

**ADVANCING PET RECYCLING:
THE APPLICATION OF NOVEL CATALYSTS IN
DEPOLYMERIZATION PROCESS**

BY
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In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

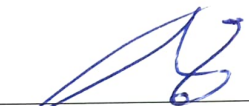
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To my parents, for their unconditional support in all my decisions.

(Ene-atama, ähli kararlaryma beren goldawy üçin)

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LIST OF ABBREVIATIONS

Ac	acetate
[AMIM]	1-allyl-3-methylimidazolium
BET	Brunauer–Emmett–Teller analysis
BHET	bis (2-hydroxyethyl) terephthalate
[Bmim]	1-Butyl-3-methylimidazolium
[Ch][Gly]	Choline Glycinate
[Cho]	Choline
[Deim]	1-Decyl-3-ethylimidazolium
DSC	differential scanning calorimetry
[Dec]0	decanoate
EG	ethylene glycol
FT-IR	fourier transform infrared spectroscopy
[Hmim]	1-Hexyl-3-methylimidazolium
IL	ionic liquids
LDH	Layered double hydroxide
[MTOA]	methyltrioctylammonium
NMR	nuclear magnetic resonance spectroscopy
PET	polyethylene terephthalate

[P ₄₄₄₄]	tetrabutylphosphonium
[P6,6,6,14]	trihexyltetradecylphosphonium
[TMPP]	bis(2,4,4-trimethylpentyl)phosphinate
XRD	X-Ray diffraction analysis

THESIS ABSTRACT

NAME: Akmuhammet Karayev

TITLE OF STUDY: Advancing PET Recycling: The Application of Novel Catalysts in Depolymerization Process

MAJOR FIELD: Chemical Engineering

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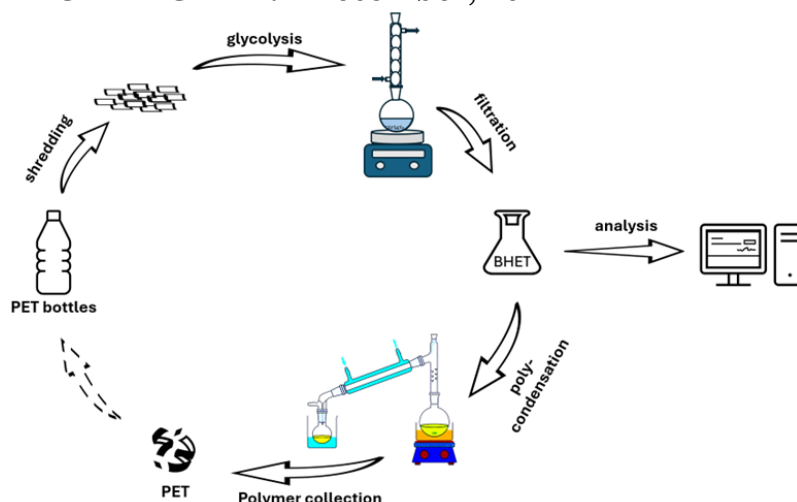


Figure 1. Graphical abstract

Polyethylene terephthalate (PET) recycling is a crucial practice for mitigating plastic pollution and advancing a circular economy. This thesis investigates the catalytic glycolysis of PET using sustainable materials, such as layered double hydroxides (LDHs) and ionic liquids, as catalysts. We explored the catalysts effectiveness and optimized the reaction parameters to enhance PET conversion and efficiency. The developed catalysts were characterized using X-ray diffraction (XRD), Fourier-

transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) analysis, nuclear magnetic resonance (NMR) spectroscopy, and thermogravimetric analysis (TGA), confirming their effectiveness in PET glycolysis. Our systematic studies optimized reaction conditions, achieving over 75% yield of bis(hydroxyethyl) terephthalate (BHET) within 2 hours at 200°C, with a catalyst loading of just 0.5-1%. Furthermore, the BHET produced was successfully repolymerized back into PET without additional catalysts, demonstrating closed-loop recycling potential. This approach represents a significant advancement in PET recycling, achieving rapid, high-yield conversions with minimal environmental impact. The work underscores the importance of catalysis and reaction engineering in sustainable materials management.

ملخص الرسالة

الاسم: اكهمت كاريف

عنوان الدراسة: تقدم إعادة تدوير PET: تطبيق المحفزات الجديدة في عملية التحلل البوليمري.

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ديسمبر 2024

تعد إعادة تدوير البولي إيثيلين تيرفثالات (PET) ممارسة بالغة الأهمية للتخفيف من تلوث البلاستيك وتعزيز الاقتصاد الدائري. تبحث هذه الأطروحة في التحلل السكري التحفيزي للبولي إيثيلين تيرفثالات باستخدام مواد مستدامة، مثل هيدروكسيدات مزدوجة الطبقات (LDHs) والسوائل الأيونية، كمحفزات. استكشفنا الفعالية التحفيزية وقمنا بتحسين معاملات التفاعل لتعزيز تحويل البولي إيثيلين تيرفثالات وكفاءته. تم فحص العوامل المحفزة المطورة باستخدام حيود الأشعة السينية (XRD)، وقياس الطيف بالأشعة تحت الحمراء (FT-IR)، وتحليل السطح بروناور-إيميت-تيلر (BET)، وتحليل الرنين المغناطيسي النووي (NMR)، والتحليل الحراري الوزني (TGA)، مما أكد فعاليتها في جليكوليز PET. من خلال الدراسات المنهجية، تم تحسين ظروف التفاعل، وتحقيق عائد يفوق 75% من ثنائي هيدروكسي إيثيل تيريفثالات (BHET) خلال ساعتين عند درجة حرارة 200 درجة مئوية، باستخدام تركيز محفز يتراوح بين 0.5-1%. علاوة على ذلك، تم إعادة بلورة BHET المنتج بنجاح إلى PET بدون عوامل محفزة إضافية، مما يظهر إمكانات إعادة التدوير المغلقة. يمثل هذا النهج تقدماً كبيراً في إعادة تدوير PET، مع تحقيق تحويلات سريعة وعالية العائد. يؤثر بيئي ضئيل. يؤكد هذا العمل على أهمية التحفيز وهندسة التفاعل في إدارة المواد المستدامة.

CHAPTER 1

INTRODUCTION

1.1 Background

The widespread use of plastics has resulted in considerable environmental and health challenges due to insufficient plastic waste management. Globally, 311 million tons of plastic are estimated to be produced annually [1]. Most plastics have a prolonged degradation time, posing a major environmental hazard. Half of the plastic production is PET (polyethylene terephthalate), which constitutes over 50 million tons and boasts a global recycling rate around or below 14% [2].

PET is a significant contributor to plastic pollution due to its prevalent use in bottles, packaging, and textile applications. Waste recycling does not only help to keep vast amounts of plastic out of landfills, it also saves precious resources by cutting down on the need for virgin polymer production [3]. As a result, greenhouse gases that are hitherto released by traditional manufacturing methods are reduced. Integrating PET recycling into the economy as a basic commodity falls under global efforts of mitigating plastic pollution, resource conservation and circular economies that incentivize sustainable systems for long-term challenges.

1.2 Problem Statement

The widespread use of plastics has resulted in considerable environmental and health challenges due to insufficient plastic waste management. Estimates indicate that a fraction of the plastics produced between 1950 and 2015 were disposed of using different techniques. Between 1950 and 2015, approximately 12% of the plastic waste was incinerated, while only 9% underwent recycling processes. This suggests that the majority of plastic are likely discarded through other means, such as landfill disposal or accumulation in the environment [4]. The inert and largely non-biodegradable nature of plastics hinder their decomposition and reintegration into the natural cycle, however, the process of decomposition can span several centuries [5]

Waste polyethylene terephthalate (PET), which accounts for 10% of the total plastic waste, has become an important environmental concern due to its extensive applications in the packaging industry and its resistance to natural degradation. In 2019, the global production capacity of PET was approximately 30.5 million metric tons. By 2024, this quantity was projected to reach nearly 35.3 million metric tons [6]. The accumulation of waste PET in landfills and its disposal into oceans pose serious ecological issues, demanding innovative strategies to facilitate sustainable solutions.

1.3 Objectives

The goal of our study is to test sustainable heterogeneous (layered double hydroxide) and homogeneous (ionic liquids) catalysts for the depolymerization of PET. This goal will be pursued through the establishment of optimal conditions for efficient recycling processes. The research will be structured around the following objectives:

1. Synthesis of LDH catalysts.
2. Undertake calcination of the synthesized LDHs to activate their catalytic properties.
3. Characterize the resultant catalysts using appropriate analytical techniques to determine their physical and chemical properties.
4. Determine the most effective catalyst for PET depolymerization through comparative analysis.
5. Establish the optimal conditions (including temperature, duration, catalyst loading, etc.) for efficient PET recycling by conducting a series of controlled depolymerization reactions.
6. Investigate the influence of ionic liquids on the depolymerization processes.
7. Determine if the catalysts are suitable to be used for multiple reaction cycles.

1.4 Contribution

This thesis contributes to the circular economy by presenting a comprehensive and sustainable approach to PET waste management. The research aims to establish a viable closed-loop system for PET recycling through the optimization of a catalyst for efficient depolymerization and the evaluation of the potential for repolymerizing the resulting monomers.

Our catalysts are selected with environmental sustainability in mind. By utilizing materials that are both effective and eco-friendly, we reduce the overall environmental footprint of the recycling process. This dual focus on efficiency and sustainability ensures that the recycled PET can seamlessly reintegrate into production cycles, supporting the development of a circular economy.

The broader implications of this work highlight the potential for similar approaches to be applied to other types of plastic waste. In summary, this thesis provides a significant step forward in addressing plastic pollution and promoting sustainable recycling practices.

1.5 Thesis organization

This thesis is structured to guide the reader through the study's background, experimental methodology, and findings in a cohesive progression. Chapter 1 provides a context on the environmental impact of PET waste, outlines the problem, objectives, and contributions of the research. Chapter 2 presents a literature review about the recycling methods and examines the environmental challenges associated with PET, identifying gaps in current approaches and establishing the need for the experimental work that follows.

Chapters 3 and 4 introduce the core experimental work, detailing PET glycolysis using layered double hydroxides (LDH) and ionic liquids (IL) as catalysts. Each chapter includes a theoretical overview, experimental methods, results, and discussions on the effectiveness and reusability of these catalysts. Chapter 5 then addresses the possibility for repolymerizing the monomers obtained from glycolysis to create high-quality recycled PET. The thesis concludes with a summary of key findings, challenges faced and future research recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1. PET and its environmental impact

PET is a condensation polymer that is generated by the polymerization of terephthalic acid (TPA) and ethylene glycol (Figure 2), or through transesterification of dimethyl terephthalate (DMT) and ethylene glycol (Figure 3). PET, which was initially developed by DuPont during the mid-1940s, has emerged as a widely produced thermoplastic material [7–9]. The production of PET at various specifications is achieved by regulating the polymerization conditions, depending on the intended use and desired qualities [10,11]. It is primarily used in the textile industry in the form of fibers, which are subsequently utilized in the manufacturing of polymer films. In addition, the polymer has been widely employed in the injection blow molding processes for the purpose of manufacturing robust and transparent bottles and jars [10,12]. The PET plastic bottles, which were patented by engineer Nathaniel Wyeth in 1973, saw rapid market adoption and have since garnered significant popularity and adaptability on a global scale. As a result, they have risen as a popular option for beverage containers.

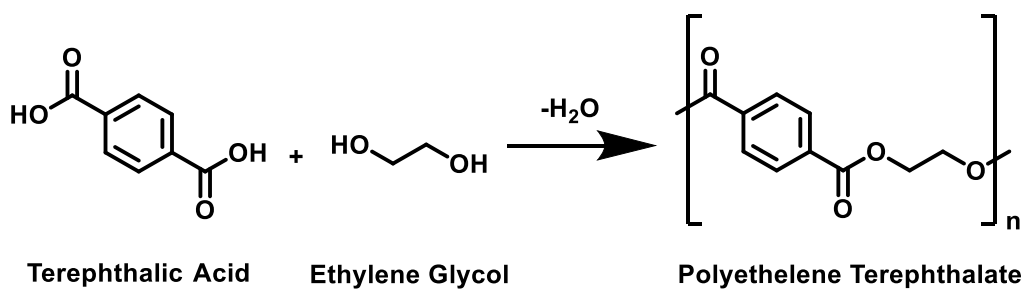


Figure 2. Formation of PET by the reaction of EG and TPA.

The growth in the market for PET packaging, mostly utilized for food and beverage packaging purposes, can be attributed to its rising adoption as a substitute for glass and metal containers. In comparison to alternative plastic materials employed in packaging, PET plastics exhibit superior attributes such as enhanced durability, transparency, lightweight composition, non-reactivity, shatterproof nature, thermal stability, cost-effectiveness, heightened pressure resistance, mechanical strength, and improved barrier properties, specifically in terms of impermeability to liquids and gases [13]. Due to its high resistance to hydrolytic and enzymatic degradation, PET exhibits very slow natural decomposition. Consequently, the vast majority of PET polymers produced today are expected to persist for several decades, potentially extending into millennia. For this reason, significant amounts of post-consumer PET plastics accumulate in landfills, oceans, and ecological systems, exerting adverse effects on both terrestrial and aquatic organisms [9,14–16].

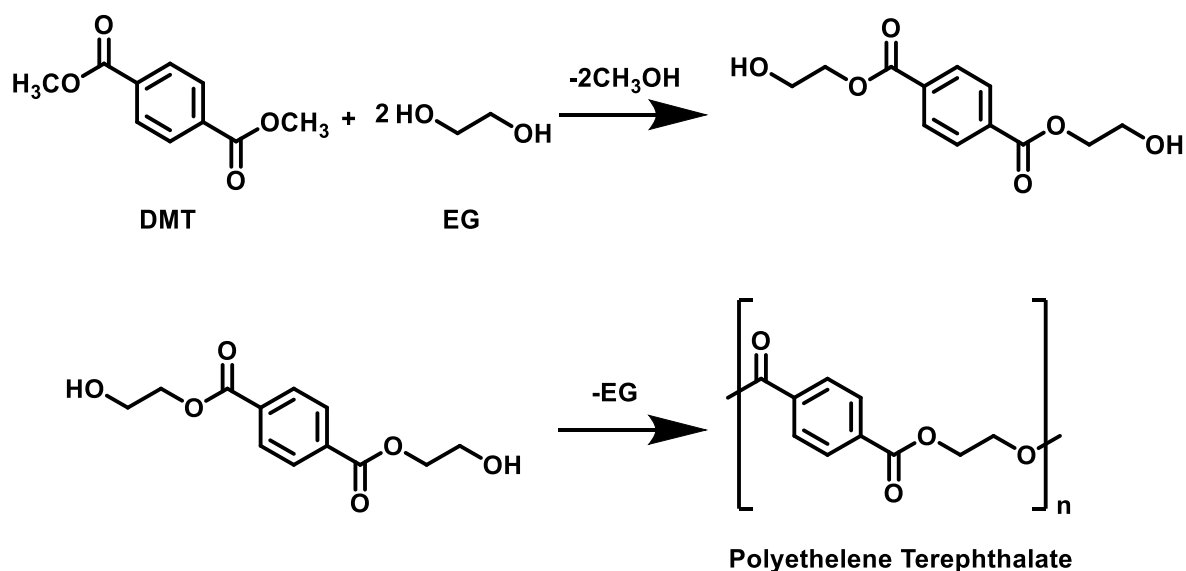


Figure 3. Transesterification reaction of DMT and EG to form PET.

Introduction of millions of metric tons of plastic waste into the ocean has resulted in the formation of extensive plastic accumulation, referred to as "the Great Pacific garbage patch." This influx of plastic debris presents a significant threat to the lives of marine animals, as shown by studies conducted by Lamb et al. [17] and Li et al. [18]. Micro- and nano-plastics generated through physical abrasion and photooxidation contribute to the contamination of marine and terrestrial ecosystems. This contamination leads to the release of harmful plastic additives and the disruption of ecosystems, affecting organisms at various trophic levels, from lower organisms to higher animals [19].

Plastics have shown to pollute the soil environment, leading to detrimental effects on soil composition, water potential, nutrient levels, and ultimately terrestrial biodiversity [20]. As the apex predators in the ecological hierarchy, humans inevitably confront the issue of plastic pollution, with an estimated ingestion of up to 5 grams of microplastics every week [21]. In light of the findings by Aguilar-Guzmán et al. [22], which demonstrate that the internalization of nanoparticles of PET by macrophage cell lines leads to oxidative stress and disruptions in cell multiplication and growth, it is essential to acknowledge the potential health hazards linked to inhaling and ingestion of PET. While direct evidence of toxic effects on humans is currently lacking, the aforementioned cellular responses suggest the possibility of adverse health effects.

As PET waste continues to grow, a circular economy offers a practical solution to address energy and resource use, reduce harmful emissions, and decrease the amount of poorly managed plastic waste entering the environment [23].

2.2. Methods of recycling

There are several PET recycling methods each with unique advantages and limitations. Mechanical recycling is one of the most cost-effective methods and is widely used in industry. This process involves collecting, washing, separating, and re-melting of PET to form pellets. However, this recycling method is considered a temporary solution because the quality of the recycled PET (rPET) drops with each cycle and is often used for secondary materials that eventually end up in landfills [4]

Chemical recycling (glycolysis, methanolysis, and hydrolysis) provides raw materials which can be re-polymerized back into high-quality PET. Depolymerization performance is essentially determined by reaction conditions, such as time, temperature, catalyst nature and amount, etc [5].

