) which can then be repolymerized into food grade new PET bottles. Chemical depolymerization methods include hydrolysis, methanolysis, ammonolysis, aminolysis and glycolysis (Neena & Thomas, 2017; Al-Sabagh, et al., 2016). They form the basis for some of the existing PET depolymerization processes that have been commercialized such as the IBM Volcat, loop industries, ioniqa/unilever/indorama/coca-cola, IFPEN, Eastman process, among several others (Ioniqa, 2019; IFPEN, 2015; Loop industries, 2014; IBM, 2019; Eastman, 2019).

The reaction mechanism for PET depolymerization consists of three reversible reactions steps (Patterson, 2007; Cornell D.D., 2003) as shown in Fig. 1.3. The first step is a rapid protonation of the carbonyl carbon in the polymer chain wherein the carbonyl oxygen is converted to a hydroxyl group. In the second step, the hydroxyl oxygen of the added hydroxyl-bearing molecule from the depolymerizing solvent such as water (hydrolysis), methanol (methanolysis), or ethylene glycol(glycolysis) slowly attacks the protonated carboxyl carbon atom. The last step is a rapid removal of the carbonyl oxygen and a proton to form water or a simple alcohol and the catalytic proton. Because the second step is the slow step, the rate of depolymerization will vary based on how fast the depolymerizing agent can attack the carboxyl carbon after protonation (Patterson, 2007; Cornell, 2003).

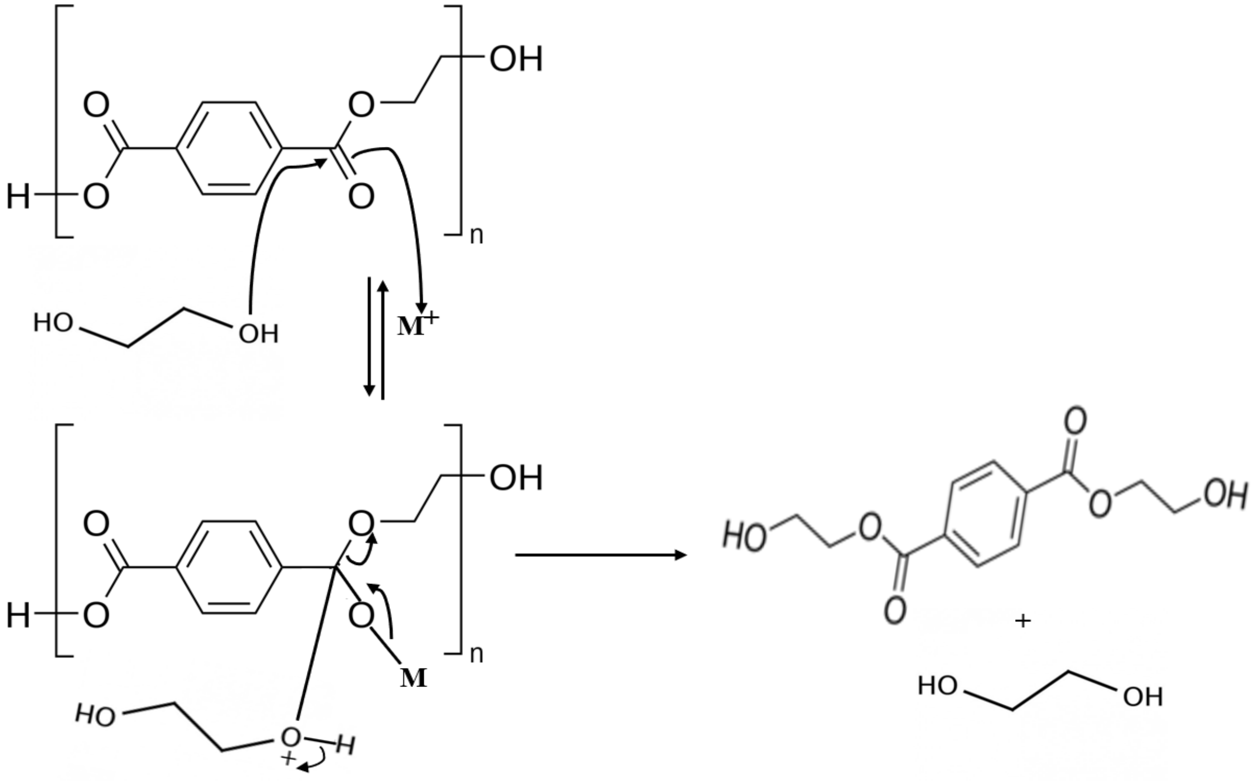


Figure 1.3: Reaction mechanism for PET depolymerization

Hydrolysis involves the depolymerization of PET to terephthalic acid (TPA) and ethylene glycol by the addition of water in an alkaline, acidic, or neutral medium. The hydrolysis products may be used to produce virgin PET or may be converted to more expensive chemicals like oxalic acid (Yoshioka et al., 2003, (Bartolome et al., 2012). Hydrolysis is slow compared to other chemical depolymerization techniques like methanolysis and glycolysis, because water is a weaker nucleophile compare to methanol and ethylene glycol used in methanolysis and glycolysis respectively. In addition, high temperature and pressure is often required, and the product formed often requires numerous purification steps (Bartolome et al., 2012).

In methanolysis, the PET is degraded to dimethyl terephthalate (DMT) and EG using methanol. One of the demerits of this method is the high cost associated with the separation and refining of the mixture of the reaction products (Bartolome et al., 2012). Also, the presence of water can poison the catalyst used and form several azeotropes (Bartolome et al., 2012).

Aminolysis of PET yields bis(2-hydroxyethylene) terephthalamide (BHETA) using primary amine aqueous solutions such as methylamine, ethylamine, and ethanolamine in the temperature range of 20–100°C (Al-Sabagh, et al., 2016). There are no known reports concerning the utilization of this process commercially in PET recycling (Al-Sabagh, et al., 2016). However, it is known that partial aminolysis has found its application in the improvement of PET properties in the manufacture of fibers with defined processing properties (Al-Sabagh, et al., 2016). When the solvent used is ammonia, it is termed ammonolysis and it equally produces a terephthalamide.

PET glycolysis most often involves the use of glycols such as ethylene glycol, Diethylene glycol, propylene glycols and dipropylene glycol to degrade waste PET in the presence of transesterification catalyst (Al-Sabagh, et al., 2016). Complete glycolysis with ethylene glycol produces bis(2-hydroxyethyl) terephthalate (BHET) as the major product as shown in Figure 1.4 (Daniel & Tadeusz,1997). Partial glycolysis sometimes results in the formation oligomers of varying chain length (Daniel & Tadeusz,1997; Al-Sabagh, et al., 2016). Glycolysis is considered the most favored and attractive chemical depolymerization method on the commercial scale because the product obtained is of higher purity, can be directly reintegrated into the polymerization process, does not generate the salt and neutralization wastes often found in other method such as hydrolysis, and requires less volatile solvents compared to those used in methanolysis (Carta et al., 2003; Lei et al., 2020).

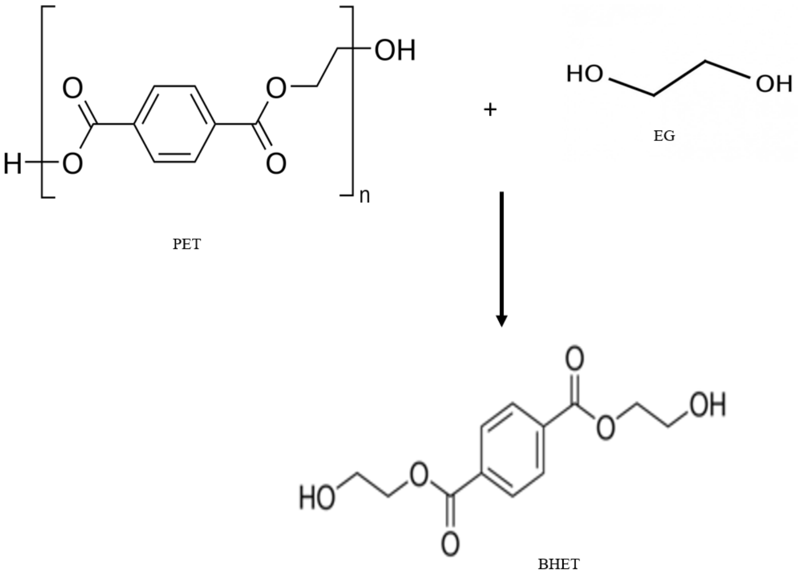


Figure 1.4: Glycolysis of poly (ethylene terephthalate) (PET) with ethylene glycol (EG) to form bis (2-hydroxyethyl terephthalate) (BHET).

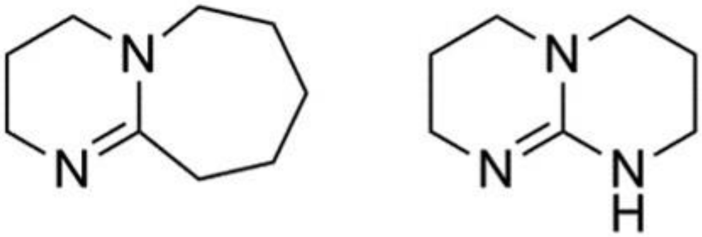
This reaction scheme is typically energy intensive requiring high temperature (180–250 °C), longer reaction time (0.5–8hrs) and about 0.5-10wt% of catalyst (Daniel & Tadeusz,1997; Neena & Thomas, 2017). Key reaction conditions that have been found to affect the rate of depolymerization and the yield of the product include the choice of catalyst, temperature, time, PET/EG ratio, and PET/ catalyst ratio (Daniel & Tadeusz,1997; Lei et al., 2020; Fukushima et a.,2011). PET glycolysis in the absence of a catalyst is typically very slow.

Oftentimes, complete depolymerization of PET to BHET may not be achieved and can form a variety of side products in form of dimers and oligomers (Al-Sabagh, et al., 2016; Neena & Thomas, 2017).

The use of several catalysts ranging from the usual heavy metal salts of acetates and chlorides (Lopez-Fonseca et al., 2010; Pingale et al., 2010), non-toxic metal salts of sodium and potassium (carbonates, bicarbonates, sulphates, chlorides) (Pingale & Shukla, 2008; Lopez-Fonseca et al., 2010), ionic liquids (neutral, basic, and acidic)(Wang et al., 2009; Wang et al., 2009; Yue et al., 2011; Yue et al., 2013) , to the more recent organic catalyst (Lei et al., 2020; Fukushima et al., 2011; Jehanno et al., 2019) have been reported, including those catalyzed by dual organocatalytic systems involving the combination of organocatalyst with acidic and basic ionic liquids (Andere et al.,2019).

