A Scalable Process for the Depolymerisation of Polyethylene Terephthalate (PET)

Joseph Wood[1]*, Guido Grause[1], Joseph Sutton[1], Ali Al-Rida Hmayed[2], Andrew Dove[2]

[1]School of Chemical Engineering; [2]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

**Corresponding author: j.wood@bham.ac.uk*

Highlights

- A novel reaction-membrane-separation process is being developed for recycling PET.
- DBU-TSA catalyst depolymerized PET powder to 99% conversion within 180 min.
- The catalyst showed good membrane retention and potential for a continuous process.

1. Introduction

There is an urgent need to devise processes for recycling plastics, with an estimated total of 8300 million metric tonnes of plastics produced to date, of which less than 10% have been recycled overall [1]. Polyethylene Terephthalate (PET) was selected as the principal polymer for depolymerisation studies in this project, owing to it being widely used, with typical applications in clothing, bottles and packaging. The world demand for PET resin is ~23.5 million tonnes and production capacity ~30.3 million tonnes, whilst only 30 % (US) – 52 %(EU) is currently recycled. However, used PET bottles are priced £222.50/tonne whilst virgin PET resin is priced £1084/tonne, making a strong economic case for chemical recycling to produce the virgin polymer, rather than mechanical or thermal recycling to a lower grade product. Chemical recycling of PET is achieved here via a glycolysis process using specially developed ionic organocatalysts, building on methods developed by the Dove group [2]. However, industrialization of the process would require scale-up and consideration of issues such as reacting solid PET particles with liquid glycols, crystallization of the product bis(2-Hydroxyethyl) terephthalate (BHET) and separation of unreacted ethylene glycol and valuable catalyst from the reaction mixture. To overcome these difficulties, the authors are undertaking a project to develop and test a membrane reactor-separator, which will facilitate process scalability.

2. Methods

Catalyst preparation: A dual catalyst was developed based on 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) and toluene sulfonic acid (TSA). A DBU-TSA catalyst was prepared by adding 58 mmol of each component to 400 mL acetone in a Schlenk flask at 65-70°C under nitrogen, followed by heating, cooling and addition of 25 mL diethyl ether. Purification under vacuum yielded an off-white solid catalyst. Depolymerization tests: PET 300 µm powder (10g, 520 mmol, 1 equiv), n-methyl pyrrolidone (NMP)(0.5mL, 5.2 mmol, 0.1 equivalents) and Ethylene Glycol (EG) (65mL) were charged to a 300mL Parr reactor. The reactor was heated to the desired temperature of 160-190°C and the organocatalyst dissolved in ethylene glycol added to the reactor to initiate the reaction. 1 mL samples were periodically withdrawn and analysed via ^{1}H NMR to calculate PET conversion. BHET was recovered at the end of the reaction by addition of boiling water, filtration on a sintered glass filter to remove unreacted PET, oven drying at 60°C to determine gravimetric PET conversion. The filtrate was cooled to yield BHET crystals. Filtration tests: A Sterlitech HP4750X cell was used to test the separation performance of model mixtures of 7.5g BHET or 4.5 g DBU and 5.5 g TSA dissolved in 150g EG. Commercial TS40 (polypiperazineamide) and TS80 (polyamide-TFC) membranes with a molecular weight cut off (MWCO) of 150 Da were utilized under a temperature range of 100-150°C and applied nitrogen pressure range of 63-3000 kPa. The flux was recorded gravimetrically and permeate analysed for BHET and catalyst concentration via ^{1}H NMR.