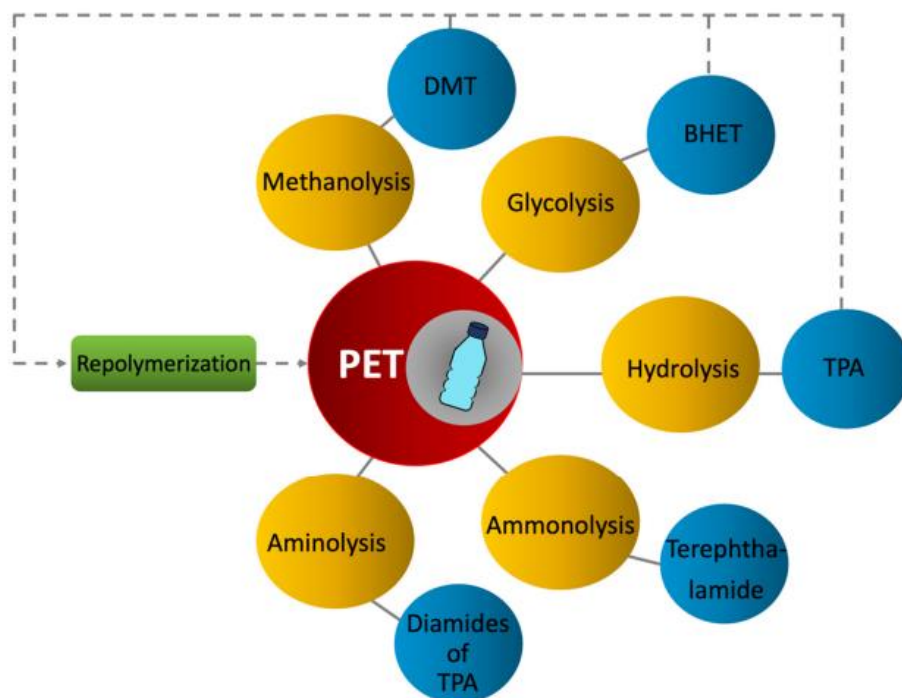


Figure 4. PET recycling methods and their products.

Hydrolysis of PET results in the formation of EG and TPA (Figure 5). The utilization of hydrolysis for the recycling of food-grade PET is not preferred due to the high purification costs of TPA and it requires extreme conditions of 1.4-2 MPa pressure, temperatures of 200-250 °C in either acidic, basic, or neutral environments [24].

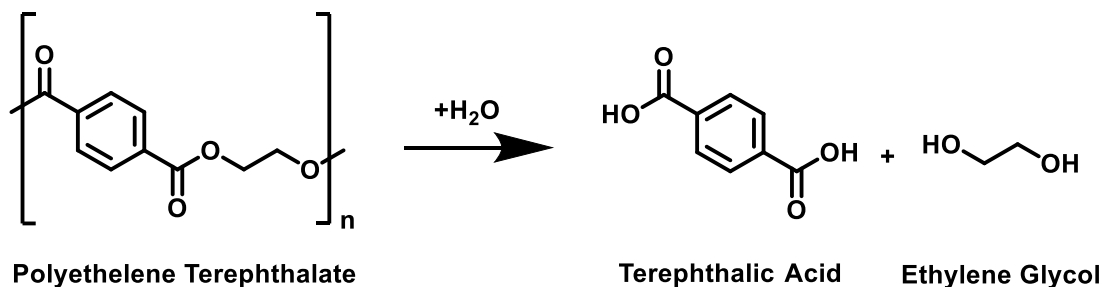


Figure 5. Reaction equation of PET hydrolysis to form TPA and EG.

Methanolysis (Figure 6) is the heating of PET in methanol at the temperatures of 180 to 280 °C [24]. The maintenance of methanol in a liquid form during the depolymerization is a challenge which is achieved by the application of high-pressure (2-4 MPa) reaction conditions. Some reactions in the depolymerization step yield a mixture of alcohols, glycols, and phthalate derivatives [25]. Methanolysis, though effective, often involves toxic reagents and costly purification steps. The procedure generally yields DMT within the range of 80 to 85%.

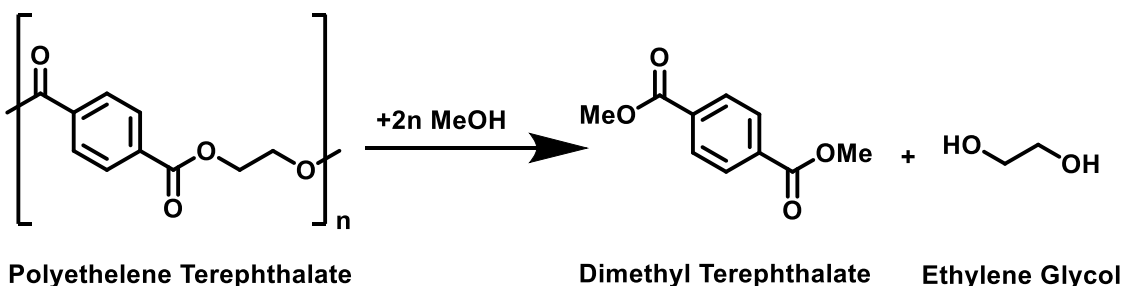


Figure 6. Reaction equation of PET methanolysis to form DMT and EG.

Aminolysis is an another approach for the chemical glycolysis of PET, however, it has received relatively less attention compared to other chemical recycling methods. Only a

limited number of studies have investigated the effects of various amines, such as allylamine, polyamines, and ethanolamine. Aminolysis involves the reaction of anhydrous amines with PET using ethylene glycol (EG) as a solvent. The reaction results in the formation of terephthalamide (Figure 7). It can then undergo conversion processes to provide terephthalonitrile, para-xylylene diamine, and/or 1,4-bis(aminomethyl)-cyclohexane [26]. This process necessitates reaction temperatures and pressures ranging from 120 to 180 °C and 2 MPa, respectively, for a duration of 1 to 7 hours [5,27,28]. Upon completion of the reaction, the amide compound is subjected to filtration, followed by rinsing with water and subsequent drying. Major disadvantage about aminolysis is that it tends to generate complex by-products, complicating the separation process [29].

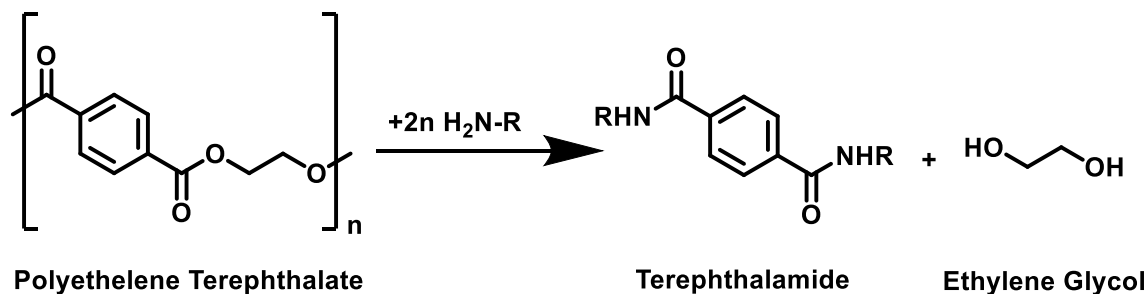


Figure 7. General reaction equation of PET aminolysis to form TPA and EG

Among previously discussed chemical recycling processes, glycolysis is distinguished as a more pragmatic and effective procedure. It operates under milder conditions, making it more energy-efficient [30]. Glycolysis uses ethylene glycol (EG) as a stable depolymerizing agent and a solvent at the same time, resulting in fewer by-products (Figure 8). This process yields bis(2-hydroxyethyl) terephthalate (BHET), a valuable monomer reusable in PET synthesis and versatile for producing textile dyes, polyurethane oligomers, foams, biocompatible materials, and other related applications [31].

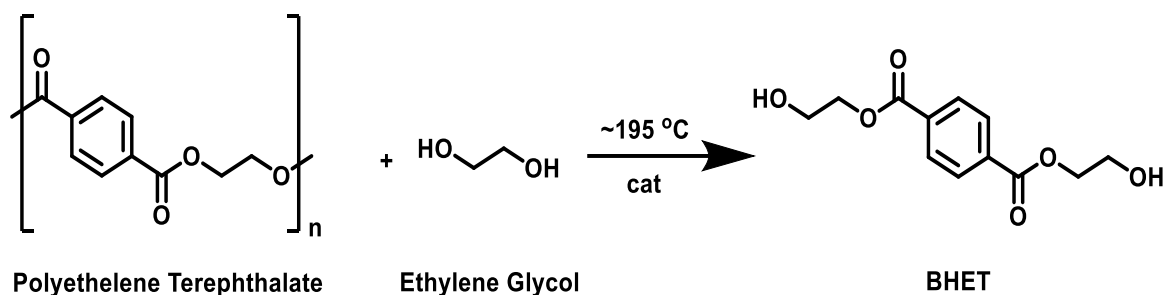


Figure 8. Reaction equation of the PET glycolysis process to form BHET.

This process is catalyzed by various agents, including metal salts, ionic liquids, and enzymes, which facilitate the breakage of the ester bonds in the PET polymer chain [30]. The reaction mechanism generally involves the nucleophilic attack of the hydroxyl group of ethylene glycol on the carbonyl carbon of the PET ester, leading to the formation of BHET and the release of ethylene glycol [29]. Previous studies in PET glycolysis have extensively explored catalysts such as metal salts, ionic liquids, and enzymes to enhance depolymerization efficiency. For instance, while traditional metal salt catalysts like zinc acetate are effective in catalytic activity, they often require extended reaction times and consume significant amounts of energy [30]. Enzyme-based glycolysis is environmentally friendly but it hasn't been implemented in large-scale due to the unpredictable nature of the process [32]. Other catalyst-free approaches like microwave-assisted glycolysis increase reaction efficiency, but the implementation in the industry solely depends on the development of the large-scale continuous microwave reactor [33], [34]. Moreover, catalysts like oxygen vacancy-rich metal oxides, despite their promising catalytic performance, still face issues such as limited recyclability and high synthesis costs [32].

CHAPTER 3

PET glycolysis in the presence of Layered Double Hydroxides

3.1. Layered double hydroxides

A catalyst plays a pivotal role in enhancing the efficiency of a glycolysis reaction. Without a catalyst, the reaction rate is significantly reduced, or it does not occur. As discussed in the last section, various materials have been tested for PET glycolysis showing different degrees of efficiency [35–38]. Nevertheless, there is a noticeable gap in the discussion of PET glycolysis effected by LDH compounds. In this work, we demonstrated the effects of various LDH materials on the glycolysis of PET.

Layered Double Hydroxides, often referred to as anionic clays, represent a class of materials characterized by their unique layered structure. These materials consist of positively charged metal hydroxide layers interspersed with anions in the interlayer spaces. The general formula for LDHs can be written as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are the metal cations, and A^{n-} represents the interlayer anions [37]. This structural configuration not only imparts significant chemical versatility but also enhances their catalytic properties. We explained the details of LDH synthesis in the experimental section.

The catalytic performance of LDHs in the glycolysis of PET can be attributed to several intrinsic features. Firstly, the presence of surface hydroxyl groups facilitates the

adsorption of PET molecules, thereby promoting the cleavage of ester bonds. This is particularly important in the context of PET recycling, where efficient depolymerization is essential for recovering monomers. Furthermore, the tunability of metal cations allows the optimization of catalytic activity by adjusting the electronic and steric properties of the active sites [35,38].

3.2. Experimental

3.2.1. Materials

Anhydrous ethylene glycol (EG) with 99.8% purity, aluminum nitrate nanohydrate - $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, potassium carbonate - K_2CO_3 , and potassium hydroxide - KOH , all of which were procured from Sigma Aldrich[®]. Zinc nitrate hexahydrate - $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was acquired from Loba Chemie[®]. Post-consumer water bottles made of PET were gathered, rinsed thoroughly to remove any contaminants, and then shredded into small pieces using a pulverizer.

3.2.2. Synthesis of LDH materials

For the synthesis of LDH, 25 ml aqueous solutions of 0.03 mole M^{2+} salt and 0.01 mole of M^{3+} salt were prepared. Separately, 50 ml solution of 1.06 g Na_2CO_3 was prepared under continuous magnetic stirring and nitrogen gas purging. The temperature was maintained at 40 °C. The metallic salt solutions were combined and transferred to a burette while another burette was filled with the NaOH solution. Both solutions were added dropwise to the Na_2CO_3 solution in the three-neck flask, maintaining the pH at 10. The mixture was then refluxed at 70 °C under a nitrogen environment for 24 hours. After refluxing, the mixture was

centrifuged and rinsed with DI water until the pH reached to 7.0; The resulting cake was washed once with ethanol, centrifuged, and then dried at 60-70 °C for 24 hours to obtain M^{2+}/M^{3+} LDH. Obtained LDH powder was subsequently screened through a 200-mesh sieve to ensure uniform particle size distribution. The catalysts were tested via X-Ray diffraction analysis (XRD), fourier transform infrared spectroscopy (FT- IR), and Brunauer–Emmett–Teller analysis (BET) to confirm the formation of pure LDH.

3.2.3. Material Characterization

The synthesized catalysts and depolymerization product samples were analyzed using Nuclear Magnetic Resonance (NMR), Gas Chromatography–Mass Spectrometry (GC-MS), Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM). NMR analysis was performed using a Jeol 600 Nuclear Magnetic Resonance spectrometer operating at 600 MHz. FTIR spectra were recorded with an iS50 6700 FTIR spectrometer over a wavelength range of 4000 to 400 cm^{-1} . XRD analysis was conducted at room temperature using a Rigaku Mini-Flex XRD system, operating at 40 kV and 15 mA with a radiation wavelength of 1.54060 Å, the diffraction angle (2θ) was scanned from 5° to 80° at a rate of 2 °/min. TGA was carried out in a nitrogen atmosphere with an SDT-Q6000 (TA Instruments), using a heating rate of 10 °C/min over a temperature range of 30 °C to 800 °C. SEM imaging was conducted with a JEOL JSM-6610LV microscope. GC-MS analysis was performed using an Agilent MassHunter GC/MS system with a 1 μL injection volume.

3.2.4. The glycolysis of PET in the presence of LDH materials

Glycolysis reactions were carried out in a two-step process which involve reflux heating followed by recrystallization. In the reflux step, 2 grams of PET along with 20 milliliters of ethylene glycol were added to a 250-milliliter RB flask maintained at 200 °C. A specified quantity of the LDH catalyst was introduced for each reaction. The reactions were performed for a duration of 30 minutes to 2 hours under atmospheric pressure.

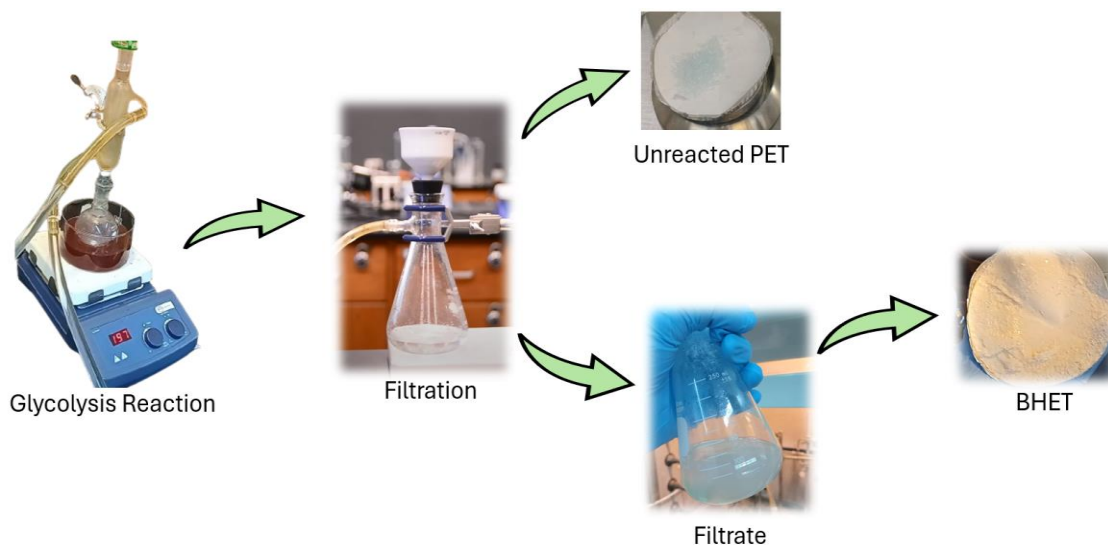


Figure 9. PET Depolymerization Process Flow

Unreacted PET was collected by rapid filtration, rinsed with water, dried, and measured to calculate the conversion by the equation:

$$Conversion (\%) = \frac{m_{PET(initial)} - m_{PET(final)}}{m_{PET(initial)}} \cdot 100\% \quad (1.1)$$

In the recrystallization step, the filtrate was stored in the fridge at 4.0 °C for 20 hours. White crystals of BHET appeared overnight and filtered off. The obtained white product was dried in a vacuum drier at 50 °C for

15 hours and measured to calculate the yield of the product:

$$Yield (\%) = \frac{m_{BHET(obtained)}}{m_{PET(expected)}} \cdot 100\% \quad (1.2)$$

$$m_{BHET(expected)} = \frac{m_{PET(initial)}}{M_{PET}} \cdot M_{BHET} \quad (1.3)$$

$$M_{PET} = 192.17 \text{ g/mol}$$

$$M_{BHET} = 254.24 \text{ g/mol}$$

3.2.5. Catalyst and solvent reusability

To assess the reusability of the catalyst and the solvent in the depolymerization reaction, the filtrates from previous filtration steps were combined, and their water content was removed using a rotary evaporator (Figure 10) to yield a dry solution of 20 ml EG. This recovered EG was then used to react with the remaining unreacted PET from the same reaction batch. To ensure consistency in the experimental setup, an additional amount of fresh PET was added, making the total mass of PET in the reaction equal to 2.0 grams.