As an emerging alternative for transesterification reactions, organocatalysts look attractive as a greener substitute for traditional organometallic complexes (Jehanno et al., 2019). While a broad range of organic catalysts find useful application in several polymerization reactions, translation to depolymerization processes is still very limited. When applied to depolymerization, specifically to transesterification reactions, organocatalysts can promote mechanisms that lead to highly pure small molecules, which are in turn suitable for subsequent polymerizations (Jehanno et al., 2019). In many cases, hydrogen-bonding interactions involved in the depolymerization mechanism promoted by organocatalysts play an important role in controlling the catalytic activity and selectivity of the depolymerization reaction, as well as the architecture of the resulting polymer (Jehanno et al., 2019). Unlike a traditional organometallic catalyst which has poor product selectivity and complex separation procedures, an organocatalyst exhibits greener character, exceptional product selectivity, and can easily be separated and recovered from the depolymerization products (Paul et al., 2020).

1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) and 1,5,7-Triazabicyclo [4.4.0] dec5-ene (TBD) (Fig.1.5) are amidine and guanidine organic super bases respectively, which have been reported to be an effective organic catalyst for a variety of organic reactions including polymer degradation (Mathew et al., 2009; Paul et al., 2020). The mode of action of these two catalysts are thought to proceed via either hydrogen bonded mechanism or through covalently bonded acyl transfer mechanism as shown in Fig. 1.6 for TBD catalyzed transesterification reaction (Fukushima et al., 2011). Fukushima et al., 2011, first reported the organocatalyzed depolymerization of waste PET with TBD using conventional heating method (oil bath). Further studies by Fukushima et al., 2013, evaluated the efficiency of other organocatalysts including DBU as a potential catalyst for depolymerization. In their work, organocatalyzed glycolysis was reported to be more rapid with less unwanted oligomers content when strong bases, with higher pKa values were used compared to bases with a lower pKa. DBU however took exception to this as higher efficiency was obtained despite its slightly lower pKa value compared to TBD. Close correlation was also reportedly observed between reactivity and the chain-length of the diols. For alcohols with a 4-carbon or longer chain, TBD exhibited higher catalytic activity than DBU on the proposition that the bifunctional acid/base character of TBD provides a simultaneous activation of the carbonyl group of the ester and the nucleophilic group of the reactant, thus leading to a faster reaction. They tested this assertion further using computational studies. In contrast, for short-chain alcohols in large excess, the diol activates the carbonyl of the polymer, undermining the bifunctionality of TBD and increasing the reaction rate (Jehanno et al., 2019; Fukushima et al., 2013).



DBU TBD

Figure 1.5: Structure for DBU and TBD

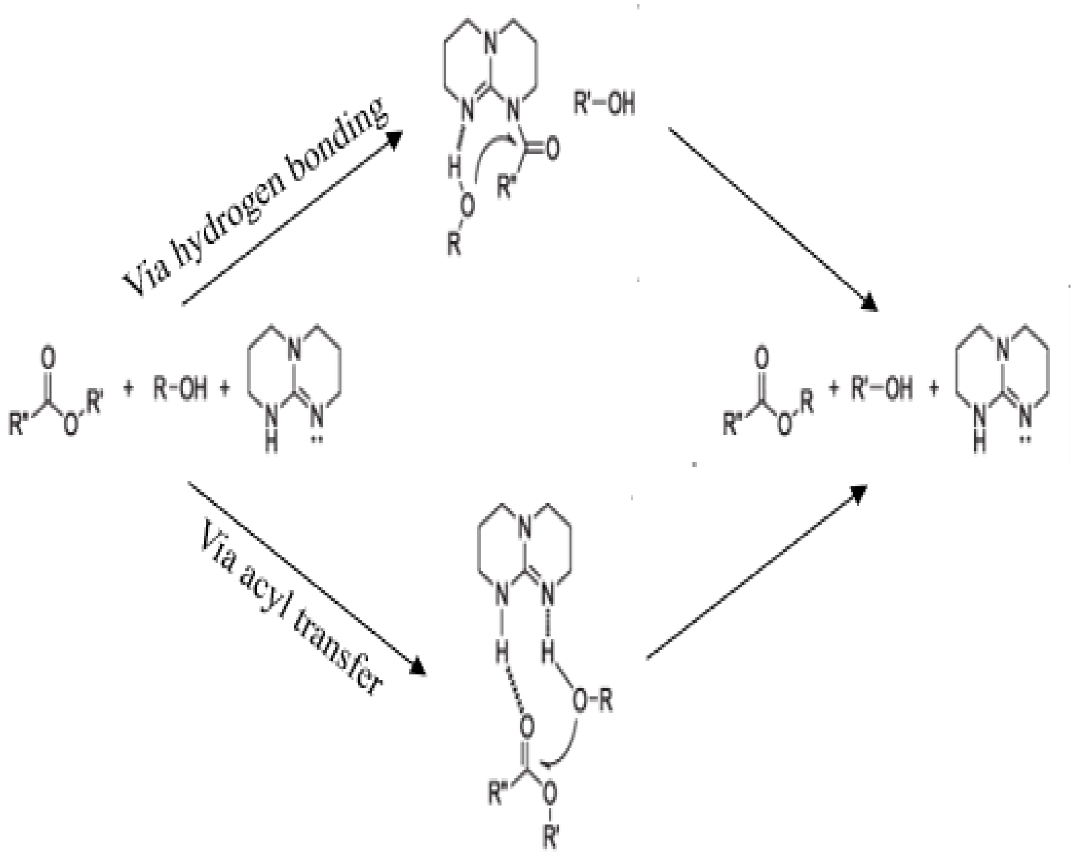


Figure 1.6: General mechanism for TBD catalyzed transesterification reaction

Microwave Assisted Depolymerization

The use of microwave energy as an energy source for heating in chemical reactions has received much attention in recent years. Microwave as a heating source promotes instant and rapid heating with high specificity, decreases reaction time and can also improve product conversions (Krzan, 1998; Pingale & Shukla, 2008). The microwaves interact directly (in-core heating) with the molecules of the reaction mixture, leading to a rapid rise in the temperature (Lidstrom et al., 2001; Jennifer & Alexander 2018). Dielectric heating plays a critical role in microwave heating and works through two major mechanisms involving dipolar polarization and ionic conduction (Jennifer & Alexander, 2018). Molecules that exhibit a permanent dipole moment will generate heat by the rotation, friction, and collision of the molecules when it aligns with the applied microwave electromagnetic field. This ability of a material (or solvent) to convert electromagnetic energy into heat by virtue of its dielectric properties is determined by its loss tangent(δ) value which can be high ($\delta > 0.5$), medium (δ 0.1-0.5), or low ($\delta <0.1$). A solvent with a high loss tangent is required for rapid microwave heating due to their strong microwave absorption (Jennifer & Alexander 2018). Ethylene glycol, the depolymerization solvent used in this work has a δ of 1.350.

Microwave-assisted depolymerizations are well-known in the literature under a variety of conditions, including using water at 220°C for 90–120 min and 20 bar catalyzed by traditional metal base esterification catalyst (Lixin et al., 2005); propylene glycol, diethylene glycol and polyethylene glycol (Saurabh et al., 2013; Krzan, 1999); ethylene glycol under reflux for 30-35 mins (Pingale and Shukla,2008) using zinc acetate as catalyst. However, there is limited report on the performance of organocatalyzed PET depolymerization under microwave conditions. In this work, we examined the catalytic performance of two organic catalyst (TBD and DBU) on the depolymerization of waste PET into BHET under microwave conditions using ethylene glycol under different reaction conditions of time, temperature, and catalyst concentrations.

Goals of the thesis

This thesis is focused on establishing reaction conditions and optimizing them for depolymerization of waste PET bottles through glycolysis into BHET using microwave irradiation and organocatalysts. PET glycolysis is one of the most widely researched areas of polymer degradation on account of its ability to produce high purity monomers, which can be directly used to produce new plastic bottles, thus promoting sustainability and circularity in the plastic economy. However, most of the available publications usually involve longer reaction times and the use of catalyst systems that present complex reaction products that requires expensive post reaction product separation techniques even in publications where microwave was reportedly used. The use of TBD, DBU and other organic catalyst for PET depolymerization is relatively new, and they are mostly reportedly used in concentrations up to 10 wt/wt %, hence optimizing these conditions can help advance large scale industrial adoption of the glycolytic process for waste PET depolymerization.

CHAPTER II

METHODOLOGY

Materials

Waste PET bottles were collected from trash bin, the cap, glue, and label removed, washed with a mild soap under running water, dried in the oven at 80°C for one hour and cut into 4 × 4 mm squares flakes. Ethylene Glycol (EG) (99% extra pure) from Acros; 1,5,7-Triazabicyclo [4.4.0] dec5-ene (TBD), and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) from TCI were purchased and used as supplied.

The Microwave Reactor

The equipment used for the depolymerization was the Anton Paar Monowave 400 as shown in Fig 2.1 The equipment has a built in IR sensor that allows for temperature monitoring as well as an external probe (ruby thermometer) that can be inserted into the reaction vessel for direct temperature monitoring. It is equipped with a magnetron capable of delivering up to 850W of continuous microwave power to achieve reaction conditions reaching up to 300 °C / 30 bar. This means that once the temperature and time of the reaction are programmed, the set temperature is maintained throughout the entire set time by an irradiation power pulse in “on/off” cycles. The air pressure for the microwave reactor was always kept at 5.5 torr. The equipment comes with a 10 ml and 30 ml borosilicate reactor vials as well as a 10 ml and 30ml silicon carbide vials. The 10ml (G10) borosilicate glass vial was used for all experiment.

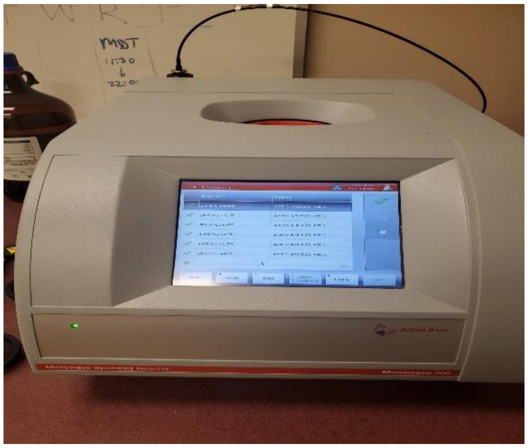


Figure 2.1: The Microwave reactor

PET Glycolysis Process

PET flakes (0.5g), ethylene glycol (5ml) and catalyst (TBD or DBU with varying concentrations from 0 to 10 wt/wt % of PET) were measured into the G10 borosilicate glass vial, magnetic stirrer inserted, sealed, and charged into the microwave to begin the reaction at a programmed temperature (180-220°C) and time (2-120 mins). After the reaction, the reaction mixture was quickly vacuum filtered to separate any unreacted waste PET and washed with 30-40 ml hot distilled water (60-80°C) into the filtrate. The unreacted PET was oven dried at 80°C until constant weight and the final weight used to calculate the % conversion as given in equation 1 below.

$$\%\ \text{PET conversion} = \frac{w_0 - w_1}{w_0} \text{ x } 100 \text{ ………………………. equation (1)}$$

where w_0 is the initial starting weight of the waste PET flakes, and w_1 is the weight of the unreacted PET residue after the reaction.

