



Department of Chemical & Process Engineering

MEng in Chemical & Process Engineering

18530

Developing new approaches on recycling of plastic waste using green solvents

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Summary

Polyethylene terephthalate (PET) is a thermoplastic polyester usually used for packaging. 12% of the global solid waste by volume consists of PET. A solution to effectively recycle PET waste with the least harmful effect on the environment has been developed over the years. Right now, the most used plastic recycling is mechanical, but its biggest drawback is the physical-thermal degradation each time it is recycled. Chemical recycling is a great sustainable alternative method that avoids the mechanical recycling disadvantages. Glycolysis is one of the best chemical recycling for PET recycling where the polymer chain is degraded to its monomer bis(2-hydroxyethyl) terephthalate (BHET). In the last few years, ionic liquids (ILs) have been discovered to work as a great sustainable catalyst for this reaction. This research aims to evaluate different conditions and conversion of PET glycolysis utilizing ILs as a green solvent catalyst to find new alternatives to plastic recycling.

Zinc-silica-based IL was synthesized ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$). The IL was used as a catalyst for the glycolysis of PET under different reaction conditions, around 170-210°C, from 1 to 4 hours, and different catalyst w/w ratios. The main product obtained was pure BHET. The IL was later supported by biochar (BC) and further tested. FT-IR was carried out to determine the functional groups of the IL, glycolysis products, and BC.

It was found that $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ worked as a great catalyst for the glycolysis of PET. The PET conversion was higher at longer periods of reaction time and higher temperatures. The biggest PET conversion obtained was 88% under optimal conditions (4 hours, 200°C, and 0.1:1:4 w/w ratio (catalyst: PET: ethylene glycol)). The highest BHET yield obtained was 28%. Yields and selectivity of BHET were low because of the difficulty encounter to filtrate the product after crystallization without the BHET dissolving in the water.

The pre-activated BC acted as great support for the IL. The FT-IR showed the BC effectively supporting $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$. The BC/ $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ showed better catalytic activity than the IL on its own. Under the same optimal conditions, the catalyst achieved complete PET conversion and 33% BHET yield. FT-IR showed that the catalyst did not suffer any change and was recovered via filtration from the medium after the reaction took place.

The project achieved satisfying results in the glycolysis of PET using IL Zn-silica-based green solvent as a catalyst that can be bonded to BC to facilitate its retrieval. The catalyst avoids two of the common problems, the final product is high-purity BHET not contaminated by the catalyst, and the structure of the IL presents an option for its easy recovery. This project helps add more information on the research gap that seeks ILs as a catalyst of glycolysis of PET more accessible.

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Introduction

Description of the organization

The organization refers to the Department of Chemical and Process Engineering (CPE) of the University of Strathclyde. It is a public research university located in Glasgow Scotland. CPE is one of the biggest chemical engineering departments in the UK. In the department, solutions for problems in society and industries are created. This research is one of the projects of module 18530 at CPE. This module requires a minimum of 12 weeks of work as part of the second semester of the fifth-year course. It is an opportunity to expand my chemical engineering experience.

The learning objectives for this project are to widen chemical engineering knowledge. This is going to be done while producing a chemical engineering report throughout the experimental investigation. This is an opportunity to apply the knowledge learned through the university degree in a non-class environment.

Background

Plastics are used in the everyday life of most humans in the world. The overuse of plastic without proper after-use treatment has created an environmental problem. The traditional method to recycle is mechanical but this method is not enough to manage the

consequences created by plastic pollution. This investigation focuses on chemical recycling of plastic using environmentally friendly methods to produce high-quality results.

Polyethylene terephthalate (PET) is a thermoplastic polyester formed by condensation of terephthalic acid (TPA) and ethylene glycol (EG) or transesterification between dimethyl terephthalate (DMT) and EG (1,2). PET is one of the most common plastics used and produced in the world due to its unique properties such as low cost of production, durability, lightweight, and chemical resistance. Global production of PET exceeds 13 million tons yearly, most of which is used as plastic packaging. 12% of the global solid waste by volume consists of only PET. This causes plastic pollution; the accumulation of plastic objects in Earth's environment to the point that they create a problem for the life on the planet. Plastic waste can release harmful chemicals onto the surrounding soil that can get into water sources causing harmful effects on the species that consume it. Plastic waste also causes various physical impacts on marine life just to name a few of the consequences that plastic pollution brings. Consequently, the treatment of PET waste has become a necessity to resolve an environmental problem (1,3).

The most common recycling method of PET plastic is mechanical, where the plastic waste is collected, sorted, washed, and ground. But this method has many disadvantages. It requires pristine and clean materials which

makes the sorting complex, and the final product suffers degradation of the plastic properties because of the thermal-mechanic degradation (4,5). A solution to effectively recycle PET waste with the least harmful effect on the environment has been developed over the years, the most successful method is chemical recycling. Chemical recycling allows for a complex stream of waste to be broken down into monomers without a reduction in its molecular weight. The problem right now is that chemical recycling is not a cost-effective process if it is not done on a high scale level and most of the traditional catalysts are not sustainable and poison the final product (6–8).

There are many kinds of chemical recycling, some of them being: glycolysis, methanolysis, amylolysis, ammonolysis, pyrolysis, hydrolysis, or biodegradation. Each of them has its advantages and disadvantages (1,9,10). For PET the best chemical recycling has been proven that is glycolysis, this is not only because glycolysis is non-toxic and non-corrosive. Compared with other chemical recycling methods it uses lower quantities of reactants, has shorter reaction times and the reaction can take place in a wide range of temperatures. Glycolysis also allows PET to be degraded to its monomer bis(2-hydroxyethyl) terephthalate (BHET) that can be directly used to produce PET (6–8). The disadvantage that glycolysis presents is the production of undesirable products and the need for non-traditional purification. But it avoids some of

the bigger problems that arise with other chemical recycling; for example, moderate temperatures and pressures that methanolysis requires, or in the case of hydrolysis, the need for complex purification of the TPA product (7).

Glycolysis of PET requires a catalyst for it not to be lethargic. These catalysts can be salts, acids, bases, transition metals compounds, or enzymes. The best results have been achieved using different kinds of metal-containing salts, especially ionic liquids (ILs) (7,11,12). ILs stand out from traditional catalysts in the glycolysis of PET because they can be an efficient and environmentally friendly way to recycle PET. ILs can be non-toxic, non-corrosive, non-flammable, and stable, they have negligible volatility, and allow to be tuned to the reaction requirements adjusting their physical and chemical properties (7).

An important quality that a catalyst needs to possess is its reusability after the reaction is complete. To achieve this, the catalyst must be retrieved and treated to be reused. The wide range of ionic liquids that can be used for the glycolysis of PET depends on the different properties specific to this purpose. To facilitate the catalyst separation, one solution is to support the IL in different mediums (7,13). Biochar (BC) is a good alternative to support ILs. BC has a porous structure with activated sites on its surface allowing it to be chemically bonded to other materials by their functional groups. Biochar is made with the thermal decomposition of

biomass without oxygen. BC made from waste is a great sustainable and low-cost alternative to other support materials like graphene or active carbon. It has a high surface area; high adsorption capacity and can exchange cations. This electron-accepting donation ability makes it perfect for binding with IL (14,15).

Research gap

A solution to effectively recycle Polyethylene terephthalate (PET) waste with the least harmful effect on the environment has been developed over the years. The most successful method is chemical recycling. For PET the best method is glycolysis where it is degraded to its monomer bis(2-hydroxyethyl) terephthalate (BHET) for it to be polymerized again. Wang et al. (12) discovered that the glycolysis of PET can achieve a much higher yield using ionic liquids (ILs) as a catalyst. The glycolysis of PET catalysed by ILs has recently gained attention over the last few years. The novel field of investigation allows a new alternative to plastic recycling. Researchers have been synthesizing different alternatives for an ionic liquid catalyst that achieve the highest yield and purity of BHET, analysing the characteristics of diverse ILs.

However, there is still a lack of empirical research, the yield and purity of BHET achieved are still insufficient to sustain its use on an industrial level, where the cost is much

lower than producing PET from primary materials.

Numerous researchers agree that this could be the course of action for the future of plastic recycling, ionic liquids working as a green and sustainable catalyst for the glycolysis of PET (16–18). Therefore, an effective and efficient degradation of the PET with novel catalysts has been sought.

The principal problems that glycolysis of PET presents right now, which stops glycolysis to be used over mechanical recycling are as follows. The first one is the higher cost of the chemical recycling process compared to traditional mechanical recycling. The second is that traditional catalysts used for glycolysis tend to leave traces of contaminants on the product BHET. And in the case of ionic liquids catalysts, there is a lack of information on the retrieval of the catalyst from the medium after the reaction is done.

Aims and objectives

Aims

This research aims to evaluate different conditions and conversion of PET glycolysis utilizing ionic liquids as a green solvent catalyst to find new alternatives to plastic recycling.