Figure 10. Removal of water via rotary evaporator.

3.3. Results and discussion

Various LDH materials were synthesized as described in section 3.2.2 and their catalytic effects were tested for PET glycolysis. ZnAl-CO₃ was found to be the highest-performing catalyst followed by MgFe and MgAl. Thus, ZnAl LDH was used for further analyses to know the optimal conditions for glycolysis.

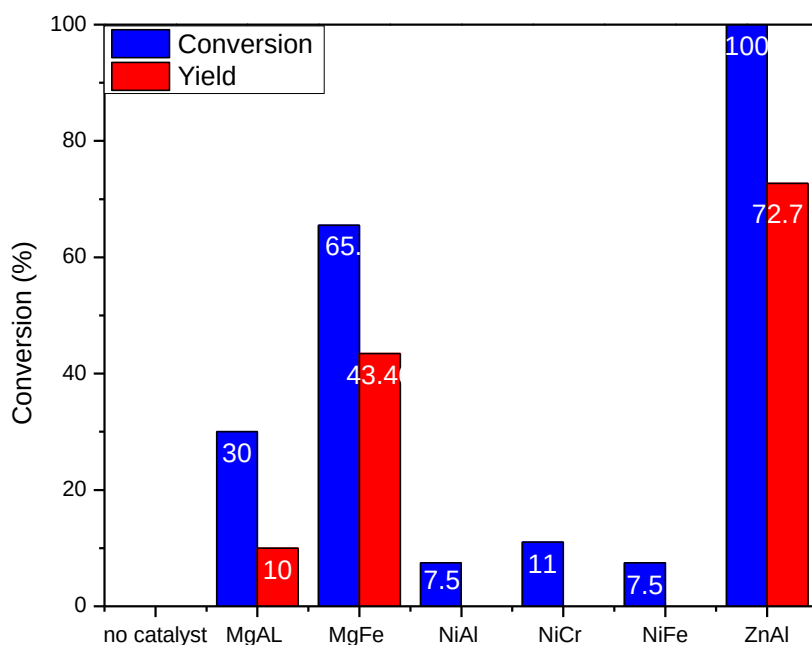


Figure 11. Effects of various LDH materials on the glycolysis of PET (200 °C, 1% cat, 2 h).

3.3.1. LDH characterization

X-ray diffraction. ZnAl CO₃ layered double hydroxide was synthesized as discussed in section 3.2.2. The catalyst was tested via XRD, FT-IR, BET, and SEM analyses. The X-ray diffraction (XRD) analysis of the ZnAl CO₃ sample is presented in Figure 12. The most prominent peaks occur at 2θ values of 11.62°, 23.40°, 31.69°, 34.43°, 36.20°, and 39.10°, corresponding to d-spacings typical of ZnAl LDH compounds. The peak observed at 11.62° indicates the presence of well-ordered layered material. Peak sharpness suggests that the prepared LDH was in a crystalline phase.

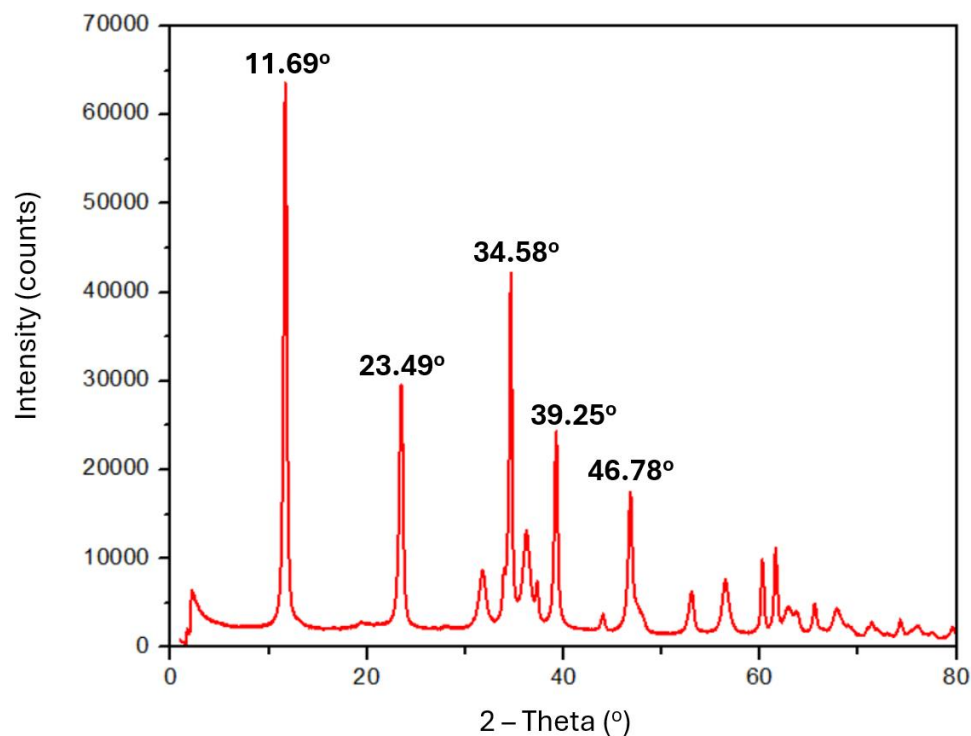


Figure 12. XRD spectrum of ZnAl LDH

Fourier transform infrared (FT-IR) spectroscopy analysis. Figure 13 illustrates the FT-IR spectrum of the synthesized ZnAl-CO₃ LDH material. The broad peak, at around 3450 cm⁻¹ is resulted from the O-H stretching vibrations [39], indicative of -OH groups and interlayer water. The bands from 1350 to 1500 cm⁻¹ are assigned as the asymmetric stretchings of interlayer carbonate ions [39], while peaks around 850 cm⁻¹ and 700 cm⁻¹ are associated with the out-of-plane and in-plane bending modes of carbonate, respectively. Moreover, the bands around 800 cm⁻¹ are attributed to the stretching vibrations of M-O and M-OH, indicating that there are metal-oxygen bonds in LDH structure [40]. These spectral features are in agreement with the synthesized ZnAl-CO₃ LDH material.

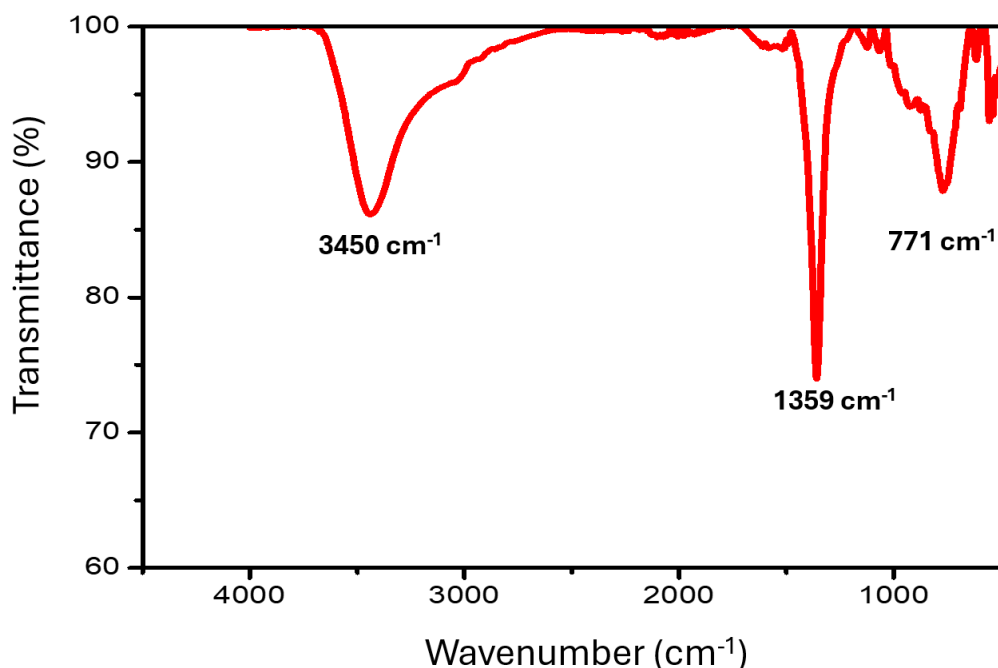


Figure 13. FT-IR spectrum of the ZnAl LDH.

Brunauer-Emmett-Teller (BET) – surface area characterization. The nitrogen adsorption-desorption isotherm for the synthesized ZnAl-CO₃ layered double hydroxide (LDH) is shown in Figure 14. As can be indicated from the figure, the material contains mesoporous structures. The isotherm demonstrates a Type IV pattern with a distinct hysteresis loop, suggesting capillary condensation within mesopores [41]. The provided BET surface area of 43.66 m²/g and Langmuir surface area of 62.49 m²/g indicate a substantial surface area that is well-suited for adsorption applications. The total pore volume of 0.1403 cm³/g, combined with the average pore diameter of approximately 27 nm, confirms the presence of a well-developed mesoporous network. These values suggest the material's potential effectiveness in processes like gas or liquid adsorption, catalysis, or separation technologies [41].

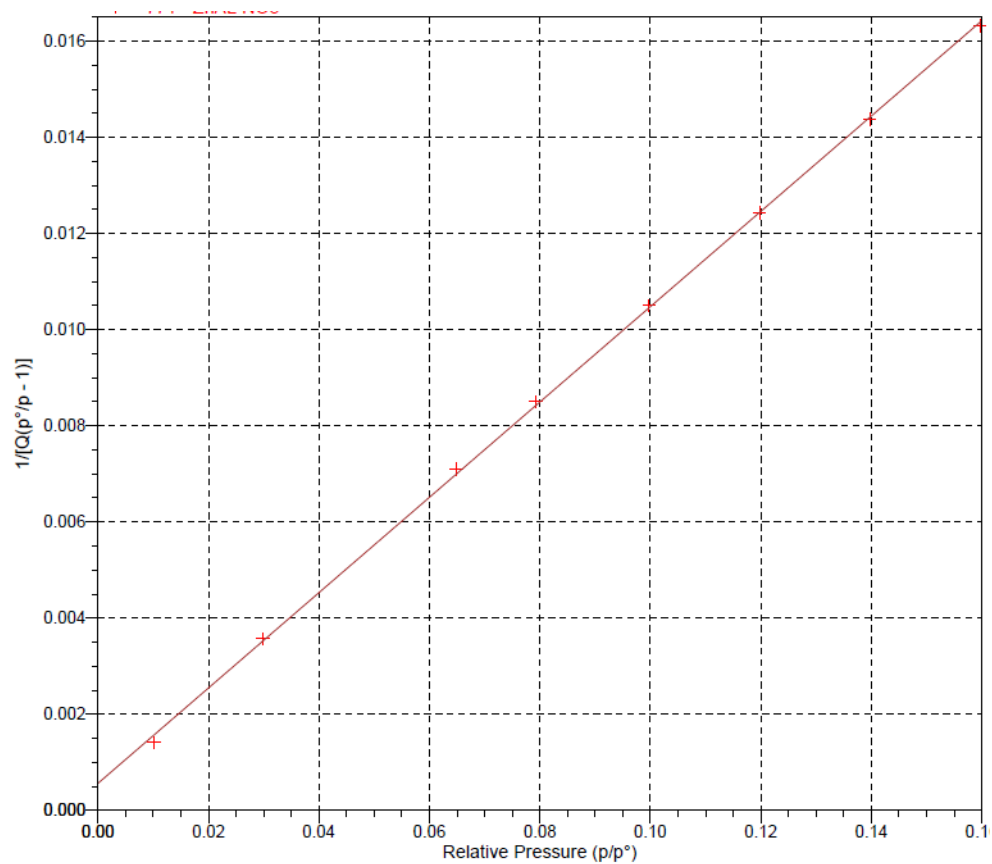


Figure 14. BET surface area plot.

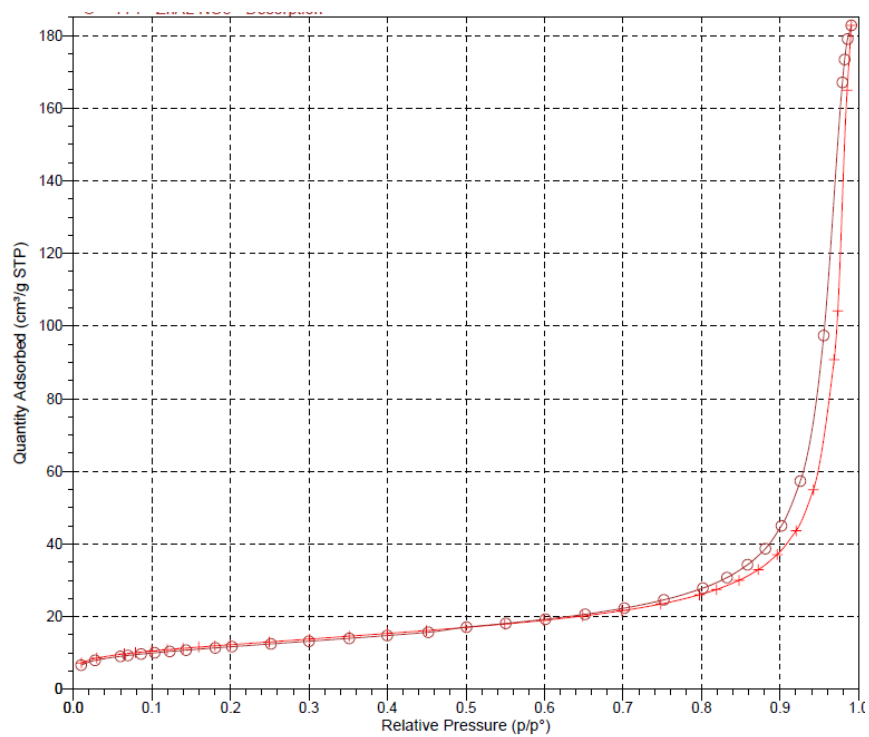


Figure 15. Isotherm linear plot of nitrogen adsorption-desorption

The thermogravimetric analysis (TGA) of the ZnAl-CO₃ LDH catalyst, used in our experiments, reveals multiple stages of weight loss corresponding to distinct thermal events (Figure 16). The first significant weight loss occurs around 177.52 °C, which is attributed to the removal of physically adsorbed water molecules, and possibly some surface-bound hydroxyl groups, from the interlayer space of the LDH structure.

A second major transition, observed at approximately 237.21 °C, is likely due to the dehydroxylation of the LDH layers and the partial decarbonation of the carbonate ions present within the interlayer space. This stage marks the onset of structural decomposition of the LDH. As the temperature increases beyond 300°C, the sample undergoes a gradual decomposition process, likely driven by the further breakdown of carbonate anions and the complete decomposition of the LDH structure.

By the time the temperature reaches 800 °C, about 28.77% of the original mass remains, indicating the presence of a thermally stable residue from the metal oxides formed after the decomposition of the LDH structure.

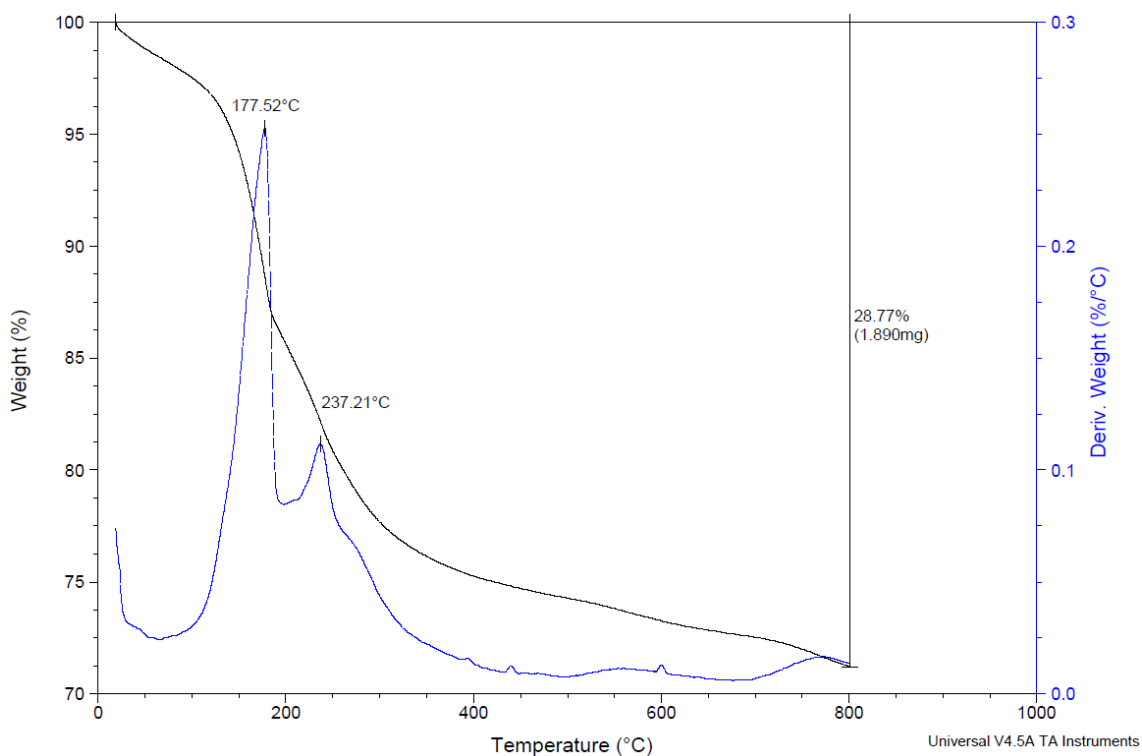


Figure 16. TGA of ZnAl LDH catalyst - weight loss and decomposition profile.

