Upcycling Waste Plastics Using Microwave: Evaluation of Glycolytic Depolymerization Conditions using TBD and DBU Catalyst

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ABSTRACT

One of the most promising and sustainable chemical depolymerization methods often proposed for the complex environmental problem arising from waste poly(ethylene) terephthalate (PET) bottles is glycolysis. However key challenges such as longer reaction times, complex separation procedures for the depolymerized products, selectivity, thermally stable catalyst, and a full understanding of the depolymerization mechanism needs to be fully explored to facilitate wide scale industrial adoption. In this work, we investigated the glycolysis of waste PET under microwave conditions using 1,5,7-Triazabicyclo [4.4.0] dec5-ene (TBD) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) as catalyst by specifically evaluating the effect of the reaction parameters (temperature, catalyst concentration and time) on PET depolymerization and product yield. The reaction was conducted using Anton Paar Monowave 400 microwave reactor at catalyst concentrations (0.5-10 wt.%), PET to ethylene glycol ratio of 1:10, temperature range 180-220°C. and time (2mins-120mins). PET was completely depolymerized within 25mins. FTIR and NMR spectra of the product shows it to be BHET with a melting point 107.4-108.8°

INTRODUCTION

Globally, over 400 million tons of plastic materials are manufactured annually. Plastic waste constitutes one of the complex global environmental challenges due to its non-biodegradability in environmental components. Available estimates show that less than 10% of this waste is effectively recycled hence the call for new, sustainable, and effective ways to recycle plastics and to preserve their material value. [1,2].

Chemical depolymerization uses chemicals to breakdown PET into its constituent monomer. In glycolysis, we use glycols such as ethylene glycol (EG) to breakdown PET into Bis(2-hydroxyethyl) terephthalate (BHET) and some dimers, oligomers and some unreacted ethylene glycols as shown in Figure 1. This system is typically energy intensive requiring high temperature and longer reaction times

Microwave-assisted recycling have been reported to provide a more efficient route to depolymerizing waste PET [3-5]. Compared to conventional heating, microwave irradiation accelerates the chemical reactions, thus shortening the reaction times and temperatures, while achieving high chemo-selectivity and high yields [2]. Using ethylene glycol is a great choice on account of its excellent loss tangent that allows for easy microwave absorption. These methods also contribute to a circular economy, as the product obtained can be used to produce new food grade PET

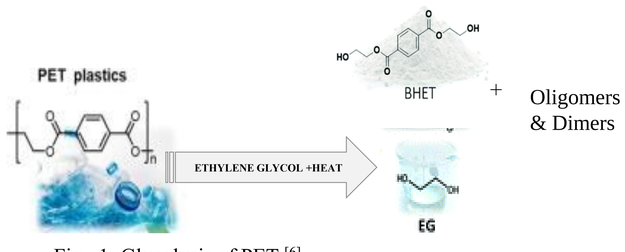

Fig.. 1: Glycolysis of PET [6]

MATERIALS AND METHODS

Materials

Discarded colorless PET bottles were collected from trash bin, the cap and label removed, washed with a mild soap under running water, dried in the oven at 80°C for 3hours and cut into flakes

Chemicals

All chemicals used were of analytical grade. They include: 99% extra pure Ethylene Glycol (EG) and the organo-catalyst 1,5,7-Triazabicyclo [4.4.0] dec5-ene (TBD), and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU)

Experimental procedure and characterization

0.5g of the PET flakes, 2.1mg TBD and 5ml EG were measured into a G10 glass vial, charged into Anton Paar Monowave 400 microwave reactor and run at different time and temperatures

Unreacted PET was filtered, washed with hot distilled water, dried and weighed

To the filtrate, 25ml cold distill water was added, kept in the refrigerator for 24hrs to crystalize out the product (BHET), filtered and recrystallized again to enhance product purity

The final recrystallized product was filtered, washed with cold water dried in a vacuum oven at 80 °C until constant weight and characterized using FTIR and NMR