Objectives

- To synthesize an effective green novel solvent catalyst silica-based ionic liquid ((SIL)/Zn-SIL) for the glycolysis of PET.
- To produce a high conversion of PET decomposition catalysed by ionic liquid ((SIL)/Zn-SIL).
- To evaluate BHET product yield and purity of PET glycolysis.
- To analyse biochar as support for (SIL)/Zn-SIL synthesised to allow easy retrieval and reuse of the catalyst.

Research questions

- How effective are zinc-silica-based ionic liquids ((SIL)/Zn-SIL) used as a catalyst in the degradation of PET?
- What is the PET conversion obtained using (SIL)/Zn-SIL as a catalyst for glycolysis?
- What impact does using biochar as support for the catalyst (SIL)/Zn-SIL have on PET glycolysis?

This project will contribute creating a circular economy, researching a way to recycle plastics using a sustainable and environmentally friendly catalysts. The IL catalyst used in this project has been used as a catalyst for other reactions, yet this is the first time used for glycolysis of PET to my knowledge. This research will add in to cover the breach of research on ionic liquids as catalysts for glycolysis.

Outline

The first chapter is an introduction to the project done in chemical engineering course. It provides a broad view of the topics that are going to be covered and the significance of the reason why the realization of the project is necessary. This chapter discussed the research gap that exists currently in the literature and the approach taken on this project to solve the problem, exhibits the aims, and objectives, and provides an outline of what is to be expected from this report.

The second chapter will cover the literature review done on the existing information and research available about the use of ionic liquid as a catalyst in the glycolysis of PET to create the foundation on which this project will be based on.

The third chapter explains the methodology used for the experiment done in the laboratory. This section describes the procedure followed on the laboratory to get the results achieved.

The fourth chapter shows the results obtained from the experiments. This section displays and discusses the results archived following the methodology.

The fifth chapter concludes the study accomplished. It exhibits the outcomes of the experiments and analysis. The conclusion chapter exhibits the findings of the study. This chapter also recommends future research that can be done on the topic and indicates the

limitations encounter while the project was carried out.

The last chapter summarises the learning outcome of the project and what skills were acquired through the process. The sixth chapter is a review of the chemical engineering project. It is reflective writing on the learning outcomes of the whole process conducted. The learning objectives established at the start of the project will be examined with else everything that was learned from this experience like skills obtained and achievements done. This reflection is done to develop new perspectives on the work realized that will affect future decision-making and career.

Literature Review

In 2009 Wang et al. (12) found that ionic liquids can be used as a catalyst in the depolymerization of PET as glycolysis. The main product obtained is the monomer bis(2-hydroxyethyl) terephthalate (BHET). The temperature of the reaction, the amount of catalyst and the glycolysis time are variables that increase with the amount of product obtained. The reaction temperature is a key element in the degradation of PET. On the contrary, the water amount in the reaction decreases the conversion of the PET (12,19).

The pH also plays a critical factor in the glycolysis of PET catalyzed by ILs. In the case of Lewis base acetate IL catalyst study by Al-Sabagh et al. 2014 (20) the reaction starts with a pH of 8 where the Lewis base facilitates the attack of the oxygen in the PET of the ester group by the synergistic effect of the cation and anion. By the end of the reaction, the pH is reduced to 6.5 due to the release of protons from the PET (20,21). A doubly bound occurs when a cation and anion form a hydrogen bond (H-bond), this occurs frequently in ILs. Ionic liquids have an extended variety of H-bonds within them where the donor is a different species of the molecule than the acceptor (22,23).

In the early years after ILs were first used to catalyze glycolysis of PET not much research was done on the topic. Different kinds of ILs were experimented on to analyse which

properties serve a better purpose in the decomposition reaction. Magnetized ionic liquids is an alternative frequently investigated, because of how accessible and fast the recovery of the catalyst results. A complete conversion of the PET can be achieved using FeCl_4 and it also has high selectivity for BHET compared to previous catalysts FeCl_3 and Cl (18). Ionic liquids catalysts that contained chloride or iron were commonly used, but they have a problem of contaminating the final product. Zhou et al. (17) studied the possibility of using different acetates acting like catalysts as an eco-friendlier alternative because they are less corrosive and toxic. Zinc acetated containing IL presented the best results out of all the metallic acetated ILs.

Yue et al. (24) proved that the particle size of the PET influences the reaction time and conversion of its degradation. They used metal-containing ionic liquids as catalysts, the best catalyst was $[\text{Bmim}]\text{ZnCl}_3$ where the smaller the PET particle the easiest it was for it to dissolve in EG, accelerating the glycolysis reaction. The optimal size found was 4mm^2 to 1mm^2 (24). A year later the two ILs that produced better outcomes were $[\text{bmim}]_2[\text{CoCl}_4]$ and $[\text{bmim}]_2[\text{ZnCl}_4]$ in the degradation of PET catalyzed by synthesized first-row metal containing ILs a complete conversion of PET was accomplished and 81.1% selectivity of BHET (25), compared to a higher BHET yield of 83.3% with a lower conversion of PET of 97.9% using ZnCl_3 in the previous year (24). Both ILs

could be reused up to six times without a decrease in the final product.

First-row metallic-containing ILs showed promising results in the previous studies but until 2015 a high conversion of PET required long periods of reaction time. Alnaqbi et al. (26) utilized microwave energy to heat the process. This allowed better control of the temperature with a much faster PET conversion under 1.75-2 hours instead of 8-10 hours that would have taken with traditional heating methods. They achieve this by applying 1-butyl-3-methyl imidazolium bromide ([bmim]Br) an IL catalyst, avoiding the problem that acetate, sodium carbonate and barium hydroxide presented when heated with microwave radiation, not allowing them to be recycled.

Furthermore Scé et al. (27) compared conventional and microwaved heating methods for glycolysis of PET catalysed by two imidazolium-based hallomellate complexes catalysts. The dinuclear iron complex was $(\text{dimim})_2[\text{Fe}_2\text{Cl}_6(\mu\text{-O})]$ and the mononuclear iron complex was $(\text{dimim})[\text{FeCl}_4]$. Both reached similar results using traditional heating methods. However, when using microwave-assisted heating, the dinuclear iron complex achieved greater conversion of the PET in a few hours compared to a whole day required with traditional heating methods (27). Similar conclusions were made with oxalate-bridged binuclear iron (III) ionic liquid. $(\text{Dimim})_2[\text{Fe}_2\text{Cl}_4(\mu\text{-ox})]$ also presented

dielectric properties which allowed high heating rates under magnetic fields (28).

In the reaction mechanism hydrogen bonds play a vital role in the glycolysis process of PET with ILs. The mechanism of the reactions shows that H-bonds are formed between the catalyst and the carbonyl oxygen of the metal (23,29). This is a vital part of the process of decomposition of PET. The imidazolium ring of the Cu- or Zn-acetate-containing ionic liquids is what form the H-bond changing the structure coordination of the metal acetate from bidentate to unidentate and facilitating the attack on the EG on the carbon cation of the ester in the PET (29).

Years later, Ju et al. (30) studied the effect that different cations and ions have in the interaction with PET, using 24 kinds of imidazolium-based and tertiary ammonium-based ILs (anions and cations). The anions have a stronger interaction with the dimer than the cation, they play a critical role in forming H-bonds resembling the conclusion done by previous studies (22,23,29).

Cations create pi-stacking with the dimer and attack the oxygen of the carbonyl. The interaction between the anion and cation of the ILs and EG makes the electronegativity of the hydroxyl in the EG stronger, making the oxygen in EG prefer to attack the carbon in the ester group (22,30).

In 2021 there were huge advances in the knowledge of the mechanism of the

glycolysis of Poly (ethylene terephthalate) using ionic liquids. The easiest pathway for PET degradation is the breakage of the C-O ester bond generating a BHET monomer. The bond is attacked by the hydroxyl oxygen of EG with a proton transfer to the carbonyl oxygen. Between the PET, EG, and the IL a four-membered ring is formed that fractures the long chain of PET (23).

PET degradation using ionic liquids based on 1,1,3,3-tetramethylguanidine (TMG) $[C_6TMG]Cl/2ZnCl_2$ yields 84% of BHET and complete conversion of PET in optimal conditions because of the stronger interaction of PET with Zn^{+2} in the $ZnCl_3^-$. The interaction between ILs and the EG; the H-bond $[C_nTMG]^+-EG$ can be altered by changing the structure of the cation. This allowed for a better understanding of the different outcomes of the reactions (16).

The number of research done on glycolysis of PET catalysed by ILs grew exponentially in the last three years. In recent years the biggest problems that ionic liquids presented when used as a catalyst for PET glycolysis was their extraction after the reaction for their recycling and avoiding leaving traces of contaminants in the product (17,18).