Scanning Electron Microscopy of ZnAl-CO₃ LDH reveals a characteristic morphology consistent with layered double hydroxides (Figure 17). At high magnifications (15,000x), the material exhibits plate-like particles with sizes in the submicron range, indicative of well-formed crystallites. Lower magnification images (1,000x and 5,000x) show larger aggregates and clusters, suggesting a hierarchical structure with both micron-sized and submicron-sized features. The porous texture observed at intermediate magnification (5,000x) implies a high surface area, making the material suitable for applications in adsorption and catalysis. These morphological characteristics are typical of LDH materials and confirm the successful synthesis of ZnAl-CO₃ LDH.

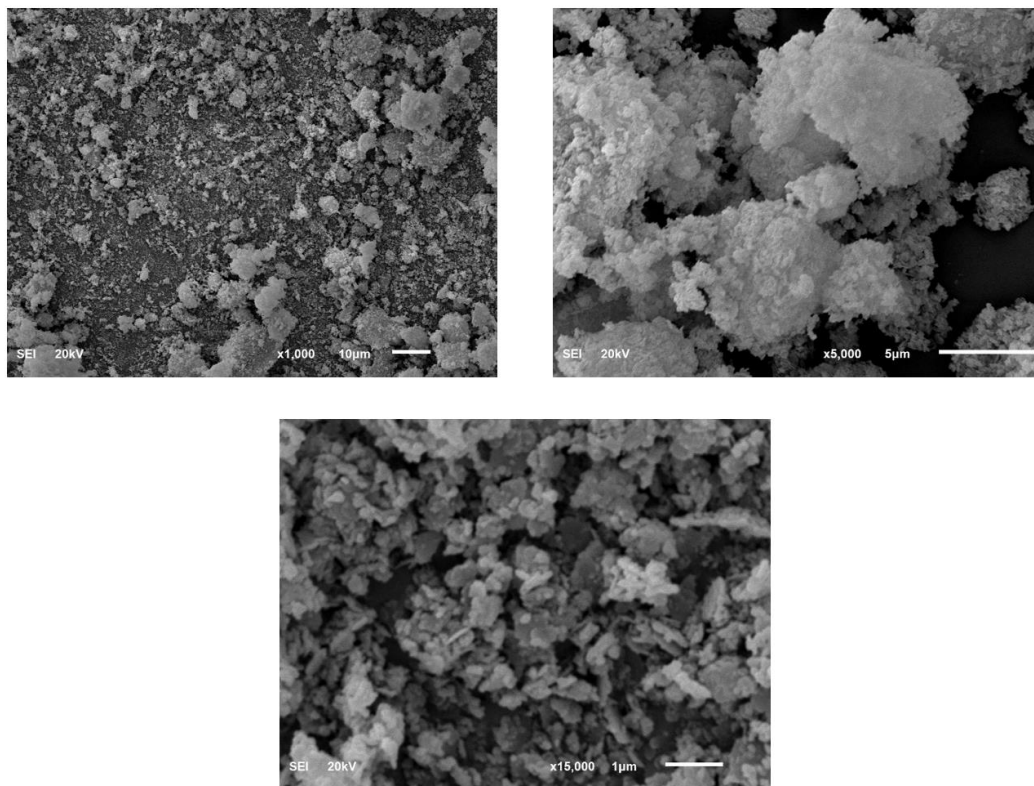


Figure 17. SEM images of ZnAl LDH

Heat treatment of LDH catalysts. The ZnAl-LDH catalysts were heated under vacuum for 2 hours to study their stabilities after heat exposure. Figure 18 compares the XRD results of ZnAl LDH before and after heating under vacuum for 2 hours at 200 °C.

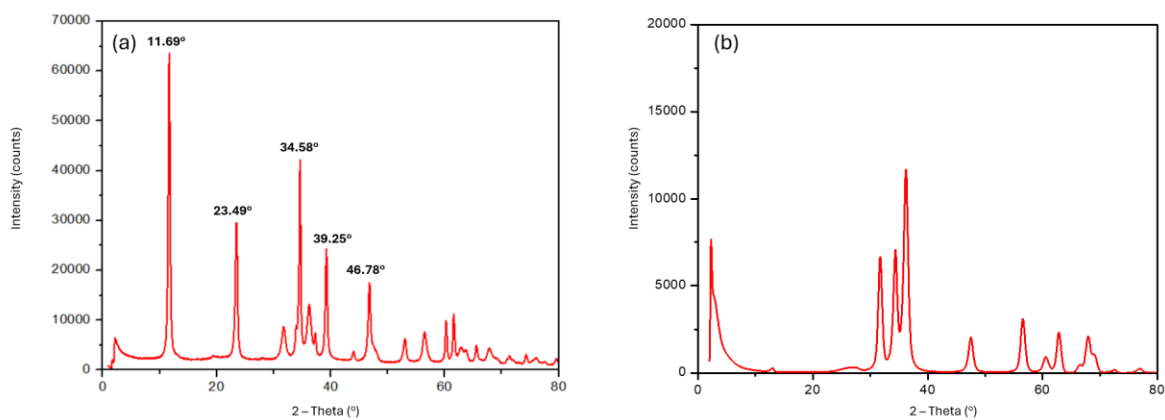


Figure 18. XRD patterns of ZnAl LDH before (a) and after (b) heating in vacuum at 200 °C for two hours.

As can be seen in the figure, the XRD patterns are significantly different. The pattern on the right (vacuum heated) shows much lower intensity and broader signals compared to the original LDH on the left. The lower intensity and broader peaks suggest that the LDH crystallinity decreases significantly after heating. The layered structure partially collapses, leading to reduced long-range order, which manifests in the diminished sharpness of the diffraction peaks. The initial sharp peaks, such as those at 23.49° , and 34.58° , which correspond to the basal reflections of the LDH structure, are much more weakened after heating. The peak at 11.69° seen in the original sample is almost lost after heating. The change in the XRD pattern indicates that the original LDH structure has undergone a transformation into an amorphous phase or another mixed oxide form. This is typical for LDH materials when they are subjected to thermal treatments, as they often convert into a combination of mixed metal oxides or spinels, depending on the conditions.

3.3.2. BHET characterization

The FT-IR analysis of the PET glycolysis product indicates the presence of BHET through characteristic absorption bands (Figure 19). The broad O-H stretching band observed around $3300\text{--}3500\text{ cm}^{-1}$ suggests hydroxyl groups, while the alkyl C-H vibration between $2800\text{--}3000\text{ cm}^{-1}$ confirms the presence of aromatic rings [42]. The strong C=O stretching band near 1700 cm^{-1} indicates the presence of ester carbonyl groups, while the C-O vibrations in the $1100\text{--}1300\text{ cm}^{-1}$ range further support the ester linkage in BHET [43]. The aromatic ring vibrations are attributed to absorption bands in the $750\text{--}850\text{ cm}^{-1}$ range. These spectral characteristics collectively validate the successful glycolysis of PET into BHET, consistent with the data reported in the literature [42–44].

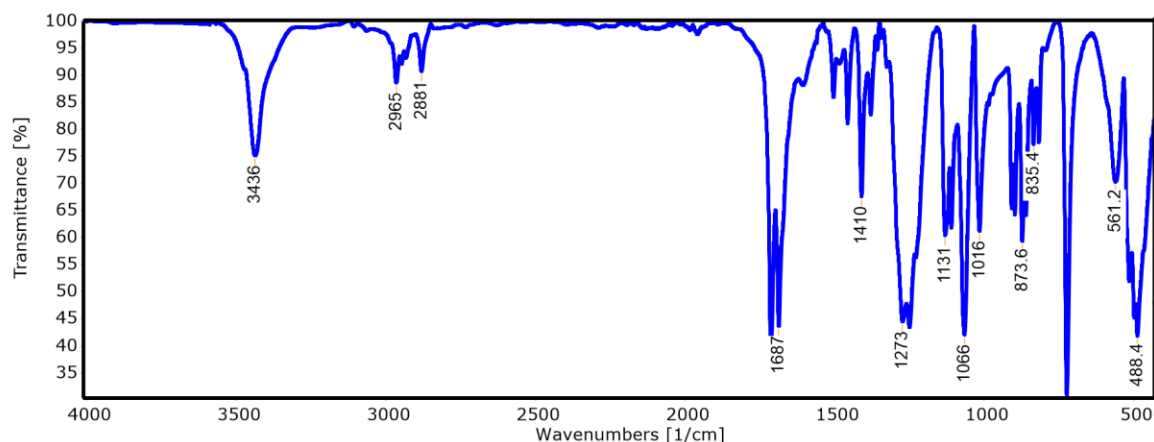


Figure 19. FT-IR spectrum of the obtained products

Proton and ^{13}C NMR analyses (Figure 20 and Figure 21, respectively) were used to confirm the formation of BHET [45]. In the proton NMR, the singlet at $\delta\text{H} = 7.98$ ppm relates to the aromatic hydrogens in the benzene ring of BHET, which are shifted downfield due to the electron-withdrawing effects of the ester groups and the delocalization of the aromatic ring [45]. The triplet at $\delta\text{H} = 4.89$ ppm is attributed to the hydroxyl group, experiencing a downfield shift due to the electronegative nature of the oxygen atom [45]. The triplet at $\delta\text{H} = 4.18$ ppm is ascribed to the methylene group adjacent to the carbonyl group, which is deshielded by the nearby carbonyl functionality [45]. The quartet at $\delta\text{H} = 3.60$ ppm is associated with the methylene group bonded to the hydroxyl group, which experiences an upfield shift [45]. The intensity ratios (2:1:2:2) of these peaks confirm that the product was synthesized in a nearly pure form.

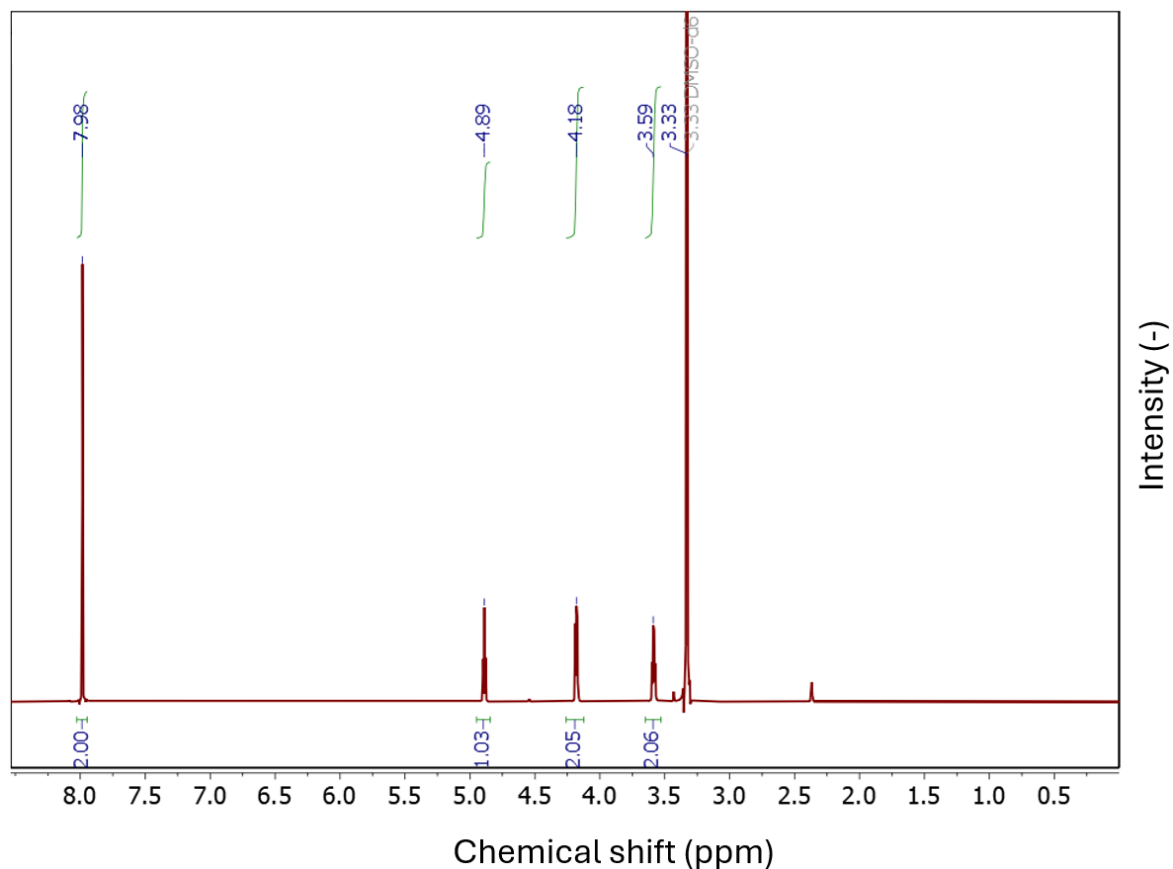


Figure 20. ^1H NMR of the product.

In the carbon NMR spectrum (Figure 21), the carbonyl carbon ($-\text{COO}-$) is represented by a peak at $\delta\text{C} = 165.35$ ppm, which is deshielded due to the electron-withdrawing nature of the carbonyl group [46]. The carbons in the benzene ring ($-\text{C}_6\text{H}_4-$) are represented by peaks at $\delta\text{C} = 133.9$ and $\delta\text{C} = 129.7$ ppm, which are shifted downfield due to the conjugation with the carbonyl group [46]. The peaks at $\delta\text{C} = 67.17$ ppm and $\delta\text{C} = 59.1$ ppm correspond to the methylene groups ($-\text{CH}_2-$), with the differences in chemical shifts reflecting their proximity to the electron-withdrawing ester and hydroxyl groups [46]. These assignments are consistent with the expected chemical environment in BHET.

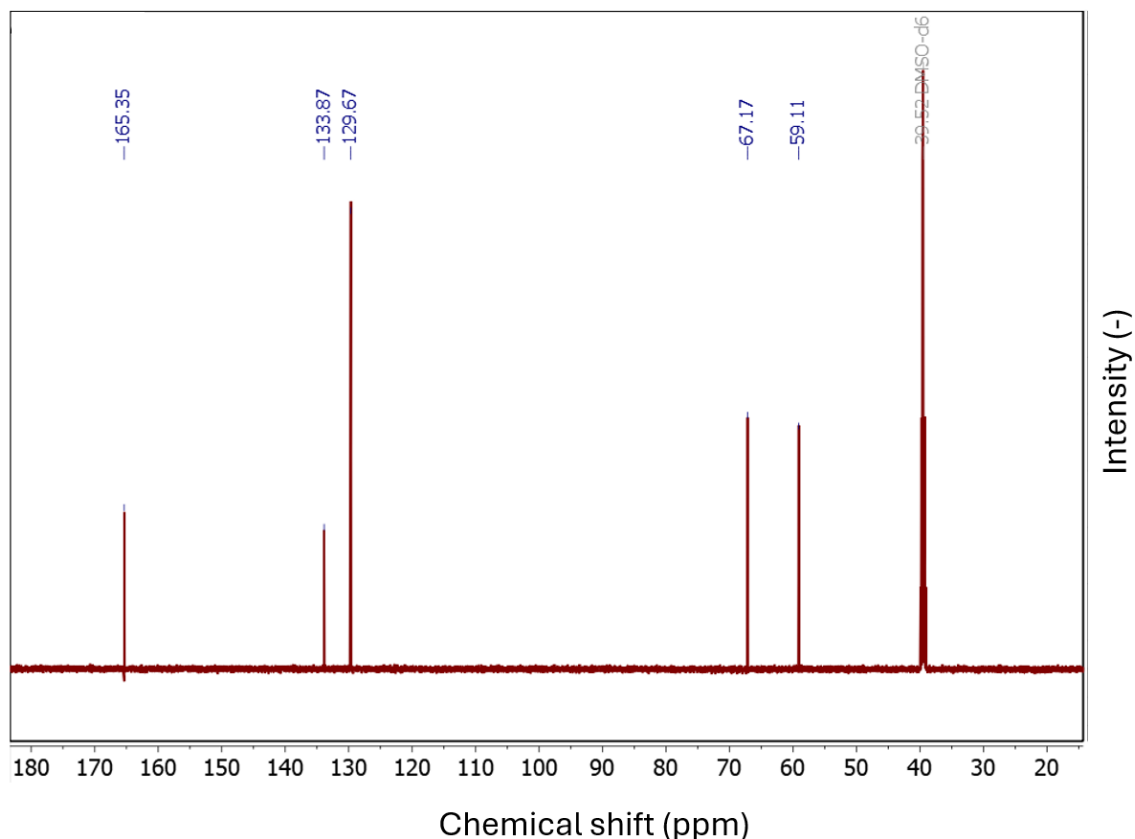


Figure 21. ^{13}C NMR of the product.

