Depolimerization of PET bottle wastes to produce high-value BHET monomer using ethylenglycol

Moral A.[a], Irusta R. [a,b,], Martín J. Mª [a], Martínez L. [a]
[a]Environmental Division, CARTIF Foundation, Parque Tecnológico de Boecillo,
47151-Valladolid, Spain
[b]Department of Chemical Engineering and Environmental Technology, ETSII,
University of Valladolid, 47011-Valladolid, Spain
albmor@cartif.es, rubiru@cartif.es, jesmar@cartif.es, lidmar@cartif.es

The main topic of this paper is the recycling of plastic wastes, focused on the chemical recycling process of polyethylene terephthalate (PET) into bis-hydroxyethyl terephtalate monomer (BHET). Although the most commonly recycling process are in-plant and mechanical methods, the benefits and opportunities offered by chemical recycling make it as one of the most interesting process to develop. In addition, consume of bottle grade PET is reaching high levels, due to its increasing applications in many industrial sectors. PET chemical recycling includes the recovery of high-value raw materials, bottle-grade, feasible from a technical, economical and environmental point of view. Although chemical recycling offers several possibilities: (methanolysis, hydrolysis, ammonolysis, aminolysis, etc…) glycolysis was selected for the present study.

The glycolysis reaction was carried out into a 1L three necked flask with reflux, a thermocouple and a N_2 line, using ethylenglycol (EG) as solvent. The temperature was 197 ºC at the beginning of the reaction, increasing after 2,5 hours up to 201 ºC. Neither stirring nor external pressure were applied.

PET:EG ratio was studied to get an overview of the reaction behaviour and yield results taking into account the solvent excess influence. Ratios EG:PET (w:w) from 1,5:1 to 5:1 were assayed. The presence of Zinc Acetate was varied to optimise the response of the system, with $ZnAc_2$:PET ratios (w:w) from 0,1:100 to 1,5:100.

Depending on the operational conditions and the reactive ratios selected, yields nearby 85 % of BHET were obtained. The process has been up-scale to a pilot plant. In this case, stirring and external pressure have been also taken into account, increasing the number of parameters to control and optimise, which allows a more complete control of the process.

Monomer and oligomers were characterized using DSC, TGA, FTIR and GC-MS techniques.

1. Introduction

PET applications have grown in the last years due to its continuous approach to different sectors, as milk, wine, oil and juices packaging, paints, construction, etc. Typical applications for soft drink bottles, textile, pharmaceutical and fibres have been consolidated and are reaching higher levels each year. Due to these new applications and the global consumption, the increasing use of plastic by consumers and industry requires cost-effective and environmentally safe recycling in order to reduce the growing pressure on the environment.

PET recycling has been tackled from the chemical point of view, offering the possibility of recovery of high-value raw materials via glycolysis.

The technical viability of the process includes several control parameters. The kinetic of the reaction (Campanelli et al., 1994; Jong-Wu- Chen et al. 1999; Mishra et al. 2002a; Goje and Mishra, 2003; Mishra and Goje, 2003b), the influence of catalyst in the depolimerization process (Kao et al. 1997), etc.

Baliga and Wong (1989) studied PET depolimerization working at 8 h reaction time and extracting BHET monomer with boiling water. Cheng-Ho Chen et al. a (2001),b (2001), c (2003) discussed about the most decisive parameters in the process, in order of influence: amount of catalyst > glycolysis temperature > reaction time. Also Gouxi et al. (2005) took in consideration reaction time, EG/PET ratio and amount of catalyst (zinc acetate) , concluding that the best results were obtained with 5:1 EG/PET mass ratio, during 3 hours adding 1:100 catalyst:PET mass ratio.

The economic viability of the process was thought to be one of the main objectives to obtain, because of the final industrial application of this study. The glycolysis process was studied trying to achieve the best combination of the parameters involved in the process, taking special care of considering lower EG:PET ratios, measuring the economical and environmental advantages and considering monomer yields decreases.

EG recovery was other important factor to evaluate, that contributes to an economical and environmental improvement.

2. Experimental

2.1 Materials

EG was Panreac synthesis grade, and Zinc acetate was Scharlau reagent grade.

PET specifications can be seen in Table 1.

The intrinsic viscosity means about 125 repeating unit, with a molecular weight value about 24.000 g/mol.

2.2 Glycolysis

The depolimerization process of PET was carried out in a three necked flask, with a N_2 line, reflux set and a thermocouple.

Table 1. PET specifications

Properties	Typical value
Intrinsic viscosity (dl/g)	0,80 ± 0,02
Melting point (ºC)	245
Acetaldehyde content (mg/kg)	< 1,0
Water content (%)	< 0,4
Fines (mg/kg)	< 200

A heating mantle provided the system the necessary temperature for the reaction, with no external pressure or stirring. Once the system reached 190-195 ºC, the reaction mass started boiling.