A solution to these problems was the synthesis of $Fe_3O_4@SiO_2@(mim)[FeCl_4]$ from silica-coated immobilizing iron-containing ionic liquid with magnetic Fe_3O_4 nanoparticles. $Fe_3O_4@SiO_2@(mim)[FeCl_4]$ is thermal stable, it also has a high surface area and high catalyst

activity. The magnetic properties allow the catalyst to have an easy recovery with an almost complete yield of BHET, without a trace of Fe on the final product and high purity under conventional heating methods. The catalyst can be reused up to twelve times in optimal conditions at 180°C obtaining up to 84% yield of BHET, with an additional fifteenth cycle at 160°C for a lower yield (11).

Synthesized 1-hexyl-3-methylimidazolium (Hmim) halometallates as Lewis acidic ionic liquids (LAIL) mixing $[Hmim]ZnCl_3$ and $[Hmim]CoCl_3$ complex gives a yield of 87.1% BHET; higher than the individual compound, due to synergetic catalytic effect between in the high reactivity of $[Hmim]ZnCl_3$ and the high selectivity added from $[Hmim]CoCl_3$. The disadvantage that $[Hmim]ZnCl_3$ has while it is used on its own is that the $[ZnCl_3]^-$ has a high catalytic activity that induces the possibility to get unconventionally broken chain by-product instead of a higher percentage of BHET (21).

Another solution for the retrieval of the catalyst was the use of polymeric ionic liquid containing $[NTf_2]^-$ that allowed the immobilization of metal ions from chloride as Lewis acid to catalyse the glycolysis of PET, allowing easy recovery with a simple filtration. Under optimal conditions, the complex has analogous results of the ionic liquid non-immobilized (31).

From the understanding that hydrogen bond is a key element to breaking the PET chain,

Yao et al. 2021 (32) designed non-metallic amino acid IL catalyst because they have several receptor and donor groups gain the capacity to form multiple H-bonds in the glycolysis of PET. They were synthesized by transesterification and neutralization. This avoids the introduction of metals in the process and achieved similar results to traditional catalysts.

The best solution that allows retrieving of the ionic liquid from the medium and avoids contaminating the product with metals is to support the catalyst on a porous material. The IL bonded to a porous material can be easily removed from the reaction medium once it is finished via filtration (13,31,33,34). This has been done before, one cobalt-based ionic liquid grafted on graphene under optimal conditions, the (rGO\([TESPMI]_2CoCl_4\)) IL gave a complete conversion of PET and 95.22% yield of BHET due to the synergistic effect of the ILs with the graphene. This way the catalyst can be easily recovered and avoids leaving contaminants in the product (13). Using graphene as a support is a good solution to retrieve the catalyst, but other supports that are more sustainable can also be used for the same purpose.

Biochar (BC) is a charcoal-like porous material, it has a high surface area, hardness, and the capacity to exchange cations, it is neutral to high pH and has low density. Biochar is made by the thermal decomposition of organic material in the absence of oxygen, and

pyrolysis of biomass. The organic material used to produce biochar can be waste biomass. Waste biochar is great for circular economy as a value-added by-product from another industrial processes. It is low-cost and has diverse properties and uses (14,35,36).

One of the uses for biochar is the immobilization support of other materials. Factors like the surface area, porous size, chemical and thermal stability on reaction conditions, and the surface functional group are properties that affect biochar's role while binding with a catalyst as a support in a reaction. Compared to other support materials such as inorganic polymers and other carbon-based supports, biochar excels in stability, it is also environmentally friendly and possesses a cation exchange capacity making it electron-accepting (35).

Biochar has been used before to support ionic liquids catalysts in reactions other than glycolysis of PET. When mixing $ZnCl_2$ with 1-(trimethoxy propyl silane)-3-methyl imidazolium chloride (IL), the ionic liquid catalyst attaches to the Zinc 1-(trimethoxy propyl silane)-3-methyl imidazolium chloride (IL-Zn) can be synthesised. This IL was successfully used as a catalyst for the hydrolysis of cellulose and bamboo. The methyl group on the structure of the IL allows it to bond with biochar and be used as support in the reaction. The $ZnCl_2$ improves the catalyst activity and the IL-Zn is flexibly bound to the biochar via BC- SO_3H bond between the IL and the BC (15). The

initial IL used can be synthesised following the methodology used by Chrobok et al. 2009 (33) mixing (3-chloropropyl) triethoxysilane and the same molar ratio of 1-methylimidazole reactants.

Methodology

The experimental project consists of three parts. The synthesis of the ionic liquid that will be used as a catalyst is 1-(trimethoxy-propyl-silane)-3-methyl-imidazolium-tetrachlorozincate ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$), the PET glycolysis reaction using the IL synthesised under different conditions, and the third part consists of binding $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ with biochar to create a support that can help retrieve the catalyst from the reaction. $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ will be synthesised, tested in PET glycolysis, and additionally tested when supported by biochar.

The ionic liquid chosen to be synthesised is 1-(trimethoxy-propyl-silane)-3-methyl-imidazolium-tetrachlorozincate ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$) because the base IL (1-(trimethoxy propyl silane)-3-methyl imidazolium Chloride ($[\text{TMSPMI}]\text{Cl}$) was used adding cobalt before by Najafi-Shoa et al. 2021 (13) where it showed great results as a catalyst grafted on graphene for support. Instead of graphene, biochar is a more sustainable carbon-based support that provides similar results because the methyl group of the silicone on the IL have the capacity to bond to both supports. Instead of using cobalt as they did, zinc-based ionic liquids give the best result as shown in the literature. Al-Sabagh et al. 2014 (29) zinc acetate ionic liquid in which the metal acetate was bonded to the same aromatic heterocyclic compound 1-

methylimidazole which allowed them to produce a great ionic liquid with excellent catalytic abilities.

For this reason, using the IL base from Najafi-Shoa et al. 2021 (11) bonding it to the zinc as it was done for Sabagh et al. 2014 (29) the ionic liquid 1-(trimethoxy-propyl-silane)-3-methyl-imidazolium-tetrachlorozincate ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$) was synthesised and tested on its catalyst activities for glycolysis of PET.

Materials

1-methylimidazole (99%), (3-chloropropyl) trimethoxysilane (98+%), n-hexane, potassium hydroxide (KOH, >85%) were supplied by Thermo Scientific, Zinc (II) Chloride (ZnCl_2) was from MP Biomedicals, dichloromethane (CH_2Cl_2) was from Merck, PET pellets were from Sigma Aldrich and the biochar before it was pre-treated for other research. The BC came from coffee waste grounds. After it was activated, the biochar had a BET surface area of 1185 m^2/g .

Synthesis of Silica Ionic liquid $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

1-(trimethoxy propyl silane)-3-methyl imidazolium Chloride ($[\text{TMSPMI}]\text{Cl}$) was synthesised following the literature (13) by mixing 1-methylimidazole and (3-chloropropyl) trimethoxy silane in a 50-ml two-necked flask

at 100 °C for 16 hours at a molar ratio of 1:1. The time reaction done was longer than the literature because the ionic liquid did not look acquire the yellow colour describe in the literature by that time, FT-IT was done while the synthesis was happening to see the reaction progress. Subsequently, it was washed with n-hexane to remove residual reactants in a separatory funnel.

The synthesis of a zinc-silica-based IL was similar to the literature (29,37). The yellow ionic liquid obtained ([TMSPMI]Cl) was mixed with ZnCl₂ at a weight ratio of 1:2 (IL: ZnCl₂) and a small amount of dichloromethane at 60 °C for 6 hours using a hot plate stirrer producing 1-(trimethoxy-propyl-silane)-3-methyl-imidazolium-tetrachlorozincate ([TMPSMIM]₂[ZnCl₄]), due to its high viscosity it was not washed as the literature indicated but dried in an oven at 60°C for 24 hours. The final ionic liquid had a blue tint with very high viscosity. The material was characterized using FT-IR recorded between the wavenumber range 400 to 4500 cm⁻¹ where the stretching of all the functional group's bonds on BHET and PET can be seen.

Conventional Heating PET glycolysis catalysed by [TMPSMIM]₂[ZnCl₄]

5g of PET pellets and various ratios of EG and IL were added to a flask and mixed at the desired temperature in an oil bath to determine the optimal conditions, around 1 to

4 hours. Once the reaction time is completed the hot mixture had to be left to cool down due to the risk of handling it at high temperatures. Once it got to 90°C, 15ml of distilled water was added and stirred for 30 min to conduct the first filtration.

The solid residue was diluted on 50ml of water and heated at 60°C to be filtered a second time after passing through a sieve. The residue left on the sieve represents the unconverted PET, it was weighed after being dried in an oven at 70°C.

The PET conversion was calculated using Eq. (1):

$$PET \text{ conversion } (\%) = \frac{W_0 - W_f}{W_0} \times 100 \quad (1)$$

where W_0 represents the initial weight of PET and W_f is the final weight of the unconverted PET.

The filtrate is concentrated in a vacuum at 70°C and refrigerated under 0°C for 12 hours. When cold, the filtrate mixture formed white crystals that were recovered by filtering and drying in an oven, and then weighed. The solid filtrated amounted to the BHET generated.