The gas chromatography data from the GC-MS spectra (Figure 22) prove the successful and pure synthesis of BHET. The mass spectrum displays prominent peaks corresponding to the molecular ions and fragments characteristic of BHET. Key fragments include the peak at m/z 211, which corresponds to $\text{C}_{10}\text{H}_9\text{O}_5^+$, indicating the loss of a terminal ethylene group from BHET [46]. The fragment at m/z 193 represents the loss of one ethylene glycol moiety, while the peak at m/z 149 signifies the terephthalate moiety with one hydroxyl group detached ($\text{C}_8\text{H}_4\text{O}_3^+$) [46]. The peak at m/z = 121 corresponds to $\text{C}_7\text{H}_4\text{O}_2^+$. Additional peaks at m/z 104 and 76 represent fragments $\text{C}_7\text{H}_4\text{O}_2^+$ and C_6H_4^2+ , respectively [46]. These fragmentations align with the expected breakdown of BHET, confirming its successful synthesis. Our data is in agreement with the reported data in the literature [46].

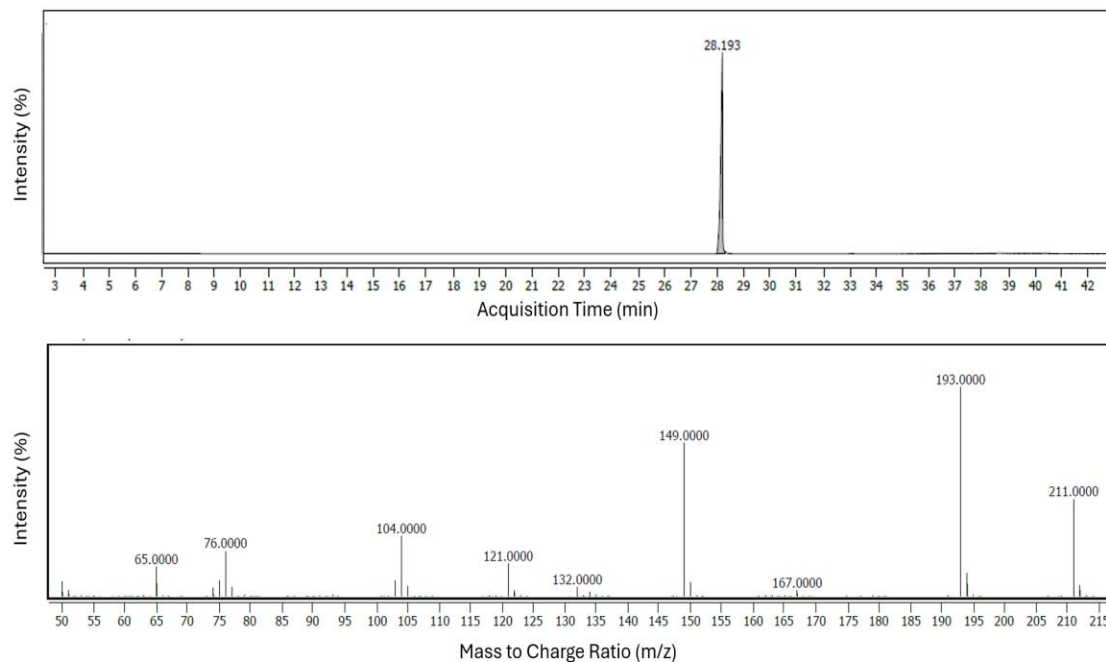


Figure 22. GC-MS spectrum of BHET.

3.3.3. Optimizations of reaction conditions

The glycolysis of PET was conducted using various amounts of ZnAl-LDH catalyst (0-1.5% mass of PET) at 200 °C for 2 hours. The experimental results in Figure 23 indicate that no reaction occurs without the catalyst, as shown by the 0% catalyst loading. With a small amount of catalyst (0.25%), there is a significant growth in the conversion (81.6%), which demonstrates the catalyst's effectiveness. The optimal catalyst loading was found to be approximately 1.00%, achieving both high conversion and yield (100% conversion and 72.6% yield). Increasing the catalyst loading to 1.5% maintained the conversion at 100%, but the yield significantly reduced to 36.5%. This suggests that while higher catalyst loading ensures complete conversion, there may be other side reactions. Therefore, using a 1.00% catalyst loading provides an optimal balance between high conversion and yield.

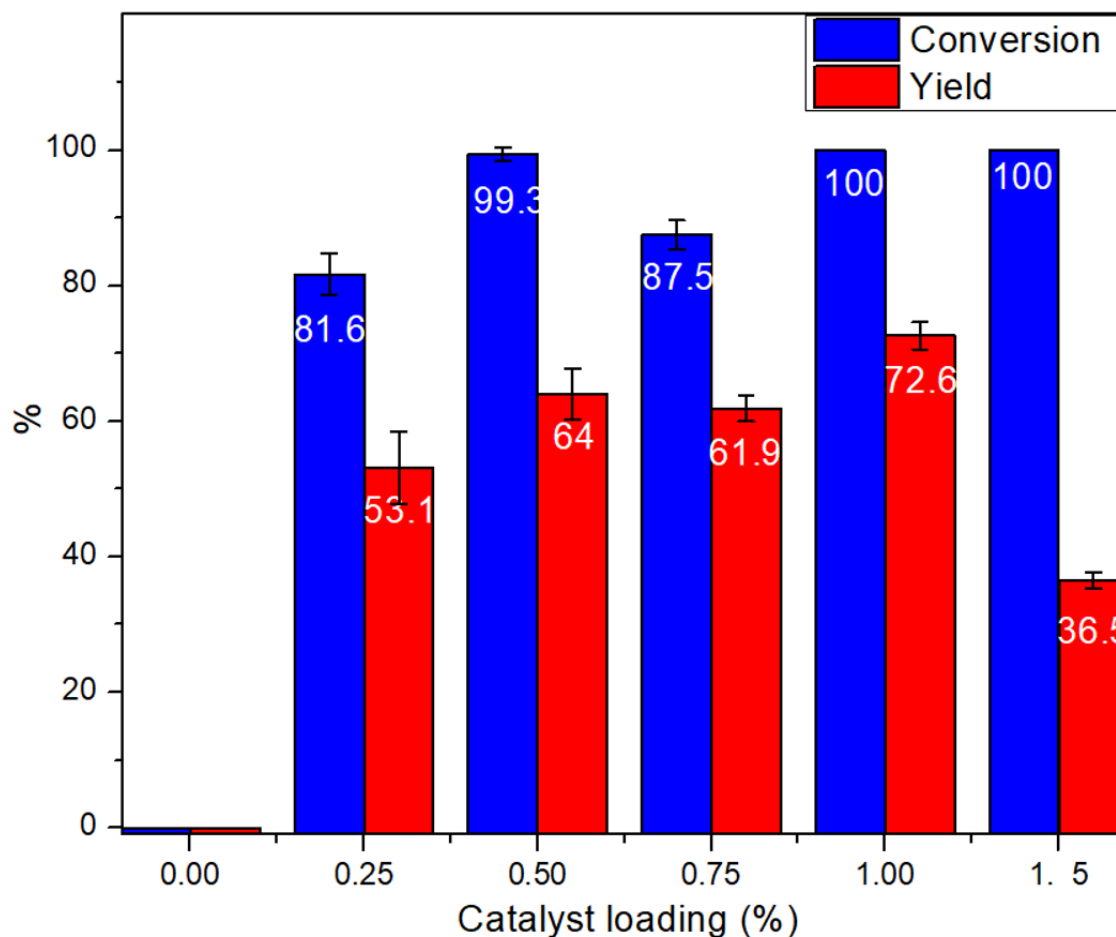


Figure 23. Glycolysis of PET with different catalyst loading at 200 °C for 2 hours of heating time

The graph in Figure 24 displays the glycolysis of PET at different reaction times (30, 60, 90, and 120 minutes) using a 1% catalyst concentration at 200 °C. After 30 minutes, the conversion reaches 33.5% with a yield of 4%, showing limited reaction progress. By 60 minutes, the conversion significantly increases to 76.1%, and the yield reaches 48%. At 90 minutes, the conversion continues to rise to 89%, with the yield improving to 56.5%. At the optimal reaction time of 120 minutes, the conversion hits 100%, and the yield peaks at 72.6%. These results suggest that longer reaction times enhance both the conversion and yield, with the most efficient glycolysis occurring at 120 minutes.

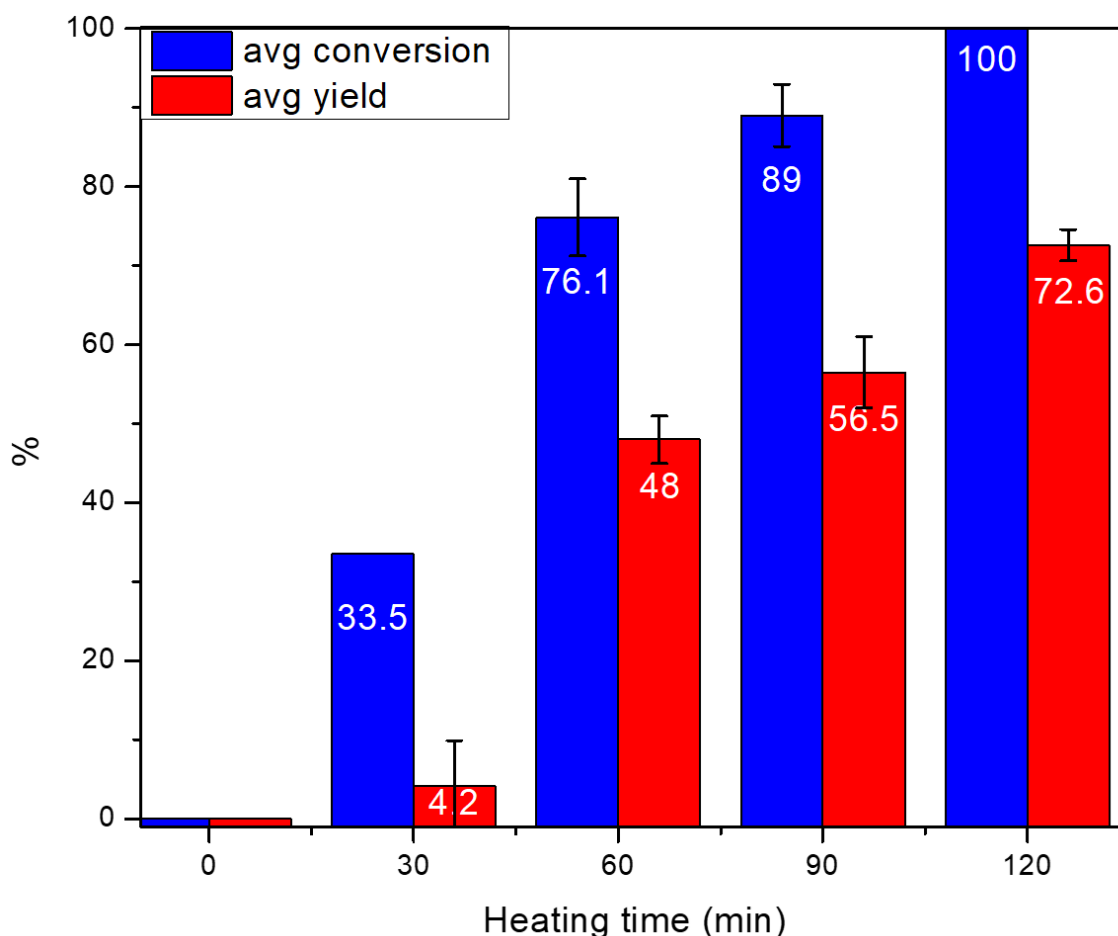


Figure 24. Glycolysis of PET at different reaction times in the presence of 1% catalyst at 200 °C

The Figure 25 represents the results of PET glycolysis conducted at varying temperatures (180 °C, 190 °C, 200 °C, and 210 °C) with the use of 1% catalyst over a reaction time of two hours. At 180 °C, the conversion rate is very low, just 8.18%, indicating that the reaction conditions are insufficient for a substantial depolymerization of PET. As the temperature increases to 190 °C, there is a marked improvement in the conversion, which rises to 25.97%. However, despite this higher conversion rate, the yield remains quite low at only 4.3%, implying that although more PET is not efficiently converted into BHET at this temperature. At 200 °C, the conversion rate reaches its maximum, with 100% of the PET being converted. The yield also shows a significant increase (72.7%). The efficiency

is similarly high at 210 °C, where the conversion remains at 100%. However, the yield decreased slightly to 66%, perhaps due to side reactions or degradation of the products. Optimal results, with high conversion and yield, are achieved at around 200 °C, beyond which there is a slight decrease in yield despite complete conversion.

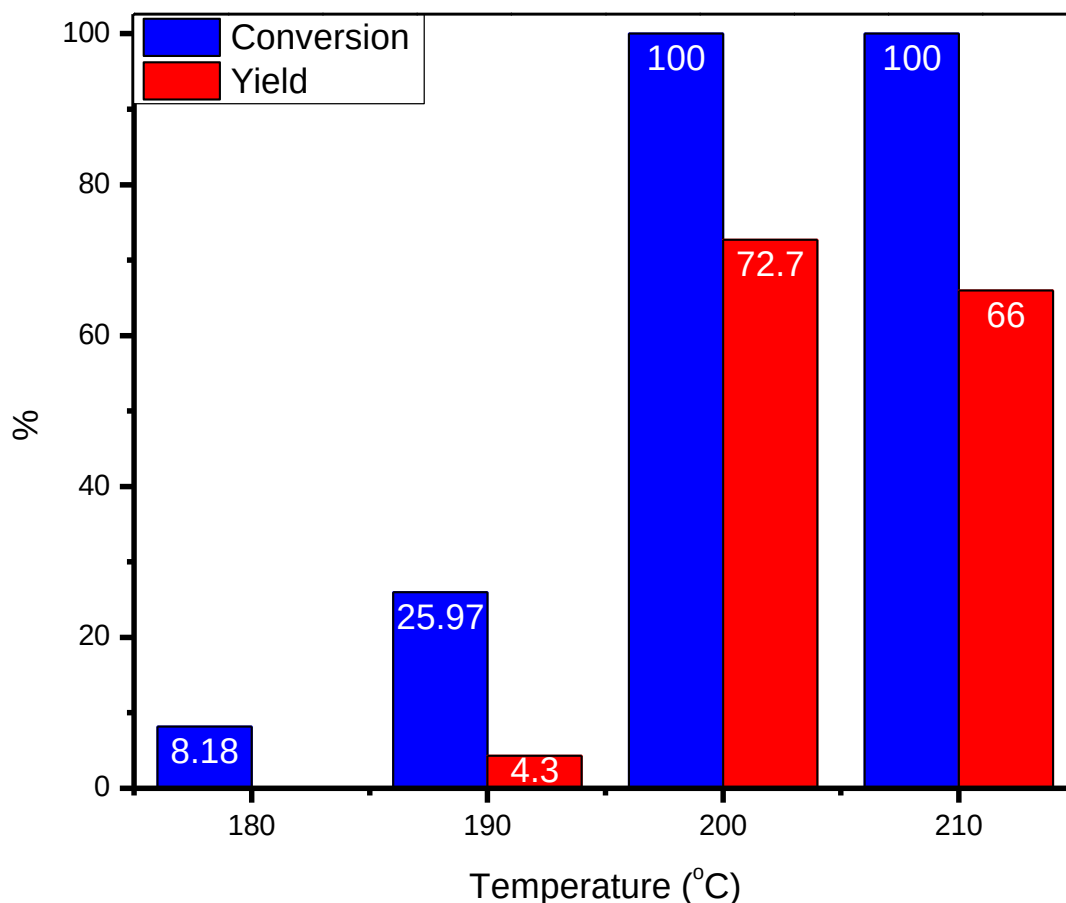


Figure 25. PET glycolysis at different heating temperatures (1% catalyst, 2h);

Figure 26 illustrates the glycolysis of PET at 200 °C for 2 hours varying the solvent volumes. The experiments demonstrate that PET conversion is nearly complete, achieving close to 100% for all the volumes. However, the yield of glycolysis products varies. At 10 ml of solvent, the yield is 60.5%, which increases to 72.7% when the solvent volume is raised to 20 ml. Further increasing the solvent volume to 30 ml results in a slight decline (67.87%). These findings suggest that the most favorable conditions

for high conversion and optimal yield occur with a solvent volume of around 20 ml.

