



Glycolysis optimisation of different complex PET waste with recovery and reuse of ethylene glycol

A. Aguado^{1,2} · L. Becerra³ · L. Martínez³

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Abstract

The poly(ethylene terephthalate) is a thermoplastic polyester, non-degradable in the environment that due to the huge amount of waste generated and accumulated in landfills, chemical recycling through glycolysis is considered the most successful method for polymer recycling. In this work, glycolysis of virgin PET and different PET waste (highly coloured PET, multilayer PET and municipal sorting waste PET) is carried out using excess ethylene glycol in the presence of zinc acetate as catalyst. Glycolysis temperature, glycolysis time, amount of catalyst and amount of solvent are important factors affecting the glycolysis of PET waste. A Taguchi orthogonal array $L_9, 3^4$, is applied to study the main interactions between these factors to optimise the yield. The process results in a good yield (79–88%) to the monomer, bis(2-hydroxyethyl) terephthalate (BHET), with optimum conditions. One of the inconvenient of the glycolysis process is the excessive use of EG, so the recovery and reuse of the remaining EG from the process are studied in order to optimise the glycolysis of PET waste making it economical and environmentally friendly. BHET is characterised by FTIR and DSC techniques confirming that is a valid and pure monomer.

Keywords PET waste · Glycolysis · Chemical recycling · BHET · Ethylene glycol

Introduction

Plastic materials, especially polyethylene terephthalate (PET), provide economic benefits as they are widely spread in daily life, and its global production is increasing rapidly due to the simple synthesis, low-priced production, robustness and durability that are beneficial for the industry, so they are often a better option than other materials (Samak

et al. 2020). Subsequently, plastics have been massively utilised in different sectors and started to be absolutely necessary for modern society (Lebreton and Andrady 2019). Despite the unexpected challenging circumstances, in 2020, the European plastics industry rapidly adapted its capacities to continue delivering safe and sustainable solutions to society. In the world, the production of plastics has increased from 1.5 million of tonnes in 1950 to 367 million of tonnes in 2020. So, the world plastic production is increased rapidly and expected to reach over 34 billion metric tonnes in 2050 (Geyer et al. 2017). As a consequence of the COVID crisis, in 2020, the European plastics value-chain experienced a decrease in its production and demand levels. Nevertheless, in Europe, plastic production was 55 million of tonnes, which represents 15% of plastic world production, being the forth in the global plastics materials production (Plastics—the facts 2021). The package industry was the main sector responsible for plastic consumption where more than 29 million tonnes of plastic post-consumer waste were collected, of which 23.4% was still sent to landfill, 42% of plastic wastes were sent to energy recovery operations, and 34.6% was sent to recycling facilities (Plastics—the facts 2021).

Statement of novelty: This article has been developed within the line of valorisation and management of waste of the CARTIF Technology Centre. This work shows a great advance in terms of the economics of the process by confirming the unlimited recovery of the solvent used in the process and validating the glycolysis with real PET waste, maintaining yields and purity of the recovered products.

✉ A. Aguado
aliagu@cartif.es

¹ CARTIF Centro Tecnológico, Boecillo, 47151 Valladolid, Spain

² ITAP Institute, University of Valladolid, 47010 Valladolid, Spain

³ Valladolid, Spain

PET is a thermoplastic polyester, non-degradable in the environment with high resistance to chemical and physical agents, with well characterised properties (e.g. excellent tensile and impact strength, light weight, transparency, low permeability of gases and appropriate thermal stability) (Chanda 2021). Due to the PET incomparable advantages, it is applied in the production of many materials such as textile fibres, copolymers, resins, carpet yarn, PET bottles and packaging films (Singh et al. 2017). In 2020, 4.14 Mt of PET was produced in Europe and the global demand for PET packaging was expected to reach 27.13 million tonnes in 2025 (The future of PET packaging to 2025 2020). So, there are a substantial amount of PET waste generated that ends up in the landfills and oceans and needs hundreds of years for degradation has attracted global concern (Seo and Park 2020). Because of landfilling is a less favoured alternative, and currently, it is gradually phased out in Europe, it is necessary to do a suitable management of waste plastic. The main goals across Europe are to reduce the amount of plastic waste in circulation by enhancing material reuse, designing for recyclability and recycling with improved quality and economic gains (The new plastics economy: Catalysing Action 2018).