The BHET yields and BHET selectivity was calculated following Eq. (2) and Eq. (3) respectively:

$$BHET \text{ yield } (\%) = \frac{W_{BHET}/MW_{BHET}}{W_0/MW_{PET}} \times 100 \quad (2)$$

BHET selectivity (%)

$$= \frac{W_{BHET}/MW_{BHET}}{(W_0 - W_f)/MW_{PET}} \times 100 \quad (3)$$

where W_{BHET} is the weight of the BHET product achieved and MW_{BHET} and MW_{PET} are the molecular weight of BHET (254 g/mol) and the molecular weight of PET (192 g/mol) respectively (16).

FT-IR was carried out for unconverted PET, the oligomers generated and the final product BHET recorded between the wavenumber range 400 to 4500 cm^{-1} .

The different scenarios used for the reaction were:

Table 1: PET Glycolysis scenarios catalysed by $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

Experiment number	Temperature ($^{\circ}\text{C}$)	Catalyst:P ET:EG (w/w)	Time (hr)
1	170	0.1:1:4	1
2	170	0.1:1:4	2
3	170	0.1:1:4	3
4	170	0.1:1:4	4
5	180	0.1:1:4	Optimal
6	190	0.1:1:4	Optimal
7	200	0.1:1:4	Optimal
8	210	0.1:1:4	Optimal
9	Optimal	0.2:1:4	Optimal
10	Optimal	0.05:1:4	Optimal

The first reaction conditions that were selected from the optimal temperature, catalyst weight ratio and time were the ones that gave the best result in the literature and then changed as the results from the experiments were coming out. As shown in Table 1, the first variable to be determined was the time, once the optimal time was determined another set of the experiment were done at different temperatures. And at last, under the optimal temperature and time the glycolysis of PET was realised for different weight of catalysts.

[TMPSMIM]₂[ZnCl₄] functionalised by biochar

The biochar was processed and activated previously for a different research project in the CPE department. The methodology followed to activate the biochar was done by pre-pyrolyzing coffee grounds for 1 hour at 600°C in a nitrogen atmosphere. The biochar was ground to be activated by KOH at a mass ratio of 1:1 (biochar: KOH). It was then put in a nitrogen atmosphere on an alumina boat crucible at high temperatures of 800°C for 2 hours. The biochar was finally washed with water and dried. All this procedure was previously done external to this project.

The biochar activated was mixed with the ionic liquid dissolved on n-hexane for 6 hours at 60°C. Then it was washed three times with n-hexane and left to dry in the oven at 70°C overnight.

FT-IR was carried out for the BC sample after it was activated and the BC supporting the IL BC[TMPSMIM]₂[ZnCl₄].

Conventional Heating PET glycolysis catalysed by BC[TMPSMIM]₂[ZnCl₄]

The same procedure followed for the glycolysis of PET utilizing IL on its own was used for the IL functionalized by the biochar. The catalyst used followed the same weight ratio that achieved the greater results, the weight

used as reference was the one the result of the final catalyst BC[TMPSMIM]₂[ZnCl₄] from the previous procedure.

The method of extraction BHET was changed to try to achieve bigger BHET yields. Once the reaction time is completed and cooled down to 90°C, 15mL of distilled water was added and stirred for 30 min to conduct the first filtration.

The solid residue from the first filtration was diluted on 15mL of water and heated at 60°C to be filtered a second time after passing through a sieve. A third filtration was done to the solid residue of the second filtration diluting it with 50mL of water and heated at 60°C.

The filtrate from the first and second filtration was put separated in the freezer at 0°C for a few hours and taken out before the water froze but left for enough time to let some of the BHET crystalize. The BHET was filtered and put in the oven to dry and be weighted.

The PET conversion, BHET yield and BHET selectivity were calculated with the same formulas as before Eq.(1), Eq. (2) and Eq. (3).

Results and Discussion

The ionic liquids, the BHET generated, the PET not converted, and the biochar were analysed by Fourier-transform infrared spectroscopy (FT-IR) between wavenumber ranges 400 to 4500 cm^{-1} .

The FT-IR gives an idea of the structure of the ionic liquid synthesized. The FT-IR of the IL can be compared to a similar ionic liquid 1-(trimethoxy propyl silane)-3-methyl imidazolium Chloride (SIL) without the ZnCl_2 added in an experiment done by Najafi-Shoa et al. (16).

FT-IR was also carried out for the unconverted PET at the end of the reaction, the product BHET, and the solid waste produced corresponding to oligomers in between BHET and PET. This analysis was realized to verify the main structure of the products obtained in the reaction. The main difference that can be found between an FT-IR of PET and BHET is that the monomer has more alcohol on its structure. Therefore, in the functional region of the BHET the O-H peak will be clear in the FT-IR, this peak can be found around 3600 – 3200 cm^{-1} . On the contrary, the fingerprint will look similar for the PET and the BHET. The FT-IR does not give information on how much PET can be in the BHET final product. Consequently, there is no certainty that in the final product, there are no traces of PET or there is still product counted as unconverted PET.

For part three of the experimental part, FT-IR was carried out to help analyse how the biochar and the ionic liquid interact with each other. The BC supporting IL was further tested and applied to a glycolysis reaction on optimal conditions for the IL on its own.

Synthesis of $[\text{TMSPMIM}]_2[\text{ZnCl}_4]$

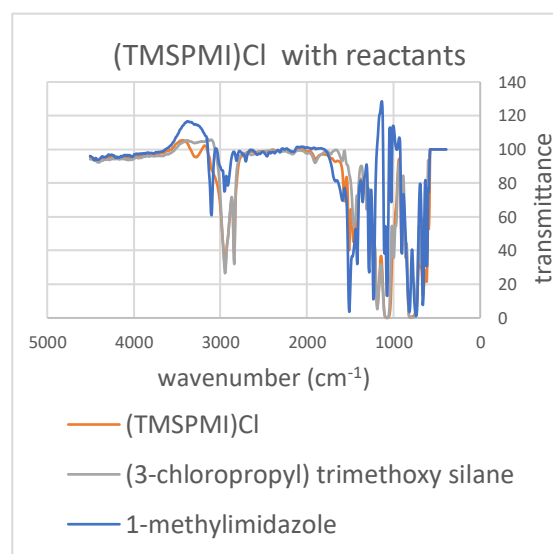


Figure 1. $(\text{TMSPMI})\text{Cl}$, 1-methylimidazole and (3-chloropropyl) trimethoxy silane

Figure 1. shows FT-IR done on the 2 reactants (3-chloropropyl) trimethoxy silane and 1- methylimidazole compared to the IL synthesized 1-(trimethoxy propyl silane)-3-methyl imidazolium Chloride ($\text{TMSPMI})\text{Cl}$. It shows that the IL has the same functional groups of the two reactants combined.

The FT-IR of 1-(trimethoxy propyl silane)-3-methyl imidazolium Chloride (SIL) shown in Figure 1, the peak on 3271 cm^{-1} that shifted as the reaction progressed represents the stretch of the bond N-H of the heterocycle amine [3490-3430] cm^{-1} , from the FT-IR of the

reactant (3-chloropropyl) trimethoxy silane and the IL (TESPMI)Cl shows the same peaks the double peak on 2947 cm^{-1} and 2839 cm^{-1} corresponding to stretching bond of alkyl C-H [$2850\text{--}3000\text{ cm}^{-1}$]. There are two peaks on the double area of the FT-IR, 1566 cm^{-1} and 1512 cm^{-1} which correspond to the aromatic ring stretch of C=N [$1590\text{--}1690\text{ cm}^{-1}$] and C=C [$1580\text{--}1615\text{ cm}^{-1}$], these two peaks are larger on the IL than the reactant 1-methylimidazole. On the fingerprint area of the FT-IR from the reactant (3-chloropropyl) trimethoxy silane and the IL (TESPMI)Cl shows the same peaks: the C-O stretch of the ether [$1050\text{--}1150\text{ cm}^{-1}$] on 1188 cm^{-1} , the silicone Si-O stretch [$1110\text{--}1080\text{ cm}^{-1}$] on 1056 cm^{-1} and Si-O-C [$740\text{--}880\text{ cm}^{-1}$] on 794 cm^{-1} (13,38–41)

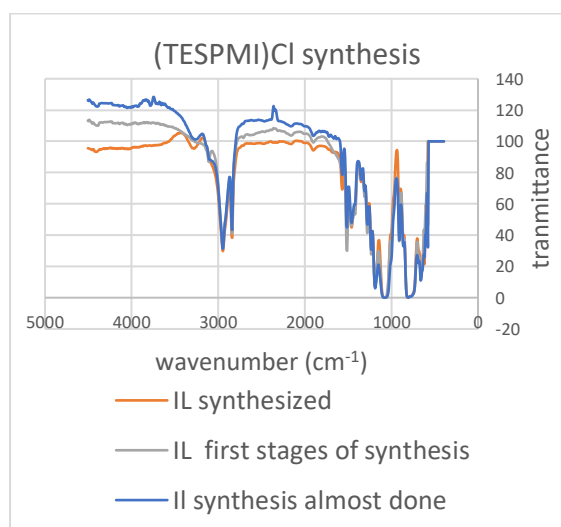


Figure 2. (TESPMI)Cl synthesis

Figure 2. presents how the functional groups change on the (TESPMI)Cl IL as the reaction is taking place. The clearest peak is the one that corresponds to the N-H 3271 cm^{-1} shifting to a higher wavenumber as the reaction is taking place.