The filtrate, after filtering out any water insoluble fraction was kept in the refrigerator at 4-5 °C for 24 hours to form white needle-like crystals which were then vacuum filtered and dried at 80°C until constant weight and characterized. The yield of the product was calculated from equation 2 below.

$$\text{Molar yield of BHET (\%)} = \frac{W_A}{W_T} x100 \text{ ………………………equation (2)}$$

Where W_A is the actual weight of the product (BHET) and W_T is the theoretical weight at 100% depolymerization given by equation 3. Fig 2.2 shows a schematic of the entire process.

$$W_T = \frac{\text{molecular weight of BHET}}{\text{molecular weight of PET repeating unit}} \text{ x weight of PET used. ……...equation (3)}$$

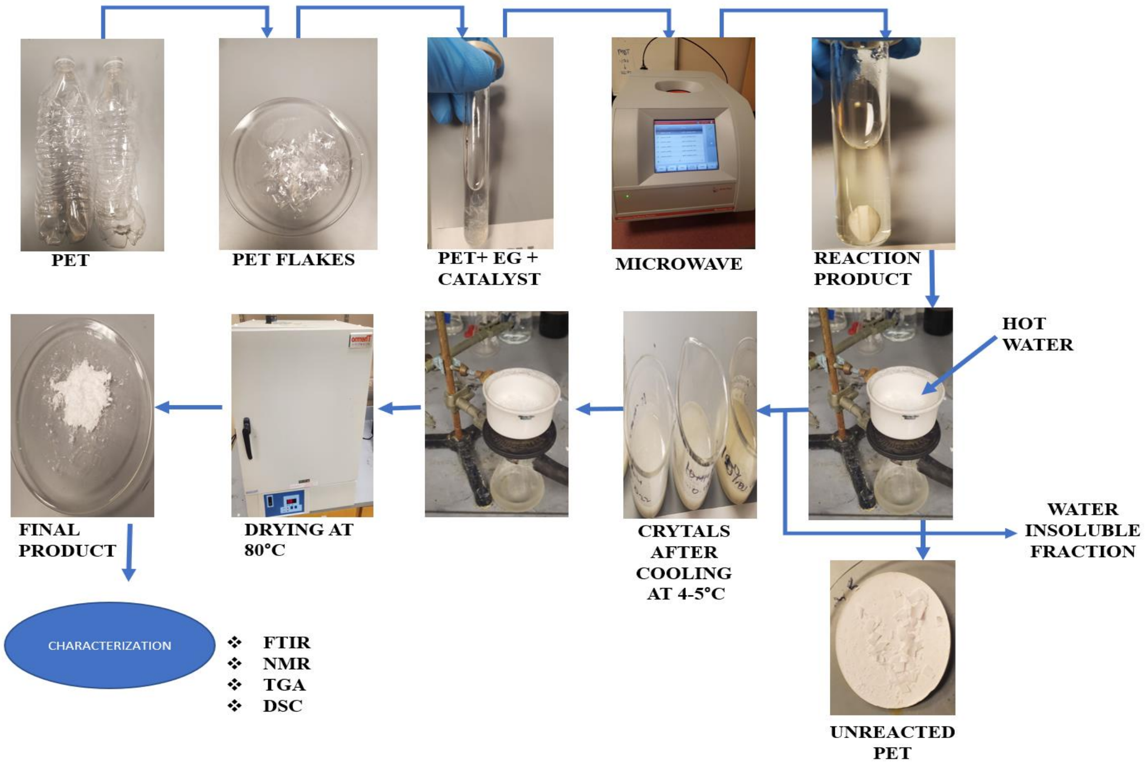


Figure 2.2: Schematic of the depolymerization process

Characterization

Fourier Transform Infrared (FTIR) Spectroscopy

Infrared Spectroscopy was done with a Bruker ALPHA Platinum ATR single reflection diamond ATR and OPUS software with the resolution set to 4 cm^{-1}, scans set to 256, and background scans set to 256. The frequency range used was 4000-400 cm^{-1}.

Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance was done with a Bruker 600 MHz FT-NMR in tubes Kimble borosilicate glass thrift N-51A 5mm NMR tubes. The number of scans were set to 16 and the chemical shift range used was 0-10 ppm. The solvent used was dimethyl sulfoxide (DMSO).

Melting Point Determination

The melting point of the product was determined using Digimelt SRS at a ramp rate of 2°C/min.

Thermogravimetric Analysis (TGA)

TGA thermograms were obtained using NETZSCH TG 209 F3 Tarsus analyzer. The experiments were performed using a small amount of sample (10mg) starting from 27°C to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere. The results were exported and plotted on OriginPro.

Differential Scanning Calorimeter (DSC)

DSC thermograms were obtained using NETZSCH DSC 214 polymer analyzer with an inbuilt temperature range of -170°C -600°C. 10mg of the sample was placed in the equipment and heated from 0°C to 270 °C under a nitrogen atmosphere at a heating rate of 10.0°C/min. The results were exported and plotted on OriginPro.

CHAPTER III

RESULTS AND DISCUSSIONS

In this study, depolymerization of waste PET bottles was done in the microwave reactor. All reactions were conducted in duplicate to ensure reproducibility. The solvent used for the depolymerization was ethylene glycol due to it high loss tangent, which allows for effective microwave absorption without pressure build-up within the microwave (an initial solvent screening done using water and methanol resulted in pressure build up that were beyond the design capacity of the microwave as the temperature increases, hence they were discontinued).

The catalysts used were TBD (bifunctional with an extra hydrogen bonding possibility) and DBU. The performance of each catalyst was evaluated by monitoring the rate of depolymerization (% PET conversion) and the molar yield of the product formed from each experimental condition under microwave irradiation. The reaction parameters evaluated were reaction time, temperature, and catalyst concentration. To determine the reaction working temperature, an initial temperature screening was done from 180°C -220 °C using reaction mixtures containing 0.5g of waste PET, 5ml ethylene glycol and 5mg of the catalyst for 1 hour as shown in Table 3.1. The reaction was deemed complete upon complete disappearance of the PET flakes (Fig.3.1).

Table 3.1: Initial temperature screening

s/n	**Description**	**Temp. (C)**	**Time mins.**	**Residue after depolymerization**	**Depolymerization (% Conversion**
1a	0.5063g PET +0.0507g TBD +5ml EG	180	60	0.3095	38.87
1b	0.5057g PET +0.0505g TBD +5ml EG	180	60	0.2924	42.17
2a	0.5054g PET +0.0509g TBD +5ml EG	190	60	0.1704	66.28
2b	0.5051g PET +0.0507g TBD +5ml EG	190	60	0.1695	66.42
3a	0.5052g PET +0.0509g TBD +5ml EG	200	60	0.0522	89.66
3b	0.5051g PET +0.0504g TBD +5ml EG	200	60	0.0451	91.07
4a	0.5050g PET +0.0505g TBD +5ml EG	210	60	-	100
4b	0.5053g PET +0.0507g TBD +5ml EG	210	60	0.0006	99.82
5a	0.5055g PET +0.0503g TBD +5ml EG	220	60	-	100
5b	0.5049g PET +0.0506g TBD +5ml EG	220	60	-	100

PET was completely depolymerized into a homogeneous clear to very pale-yellow solution at 220°C as shown in Figure 3.1 Possible oxidation/degradation of the catalyst might be responsible for the observed crude product color. To verify this color change, we heated just the solvent only with and without catalyst for 5 mins at 220°C and observed similar color change as those obtained after PET depolymerization as shown in Fig. 3.2, suggesting that the reaction resulting in the color changes probably occur faster or quite early in the reaction involving DBU than that of TBD, meaning that DBU likely oxidizes faster than TBD.

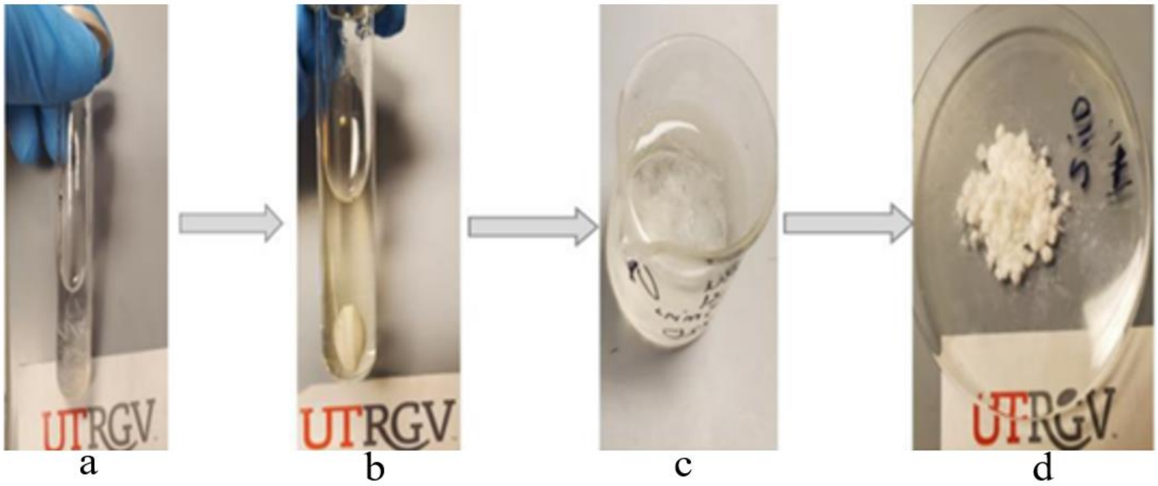


Figure 3.1 Reaction product and work up showing a) mixtures of ethylene +PET flakes + catalyst, b) clear product after complete depolymerization, c) crystals formed and d) final dried recrystallized product.

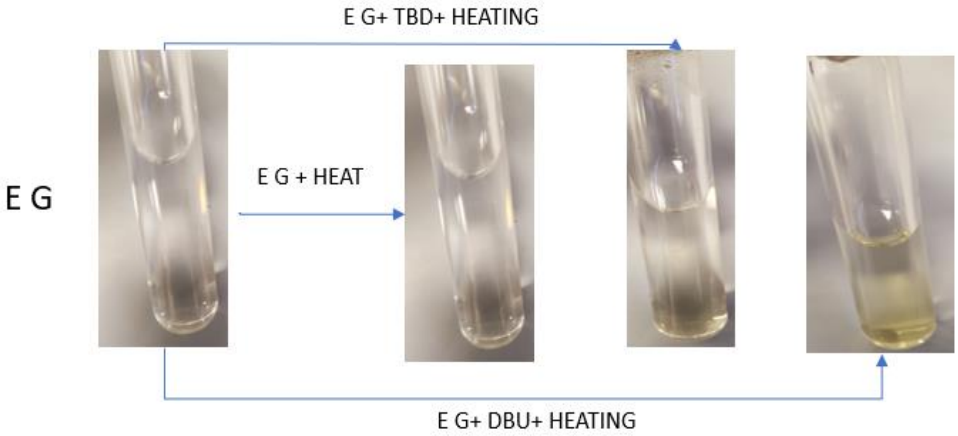


Figure 3.2 Color changes arising from the catalyst usage

Addition of water to the crude clear solution precipitated out very small amounts of water insoluble fraction (possibly arising form side reactions or from additives such as isophthalic acid, diethylene glycol, and cyclo-hexane dimethanol added to enhance PET moldability) (Fukushima et al., 2011) which was filtered out. After cooling the filtrate for 24 hrs at 4-5 °C in a refrigerator, white needle-like crystals were formed (Fig 3.1) which was filtered, dried until constant weight and characterized. The dried white crystals gave a very narrow melting point of 107.4°C -108.8°C, an indication of the product purity. The result of the melting point was within the 106°C -109°C experimental value reported in literature (Nahrain, et al., 2010).