PET waste can be recycled through four main methods: primary recycling (re-extrusion), secondary recycling (mechanical), tertiary recycling (chemical) and quaternary recycling (energy recovery through incineration) (Meys et al. 2020; Al-Sabagh et al. 2016; Langer et al. 2020; Das et al. 2021). Primary Recycling is the recycling of clean, uncontaminated single-type waste industrial scrap. This method ensures simplicity and low cost. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as a second-grade material (Neale et al. 1983). In the mechanical recycling, PET waste is cleaned to remove contaminants and then, grinding. The material obtained is remelted and spun to produce rPET fibres or aggregate in concretes mixes (Shamsaei et al. 2017). Although the

mechanical recycling is still the dominant way to recycle PET waste because is the easiest way to recycle, its main disadvantage is the deterioration of product properties in every cycle due to normally suffers from quality loss caused by thermal and hydrolytic degradation (Ragaert et al. 2017; Grigore 2017).

Chemical recycling is the process with more expectations and leading to total depolymerisation of polymer to the monomers which can be repolymerised to regenerate the original polymer, or partial depolymerisation to oligomers and other chemical substances (Solis and Silveira 2020; George and Kurian 2014; Bartolome et al. 2012; Raheem et al. 2019). There are several processes for chemical depolymerisation of PET, such as glycolysis, methanolysis, ethanolysis, aminolysis and hydrolysis, summarised in Table 1. Glycolysis is one of the most promising way for industrial-level depolymerisation of PET due to its mild reaction conditions (Chen et al. 2001a; Sheel and Pant 2019; Payne and Jones 2021). The glycolysis reaction is the molecular degradation of PET polymer by transesterification between ester groups and a glycol in excess to obtain the monomer, bis(2-hydroxyethyl) terephthalate (BHET). PET degradation is carried out most frequently using ethylene glycol (EG) as solvent due to its high efficiency (Duque-Ingunza et al. 2014; Ghaemy and Mossaddegh 2005; Palhano Zanela et al. 2018; Pingale et al. 2010) although other solvents also are used such as diethylene glycol, propylene glycol and dipropylene glycol (Reséndiz and Monje 2012; Abdelaal et al. 2011). Studies on the kinetics of PET glycolysis have shown that glycolysis without a catalyst is very slow, and complete depolymerization of PET to BHET cannot be achieved. So, glycolysis is most frequently carried out with zinc acetate ($ZnAc_2$) as catalyst due to it considered the benchmark (Payne and Jones 2021; Duque-Ingunza et al. 2014; Palhano Zanela et al. 2018). Other metal salts and ionic liquids have been also investigated (Guo et al. 2018; Khoonkari et al. 2015; Imran et al. 2013; Wang et al. 2015).

Table 1 Different methods of chemical recycling of PET

Process	Reagent/solvent	Temperature/pressure	
Methanolysis (Mishra and Goje 2003; Genta et al. 2005, 2007)	Methanol	High > 200 °C/High > 2 MPa	Dimethyl terephthalate and ethylene glycol
Ethanolysis (Castro et al. 2006; Fernandes et al. 2020)	Ethanol	Supercritical conditions	Diethyl terephthalate
Aminolysis (Hoang and Dang 2013)	Amines	20–100 °C	Bis(2-hydroxy ethylene) terephthalamide (BHETA)
Hydrolysis (Kumar and Rao 2003; Ügdüler et al. 2020; Čolnik et al. 2021; Goto et al. 2006; Goto 2009)	NaOH or KOH, H ₂ SO ₄ Sub- and supercritical fluids	Alkaline, acidic and neutral conditions	Terephthalic acid
Glycolysis (Chen et al. 2001a; Sheel and Pant 2019; Payne and Jones 2021)	EG	Aprox. 197 °C, Patm	Bis hydroxyethyl terephthalate (BHET)

Finally, incineration, aiming at the recovery of energy, is currently the most effective way to reduce the volume of organic materials. This method has been widely accused of being ecologically unacceptable owing to the health risk from air born toxic substances such as dioxins (in the case of chlorine containing polymers) and antimony and phthalate esters (Mihucz and Zaray 2016). In the lack of other PET recycling possibilities, incineration energy recuperation is preferring to landfilling but incineration can never give zero emission, hence the necessity to consider other options.