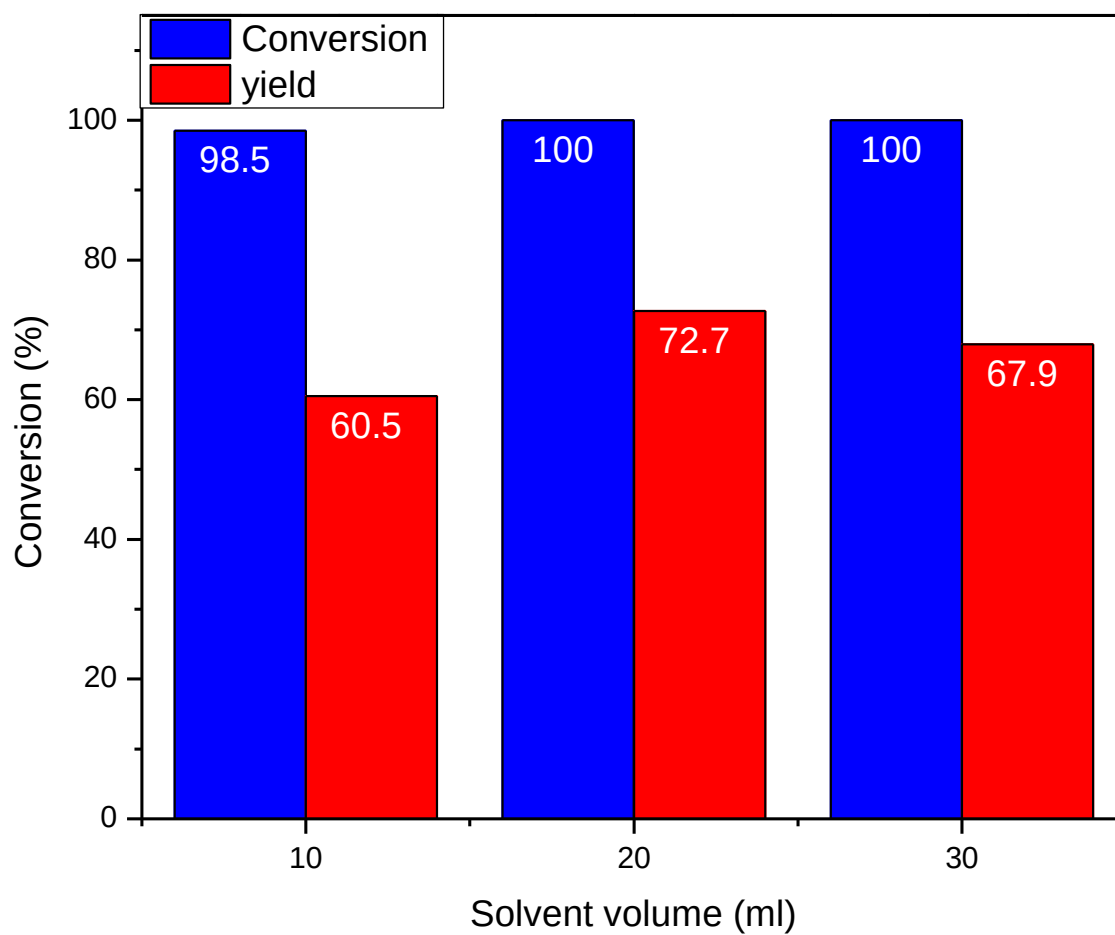


Figure 26. Glycolysis of PET in different volumes of EG solvent (1% catalyst, 200 °C, 2h).

3.3.4. Attempts to reuse the LDH catalysts

We investigated the reusability of the ZnAl LDH catalyst in the glycolysis of PET. Each run involved sequential reactions to assess how effectively the catalyst could perform over multiple uses. As can be seen in the Figure 27, the initial reactions achieved 100% PET conversion with moderate yields of around 65% on average. However, the efficiency dropped in the subsequent reactions. For instance, the second reaction in the first and second runs reached 57% and 67.2% conversions, The third and fourth runs showed much reduced effectiveness in the successive reactions likely because most of the catalyst was trapped in the filter paper. These results highlight the challenges associated with reusing the catalyst under these conditions. To avoid this unpredictable reaction performance and achieve consistent outcomes, more reliable method of catalyst recovery is necessary. This could include improved filtration steps or the development of a fixed-bed catalyst.

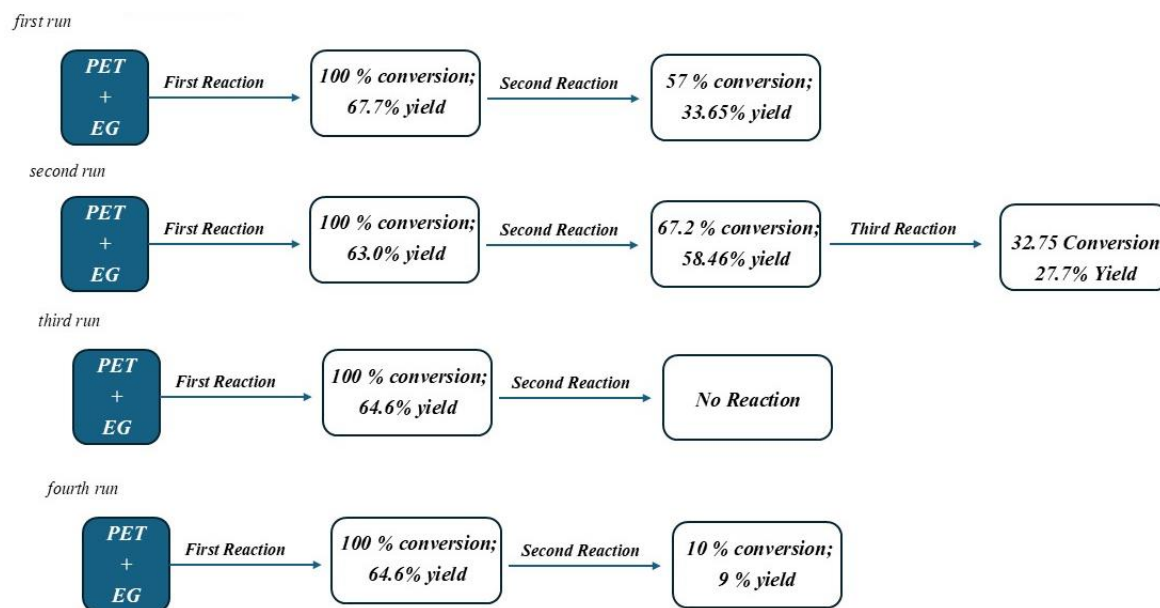


Figure 27. Trials in catalyst reusability for PET depolymerization reactions.

Chapter 4

PET glycolysis via ionic liquids as catalysts

We investigated the depolymerization of PET utilizing basic ionic liquids (ILs) as catalysts. Effectiveness of several ILs have been tested. Among these, trihexyltetradecylphosphonium decanoate demonstrated the highest catalytic activity, achieving 100% conversion of PET and a BHET yield of 75% under optimal conditions — 5 wt% catalyst dosage, reaction temperature of 200 °C, and reaction time of 3 hours. The effectiveness of these catalysts was determined through FT-IR, ^1H , ^{13}C NMR, and GC-MS analysis of the main product.

This work suggests that ionic liquids can serve as an efficient, environmentally friendly catalyst for PET recycling, offering a potentially valuable solution to managing PET waste.

4.1. A Review of the Effects of Ionic Liquids on PET Glycolysis

ILs are a kind of salts with a melting point under 100 °C. The distinctive qualities of these substances, such as low volatility, excellent thermal stability, and adjustable chemical structures, have recently gained attention in a range of chemical processes. ILs play a crucial role as catalysts in the glycolysis process of polyethylene terephthalate (PET), effectively enhancing the rate of depolymerization.

The primary study of ILs centered on its utilization in the cleansing of glycolysis byproducts [47]. The effectiveness of [BMIM]OH as a catalyst for glycolysis has been proven by obtaining total conversion of PET within a 2-hour reaction time under normal pressure and a temperature of 190 °C. Moreover, the catalyst possesses the capacity for multiple applications. Other IL catalysts assessed for their suitability in glycolysis depolymerization include [BMIM]HCO₃ and [BMIM]Cl, [BMIM]-FeCl₄, [BMIM]Br, [BMIM]Ac [48–50]. Additionally, there have been more catalysts investigated as well [51–56]. Table 1 provides a concise overview of previous efforts in the field of PET glycolysis.

Table 1. Previous studies on the depolymerization of PET in ethylene glycol using IL catalysts.

No	Ionic liquids used	Depolymerization conditions	Conversion (%)	Product yield	Ref
1.	[BMIM]OH	2.0g PET, 20.0g EG, 0.1g IL. 2h 190°C	100%	71.2%	[48]
	[BMIM]HCO ₃		82.8%	14.1	
	[BMIM]Cl		28.9%	6.0	
	[BMIM]Br		10.7%	10.7	
2.	Cholinium ILs, [Ch][Gly]	PET:IL ratio 5:1, and 0.4 g of EG were added, 150°C, 6 h	85	51	[52]
3.	[Deim][Zn(OAc) ₃]	16.67% IL, 180°C. 1.5h	98.05	70.94	[53]
4.	[BMIM]-FeCl ₄	5-10% catalyst, 178 °C, 7 h		76.4	[49]

5.	[BMIM]ZnCl ₃	0.16 wt % cat, 190°C, 5h	100	83.8	[54]
6.	1,3-dimethylimidazolium-2-carboxylate	1 h at 180°C under nitrogen	100	50	[55]
7.	protic ILs (PIL3)	5 g PET, 30 g EG. 10% cat, 30 mins, 190°C	100	87.3	[56]
8.	[P ₄₄₄₄]Ace	200 °C and 2 h.	100	37.8	[57]
9.	Equimolar [Hmim]ZnCl ₃ and [Hmim]CoCl ₃ mixture	1% catalyst, 190 °C for 2 h.	100	87.1%	[58]
10.	[Cho][OAc]	10% catalyst, 3 h, 180 °C.	100	66.7 %	[59]

The results presented in the table above indicate that the processes tested either suffer from low yield or require high amount of catalyst. In contrast, the ionic liquids we evaluated for PET glycolysis are free of metals, offering a sustainable and environmentally friendly alternative. These ionic liquids demonstrated remarkable efficiency, achieving a complete conversion of PET to BHET with a 100% conversion rate.

4.2. Experimental

4.2.1. Materials

Anhydrous ethylene glycol (EG) with 99.8% purity, ionic liquids, 1-allyl-3-methylimidazolium chloride - [AMIM]Cl, 1-butyl-3-methylimidazolium acetate - [BMIM][OAc], trihexyltetradecylphosphonium decanoate - [P6,6,6,14][Dec], trihexyltetradecylphosphonium chloride - [P6,6,6,14]Cl, trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate - [P6,6,6,14][TMPP], methyltrioctylammonium chloride - [MTOA]Cl were procured from Sigma Aldrich® and were used without any purification. PET flakes were obtained from shredding the post-consumer water bottles.

4.2.2. Glycolysis of PET in the presence of ILs as catalysts

Glycolysis reactions using ionic liquids as catalysts were carried out in a similar procedure as described in section 3.2.3. In the reflux step, 2 grams of PET along with 20 milliliters of ethylene glycol were added to a 250-milliliter round-bottom flask reactor maintained at 200 °C. A 5-10% of the ionic liquids were introduced for each reaction. The reactions were performed for the duration of 2-3 hours under atmospheric pressure. Unreacted PET was collected by rapid filtration (see Figure 9), washed with water, dried, and measured to calculate the conversion by the following equation:

$$Conversion (\%) = \frac{m_{PET(initial)} - m_{PET(final)}}{m_{PET(initial)}} \cdot 100\% \quad (2.1)$$

In the recrystallization step, the filtrate was stored in the fridge at 4 °C for 20 hours. White crystals of BHET were formed overnight and filtered off. The obtained white product was dried and measured to calculate the yield of the product:

$$Yield (\%) = \frac{m_{BHET}(obtained)}{m_{PET}(expected)} \cdot 100\% \quad (2.2)$$

$$m_{BHET}(expected) = \frac{m_{PET}(initial)}{M_{PET}} \cdot M_{BHET} \quad (2.3)$$

$$M_{PET} = 192.17 \text{ g/mol}$$

$$M_{BHET} = 254.24 \text{ g/mol}$$

Among the tested ionic liquids, 1-butyl-3-methylimidazolium acetate - [BMIM][OAc] and trihexyltetradecylphosphonium decanoate – [P6,6,6,14][Dec] gave the best results. Conversion of the glycolysis using trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate - [P6,6,6,14][TMPP] was high, however the product could not be isolated in a pure form. Further details will be discussed in the subsequent sections.

4.2.3. IL and solvent reusability

To evaluate the reusability of the IL catalysts and the EG solvent in the glycolysis procedure, the filtrates from prior filtration steps were combined, and their water content was eliminated using a rotary evaporator, resulting in a dry solution of 20 ml ethylene glycol. The recovered ethylene glycol was subsequently utilised to react with the residual unreacted PET from the identical reaction batch. To maintain uniformity in the experimental setup, an extra quantity of fresh PET was incorporated, resulting in a total mass of 2.0 grams of PET in the reaction.

4.3. Results and discussion

4.3.1. IL characterization

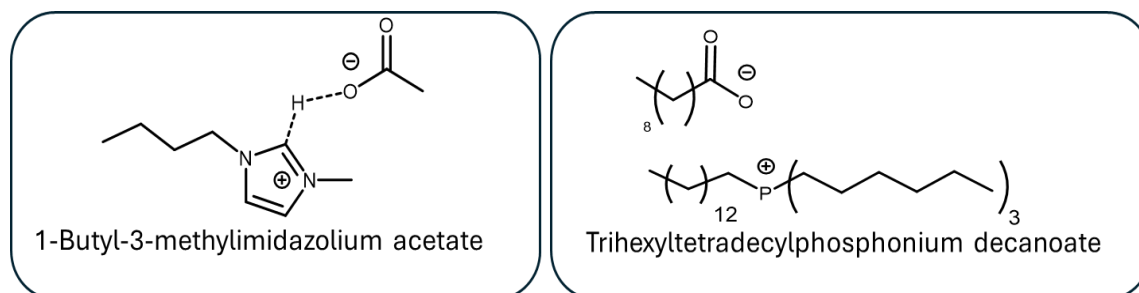


Figure 28. Molecular structures of [BMIM][OAc] (left) and [P6,6,6,14][TMPP] (right)

^1H NMR of the [BMIM][OAc] ionic liquid is presented in the Figure 29. The singlet peak at 10.2 ppm corresponds to the acidic proton of the imidazolium ring, which is deshielded due to the electron-withdrawing effect of the adjacent nitrogen atoms. The doublet peak at 7.9 ppm represents the aromatic protons of the imidazolium ring. These two protons are in positions 4 and 5 of the imidazolium ring, and they appear downfield due to the positive charge of the nitrogen. The triplet peak at 4.2 ppm belongs to the methylene group ($-\text{CH}_2-$) linked to the butyl chain directly attached to the nitrogen atom of the imidazolium ring, and this peak is slightly deshielded due to its proximity to the positively charged nitrogen. The sharp singlet at 3.9 ppm represents the methyl group ($-\text{CH}_3$) attached to the nitrogen on the imidazolium ring, where the positive charge on the nitrogen causes slight deshielding of this methyl group. Moving to the peaks at around 1.7 ppm, this region corresponds to the methylene group ($-\text{CH}_2-$) that is adjacent to the methylene group directly attached to the imidazolium ring, and these protons are more shielded as they move further from the influence of the charged ring. Lastly, the peaks at 1.1 ppm and 0.8 ppm

correspond to the terminal methylene (-CH₂-) and the methyl group (-CH₃) on the butyl chain, respectively, with the terminal methyl group being the most shielded, which results in an upfield chemical shift.

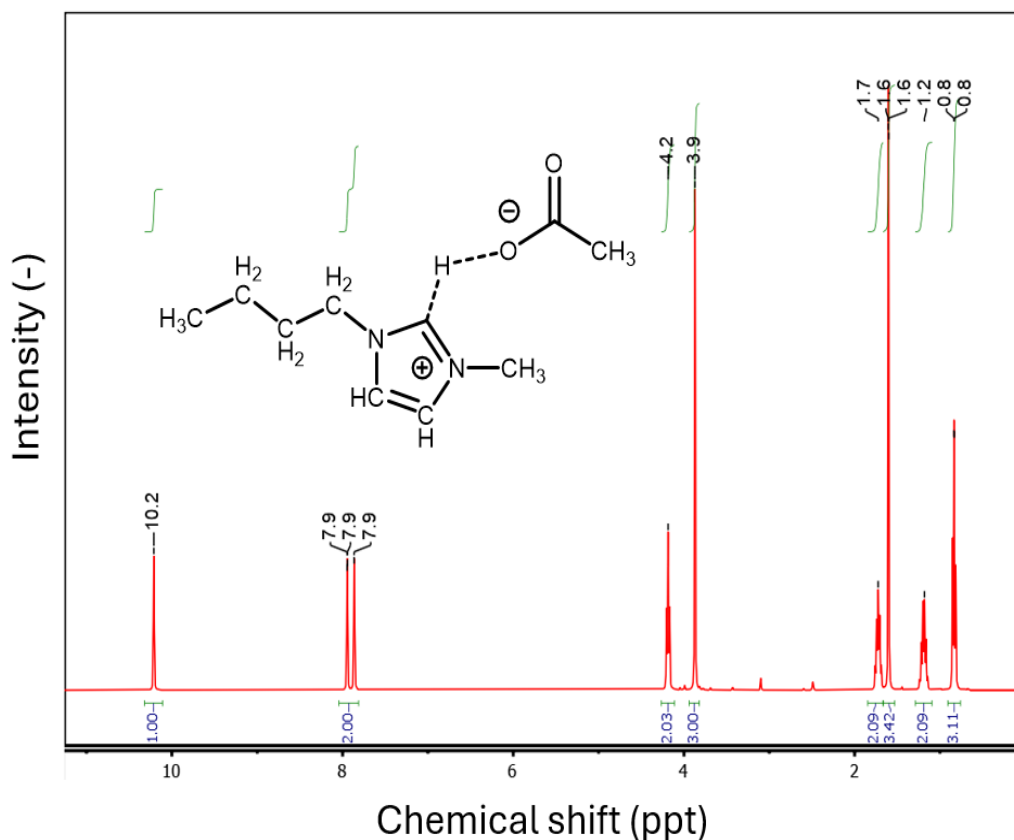


Figure 29. ¹H NMR of the [BMIM][OAc] ionic liquid

Figure 30 illustrates the ¹³C NMR of the [BMIM][OAc] ionic liquid. The peak at 173.9 ppm corresponds to the carbonyl carbon of the acetate anion, which is highly deshielded due to its attachment to the electronegative oxygen atoms. The peak at 138.4 ppm can be assigned to the C2 carbon, which is bonded to both nitrogen atoms, and thus is more deshielded. The peaks in the range 122.7-124.0 ppm correspond to the C4 and C5 carbons of the imidazolium ring. These carbons are less deshielded compared to C2 but still experience the influence of the adjacent nitrogen atoms. The

peak at 48.6 ppm corresponds to the methylene carbon attached directly to the imidazolium nitrogen, as this carbon is relatively close to the positive charge of the imidazolium ring. Moving downfield, the peaks at around 31.9, 26.0, 19.2, and 13.7 ppm correspond to the carbons of the butyl chain. This spectrum is consistent with what is expected for the carbon environment of [BMIM][OAc] (Figure 28), with each distinct carbon resonance showing up according to the level of shielding or deshielding effects experienced by the respective carbons.