Characterization

FTIR

FTIR analysis for the PET flakes and the product is as shown in Fig.3.3. The PET flakes show absorption peaks which were within the spectra bands observed for those of BHET except for the absence of the O-H stretching vibration peak at 3449cm^{-1}. BHET spectrum shows significant absorption peaks at 3449cm^{-1}, 2969cm^{-1}-2884 cm^{-1}, 1712 cm^{-1}, and 1506-1450 cm^{-1} representing O-H stretching vibration at chain termination, alkyl C-H asymmetric and symmetric stretching vibrations, C=O stretching and aromatic C=C bending vibration from the aromatic ring respectively found on BHET.

NMR

Further NMR analysis (Figure 3.4) shows chemical shifts confirming the chemical nature of BHET with a, b, c, and d representing protons of the aromatic ring (δH = 8.16 ppm, s, 4H), hydroxyl groups (δH = 5.00 ppm, t, 2H), methylene ($-CH_2-$) adjacent to the -COO groups (δH = 4.37 ppm, t, 4H), and methylene ($-CH_2-$) adjacent to the -OH groups (δH = 3.77 ppm, m, 4H), respectively. 2.54 ppm is DMSO while 3.36ppm is likely from residual water from PET production (Gabrielle, et al., 2017; Wang, et al., 2015).

TGA and DSC

The result of the thermogram from both TGA and DSC analysis is as shown in Fig. 3.5 and Fig. 3.6 respectively. The TGA graph shows that PET degraded in a single step at about 450°C, while the degradation of BHET was in two steps at around 248°C-250°C, which represent the degradation of the BHET monomer (Gabrielle et al., 2017) and at 450°C because of the repolymerization of the BHET monomer to PET which then degrades as PET during analysis (Gabrielle et al., 2017; Imran, et al., 2013). The absence of other degradation steps in the product further confirms the NMR spectra showing the product was purely BHET monomer.

Similarly, the DSC curve for BHET showed a sharp endothermic peak at 109°C corresponding to the melting point of BHET. This result was within BHET reported melting point range and correlated well with those obtained using the Digimelt equipment. For the PET, the sharp endothermic peak observed at 248°C corresponds to its melting peak.