So, due to the chemical recycling of post-consumer PET has been considered the most successful method for polymer recycling according to the previous literature, it has been the chosen for this work to study the viability and efficiency of the different PET waste.

Materials and methods

Materials

Virgin PET used has been supplied by NOVAPET, and samples of different PET waste [highly coloured, complex multi-layer and municipal solid waste (MSW)] have been provided by ECOEMBES, the Spanish integrated management system for the light packaging waste. The size of PET waste was less than 5 mm, and the size of virgin PET was between 3 and 5 mm approximately.

The composition of the different types of post-consumed PET used is shown in Table 2.

Zinc acetate (min 97%) has been purchased from SCHAR-LAB; ethylene glycol has been supplied by PANREAC and commercial BHET (99.8%) by SIGMA ALDRICH.

Methods

Glycolysis process

Glycolysis experiments are carried out in a 2L stainless steel batch reactor with an electrical resistance to heat and control the temperature and a stirrer to assure the correct mixing of the components with an agitation rate constant of 900 rpm. An initial purge of nitrogen is used to prevent possible oxidation of the reaction products. The system can operate at a

pressure up to 6 bars. In each experimental run, about 200 g of PET are depolymerised, EG is used as solvent and ZnAc₂ as catalyst which have been reported previously as the most active and suitable solvent and catalyst. The starting time for the reaction is taken when the temperature is the desired one. Temperature and stirring are maintained constant during the whole reaction. Once the reaction is finished, an extraction with hot water is carried out to recover the BHET. So, boiling water is added in excess inside the reactor under vigorous stirring in order to dissolve the BHET monomer. Afterwards, the mixture is quickly filtrated, using 0.45 micras Millipore filter paper, to separate unreacted PET and solid oligomers above the filter, and a liquid phase composed of BHET and EG–H₂O below the filter. This recovered liquid is refrigerated to achieve the crystallization of the BHET. BHET monomer crystals formed, are filtered again to separate from EG and then, dried at 65 °C until constant weight. The yield of monomer, is calculated in Eq. (1), where $W_{\text{BHET},t}$ and $W_{\text{PET},0}$ refer to the weight of BHET at a certain reaction time and the initial weight of PET, respectively. MW_{BHET} and MW_{PETu} are the molecular weights of BHET (254 g·mol⁻¹) and PET repeating unit (192 g·mol⁻¹), respectively:

$$\text{Yield of BHET(\%)} = \frac{W_{\text{BHET},t}/MW_{\text{BHET}}}{W_{\text{PET},0}/MW_{\text{PET}}} \times 100 \quad (1)$$

Besides assessing the feasibility of glycolysis, the economics of the process is considered. As the solvent used in the reaction is higher than the stoichiometric needed, EG recovery from the EG–H₂O solution is needed. For this, a distillation performed at atmospheric pressure has been carried out to recover the remaining EG using a vacuum rotary evaporator (Buchi) at 75 °C and during 30 min and thus, reuse it in the following glycolysis runs.

Glycolysis optimisation by Taguchi's methodology

When an experiment has several factors that are relevant, the factorial Design of Experiments (DoE) are the best option to identify interactions between variables. So, the glycolysis of PET has been carried out using the Taguchi's parameter design methodology (Park et al. 2020). The main goal of this study is to find the best conditions for the process to obtain the higher yield of BHET with optimum purity. These control factors (glycolysis temperature, reaction time, mass ratio solvent to PET and percentage ratio catalysts to PET) and their levels are chosen based on its effectiveness in previous studies (Chen et al. 2001a; Abdelaal et al. 2011; Khoonkari et al. 2015; Aguado et al. 2014; Goje and Mishra 2003; Awaja and Pavel 2005; Carta et al. 2003; Chen 2003). These factors and levels used are appears in Table 3. The configuration of the orthogonal array L₉ combining the different selected levels of each control factor is showed in Table 4.