After 2,5 hours reaction time, the glycolysed products were cooled to room temperature and mixed with boiling water during 45 min. After the extraction, the mixture was filtered under vacuum. This filtration process was carried out avoiding the mixture cooling. After several experiences, it was found that filtrating below extraction temperature lead to a decrease of BHET monomer in the filtrate, reducing reaction yields considerably. The solid obtain was washed with boiling water, dried until constant weight and labelled as Fraction A.

The filtrate was cooled in a refrigerator for 16 hours, obtaining white crystals of BHET, that were filtered and washed with cooled water under vacuum, dried until constant weight and labelled as fraction B.

The filtrate, a mixture of EG and water, was distilled under vacuum, recovering the EG excess from the glycolisis reaction, thinking about the possibility of its reuse in consecutive depolimerizations.

2.3 Analysis

The equipment used in Fourier Transform Infrared (FTIR) was a Shimadzu IR Prestige-21 (KBr), using the Diffuse Reflectance technique from 600 to 4000 cm-1.

IR(KBr): ν 3446 cm-1 (-OH terminal alcoholic group), 2962-2877 cm-1 (-CH2-alquilic chain in the ethylene ester group), 1712 cm-1 (C=O ester, carbonilic), 1274-1253 cm-1 (C-O ester asymmetric vibration), 1134-1072 cm-1 (C-O ester symmetric vibration), 725 cm-1 (C-H, position para in aromatic ring).

The Thermo Gravimetric Analysis (TGA) equipment used for this analysis was a Shimadzu DTA-TG – 60H, using air atmosphere, with a gas flow 50 mL/min in an aluminium pan, starting at 26ºC with a 10ºC/min, until 550ºC, holding this final temperature for 5 min. The thermograph can be seen in figure 1.

GC-MS was carried out in a GC Agilent 6890N, in a HP5-MS column, scan mode, with a MS Agilent 5793N. Chromatogram can be seen in figure 2. Ramp in the GC oven can be seen in table 2

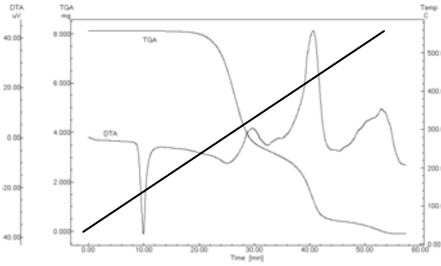

Figure 1. BHET monomer TGA analysis

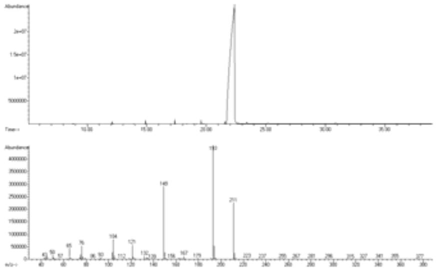

Figure2. BHET monomer GC-MS analysis

Table 2. GC oven ramp in BHET characterization

Rate (ºC/min)	Final temp (ºC)	Final time (min)
Initial temp 70ºC, Initial time 1 min		
10,00	110	1,00
10,00	290	15,00

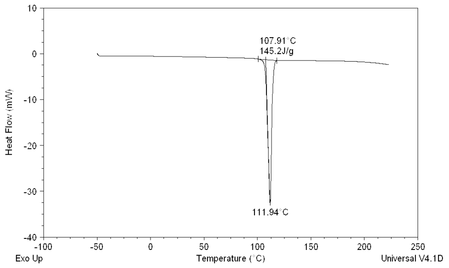

Figure 3. BHET monomer DSC

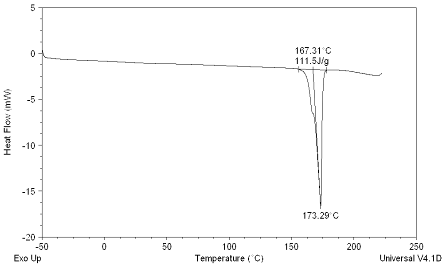

Figure 4. Oligomer DSC

Differential Scanning Calorimetry (DSC) equipment was TA-instruments Q100, equilibrating at –50ºC with 10 ºC/min ramp to 225ºC.

In the figures 3 and 4 it can be seen the melting points of each fraction.

3. Results and discussion

The first experience carried out was according to Gouxi et al (2004). EG/PET (w:w) ratio was 5:1, the weight ratio catalyst to PET was 1 % and 3 hours reaction time, obtaining yields of 84,47 % BHET monomer.

Even taking into account the high BHET yield obtained in this experience, economical viability at industrial scale and environmental consequences are not as positive as the yields obtained.

Due to these cost and environmental factors, the experiences turned into lower EG/PET ratios, decreasing reaction time and on the side of EG recovery possibilities.