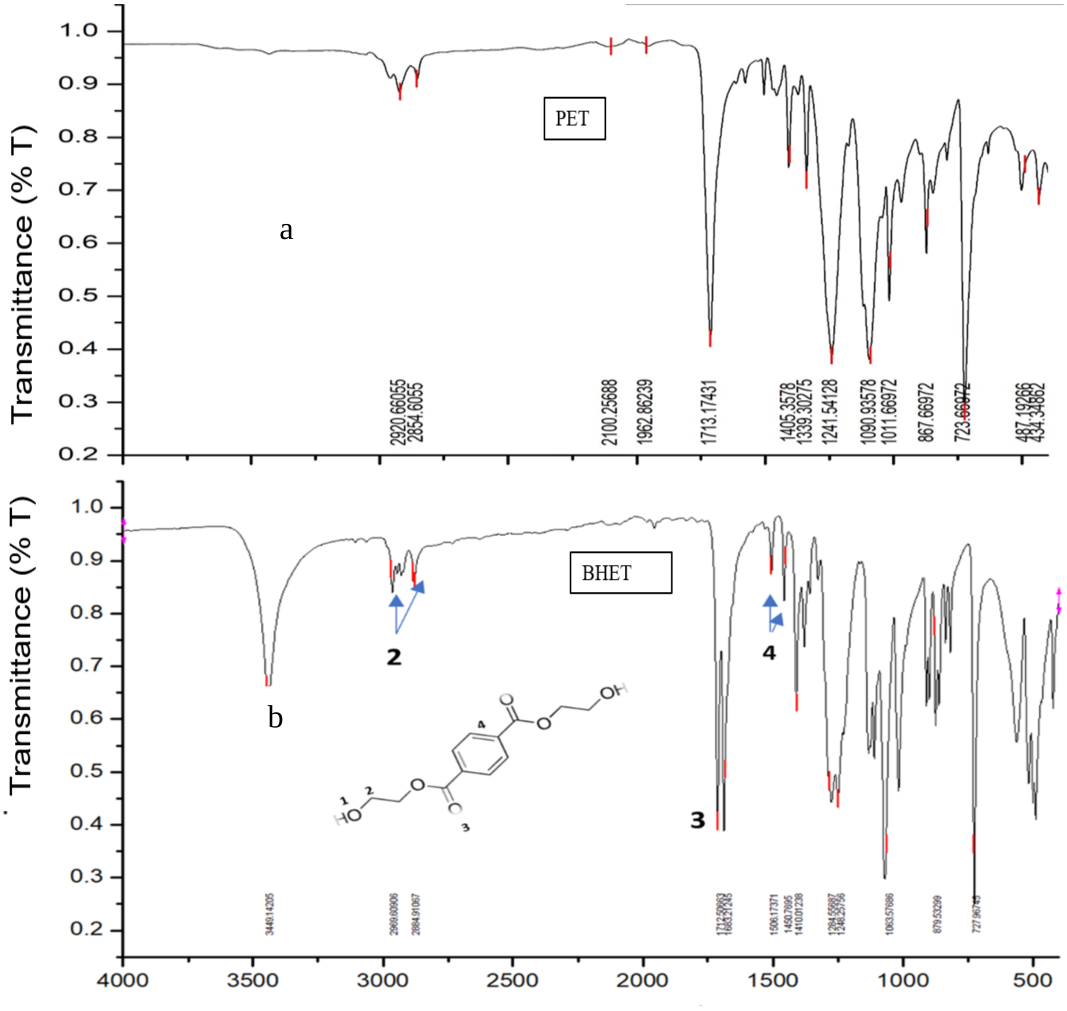


Figure 3.3 FTIR spectra of starting PET and BHET product

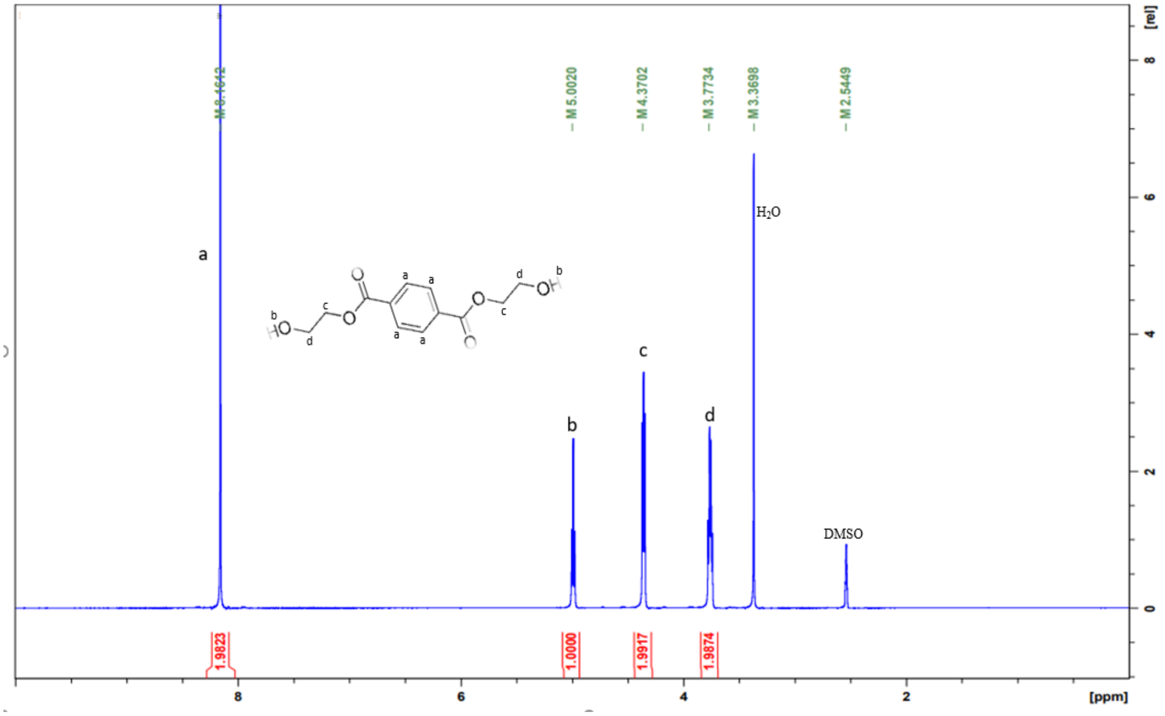


Figure 3.4: NMR spectrum of the BHET

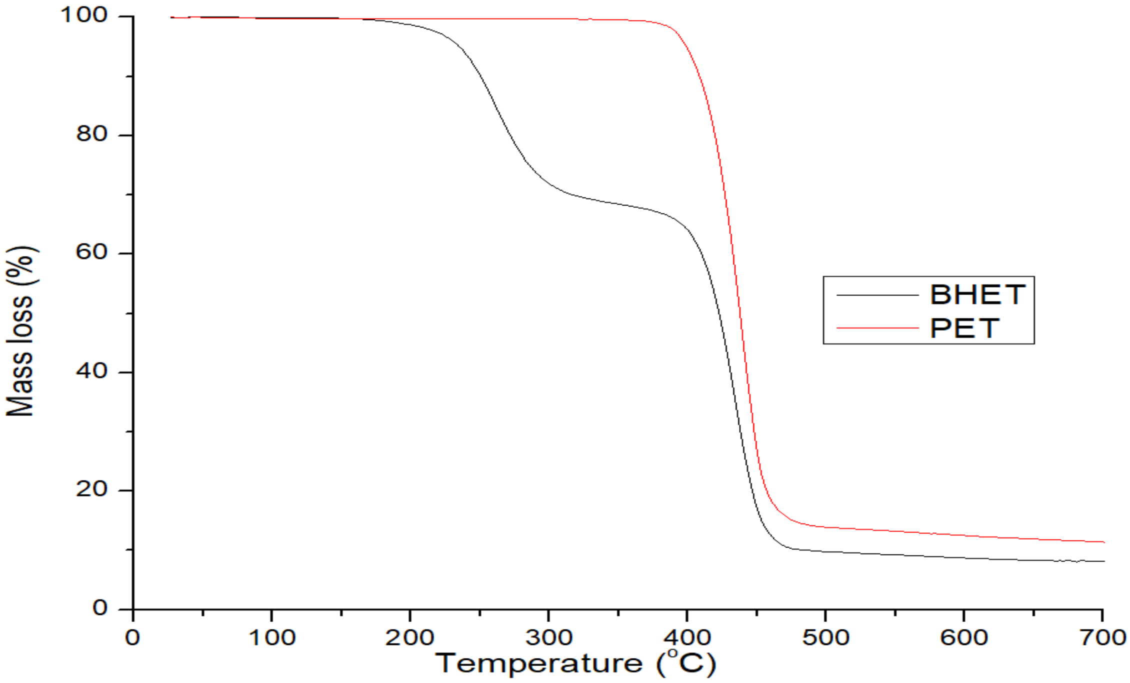


Figure 3.5: TGA degradation for PET and BHET

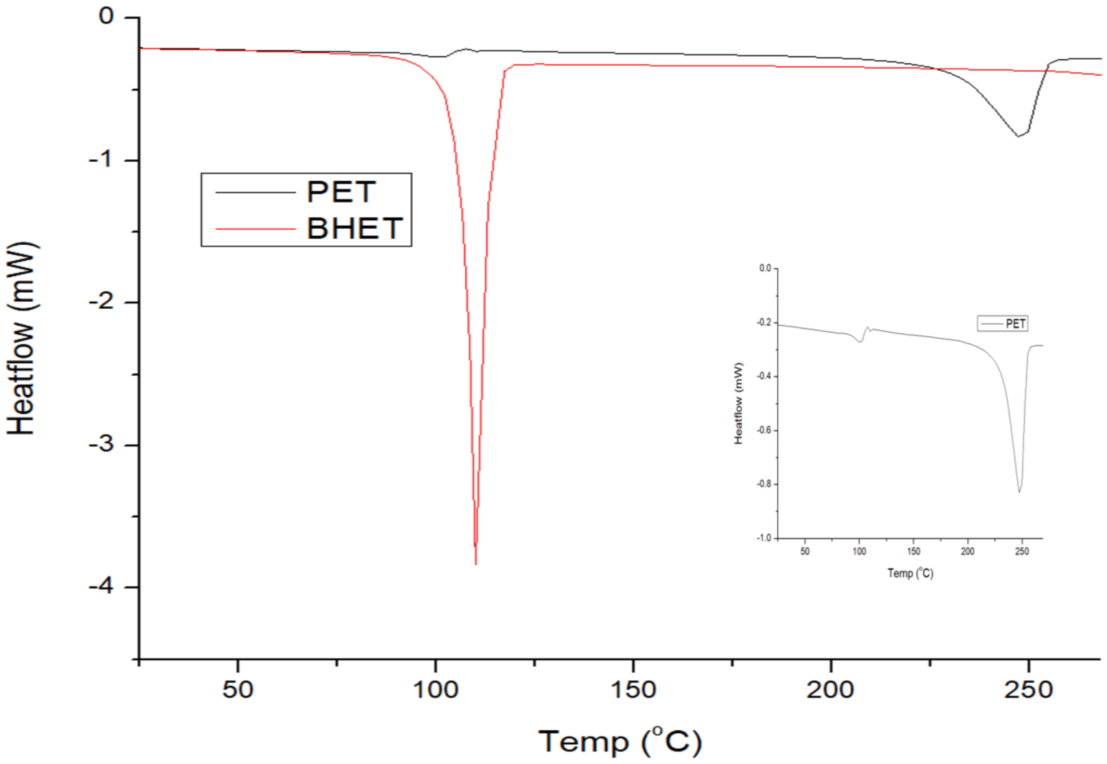


Figure 3.6: DSC thermogram for PET and BHET

Effect of Catalyst Concentration

Table 3.2 and 3.3 shows the reaction parameters for the variation of concentration of TBD and DBU respectively at 220°C, Fig. 3.7 and 3.8 shows the reactions progress, while Fig. 3.9 shows the % PET conversion and molar yield of BHET for the microwave assisted glycolysis of PET for TBD and DBU respectively over various catalyst concentration (0.5-10 wt/wt%).

Table 3.2: Variation in concentration-TBD

s/n	Sample Description	Temp. (C)	Time (mins)	TBD Conc. (wt%)	Residue after depolymerization (g)	% PET conversion	Weight of product obtained(g)	Av. Weight of product	Molar Yield of BHET (%)
1a	0.5069g PET +0.0027g TBD +5ml EG	220	60	0.53	0.1788	64.72	0.2334	0.2368	35.32
1b	0.5076g PET + 0.0025g TBD + 5ml EG	220	60	0.5		66.4%	0.2401		
2a	0.5063g PET +0.0055g TBD +5ml EG	220	60	1.08	0.0934	81.55	0.3944	0.3635	54.39
2b	0.5043g PET + 0.0053g TBD + 5ml EG	220	60	1.05		82.6%	0.3325		
3a	0.5075g PET +0.0119g TBD +5ml EG	220	60	2.3	0.0018	99.64	0.4388	0.4398	65.51
3b	0.5077g PET + 0.0113g TBD +5ml EG	220	60	2.23		100%	0.4407		
4a	0.5063g PET +0.0219g TBD +5ml EG	220	60	4.33	-	100	0.4614	0.4648	69.34
4b	0.5072g PET + 0.022g TBD + 5ml EG	220	60	4.34		100%	0.4682		
5a	0.5040g PET +0.0312g TBD +5ml EG	220	60	6.2	-	100	0.4599	0.4586	68.91
5b	0.5023g PET + 0.0316g TBD + 5ml EG	220	60	6.3		100%	0.4572		
6a	0.5074g PET +0.0374g TBD +5ml EG	220	60	7.3	-	100	0.4677	0.4643	69.21
6b	0.5070g PET +0.0370g TBD +5ml EG	220	60	7.3		100%	0.4610		
7a	0.5051g PET +0.0509g TBD +5ml EG	220	60	10.07	-	100	0.4432	0.4515	67.45
7b	0.5070g PET +0.0512g TBD +5ml EG	220	60	10.09		100%	0.4596		

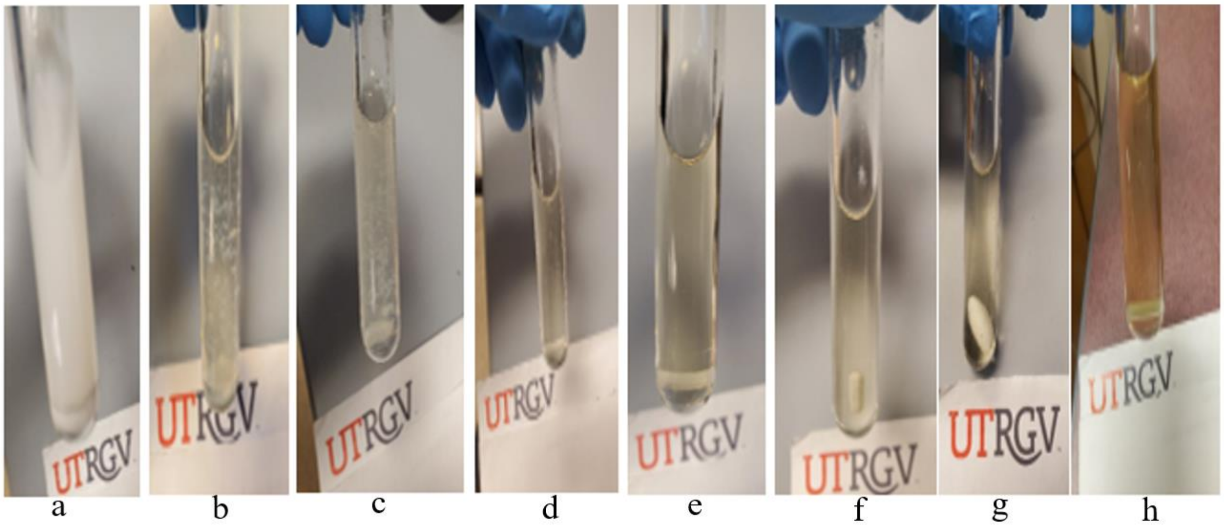


Figure. 3.7: Describes the crude product after deploymerization at various TBD concentration for a) 0%, b) 0.51%, c) 1.07%, d) 2.25%, e) 4.25%, f) 6.25%,g) 7.3% and h) 10.08%

Table 3.3: Variation in catalyst concentration-DBU

S/N	Sample description	Temp. (C)	Time (mins)	DBU conc. (wt%)	Residue after Depolymerization	%conversion (calculated)	Weight of Product (g)	Average weight of product	Molar yield of BHET
1a	0.5053g PET + 0.0511g DBU + 5ml EG	220	60	10.28	0.00	100%	0.3791	0.3898	58.34
1b	0.5050 PET + 0.050 DBU + 5ml EG	220	60	10	0.00	100%	0.4005		
2a	0.5048g PET + 0.0373g DBU +5ml EG	220	60	7.39	0.00	100%	0.4084	0.4043	60.51
2b	0.5055g PET + 0.0375g DBU +5ml EG	220	60	7.39	0.00	100%	0.4003		
3a	0.5051g PET +0.031g DBU +5ml EG	220	60	6.14	0.0059	98.83%	0.4055	0.4117	61.63
3b	0.5050g PET +0.0315g DBU +5ml EG	220	60	6.24	0.0091	98.19%	0.4179		
4a	0.5047g PET + 0.0218g DBU + 5ml EG	220	60	4.32	0.00	100%	0.4184	0.4275	63.98
4b	0.5056g PET +0.0220g DBU +5ml EG	220	60	4.35	0.00	100%	0.4365		
5a	0.5051g PET +0.011g BDU +5ml EG	220	60	2.18	0.00	100%	0.3876	0.3787	56.68
5b	0.5053g PET + 0.0117g DBU +5ml EG	220	60	2.31	0.0052	98.97%	0.3698		
6a	0.5052g PET +0.0055g DBU +5ml EG	220	60	1.09	0.0321	93.61%	0.3703	0.3588	53.71
6b	0.5049g PET + 0.0056g DBU +5ml EG	220	60	1.11	0.0447	91.11	0.3473		
7a	0.5054g PET +0.0025g DBU +5ml EG	220	60	0.50	0.1507	70.31%	0.3397	0.3505	52.46
7b	0.5048g PET + 0.0025g DBU +5ml EG	220	60	0.49	0.1343	73.52%	0.3612		

Figure. 3.8: Describes crude product at various DBU concentration for a) 0%, b) 0.50%, c) 1.10%, d) 2.25%, e) 4.34%, f) 6.19%, g) 7.39% and h) 10.14%

Optimal concentration for PET depolymerization was achieved at 4.33wt/wt% for both TBD and DBU as PET was completely degraded at this concentration, hence using these catalysts above this concentration at the given conditions does not make any significant contribution to both PET conversion and the yield of BHET. Both catalysts exhibited rising product yield with increasing catalyst concentration up to the optimum concentration at a molar yield of 69.34% for TBD and 63.98% for DBU, after which a reduction in yield was observed. Below the optimum concentration, DBU was interestingly effective at degrading PET with % PET conversion (reaching 71.93% and 92.43% at 0.5wt/wt% and 1wt/wt% concentration respectively and molar yield of 52.46% and 53.71% respectively.