Table 2 Content of polymers in the different types of PET waste

Type of PET waste	Content			
	% PET	% PE	% PA	% PP
Highly coloured PET	90	10	–	–
Complex multilayer PET	82–96	5–10	1–5	–
MSW PET	92	6.2	0.05	1.75

Table 3 Factors and levels used in the factorial design experiments

Factors	Level 1	Level 2	Level 3
Temperature [°C]	195	208	220
Time [min]	150	180	210
EG/PET [w/w]	2	4	6
ZnAc ₂ /PET [%w/w]	0.2	0.6	1.0

Table 4 Experimental conditions for the glycolysis reaction with different PET waste

Run	Temperature [°C]	Time [min]	Solvent [w/w]	Catalyst [%w/w]
#1	195	150	2	0.2
#2	195	180	4	0.6
#3	195	210	6	1
#4	208	150	4	1
#5	208	180	6	0.2
#6	208	210	2	0.6
#7	220	150	6	0.6
#8	220	180	2	1
#9	220	210	4	0.2

By using orthogonal arrays, the number of experimental parameters can be reduced significantly. Each experiment is repeated three times in order to observe the reproducibility of the glycolysis process. The analysis of variance of the results is performed using Minitab Software to obtain the contribution of the factors and their interactions over the response variable (BHET yield) and to determine the levels that maximise the BHET production.

Analysis of products

A Differential Scanning Calorimetry, DSC, (TA Instruments DSC Q100 Model) is used for thermal analysis to determine the BHET purity. A Fourier-Transform Infrared Spectrometer, FTIR, (Varian 670-IR with ATR Pike accessory) is used to identify the chemical structure of BHET. Commercial BHET is used to compare with the recovered products.

Results

Optimisation glycolysis process

The glycolysis results obtained with each type of PET waste are submitted to a Taguchi methodology to determine the levels that maximise the BHET production. In a Taguchi design, the mean is the average response for each combination of control factor levels. So, the means provide an

estimate of BHET yield at each factor level to know how the four control factors affect the yield of BHET. Delta is the difference between the highest and lowest average response values for each factor. Table 5 shows the response for the means, where the ranks are based on Delta values: Rank 1 to the highest Delta value, Rank 2 to the second highest, and so on, to indicate the relative effect of each factor on the response. Figure 1 illustrates the influence of the conditions on the yield of BHET.

According to the results obtained by Taguchi (Table 5 and Fig. 1), it is observed that the EG to PET mass ratio (EG/PET) is the most significant factor in all studied PET waste, with a great difference with respect to the others in the Delta value. The next most influential factor is time (in all cases except MSW PET), followed by the ZnAc₂ to PET mass percentage ratio (ZnAc₂/PET). Finally, the least influential factor is temperature, although these last three factors have a very similar and low influence (similar values of Delta) on BHET yield (Park et al. 2020; Chen et al. 2001b). Therefore, through these results, it can be confirmed that the behaviour of the factors studied is the same with all types of PET waste, as well as virgin PET, according to other authors (Duque-Ingunza et al. 2014; Chen 2003).

Table 5 Means table response for the glycolysis PET waste

Level	T [°C]	t [min]	EG [w/w]	ZnAc ₂ [%w/w]
<i>Virgin PET</i>				
1	76.59	78.79	67.62	77.11
2	77.19	76.27	76.54	76.04
3	77.02	75.74	86.64	77.65
Delta	0.60	3.05	19.02	1.61
Rank	4	2	1	3
<i>Multilayer PET</i>				
1	66.83	68.15	57.21	66.61
2	66.76	65.35	65.10	65.07
3	65.34	65.42	76.62	67.25
Delta	1.49	2.8	19.41	2.17
Rank	4	2	1	3
<i>Highly coloured PET</i>				
1	74.26	76.00	64.43	74.35
2	74.29	73.28	73.77	72.84
3	74.04	73.31	84.40	75.41
Delta	0.25	2.72	19.97	2.57
Rank	4	2	1	3
<i>MSW PET</i>				
1	73.92	74.79	64.36	72.96
2	73.26	72.64	72.69	72.30
3	72.82	72.56	82.94	74.74
Delta	1.10	2.23	18.58	2.44
Rank	4	3	1	2