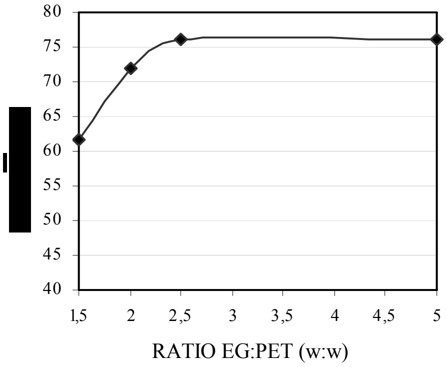

Figure 5. BHET yields varying PET:EG

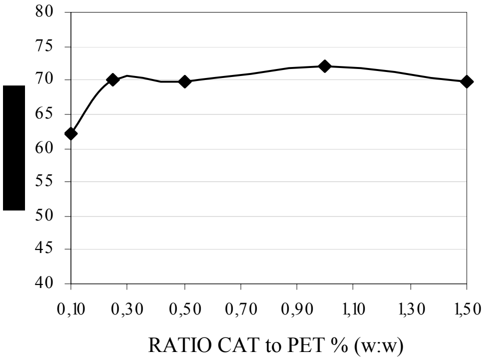

Figure 6. BHET yields varying CAT:PET

EG:PET (w:w) ratios run from 1,5:1 to 5:1, with a constant amount of catalyst Zinc acetate (weight ratio catalyst to PET) 1 %. BHET monomer yields obtained can be seen in figure 5.

In the second serial of trials, EG:PET ratio was constant 1:2, and the catalyst varied from 0,1% to 1,5 % ratio CAT to PET (w:w), (figure 6).

After the glycolysis reaction according to Gouxi et al. (2004) best experience, (EG/PET (w:w) ratio 5:1, ratio catalyst to PET (w:w) 1 %), EG excess was recovered via distillation under vacuum, retrieving the 82,5 % of the solvent involved in the experience. The recovered solvent was used in a new experience in the same conditions, 2,5 hours reaction time. BHET monomer yields decreased from 76,09 % using fresh EG to 65,71 % using recovered EG.

The process was upscale to a pilot plant in a 50 L stirring tank

In the figure 7 it can be seen the process implanted at pilot scale.

In the first experiment carried out at pilot scale, the improvement of the yield obtained was significant. The PET mass treated in the reactor was 8 kg.

In the experience, EG:PET ratio (w:w) was 1:2,5, with 0,25 catalyst per 100 PET (w:w).

The reaction time was 2,5 hours, working at 1,75 bar of pressure with stirring.

Two extraction were realized. In the first one 7,580 kg were obtained, and in the second one, carried out from the supposed oligomer, 1,180 kg were obtained.

The complete BHET obtained was 8,760 kg, which corresponded to 82,90% yield.

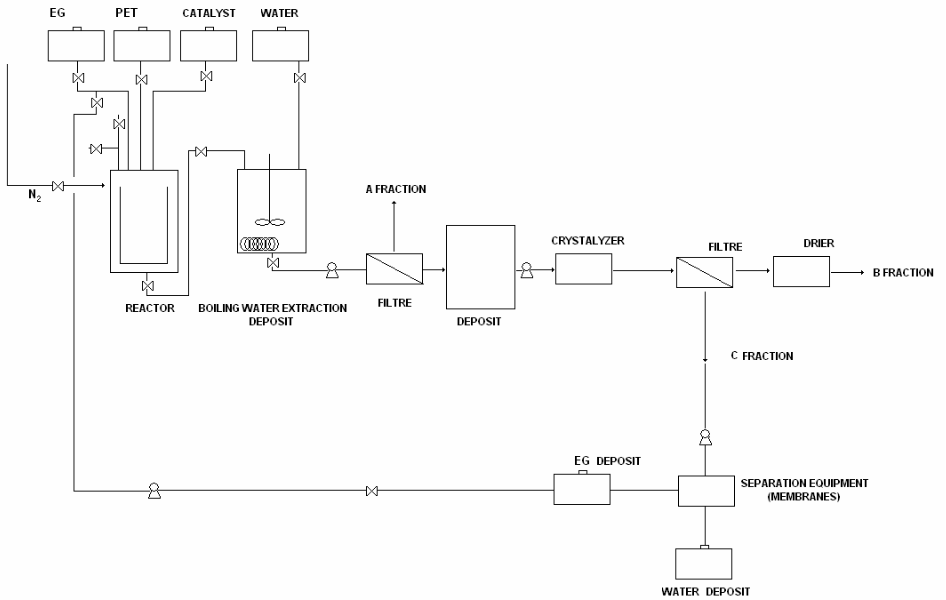

Figure 7. Pilot plant diagram

4. Conclusions

After the performance of several experiments in different conditions, the viability of PET waste recycling into its monomer BHET was studied, at laboratory and pilot scale. Yields obtained at laboratory scale, taking into account that no pressure or stirring was applied were improved at pilot scale.
From 76 % obtained at laboratory scale, BHET yield turned up to 82,90% at the pilot scale plant, where stirring and pressure were the key factors for this improvement.

The possibility to improve the extraction process and the use of EG recovered from previous glycolysis reactions via distillation, membranes or other separation method could take us to a better economical an environmental process.

5. References

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