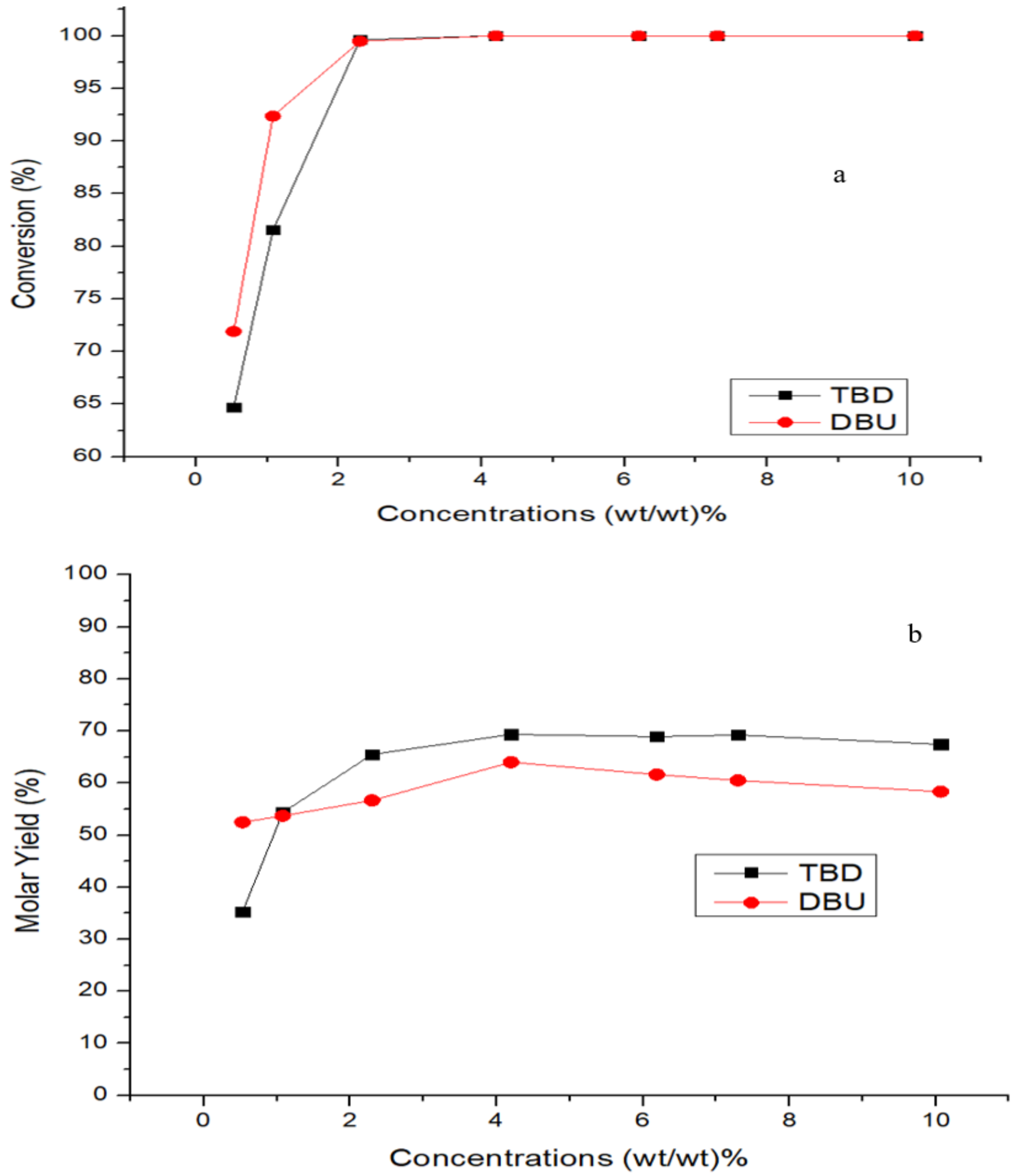


Figure. 3.9: Effect of catalyst loading on PET depolymerization (%conversion (a)) and product molar yield (b) using DBU and TBD respectively.

(Reaction conditions: PET:EG of 1:10, at 220°C for 1hr. The concentrations are in wt/wt% of the starting weight of the PET)

Effect of Reaction Temperature

The impact of temperature on the conversion and BHET yield is shown in Fig 3.12 for TBD and DBU respectively. The reaction's parameters and results are as shown in Table 3.4 and 3.5, while Fig. 3.10 and 3.11 shows the reaction product after depolymerization. Both catalysts exhibited similar profile in conversion and BHET yield with rising temperature. 100% PET depolymerization was achieved at 220°C for both catalysts. Although DBU exhibited slightly higher conversion for each temperature examined up to 210°C, the slight edge did not result in significant higher BHET yield for DBU. At 180°C for instance, while the % conversion of PET was 29.35% and 20.52% for DBU and TBD respectively, BHET yield at 180°C was only 5.09% and 4.66% for DBU and TBD respectively. At the optimum temperature of 220°C, slightly higher yield of 68.92% was obtained using TBD, compared to 67.06% obtained using DBU.

Table 3.4: Reaction's parameters and result for effect of Temperature on TBD

	Description	**Temp. (C)**	**TBD Conc. Wt%**	**Residue after depolymerization**	**Conversion(%)**	**Weight of product**	**Av. Weight of product**	**%yield of product (wt/wt)**	**Molar Yield of BHET (%)**
1a	0.5055g PET +0.0216g TBD +5ml EG	220	4.27	-	100	0.4614	0.4606	90.97	68.92
1b	0.5049g PET +0.0211g TBD +5ml EG	220	4.18	-	100	0.4598			
2a	0.5050g PET +0.0213g TBD +5ml EG	210	4.22	0.0060	98.81	0.4423	0.4360	86.17	65.25
2b	0.5053g PET +0.0216g TBD +5ml EG	210	4.28	0.0076	98.50	0.4296			
3a	0.5052g PET +0.0216g TBD +5ml EG	200	4.28	0.1654	67.38	0.2553	0.2516	49.63	37.65
3b	0.5051g PET +0.0214g TBD +5ml EG	200	4.24	0.1863	63.28	0.2478			
4a	0.5048g PET +0.0216g TBD +5ml EG	190	4.29	0.2938	42.12	0.1121	0.1093	21.53	16.35
4b	0.5053g PET +0.0213g TBD +5ml EG	190	4.22	0.3025	40.13	0.1064			
5a	0.5054g PET +0.0220g TBD +5ml EG	180	4.35	0.4017	20.52	0.0377	0.0311		4.66
5b	0.5051g PET +0.0217g TBD +5ml EG	180	4.30	0.4014	20.52	0.0245			

Figure 3.10: Describes the glycolytic product after depolymerization with TBD at a) 180°C , b) 190°C , c) 200°C , d) 210°C, and e) 220°C.

Table 3.5: Reaction's parameters and result for effect of Temperature on DBU

	Description	Temp. (C)	Time (mins)	DBU Conc.	Residue after depolymerization	Conversion(%)	Weight of product	Av. Weight of Product	Molar Yield of BHET (%)
1a	0.5059g PET +0.0209g DBU +5ml EG	220	60	4.13	-	100	0.4365	0.4481	67.06
1b	0.5044g PET +0.0220g DBU +5ml EG	220	60	4.36	-	100	0.4597		
2a	0.5054g PET +0.0236g DBU +5ml EG	210	60	4.67	-	100	0.4383	0.4297	64.30
2b	0.5050g PET +0.0220g DBU +5ml EG	210	60	4.36	-	100	0.4211		
3a	0.5053g PET +0.0220g DBU +5ml EG	200	60	4.35	0.1109	78.07	0.2838	0.2792	41.78
3b	0.5050g PET +0.0219g DBU +5ml EG	200	60	4.34	0.1203	76.25	0.2746		
4a	0.5054g PET +0.0221g DBU +5ml EG	190	60	4.37	0.2569	49.16	0.1076	0.1070	16.01
4b	0.5051g PET +0.0220g DBU +5ml EG	190	60	4.36	0.2800	44.67	0.1064		
5a	0.5053g PET +0.0218g DBU +5ml EG	180	60	4.31	0.3570	29.35	0.0344	0.0341	5.09
5b	0.5052g PET +0.0220g DBU +5ml EG	180	60	4.35	0.3555	29.63	0.0338		

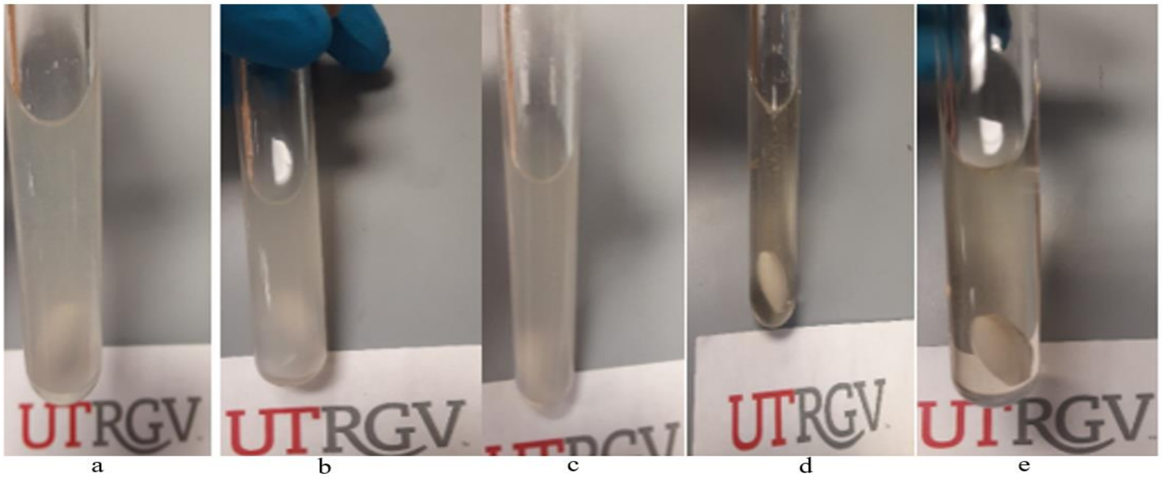


Figure 3.11: Describes the glycolytic product after depolymerization with DBU at a) 180°C , b) 190°C , c) 200°C , d) 210°C, and e) 220°C.