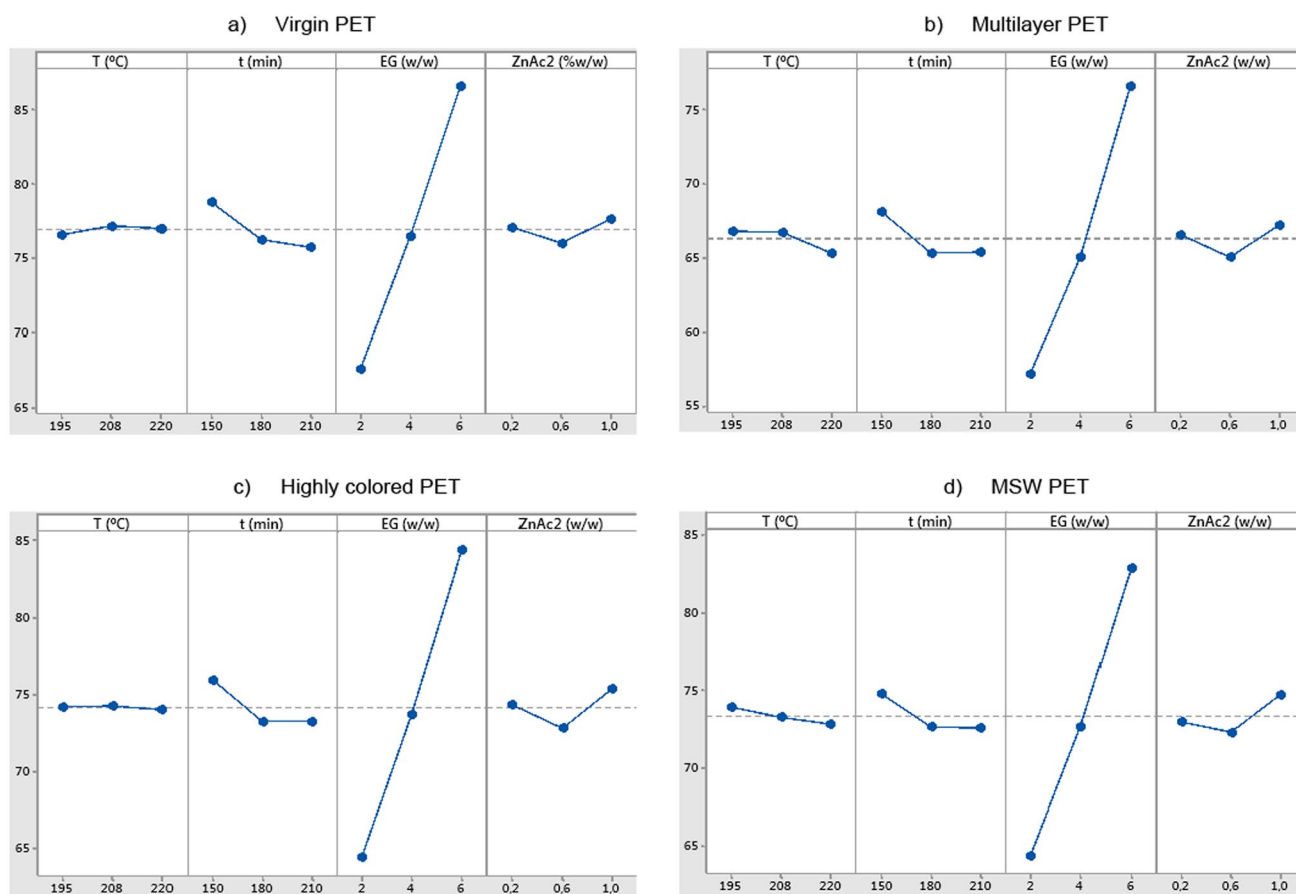


Fig. 1 Influence of the conditions on the yield of BHET

Focussing on the EG to polymer mass ratio, the best level to achieve the highest BHET yield is the one with the highest amount of solvent used (6 w/w) due to the yield of the reaction increase with the amount of EG as show the Taguchi results in Fig. 1. As expected and according to literature, the use of an excess of EG is the most important parameter due to the polycondensation step is reversible and in the presence of excess of EG, glycolysis of PET occurs to promote the reverse reaction to give BHET (Payne and Jones 2021; Ghaemy and Mossaddegh 2005; Park et al. 2020; Carta et al. 2003; Shukla and Harad 2005; Xi et al. 2005).

About other factor studied, Fig. 1 illustrates that an increase in time reaction decrease BHET yield. According to the literature, as reaction time continues increasing, BHET starts to dimerise and polymerise into oligomers (Imran et al. 2013). A similar observation was made by other authors, who found that after a long time of reaction, equilibrium is attained in the obtaining of BHET (Pingale et al. 2010; Goje and Mishra 2003; Baliga and Wong 1989). So, this is the reason why in this work, the highest yield is obtained with the lowest time, due to with a suitable temperature and catalyst; 150 min time is enough time

to obtain the maximum yield. On the other hand, if lower times had been used, an increase in BHET yield would have been observed with the increase in time (Carta et al. 2003).

The effect of using catalyst in the reaction is touchable which decreases the reaction time required (Khoonkari et al. 2015). Sometimes, with further increase in the amount of a catalyst, the yield of BHET decreased (Shukla and Harad 2005), but in other case increase (Goje and Mishra 2003; Xi et al. 2005). This is because this factor