RESULTS AND DISCUSSION

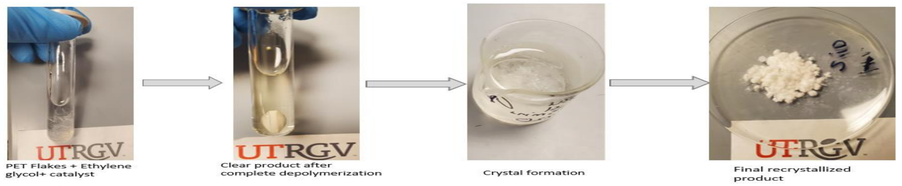

Fig.2

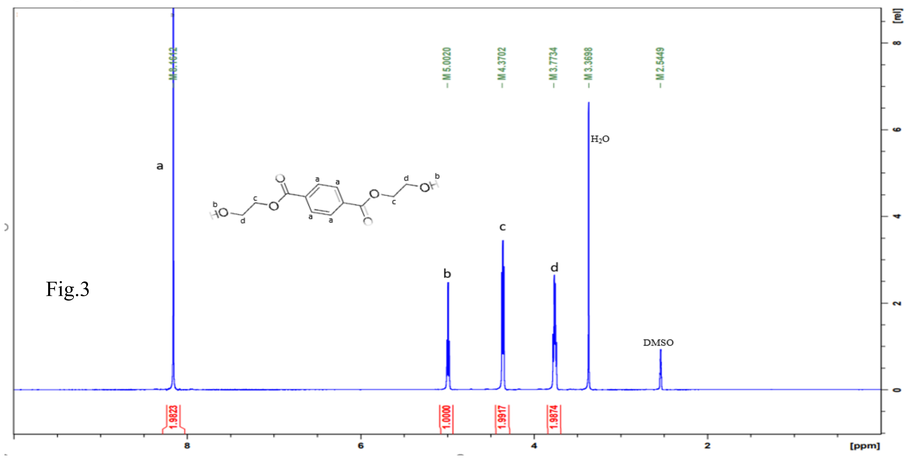

Fig.3

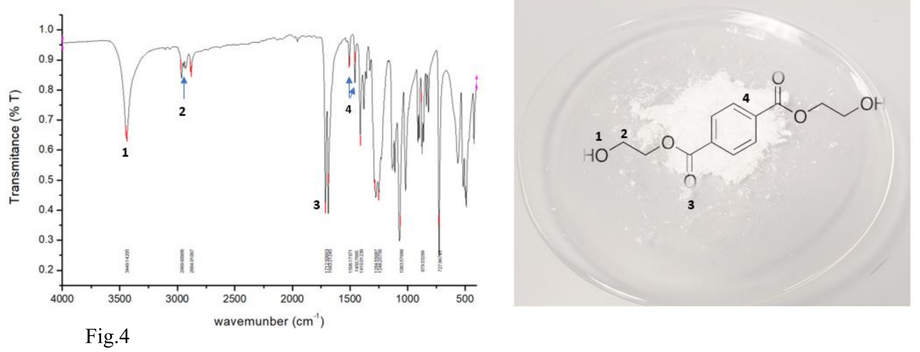

Fig.4

Effect of Catalyst concentration

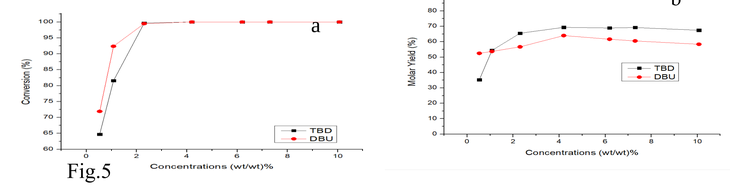

Fig.5

Effect of Reaction Temperature

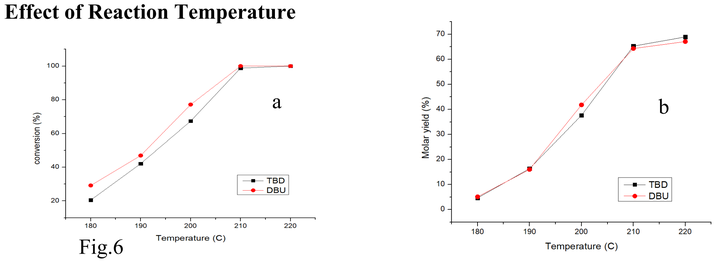

Fig.6

Effect of Reaction Time

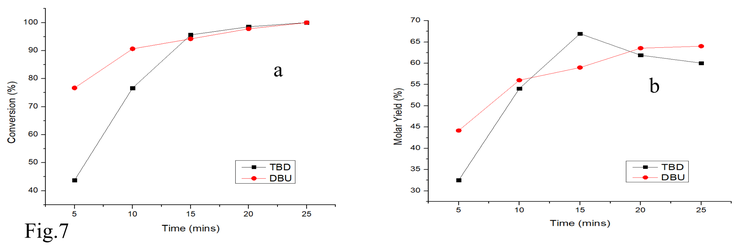

Fig.7

Figure 2 shows the reaction's product, while Fig. 2 and 3 shows its NMR and FTIR characterization confirming BHET. Complete PET depolymerization was achieve at a concentration of 4.33wt% (Fig.5a) for both catalysts under microwave conditions compare to 7-10wt% reported using conventional heating. The BHET yields also shows similar pattern as the concentration varies (Fig 5b). As the temperature varies DBU slightly outperform TBD in conversion (Fig.6a), while no significant difference was observed for molar yields as shown in Fig 6b. Furthermore, complete PET depolymerization was achieved within 25mins for both catalysts (Fig. 7a), however DBU does appear to initiates the depolymerization process quite earlier which probably resulted in the higher conversion seen within 10mins into the reaction at 220 °C which also correlated with the molar yield as shown in Fig. 7b

CONCLUSION

Complete PET depolymerization was observed at a time of 25minutes and a temperature of 220°C. FTIR and NMR spectra measured for the product shows similar transmittance bands representative of BHET

ACKNOWLEDGEMENT

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