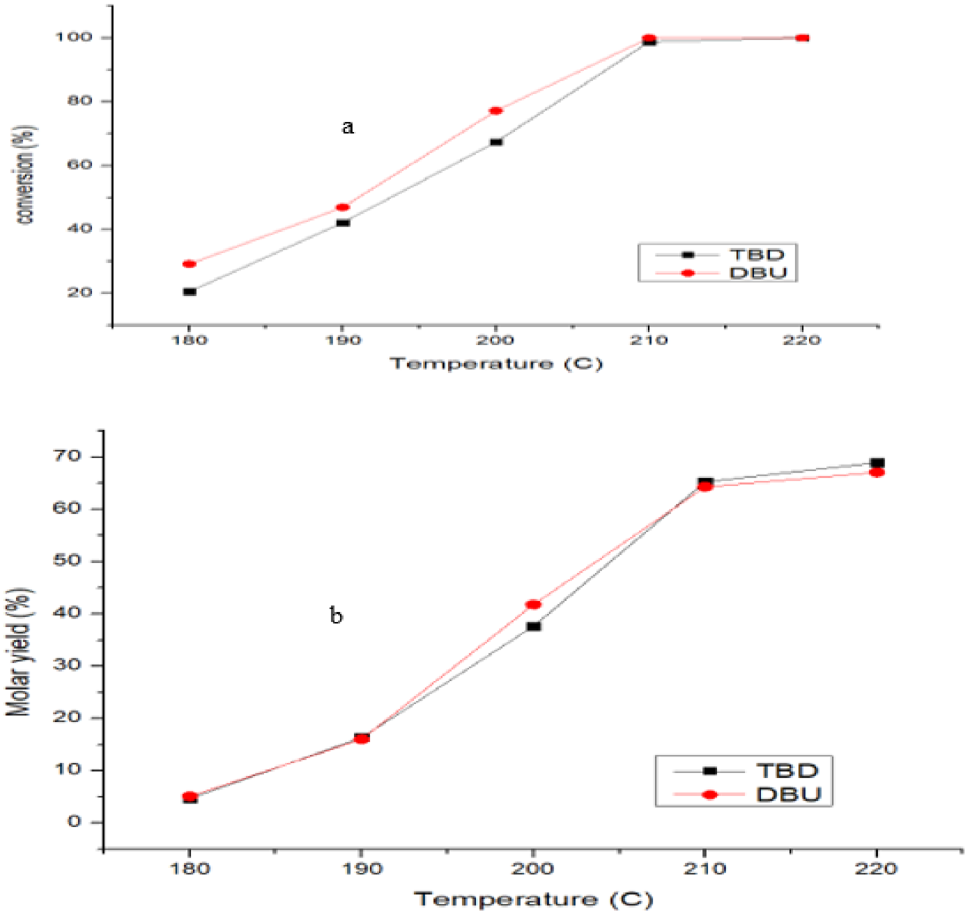


Figure.3.12: Influence of temperature on the PET conversion (a) and Molar yield of BHET (b) using TBD and DBU respectively.

Effect of Reaction Time

Fig.3.15 shows the variation of reaction’s time with PET conversion and BHET formation for TBD and DBU. We first investigated the effect of time at the optimum reaction concentration of 4.3% and 220°C. The reactions parameters and results are shown in Table 3.6 and 3.7 for TBD and DBU respectively, while Fig. 3.13 and Fig. 3.14 shows the reaction product after depolymerization. Complete PET depolymerization (y% PET conversion) was achieved in 25 mins for both catalyst with molar yield reaching 64.30% and 60.60% for DBU and TBD respectively. At about 5 mins into the reaction, DBU exhibited higher catalytic efficiency with a conversion of 76.99% and yield of 43.92% compared to 43.75% conversion and 32.5% molar yield observed with TBD, suggesting that DBU probably initiates the depolymerization process faster than TBD.

To further probe the influence of time, we extended the catalyst concentration to about 10% and evaluated the conversion and yield over an extended period (Fig 3.16). In this case, although the reaction time was further reduced to 15 mins, with DBU showing higher conversion quite early into the reaction, the overall BHET yield were lower than those obtained using the optimum catalyst concentration of 4.3%. In addition, a gradual decrease in BHET molar yield was observed after 15 mins for DBU and 30-60 mins for TBD, suggesting that running the reaction for a longer time does not enhance both PET conversion and BHET yield.

Table 3.6: Variation in reaction time and result at optimum TBD concentration

S/N	**Description**	**Temp. (C)**	**Time (mins)**	**Residue after depolyme-rization**	**PET (%) (conversion)**	**Weight of Glycolitic Product (GP)**	**Av. Weight of Product**	**Molar Yield %**
1a	0.5050g PET +0.0216g TBD +5ml EG	220	5	0.2989	40.81	0.2007	0.2171	32.47
1b	0.5061g PET +0.0215g TBD +5ml EG	220	5	0.2693	46.69	0.2334		
2a	0.5042g PET +0.0215g TBD +5ml EG	220	10	0.1118	72.83	0.3606	0.3611	54.10
2b	0.5050g PET +0.0217g TBD +5ml EG	220	10	0.0985	80.50	0.3616		
3a	0.5064g PET +0.0215g TBD +5ml EG	220	15	0.0277	94.53	0.4482	0.4473	67.03
3b	0.5025g PET +0.0216g TBD +5ml EG	220	15	0.0165	96.72	0.4464		
4a	0.5053g PET +0.0219g TBD +5ml EG	220	20	0.0069	98.63	0.3928	0.4135	61.76
4b	0.5069g PET +0.0218g TBD +5ml EG	220	20	0.0081	98.40	0.4342		
5a	0.5076g PET +0.0217g TBD +5ml EG	220	25	-	100.00	0.4011	0.4066	60.60
5b	0.5069g PET +0.0215g TBD +5ml EG	220	25	-	100.00	0.4120		

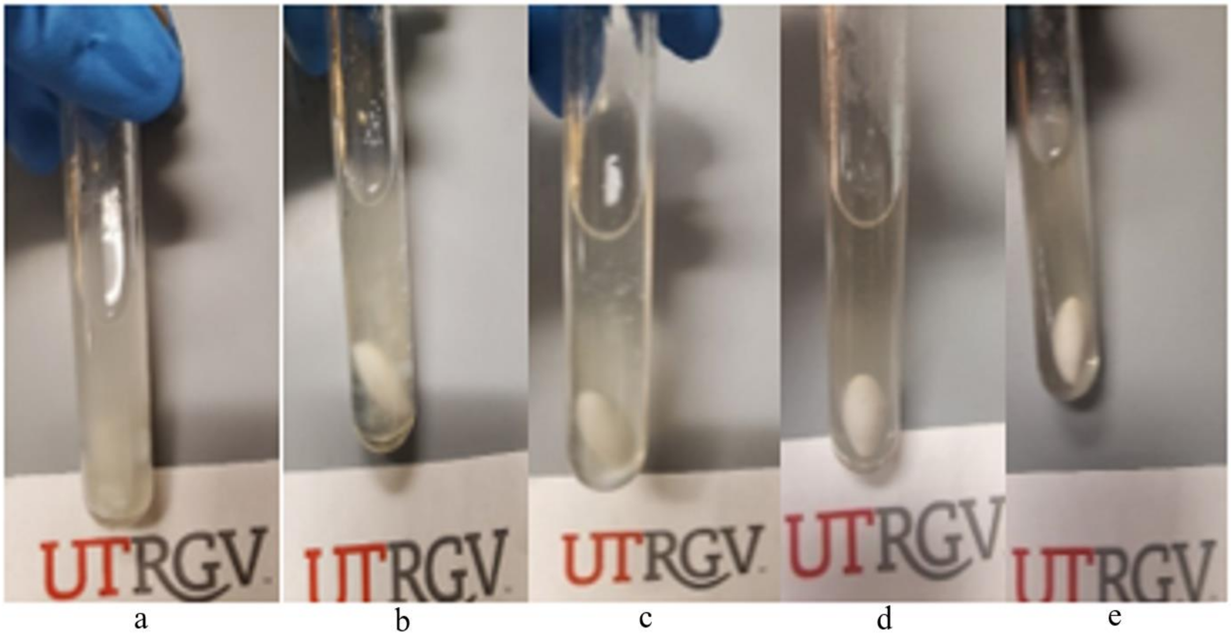


Figure 3.13: Describes the glycolytic product after depolymerization with TBD at a) 5 mins, b) 10 mins, c) 15 mins, d) 20 mins and e) 25 mins.
(PET:EG = 1:10; TBD conc. =4.33wt/wt%)

Table 3.7: Variation in reaction time and result at optimum DBU concentration

S/N	Description	Temp. (C)	Time (mins)	Residue after depolyme-rization	%conversion	Weight of Glycolitic Product (GP)	Av. Weight of product	% Molar Yield of BHET
1a	0.5050g PET +0.0220g DBU +5ml EG	220	5	0.1225	75.74	0.2924	0.2935	43.93
1b	0.5051g PET +0.0215g DBU +5ml EG	220	5	0.1123	7776	0.2947		
2a	0.5049g PET +0.0216g DBU +5ml EG	220	10	0.0611	87.90	0.3655	0.3746	56.07
2b	0.5052g PET +0.0220g DBU +5ml EG	220	10	0.0434	91.41	0.3838		
3a	0.5053g PET +0.0215g DBU +5ml EG	220	15	0.0289	94.29	0.3891	0.3951	59.16
3b	0.5045g PET +0.0217g DBU +5ml EG	220	15	0.0299	94.07	0.4011		
4a	0.5050g PET +0.0219g DBU +5ml EG	220	20	0.0153	96.97	0.4176	0.4270	63.84
4b	0.5063g PET +0.0216g DBU +5ml EG	220	20	0.0073	98.56	0.4363		
5a	0.5043g PET +0.0215g DBU +5ml EG	220	25	-	100	0.4296	0.4297	64.30
5b	0.5060g PET +0.0214g DBU +5ml EG	220	25	-	100	0.4301		