is very related and depends on the temperature and reaction time used. For example, ZnAc₂ has the best efficiency when the temperature range is between 180 °C and 195 °C (Khoonkari et al. 2015; Imran et al. 2013). In this work, ZnAc₂ has the best efficiency using the highest mass percentage ratio to PET (1%w/w) as it is shown in Fig. 1 and which is according to the literature (Ghaemy and Mossaddegh 2005; Xi et al. 2005). However, decreasing the mass percentage ratio of ZnAc₂/PET to the lowest (0.2%w/w) only decreases the yield by 0.6% show a little influence of this factor on the glycolysis. So, due to economic and environmental reasons, it is not worth using the maximum level of catalyst.

Finally, temperature is the least influential factor on yield of BHET, having practically no influence compared to the others factors (Bartolome et al. 2012; Khoonkari et al. 2015). Temperatures under 190 °C produce an excess of sub-products and decrease the yield of BHET (Aguado et al. 2014; Wang et al. 2009), and higher temperatures over 208 °C do not increase the yield of BHET (Lebreton and Andrady 2019; Khoonkari et al. 2015; Goje and Mishra 2003). This is in accordance with most of the reported works on glycolysis of PET which have been carried out at relatively low temperatures in the range of 190–200 °C due to the yield of BHET at softening point temperatures is almost constant (Park et al. 2020). So, the best level chosen as optimum for this factor is the lowest (195 °C) which agrees with literature (Mihucz and Zaray 2016).

According to Taguchi's methodology, if the best levels of control factors are used (195 °C, 150 min, 6 w/w EG/PET and 0.2%w/w ZnAc₂/PET), a maximum BHET yield will be obtained whose value would be between 79 and 88% depending the type of PET used. As expected, virgin PET gives the highest BHET yield (88.33%), followed by highly