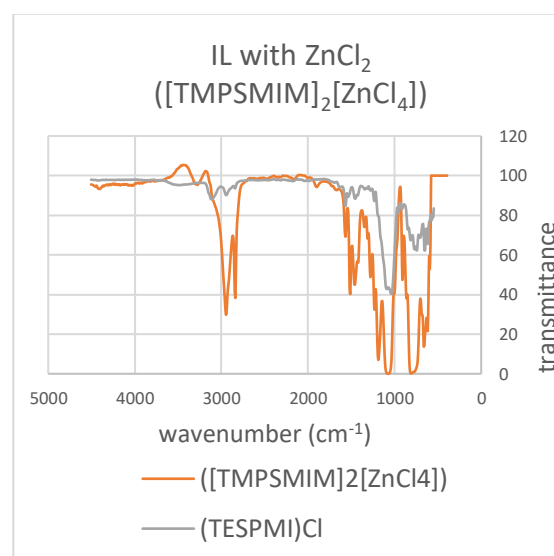


Figure 3. IL with ZnCl₂

Figure 3. compares the ionic liquid analysed before (TESPMI)Cl and the ionic liquid after the ZnCl_2 was added ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$). After the final ionic liquid was synthesised, it acquired a blueish colour with a very viscous consistency. The $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ was so viscous that it behaved almost a solid, so the FT-IR done on this sample was for solids, instead of the liquid FT-IR previously done on the other ILs. The main peaks identified in Figure 3 are present on the $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ FT-IR shifted slightly. On the single bond zone, N-H peak is 3116 cm^{-1} , the double C-H peak is 2939 cm^{-1} and 2839 cm^{-1} , C=N and C=C are on 1566 cm^{-1} and 1458 cm^{-1} . The biggest peak belongs to the C-O and Si-O of the silicon on 1087 cm^{-1} and 1033 cm^{-1} , the peak Si-O-C blends on the finger zone with other peaks (41).

Glycolysis of PET catalysed by [TMPSMIM]₂[ZnCl₄]

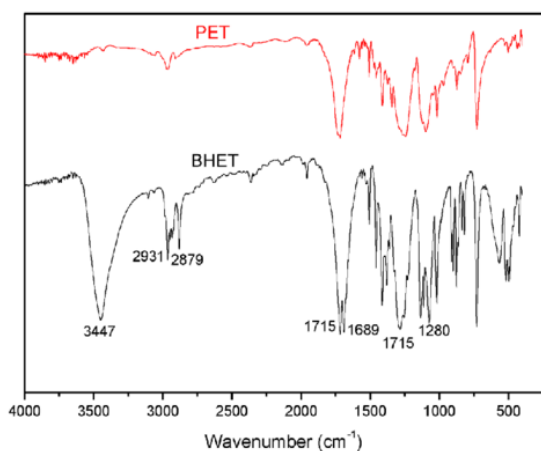


Figure 4. FT-IR BHET and PET (17)

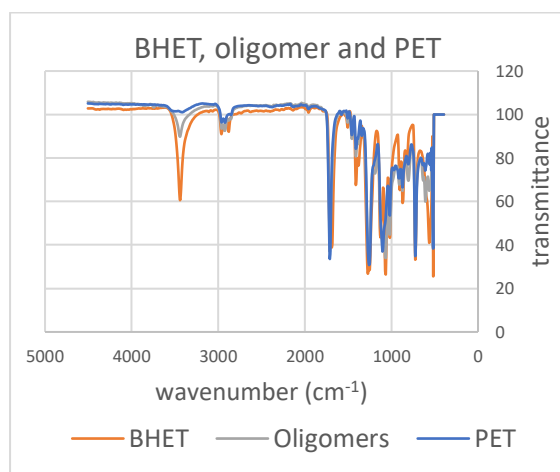


Figure 5. FT-IR of PET, BHET and oligomers

Figure 5 where the transition of the functional bonding groups from PET to BHET in the glycolysis process can be seen, this can be compared to one taken from the literature in Figure 4 (17). Figure 5 shows an intermediate product from the glycolysis reaction, oligomers that are PET degraded but the carbon polymers are not short enough to be BHET. This product amounts to solid waste on the second filtration.

The clearest difference between BHET and PET is the peak on 3440 cm^{-1} , which represent the stretching of the O-H bond of primary alcohol $[3600-364]\text{ cm}^{-1}$. When the polymer of PET is degraded new O-H bonds forms, and as the polymer gets shorter more O-H groups appear. Therefore, the peak O-H has a greater absorbance making it bigger on the FT-IR. The appearance of new O-H bonds can also be seen on the new peak that appears on 1064 cm^{-1} of the BHET forming a triple peak with the other two peaks before. This third peak is the stretching of the C-O bond on the alcohol $[1180-1300]\text{ cm}^{-1}$. The two peaks that were before 1110 cm^{-1} and 1018 cm^{-1} are the stretching of the symmetric C-O bond of the ester $[1050-1150]\text{ cm}^{-1}$ (17,41,42).

Other peaks can be found on the BHET and PET taking reference from the BHET FT-IR in Figure 5. The double peak on 2962 cm^{-1} and 2931 cm^{-1} belongs to the stretch of C-H on the alkyl groups $[2970-2950/2880-2860]\text{ cm}^{-1}$, on the double bond zone the stretch of the C=O carbonyl compound of the ester $[1750-1725]\text{ cm}^{-1}$ can be seen on 1702 cm^{-1} , the double peak 1272 cm^{-1} on the fingerprint zone corresponds to C-O-C bend $[1350-1260]\text{ cm}^{-1}$. There are skeletal vibrations of the benzene between $1500-1300\text{ cm}^{-1}$ and the bend of C-H and C=C between $900-700\text{ cm}^{-1}$ (17,41,42).

Effect of time on glycolysis of PET catalysed by $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

For the reaction time of one hour, the BHET extraction was extracted with only 15 mL of water doing one extraction. Once the experiment was run a few more times under different conditions it was evident that it was not enough water to separate all the product from the unconverted PET, for this reason, more water amount was added to a second filtration and sieve following the procedure explained on the methodology chapter. Adding more water to dissolve the BHET solved the problem of extracting the BHET product from the unconverted PET but created a new problem. When the BHET was filtered after it was crystalized on the fridge at 5°C, great quantities of the product would dissolve again in the water and be lost as liquid waste. A solution found in the literature for this problem is by extracting water before crystalizing the BHET using rotatory evaporation. This was not an available solution for the experiment because the rotatory evaporator was inaccessible at the time the experiments were being carried out.

Therefore, comparing the result obtained, the one-hour results with the other experiments where the PET conversion is higher for 2 hours or 3 hours reaction time, but the BHET yield, and selectivity obtained were lower. It can be concluded that there are big amounts of product that was unable to be extracted from the water explaining the low

BHET yield and BHET selectivity obtained in all the experiments. Also, because of the same problem of the BHET being easily diluted in water, the result achieved with the BHET product is less unreliable than the results obtained by looking at the PET conversion. For this reason, all decisions made are based on the PET conversion rather than the BHET yield and selectivity.

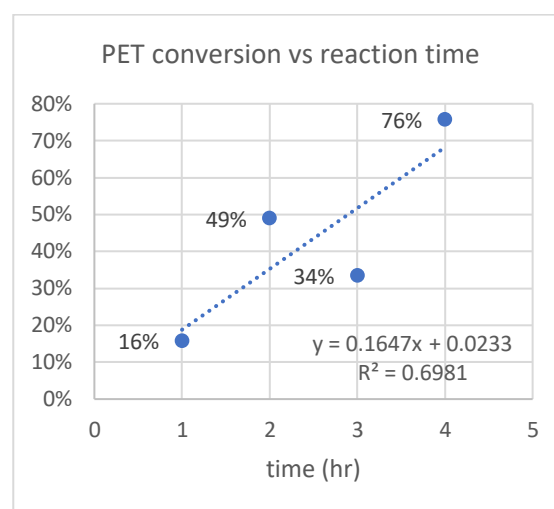


Figure 6. PET conversion at different reaction times

As shown in Figure 6 the PET conversion is higher as the reaction time increases. When the reaction was performed for 1 hour, the PET conversion was 16% much lower than compared when the reaction time was 4 hours achieving a PET conversion of 76%.