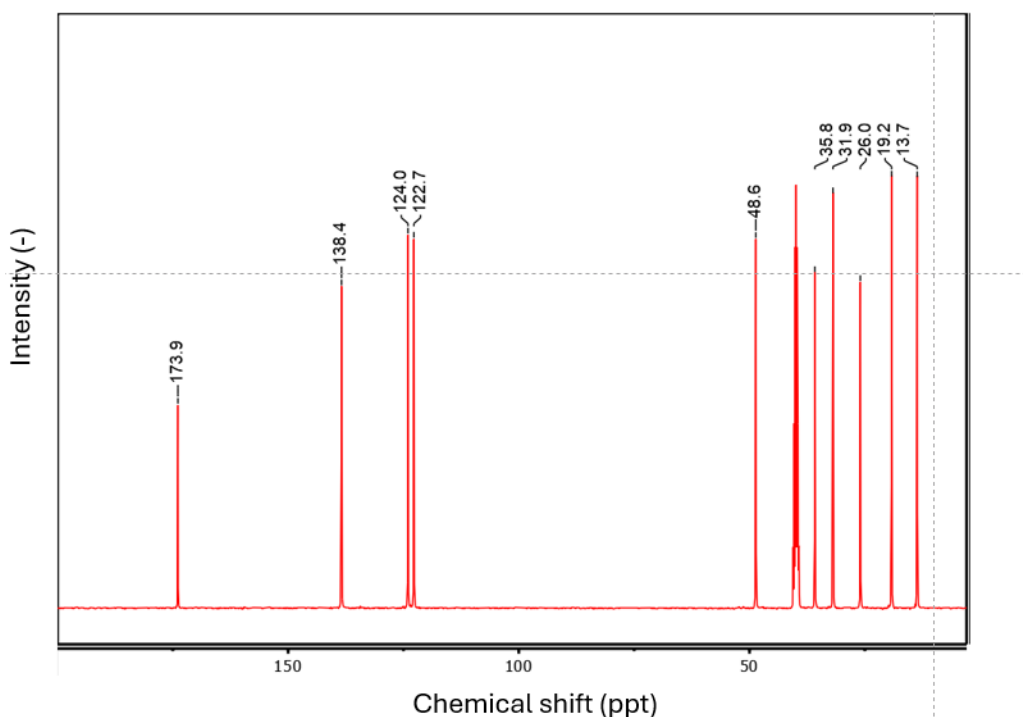


Figure 30. ^{13}C NMR of the [BMIM][OAc] ionic liquid.

The carbon and proton NMR spectra of the ionic liquid [P6,6,6,14][TMPP] were highly complex and provided limited information due to the presence of phosphorus, which introduces additional coupling, and the extensive carbon chains, which lead to overlapping signals. Therefore, the spectra are not presented in this work.

4.3.2. Glycolysis results

The glycolysis of PET was studied using several ionic liquids as catalysts: [AMIM]Cl, [BMIM][OAc], [P6,6,6,14][Dec], [P6,6,6,14]Cl, [P6,6,6,14][TMPP], [MTOA]Cl. The experiments were conducted under identical conditions, with a temperature of 200 °C, a catalyst concentration of 5%, and a reaction time of 3 hours. The results reveal significant differences in the performance of these liquids in terms of conversion and yield. [BMIM][OAc] and [P6,6,6,14][Dec] were identified as the most effective catalysts (Figure 31). While [P6,6,6,14][TMPP] achieved a conversion rate of approximately 60%, the final product could not be isolated due to a high level of impurities. Other materials, such as [AMIM]Cl, [P6,6,6,14]Cl, and [MTOA]Cl, were found to be ineffective for this reaction.

The ionic liquid [BMIM][OAc] resulted in a complete conversion of PET, reaching 100% conversion. The yield of the target product was 33.58%. This result suggests that although [BMIM][OAc] is highly effective at breaking down PET, a significant portion of the product either undergoes side reactions or forms undesired by-products, limiting the yield of the desired glycolysis product.

On the other hand, [P6,6,6,14][Dec] also achieved a 100% conversion of PET, indicating its comparable effectiveness in catalyzing the depolymerization process. However, unlike [BMIM][OAc], [P6,6,6,14][Dec] produced a significantly higher yield of 72.4%, implying better selectivity towards the desired product. This suggests that [P6,6,6,14][Dec] not only effectively depolymerizes PET but also enhances the overall efficiency of the glycolysis process by minimizing side reactions and maximizing the yield. These findings suggest that [P6,6,6,14][Dec] could be a more

suitable catalyst for industrial applications where maximizing product yield is crucial.

IL Used	Abbreviation	Conversion (%)	Yield (%)
no catalyst	-	>1	~0
1-Butyl-3-methylimidazolium acetate	[BMIM][OAc]	~100	33.6
Trihexyltetradecylphosphonium decanoate	[P6,6,6,14][Dec]	~100	72.4
trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate	[P6,6,6,14][TMPP]	~56	0
1-Allyl-3-methylimidazolium chloride	[AMIM]Cl	0	0
Trihexyltetradecylphosphonium chloride -	[P6,6,6,14]Cl	0	0
Methyltrioctylammonium chloride	[MTOA]Cl	0	0

Figure 31. Effects of ionic liquids on the glycolysis of PET (200 C, 5% cat, 3 h).

Qualitative analyses of the obtained products were conducted using FT-IR, NMR, and GC-MS analyses. The results from these analyses were identical to those presented in the previous chapter (Section 3.3.2).

4.3.3. Characterization of the glycolysis product

The FT-IR analysis of the PET glycolysis product indicates the presence of BHET through characteristic absorption bands (Figure 32). The broad O-H stretching band observed around 3300-3500 cm^{-1} suggests hydroxyl groups, while the alkyl C-H vibration between 2800-3000 cm^{-1} confirms the presence of aromatic rings [42]. The strong C=O stretching band near 1700 cm^{-1} indicates the presence of ester carbonyl groups, while the C-O vibrations in the 1100-1300 cm^{-1} range further support the ester linkage in BHET [43]. The aromatic ring vibrations are attributed to absorption bands in the 750-850 cm^{-1} range. These spectral features collectively confirm the successful glycolysis of PET into BHET, consistent with the data reported in the literature [42–44].

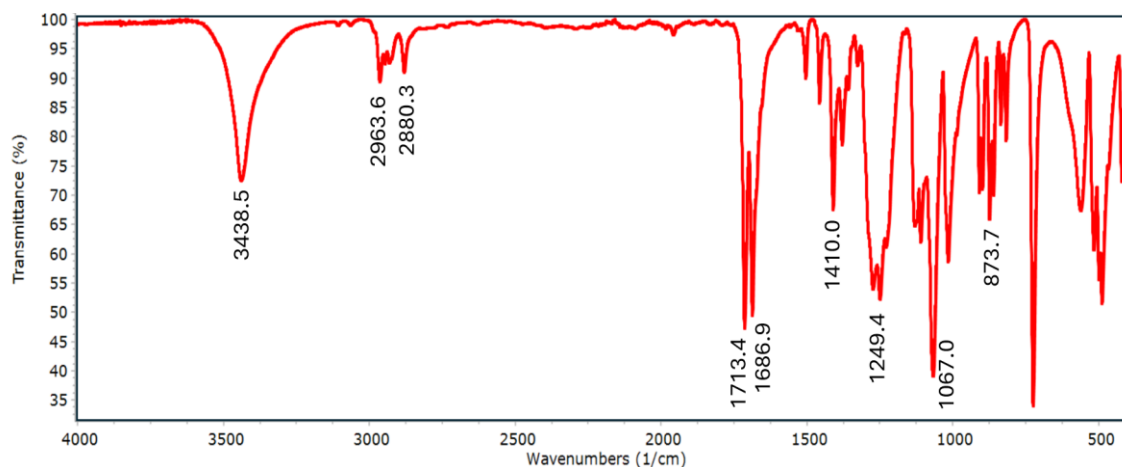


Figure 32. FT-IR spectrum of the obtained products

Proton and ^{13}C NMR analyses (Figure 33a and b, respectively) were used to confirm the structure of BHET [45]. Singlet at $\delta_{\text{H}} = 7.98$ ppm belongs to the hydrogen atoms in the aromatic ring. The triplet at $\delta_{\text{H}} = 4.89$ ppm is attributed to the -OH hydrogen, while the triplet at $\delta_{\text{H}} = 4.18$ ppm is assigned to the methylene group adjacent to the carbonyl group [45]. The quartet peak at $\delta_{\text{H}} = 3.60$ ppm is associated with the other methylene group [45]. The intensity ratios of these peaks indicate that the product was synthesized in a nearly pure form. In the carbon NMR spectrum (Figure 33b), the carbonyl carbon (-COO-) is represented by a peak at $\delta_{\text{C}} = 165.35$ ppm [46], and the carbons in the benzene ring (-C₆H₄-) are represented by peaks at $\delta_{\text{C}} = 133.9$ and $\delta_{\text{C}} = 129.7$ ppm [46]. The peaks at $\delta_{\text{C}} = 67.17$ ppm and $\delta_{\text{C}} = 59.11$ ppm correspond to the methylene groups (-CH₂-) [46].

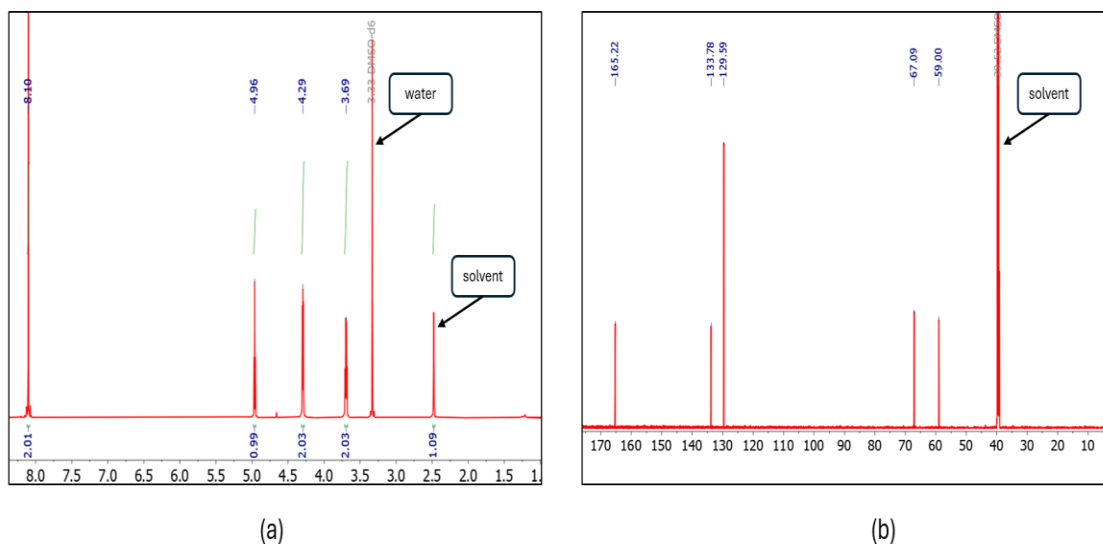


Figure 33. (a) Proton and (b) Carbon NMR spectra of the obtained product (BHET).

GC-MS spectrum in Figure 34 further confirms the product purity and the structure of BHET. The gas chromatography from the GC-MS spectra (Figure 34a) proves the successful and pure synthesis of BHET. The mass spectrum displays prominent peaks corresponding to the molecular ions and fragments characteristic of BHET. Key fragments include the peak at m/z 211, which corresponds to $C_{10}H_9O_5^+$, indicating the loss of a terminal ethylene group from BHET [46]. The fragment at m/z 193 represents the loss of one ethylene glycol moiety, while the peak at m/z 149 signifies the terephthalate moiety with one hydroxyl group detached ($C_8H_4O_3^+$) [46]. The peak at m/z 121 corresponds to $C_7H_4O_2^+$. Additional peaks at m/z 104 and 76 represent fragments $C_7H_4O_2^+$ and $C_6H_4^2+$, respectively [46]. These fragmentations align with the expected breakdown of BHET, confirming its successful synthesis. Our data is consistent with the reported data in the literature [46].

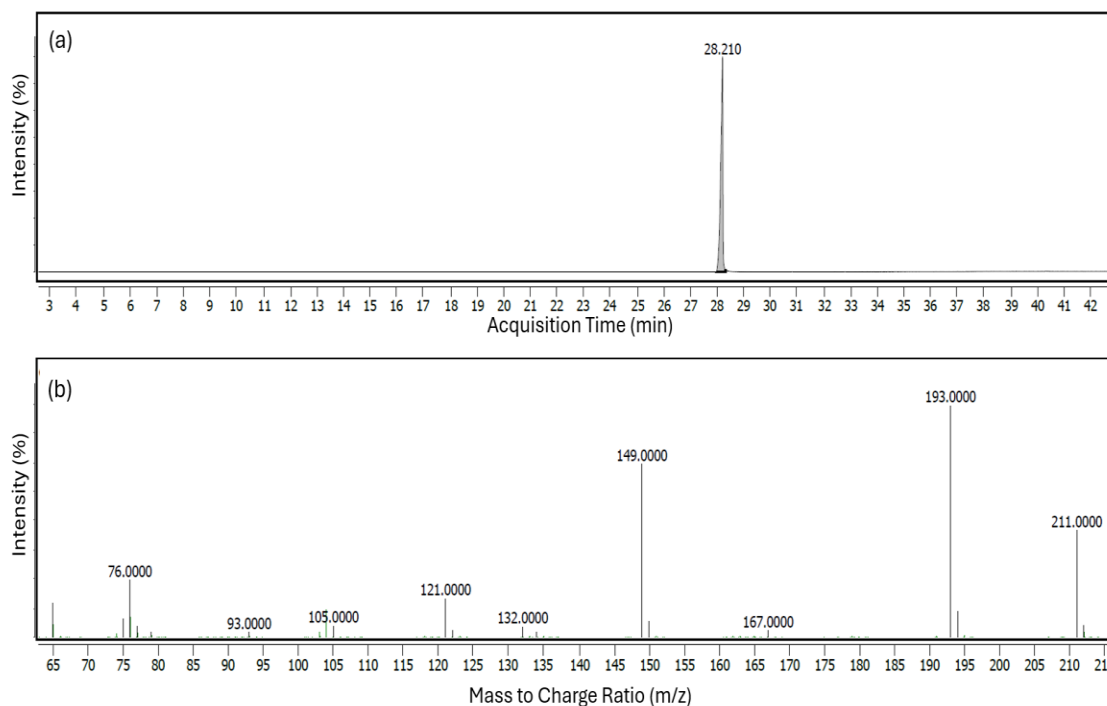


Figure 34. GC-MS analysis: (a) – gas chromatography spectrum, (b) – mass spectrum of the product

4.3.4. Exploring the Reusability of Ionic Liquids

As discussed in section 4.2.3, we examined the reusability of ILs in the glycolysis of PET through multiple trials, each consisting of sequential reactions. The goal was to determine how effectively the catalyst could sustain its activity over multiple cycles. Figure 35 shows the results of this attempt using [BMIM][OAc] ionic liquid as a catalyst. As expected, the initial reactions for all the trials achieved complete PET conversion with a yield of around 30%. However, further reactions were observed to be inconsistent among the trials. The second trial showed the plausibility of the reusing of this ionic liquid. The catalyst showed partial activity in the second and third reactions, reaching 77.4% conversion with 16.92% yield and then 92% conversion with a high yield of 98.8%. Yet, by the fourth reaction, the conversion dropped drastically to 5%, with only a 5% yield. This steep decline points to significant loss or deactivation of the catalyst over successive

reactions. Unfortunately, we could not repeat these results in the other trials.

The first and third trials were followed by no reaction in subsequent steps, suggesting substantial catalyst loss during the filtration process. These findings underscore the limitations of the [BMIM][OAc] catalyst under current reuse conditions. While initially effective, the catalyst's performance deteriorates in successive reactions, likely due to progressive loss or deactivation. To achieve consistent catalytic activity over multiple cycles, improved recovery methods are needed to prevent catalyst loss and maintain stable reaction performance.