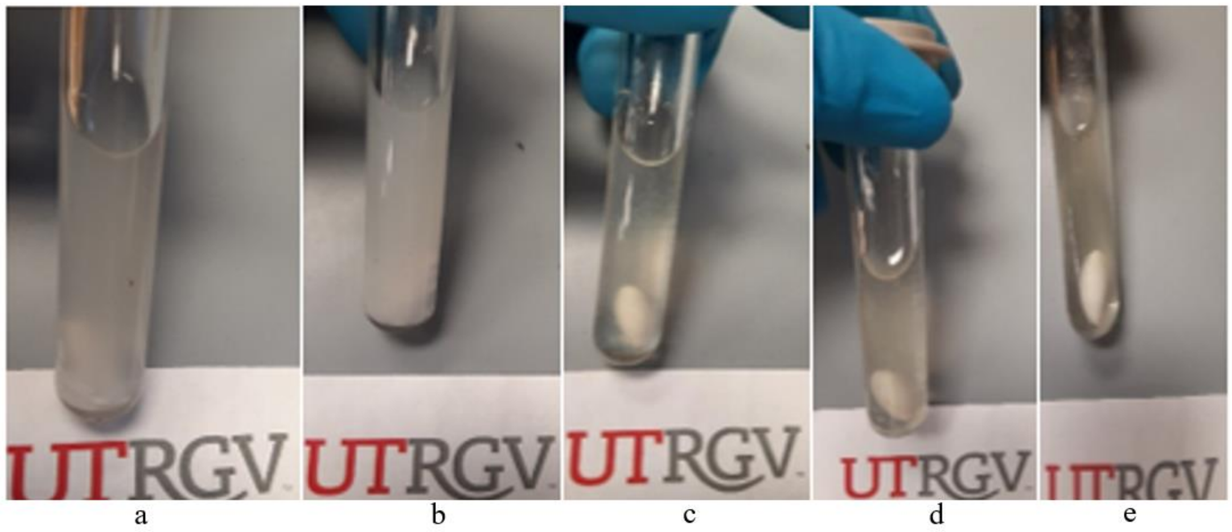


Figure 3.14: Describes the glycolytic product after depolymerization with DBU at a) 5 mins, b) 10 mins, c) 15 mins, d) 20 mins and e) 25 mins.
(PET:EG = 1:10; DBU conc. =4.33wt/wt%)

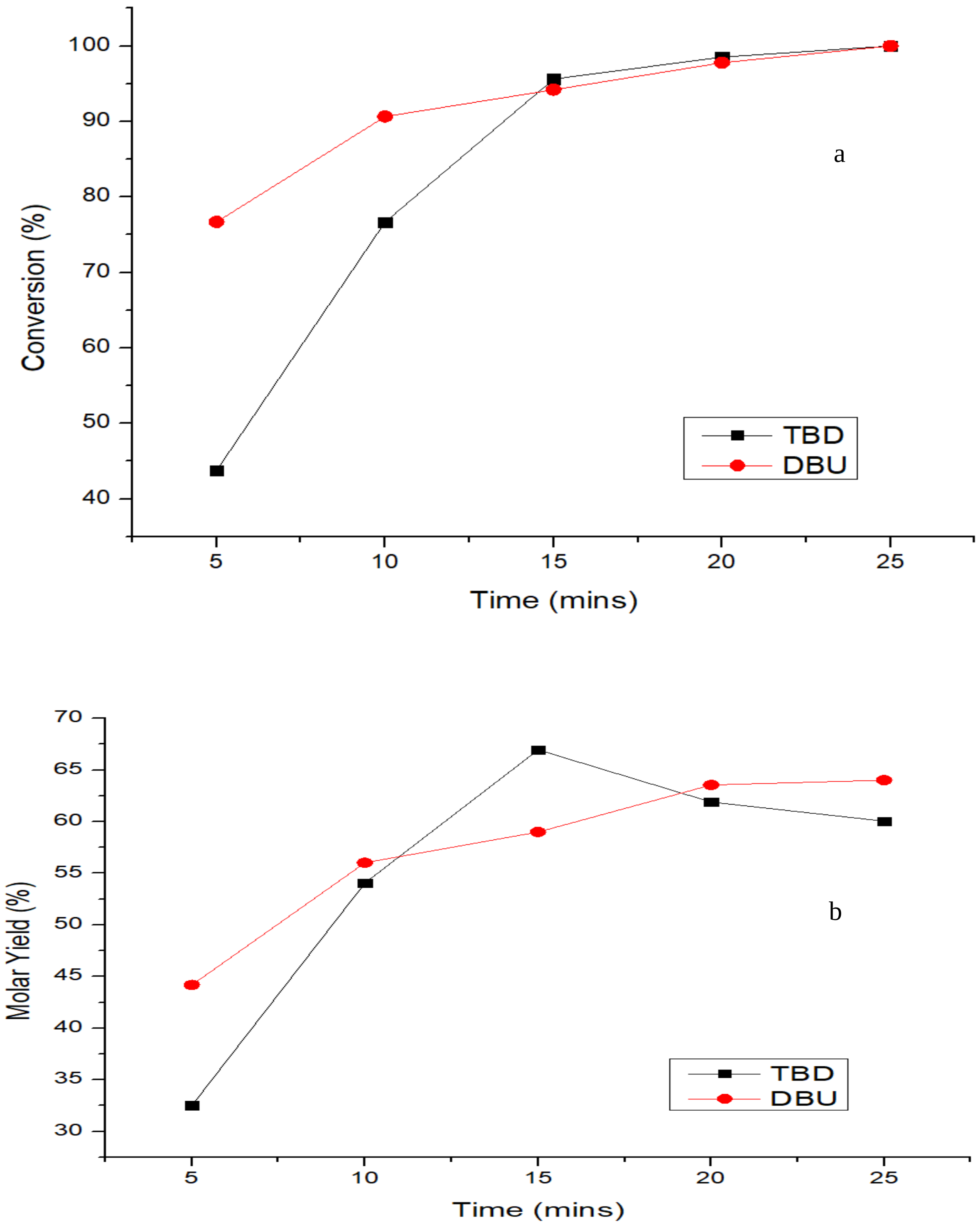


Figure. 3.15: Influence of reaction time on PET conversion (a) and BHET molar yield (b) at 4.33 wt/wt% catalyst concentration.

(The reactions conditions are PET:EG of 1: 10, Temp of 220°C)

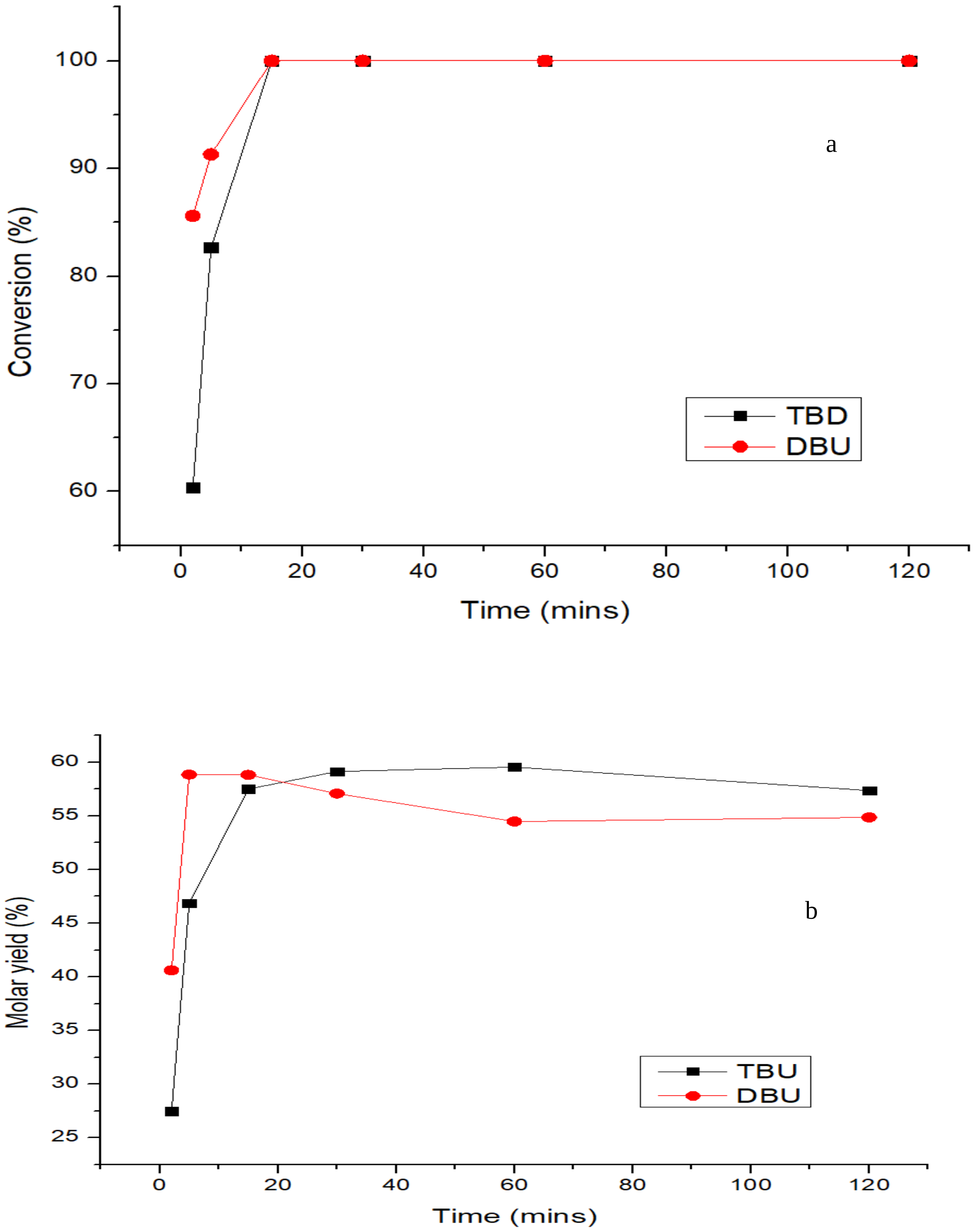


Figure. 3.16: Influence of reaction time on PET conversion (a) and BHET molar yield (b) at 10 wt/wt% catalyst Conc.

CHAPTER IV

CONCLUSIONS

In summary, we investigated the glycolysis of waste PET bottles under microwave irradiation using TBD and DBU. The aim was to evaluate the performance of the two organocatalyst with a view to optimizing reaction conditions for PET depolymerization and the yield of the product BHET. The reaction was carried out using PET: EG of 1:10 and was optimized at a temperature of 220°C for 25 mins at a catalyst concentration of 4.33 wt/wt% of the initial starting weight of the PET. The product was characterized as BHET with a very narrow melting point of 107.4-108.8°C showing the product was of high purity. From our initial assessment, we anticipated TBD to be more effective at depolymerization, given it higher basicity (pKa value) and it bifunctionality(from both the nucleophile and the additional hydrogen bonding possibility from the secondary ammine) Unexpectedly, DBU showed better catalytic performance in terms of reaction time, PET conversion and product yield in most of the conditions evaluated,, suggesting that the catalytic pathway might not necessarily be enhanced through hydrogen bonding from the bifunctional TBD.

Overall, the optimized reaction parameters showed significant reduction in the reaction time for the glycolytic depolymerization of PET which traditionally takes up to 4-8 hrs or more to degrade. In addition,, we were able to reduce the catalyst concentration from about 7-10 wt/wt% to just 4.33 wt/wt% under microwave conditions. In the future, we will extend this established optimized depolymerization conditions to incorporate the use of Lewis acid-DBU/TBD combinations, imidazole, and other nitrogen-based catalyst, explore simultaneous glycolysis-hydrolysis of PET using TBD/DBU, explore the depolymerization of colored PET bottles using conditions from this research, explore glycolytic depolymerization using Si carbide vials and possibly compare their performance with those of the glass vials and finally explore possibility of upcycling BHET obtained from this research into materials for hydrogen storage and other applications.

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BIOGRAPHICAL SKETCH

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