3. Results and discussion

Fig 1a displays the conversion of PET determined by NMR for the temperatures 160-190°C, illustrating that at 190°C initial conversion of up to 40% occurs in just a few minutes, followed by a slowing of the reaction rate, eventually reaching up to 99% conversion at 180 min. The other temperatures exhibit similar but slower kinetic behavior, with final conversions of ~55%, 75% and 95% at temperatures of 160, 170 and 180°C respectively. It was shown that the kinetics of the reaction follow a shrinking core mechanism, with linearized kinetics fits shown in Fig 1b. Further analysis has suggested that the reaction rate may be influenced by polymer crystallinity and the slowed by the presence of water. The developed filtration rig is shown in Fig 1c. Potentially selecting membranes of appropriate cut-off could be used to retain catalyst, PET particle and/or BHET product within the reaction cell, whilst passing EG in the permeate to facilitate recycling. Tests with BHET showed a flux rate of up to 50g/h at a temperature of 125°C and pressure of 500 kPa although an insignificant reduction of the BHET concentration in the permeate, thus requiring alternative membranes. Ionic catalysts are retained in the solution by more than 80% (Fig. 1d) with the TS40 membrane. Caused by a strong polarization, pressures up to 3000 kPa are required to maintain a high flux. In order to reduce the required pressure, novel supported catalysts are being developed, which will have a higher molecular weight and facilitate easier separation via membranes, together with testing a wider range of membrane MWCOs.

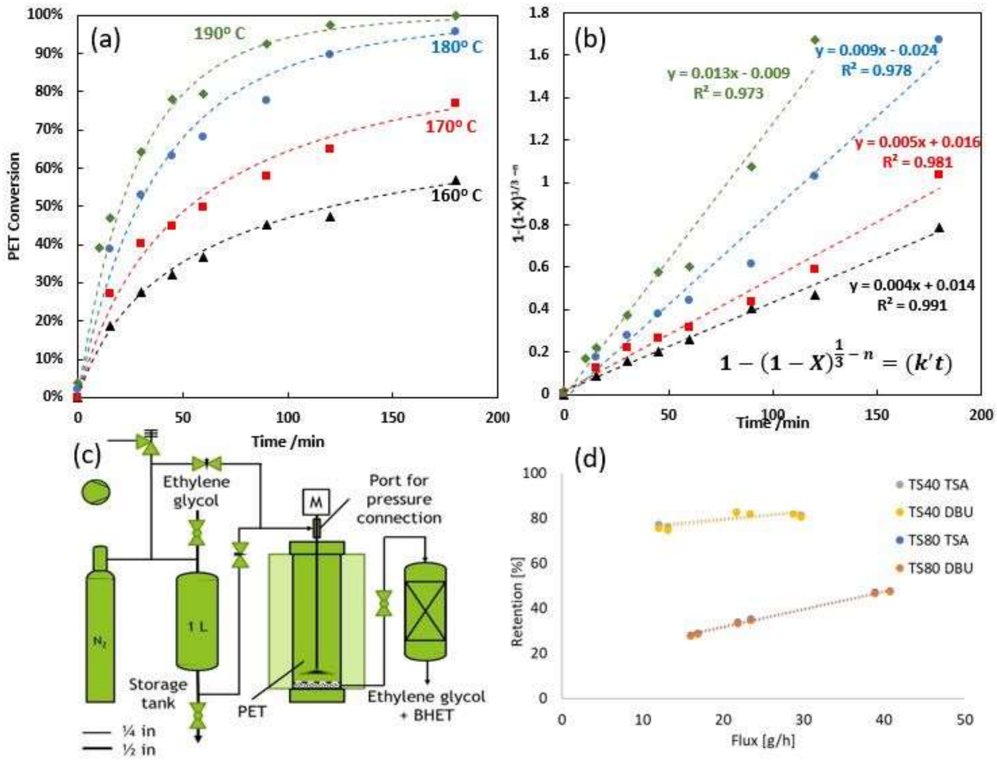

Figure 1. (a) PET conversion vs time for 300 μm powder with DBU-TSA catalyst (b) Plot of fit of kinetic data to shrinking core model, via the stated equation. *X* = PET Conversion, *n* = model exponent, *k'* = rate constant, *t* = time. (c) developed filtration rig based on Sterlitech HP4750 cell (d) retention of catalysts by membranes at 125 °C.

4. Conclusions

A dual DBU-TSA catalyst was shown to be effective for depolymerizing PET powder, at 190°C with conversion of up to 99% within 180 min. The reaction follows a shrinking core mechanism. A project concept to harvest the product mixture whilst retaining the catalyst and facilitate scalability was demonstrated. The selected membrane was effective for retaining the DBU-TSA catalyst and potentially a continuous scalable process could be developed based on membrane technology.

References

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Keywords
PET; depolymerization; dual catalyst; membrane separation