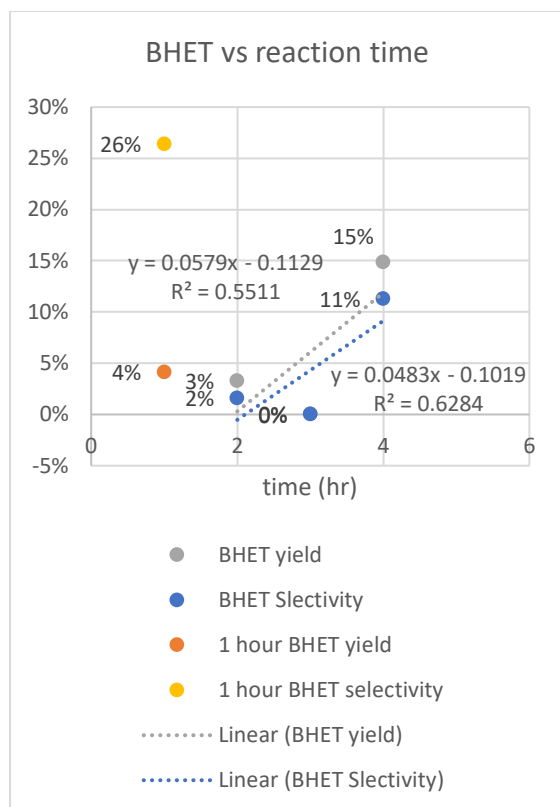


Figure 7. BHET yield and selectivity at different reaction times

Excluding the results obtained with the experiment for only one hour of reaction time, Figure 7 shows that the BHET yield and selectivity grow with the reaction time concurring with the tendency observed for the PET conversion. For the 2 hours and the 3 hours experiments, the BHET product obtained is so low that even if the BHET crystals could be seen from when the mixture was in the fridge, once it was taken out to be filtrated, the BHET would dissolve in the water again.

Effect of temperature on glycolysis of PET catalysed by $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

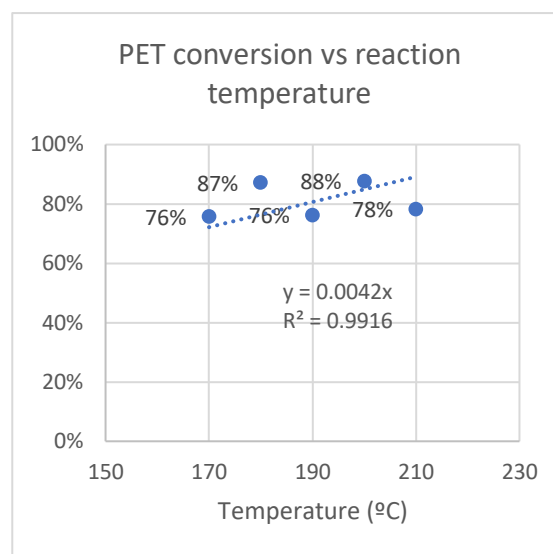


Figure 8. PET conversion at different temperatures

As shown in table Figure 8, PET conversion tends to grow the higher the temperature. The highest PET conversion being 88% observed at 200°C. Regardless of PET conversion tendency to be higher when the temperature is higher, the inclination of the line is low. Considering the tendency, it is to be assumed that all experiments were done close to the optimal values taken from the literature, Presumably under these temperatures the PET conversion is much lower as it can be seen with the lowest temperature used 170°C obtaining lowest result 76% PET conversion.

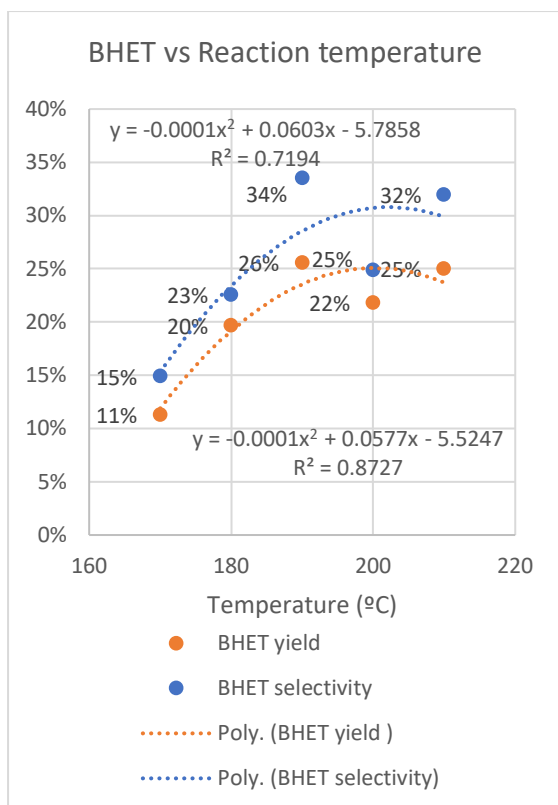


Figure 9. BHET yield and selectivity at different temperatures

From Figure 9, the optimal temperature ranges between 190°C and 210°C where the PET conversion, BHET yield, and BHET selectivity are the highest. Figure 9 shows an exponential growth from the lowest temperature to the highest where it stabilizes.

A reverse reaction can explain the decrease in BHET yield and selectivity for high temperatures. As a safety precaution, the experiment was left to cool down once the reaction was finished because it was dangerous to handle the set-up over the hot temperatures of the oil bath. For the temperatures over 190°C the time to reach the temperature and to cool down was much higher than the rest. Because in the flask there is BHET, and ethylene glycol mixed a reverse reaction can happen

where the BHET starts to polymerize again. It is important to note that this could be happening with all the experiments, but it is more prominent for high temperatures as it takes longer to reach a set temperature and to cool down.

Following the criteria that the PET conversion is more reliable as seen in Figure 8, the optimal temperature achieved was 200°C.

Effect of catalyst amount [TMPSMIM]₂[ZnCl₄] on glycolysis of PET

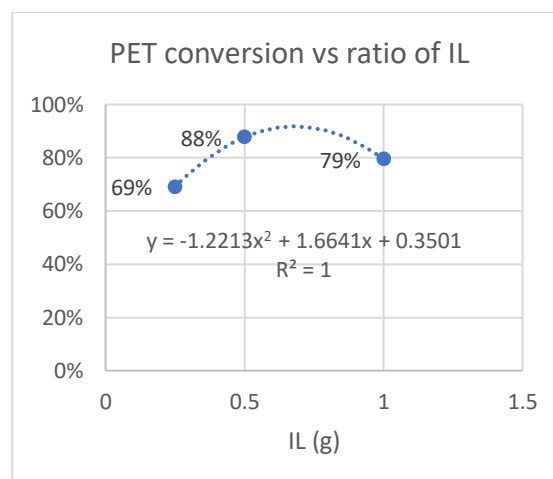


Figure 10. PET conversion at different catalyst weight ratios

As shown in Figure 10, the amount of catalyst versus the PET conversion creates a curve. In which 0.25 g (0.05:1:4) w/w ratio of the catalyst decreases the PET conversion and a big amount of catalyst (0.2:1:4) w/w ratio tends to also decrease the PET conversion. The optimal point in the curve is 0.68128g of catalyst to obtain the highest PET conversion,

which means the optimal weight ratio is 0.136:1:4 of (catalyst:PET:EG).

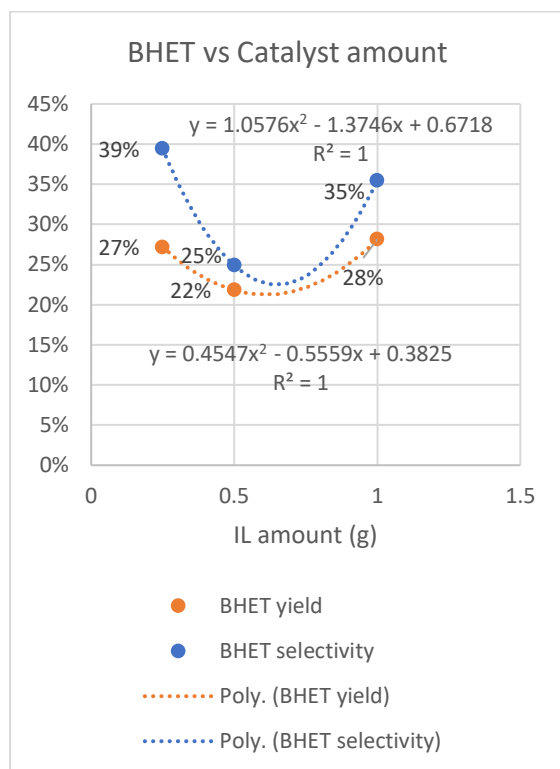


Figure 11. BHET yield and selectivity at different catalyst weight ratios

From Figure 11, the BHET yield and selectivity follow a curve contrary to the PET conversion. The experiment done using 0.5 g (0.1:1:4) w/w ratio of IL is the same ratio as the one used for the different temperatures. In both cases, the yield and selectivity of BHET achieved are much lower than what the tendency implies, especially compared to the amount of PET converted in that experiment.