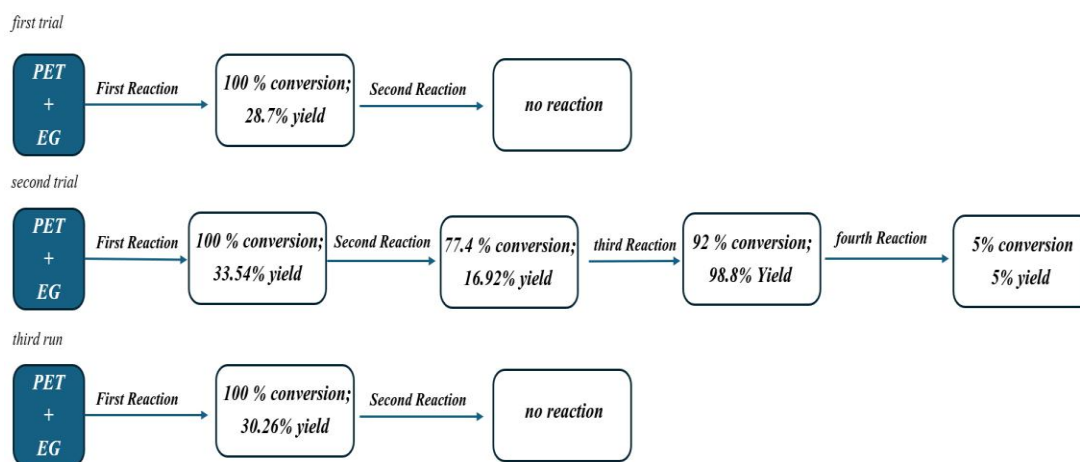


Figure 35. Attempts to reuse BMIM OAc

Investigations on the reusability of a [P6,6,6,14][Dec] ionic liquid is shown in Figure 36. Similar to the performance of [BMIM][OAc], the initial reactions consistently achieved 100% PET conversion, with yields of about 70% on average. However, catalyst activity declined significantly in subsequent reactions

In the second trial, some catalytic activity was retained, as indicated by a 25% conversion and a 15% yield in the second reaction. The first and third trial showed minimal activity in the second reaction, suggesting rapid loss of the catalyst.

These observations emphasize the limitations of reusing this catalyst under the current

experimental setup. To ensure consistent catalytic activity across multiple cycles, better recovery methods are necessary to minimize catalyst loss and maintain consistent reaction outcomes.

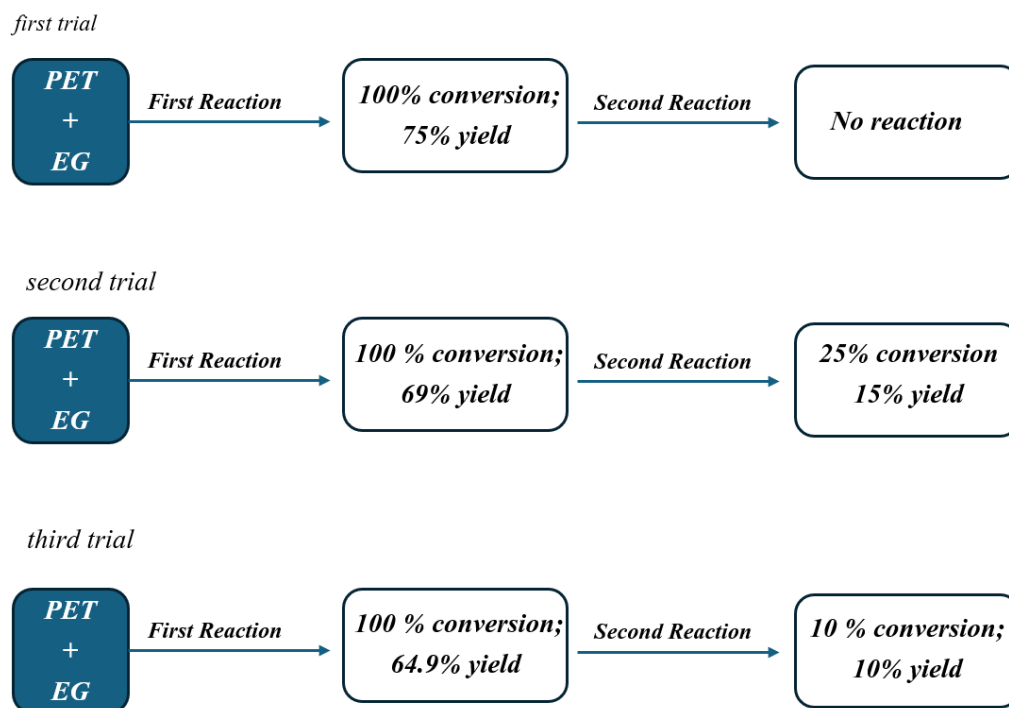


Figure 36. Attempts made in order to reuse [P6,6,6,14][Dec].

Chapter 5

Repolymerization of the obtained monomers

5.1. Experimental

3 grams of BHET from the previous reactions were introduced into a conical flask fitted with a magnetic stirrer. The flask was connected to a distillation setup and heated to 200 °C under nitrogen flow until the BHET melted completely. Once fully melted, the temperature was raised to 270 °C, nitrogen supply was halted, and a vacuum was applied. After 50 minutes, the heating was discontinued and the reaction flask was quenched with DI water. The product was then filtered and dried in a vacuum chamber at 100 °C. The obtained polycondensation product was characterized using TGA, FT-IR, and NMR. The results were compared with the initial PET flakes and were found to be identical.

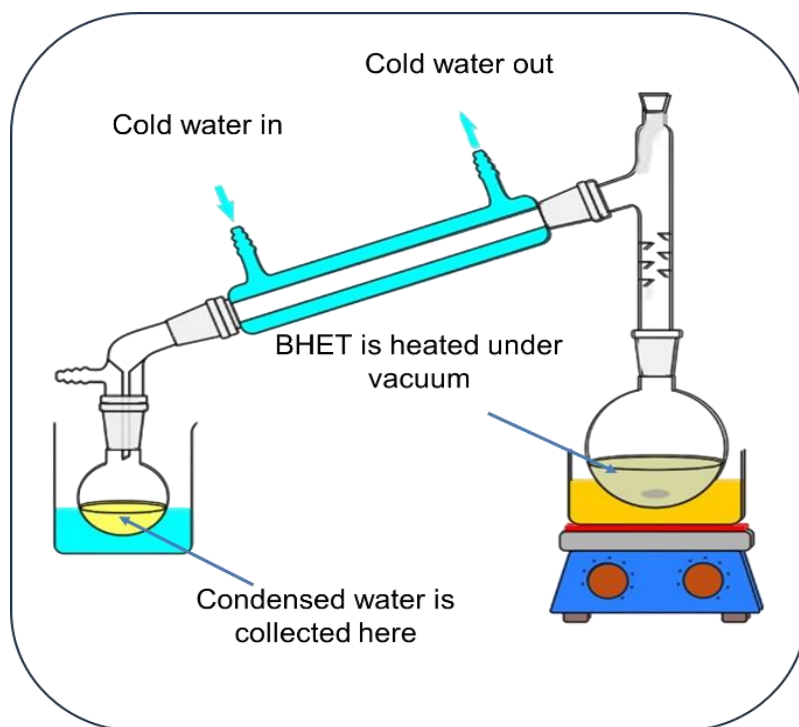


Figure 37. Schematics of polycondensation reaction of the formed monomers.

5.2. Characterization of the polymerization product

The synthesized BHET monomers from each reaction were combined and used for polycondensation. The resulting polymer was analyzed using FT-IR, Thermogravimetric Analysis (TGA), and solid-state NMR spectroscopy. Those results were then compared with those of the original PET.

Figure 38 shows the FT-IR spectra of BHET, original PET, and the re-polymerization product of BHET. As can be seen from the figure, the wide peak at around 3500 cm^{-1} belonging to hydroxyl groups are missing in the FT-IR spectrum of the re-polymerization product. Moreover, there is a striking similarity between our product and the PET from water bottles suggesting the re-polymerization from BHET to PET was successful.

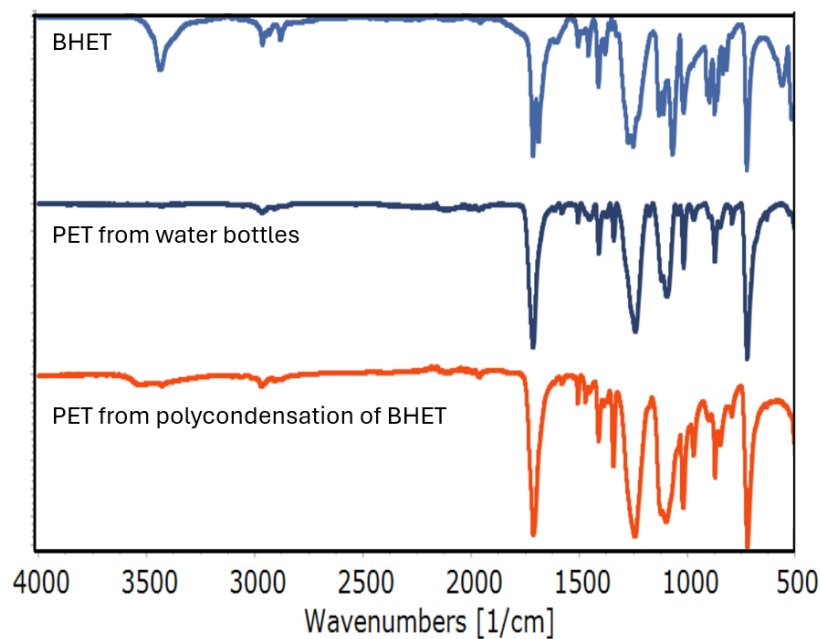


Figure 38. Comparison of the FT-IR spectra of the BHET monomers (blue), original PET from water bottles (navy blue) and PET from the re-polymerization (red).

Figure 39 illustrates a comparison of the thermal properties of the polycondensation product with those of PET and BHET. The TGA results indicate that the polycondensation product exhibits thermal properties similar to those of PET, while showing significant differences from those of BHET.

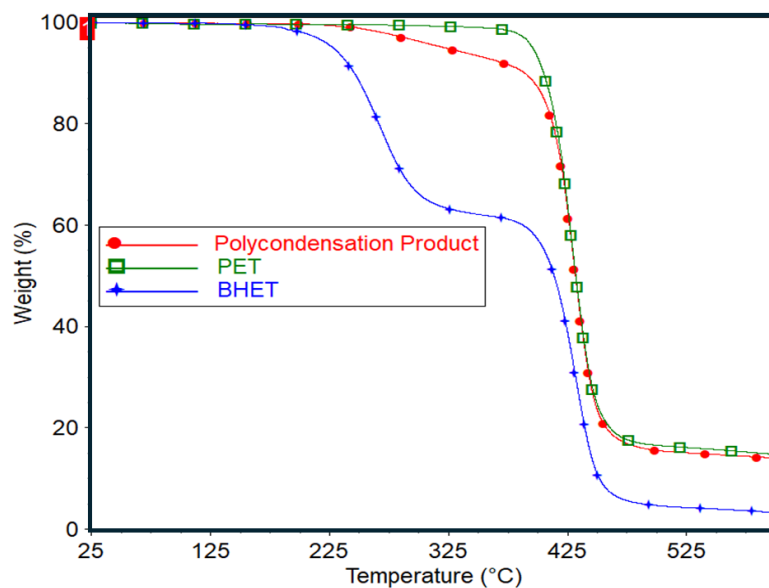


Figure 39. TGA Comparison of the TGA results of the PET polymer (green), re-polymerisation product (red) and BHET (blue).

Figure 40 shows a comparison between the solid-state carbon-13 NMR spectra of the polycondensation product and the original polyethylene terephthalate (PET). The spectra of the polycondensation product closely resemble those of the original PET, indicating a successful replication of PET's chemical structure through the polycondensation process. Key peaks in both spectra align well. This confirms that the polycondensation of BHET monomers effectively reproduces the original PET polymer structure.

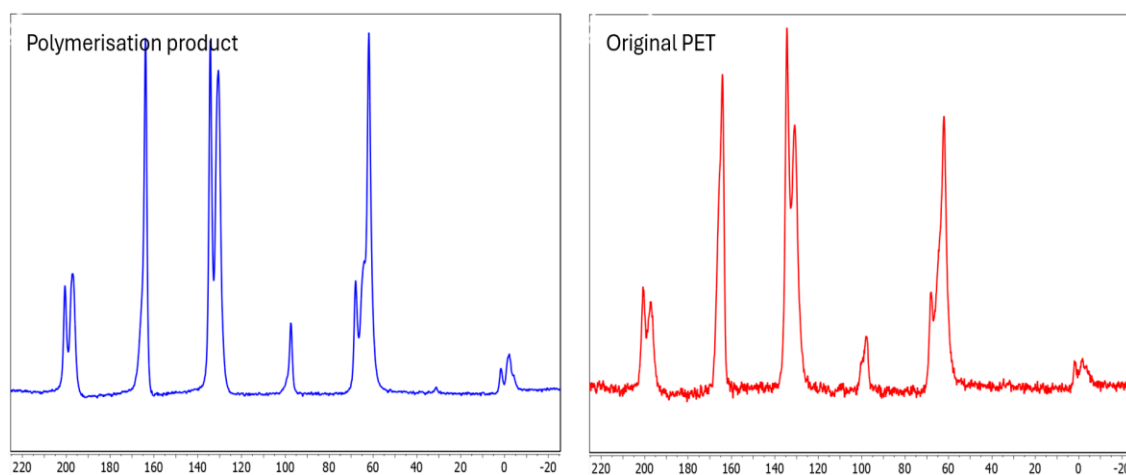


Figure 40. Comparison of the solid carbon NMR spectra of the polycondensation product (blue) and the original PET (red).

Conclusion

Our objective to tackle the global problem of plastic waste led us to explore the depolymerization of PET as a means to ensure a cleaner environment for the future. Through an extensive literature review, we identified chemical recycling via depolymerization as a highly effective method to address this issue, with a particular focus on finding the most suitable catalysts.

Our research revealed that the LDH catalysts, known for their sustainability and prior use in the pyrolysis of other plastics, was highly effective for PET glycolysis. ZnAl LDH achieved 100% conversion in just 2 hours at 200°C.

Further investigation into homogeneous metal-free catalysts led us to test the ionic liquids. [P6,6,6,14][Dec] also achieved a 100% conversion of PET and 72% yield within 3 hours at the same temperature.

Furthermore, the repolymerization of BHET resulted in the formation of rPET, as confirmed by FT-IR, TGA, and NMR analyses. The rPET exhibited properties comparable to those of the virgin polymer. The successful recycle of waste PET to rPET through the IL based PET depolymerization poses as a sustainable PET recycling techniques.

However, one of the main challenges encountered was the recovery of the catalysts. The inclusion of multiple filtration steps in the glycolysis process resulted in significant mass loss during catalyst recovery. To address these limitations, future research should focus on developing a reactor design that minimizes catalyst loss, possibly through the use of fixed-bed catalysts or improved filtration methods.

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APPENDIX A

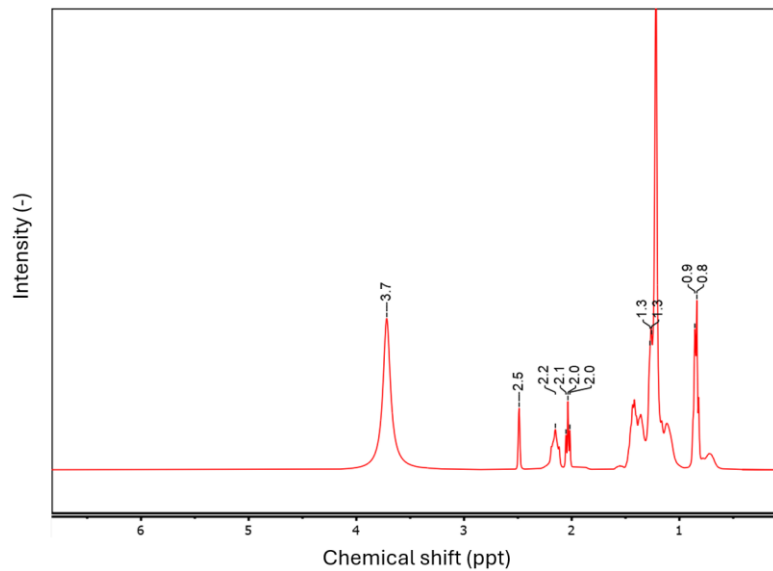


Figure 41. ¹H NMR of trihexyltetradecylphosphonium decanoate – [P6,6,6,14][Dec] - ionic liquid.

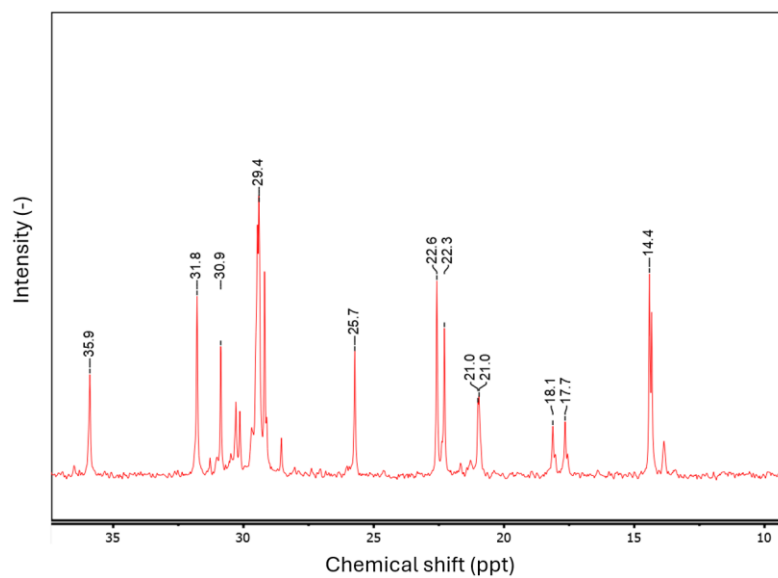


Figure 42. ¹³C NMR of trihexyltetradecylphosphonium decanoate – [P6,6,6,14][Dec] - ionic liquid.

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PET bottles”