The highest PET conversion obtained was 88% using 0.5 g (0.1:1:4) w/w ratio of IL at 200°C for 4 hours. For this experiment, the yield of BHET was 22% and the selectivity of BHET was 25%. The highest BHET selectivity was 39% using the lowest catalyst amount of

0.25g (0.05:1:4) w/w at 200°C for 4 hours with a PET conversion of 69% and BHET yield of 27%. And the highest BHET yield was 28% using the biggest catalyst amount 1g (0.2:1:4) w/w at 200°C for 4 hours with a PET conversion of 79% and BHET yield of 35%.

Biochar supporting $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ (BC/ $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$)

Zhang et al. (43) concluded that the interactions when IL was functionalized by biochar are hydrogen bonds.

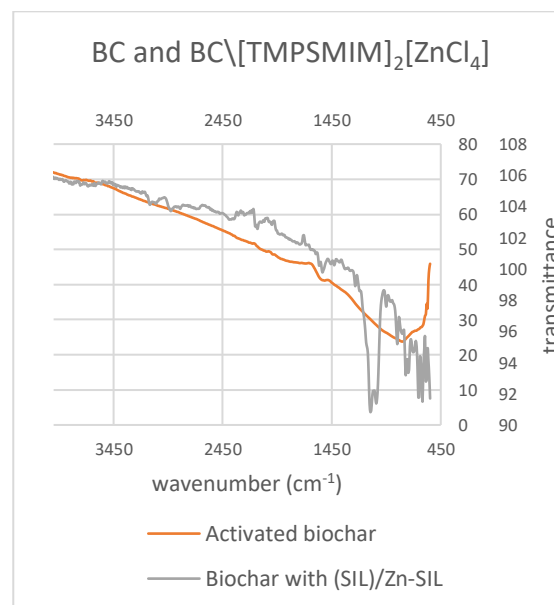


Figure 12. BC and BC/ $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

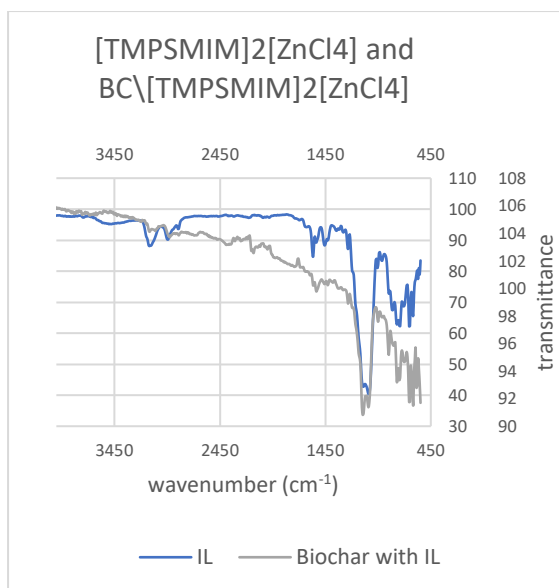


Figure 13. $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ and $\text{BC}[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

Figure 12 shows the activated biochar changes when it bonds to the IL ($\text{BC}[\text{TMPSMIM}]_2[\text{ZnCl}_4]$). The activated biochar on its own does not give a good resolution result on the FT-IR. For this reason, it is shown with another vertical axis so it can overlap with the other results. Even though the resolution is not good the FT-IR shows clearly when the ionic liquid was bonded to it. In Figure 13 the FT-IR from the IL and the FT-IR from the biochar bonded to the ionic liquid can be compared. All the peaks identified for the IL previously appear on the biochar supporting the IL. The biggest peaks 1041 cm^{-1} and 1095 cm^{-1} belong to Si-O and C-O bonds respectively, the N-H stretching can be seen on the 3116 cm^{-1} by the side of the double peak 2923 cm^{-1} and 2839 cm^{-1} from the C-H bond. The fingerprint zone has a similar aspect where the Si-O-C from the silicon shows up. And C=N and C=C stretches appear slightly on 1527 cm^{-1} and

1535 cm^{-1} respectively. This affirms that the biochar is supporting the ionic liquid and it was not washed out with the solvent (14,41).

Glycolysis of PET catalysed by $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

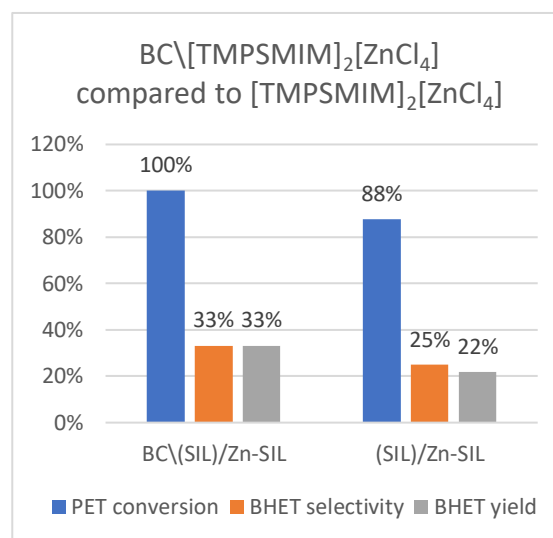


Figure 14. Glycolysis results $\text{BC}[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ compared to $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$

Figure 14 compares the results using the same reaction conditions of using $\text{BC}[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ as a catalyst instead of $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$. The ionic liquid bonded to the biochar obtained better results than the ionic liquids on its own. This can be tied to the catalytic ability that the BC added to the support given to the IL. Complete PET conversion was reached with 33% BHET selectivity and yield. FT-IR showed that there are no catalyst traces on the BHET product.

The catalyst was recovered in two parts. Half of the catalyst was recovered from the medium in the first filtration. A big clump of catalyst was attached to the magnet and did

not pass through the sieve before the second filtration. The second part of the catalyst was the solid product of the third filtration added which seems to be mixed with traces of oligomers from the reaction. A third filtration allowed for the catalyst retrieve with fewer oligomers and BHET mixed with it.

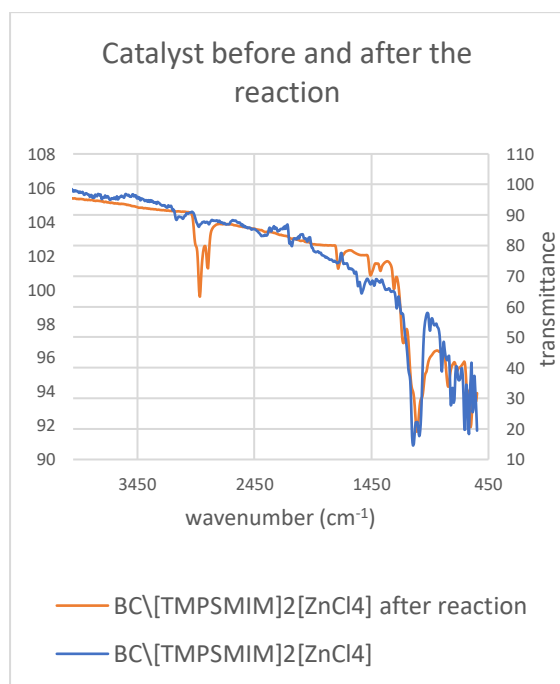


Figure 15. Catalyst before and after the reaction

Figure 15 shows the FT-IR done on the catalyst recovered on the second filtration after the reaction was done compared to the catalyst before. The catalyst $\text{BC}\text{[TMPSMIM]}_2\text{[ZnCl}_4\text{]}$ did not suffer any changes. All the important peaks identified are still present in Figure 12. The biochar was still attached to the ionic liquid when the reaction ended. On the FT-IR done on the catalyst after the reaction shows the double peak on 2916 cm^{-1} and 2846 cm^{-1} that appears more prominent than the FT-IR before the reaction belongs to the stretching of the alkyl C-H that

can be easily identified on the FT-IR done on the ionic liquid before adding the ZnCl_2 on Figure 3 (14,41).

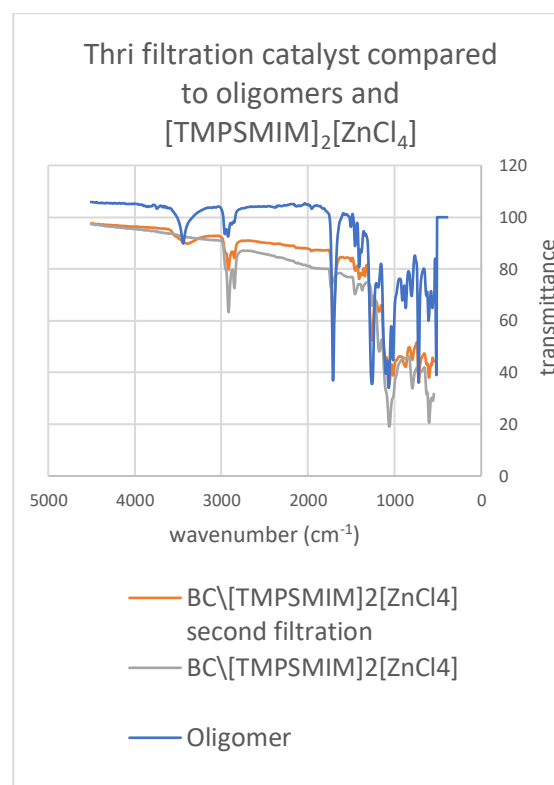


Figure 16. $\text{BC}\text{[TMPSMIM]}_2\text{[ZnCl}_4\text{]}$, $\text{[TMPSMIM]}_2\text{[ZnCl}_4\text{]}$ and oligomers

Figure 16 compared the FT-IR done on the catalyst retrieved from the third filtration with the catalyst before the reaction and FT-IR done on the oligomers from another experiment. The third filtrated solid consists of mostly the catalyst as it has the same prominent peak identified from the catalyst before. There is one small peak on 3425 cm^{-1} that belongs to the stretching of O-H from oligomers or BHET. This means that there are small traces of plastic that can be oligomers of BHET products with the catalyst (14,41).

The sum of both catalysts retrieved is the same as the initial catalyst used for the

reaction. There were no signs of catalyst dissolving on the FT-IR of the product of the reaction, this could mean that most of the solid filtrated consist of the catalyst and there are only small traces of oligomers left.

Conclusion

This research aimed to evaluate different conditions and conversion of PET glycolysis utilizing ionic liquids as a green solvent catalyst to find new alternatives to plastic recycling. Based on the quantitative analysis, the results obtained were satisfactory. The ionic liquid ($[\text{TMPSMIM}]_2[\text{ZnCl}_4]$) was effectively synthesised and worked as a great catalyst for the glycolysis of PET, high conversions of PET were achieved under optimal conditions. $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ can be bonded to biochar as a support for the glycolysis reaction. The product obtained during the depolymerization of PET utilizing the catalyst and ethylene glycol was pure BHET. The yield obtained is very low compared to recent literature and the PET conversions achieved for the same experiments, this is owing to the fact that the BHET could not be effectively retrieved from the solution used to extract it from the unconverted PET.

$[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ was successfully synthesised following the methodology taken from the literature and used as a catalyst for PET glycolysis for the first time to my knowledge. After the reaction is done the final product does not have any contaminants thanks to the green catalyst ionic liquid used.

Using $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ as a catalyst on its own, the highest PET conversion achieved was 88% using 0.1:1:4 molar weight (catalyst: PET pellets: EG) at 200°C for 4 hours.

Under this condition, the selectivity of BHET was 25% and the BHET yield was 22%. Under the same conditions with a greater catalyst amount of 0.2:1:4 the conversion of PET was lower at 79% but the yield of BHET was the highest at 28%. It is important to notice that the BHET result are unreliable because the complete extraction of the product was unsuccessful due to the fact that after it was crystalized the BHET would dilute on the mixture again while it was being filtrated.

The ionic liquid bonded satisfyingly to biochar previously activated. The functional groups that keep their interaction together are hydrogen bonds. This interaction allows a solution for the retrieval of the catalyst from the medium after the reaction is done. The catalyst made with the functionalised biochar showed better catalytic activity than the $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ on its own due to the catalytic activity that the BC added. Under the optimal conditions for the IL on its own, the catalyst BC\ $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ obtained a complete conversion of PET and 33% of BHET yield and selectivity. This experiment achieved the best results, and the retrieval of the catalyst after the reaction was finished could be easily done with two filtrations. FT-IR showed that BC\ $[\text{TMPSMIM}]_2[\text{ZnCl}_4]$ did not suffer any important changes in its structure after the reaction. It was not determined how many times this catalyst can be reused.

This project helped add more information on the research gap on the area

that pursues making the use of ionic liquids over mechanical recycling or producing plastic from raw materials more achievable. It avoids two of the problems encountered in previous studies, the final BHET product is not contaminated by the catalyst and the structure of the ionic liquid presents a viable option for its recovery.

The biggest limitation of this research was the time frame. Because of external reasons and the inability to acquire the chemicals for the experiment on time, even though the work done on the literature review and planning had started before, the start of the experimental part began very late. The time constraint did not allow to repeat the experiments if the result had abnormal outcomes or to make all the experiments necessary that would have allowed a broader view of the glycolysis for the different reaction conditions. Another important limitation was the lack of tests done on the sample. For example, NMR testing would have helped determine a better quantification of the structures present in the product. And especially further testing on the biochar supporting the IL would have been ideal. This could not be done because of the same limitation explain before about time limit. Lab materials were also limited, this especially affected the BHET yield reached, the BHET extraction is usually done on a rotatory evaporator in most literature, this helps to avoid the problem of the BHET dissolving while

it is being filtered. A rotatory evaporator was not available at the time when the experiments were taking place. Other limitation is that the laboratories do not have the capacity to realize microwave heating glycolysis of PET, this is the most effective method for heating glycolysis reaction found up to date. Therefore, the results that can be archived using traditional heating methods are not as good as the ones published in recent years.

Based on this conclusion future research could be beneficial on how the biochar affects the glycolysis of PET and what are the optimal conditions for the reaction in this case. In the research gap was expressed how glycolysis of PET catalysed by ionic liquids is not yet cost-effective at an industry level because mechanical recycling is cheaper. Further exploration should be done on how to translate the concept to a large-scale level implementation.

To conclude, the project achieved satisfactory results in the glycolysis of PET using a synthesized ionic liquid zinc-silica-based green solvent as a catalyst that can be bonded to biochar for its retrieval. Results for different reaction conditions of temperature, catalyst amount and time were analysed. Under optimal conditions PET conversion was achieved using $BC\{[TMPSMIM]_2[ZnCl_4]\}$ as a catalyst compared to 88% of PET conversion for $[TMPSMIM]_2[ZnCl_4]$. $BC\{[TMPSMIM]_2[ZnCl_4]\}$ is an effective and efficient catalyst for the glycolysis of PET.

Reflection and Review

I am proud to say that the learning objectives I set for myself for the realization of this project were gratifyingly achieved. I was able to apply the knowledge that I have accumulated through my university course in a non-class environment, not only producing an experimental chemical engineering project but conducting research, experiments, and analysis on my own study. All this work put on through this semester; not only on the lab report but on the decision making and carrying out experiments, helped me widen my chemical engineering knowledge.

The research conducted was an experimentation base chemical engineering project that is part of the chemical engineering course. The topic chosen was of my own interest, backed up by the supervision and guidance of experienced researchers. The lab work was based on research conducted from previous literature, analysis using chemical engineering knowledge and decision making.

I found the experience challenging and exhilarating. As it was my first project conducted of this magnitude, my first time using my second language English for my chemical engineering degree and my first time being able to make and prove my own theories and ideas. The guidance that I received from my project supervisor and a senior engineering PhD student helped me overcome the obstacles presented through the process.

I don't have any regrets, but I wish I could have had more time. Because of the tight time frame that I talked about on the limitations I was not able to repeat the experiments to achieve the best result possible as it took a week since the experiment started to get the results and there was also limited catalyst, to synthesise more catalyst the experiments would have to be put on hold as there was only one set-up for both. If I had more time, I would have repeated the experiments and tried different methods to get more BHET yield. I also wish I could have been able to make more experiments using the IL functionalized by biochar. I would have done more experiments to determine how many times the catalyst can be reused and how the results and the catalyst change with every use. And I would have done more experiments on different reaction conditions to determine the optimal properties of the IL-functionalized biochar catalyst. Another limitation that affected the results is the lack of tests done on the samples. FT-IR does not allow me to know the exact composition of the sample, and the drawback from this was that there was no certainty that there were no traces of BHET anywhere else.

I have learned how to conduct research to make decisions utilizing my engineering knowledge and the literature available. But this work has not only left me with new information related to my degree. I have also acquired and developed skills related to a working

environment. Being around peers that work hard seeking achievements in our field of study has inspired me and taught me different ways of working and approaches to obstacles.

For me this study not only represented a challenging project. It was done in a completely different environment that allowed me as an exchange student to learn a new culture, get used to fast changes, and experience how is the university life in a different country.

From all the skills that I have worked on and achieved in this process, the most used skill that is deep-rooted in me is problem solving. Thanks to this project I have established a familiar and effective method of identifying, searching for a fundamental cause, brainstorming, prioritizing, and making decisions while working.

I am very grateful for the opportunity that this course gave to execute my own chemical engineering project. I am highly interested in applying everything that I have learned in the making of this project to my future career path. I will not doubt to take any opportunity to participate in or carry out research in the future. To see my knowledge and ideas come to life in the laboratories has reminded me and made me fall in love again with the beauty of chemical engineering that I had once forgotten focusing on textbooks and exams during my undergraduate studies.

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