coloured PET (86.41%), MSW PET (84.61%) and multilayer PET (79.28%). In order to demonstrate the theoretical results of Taguchi's study, a confirmatory experiment is carried out with the optimum conditions to verify the BHET yield expected. In this last confirmatory experiment, the results are close to the theoretical, with yields between 77 and 87%. These results have only a difference of 2% compared to theoretical as it is shown in Fig. 2. More in detail, virgin PET also gives the highest BHET yield (86.82%), followed by highly coloured PET decreasing yield by only 2.6% (84.52%), MSW PET decreasing by 4.8% (82.65%) and the last is multilayer PET with more difference, decreasing by 11.4% compared to the virgin PET (76.93%), due to has more impurities in its composition. The yield of BHET obtained is similar or even higher considering the literature with similar conditions (Duque-Ingunza et al. 2014; Ghaemy and Mossaddegh 2005; Palhano Zanela et al. 2018; Arnaiz et al. 2009; Shukla and Harad 2005; Xi et al. 2005; López-Fonseca et al. 2010, 2011; Shukla and Kulkarni 2002; Ghaemy and Behzadi 2002; Viana et al. 2011; Stoski et al. 2016), and a summary is shown in Table 6. It has been

Fig. 2 BHET yield with optimal conditions (195 °C, 150 min, 6 w/w EG/PET and 0.2%w/w ZnAc₂/PET)

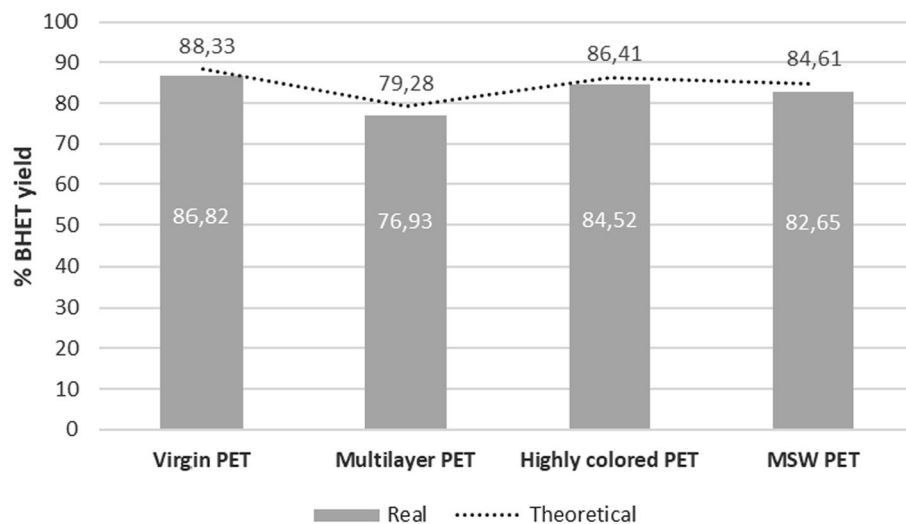


Table 6 Comparison of BHET yield considering the literature

References	Yield BHET (%)	Temperature (°C)	Catalyst
Duque-Ingunza et al. (2014)	63–80	196	Sodium carbonate
Ghaemy and Mossaddegh (2005)	75	198	Metal acetate
Palhano Zanela et al. (2018)	75	190	ZnAc ₂
Arnaiz (Arnaiz et al. 2009)	80	196	ZnAc ₂
Shukla and Harad (2005)	60		Sodium sulphate
Xi et al. (2005)	86	196	ZnAc ₂
López-Fonseca et al. (2010)	70	196	ZnAc ₂
Shukla and Kulkarni (2002)	67	190	ZnAc ₂
Ghaemy and Behzadi (2002)	92	198	ZnAc ₂
López-Fonseca et al. (2011)	80	196	Sodium carbonate

demonstrating that PET nature, colour and multilayer material has low influence on BHET yield, being the results of complex PET waste similar to virgin PET (Duque-Ingunza et al. 2014; Arnaiz et al. 2009).

Recovery and reuse of EG

One of the inconvenient of the glycolysis process is the excessive use of EG to obtain high yield of BHET. According to the study carried out in this work and the results obtained by Taguchi with the virgin PET, with an EG/PET mass ratio of 6 w/w, the BHET yield obtained is 88.33%. When the EG/PET mass ratio decreases to 4 w/w, the BHET yield also reduces by 11.4% (78.23%), reaching a reduction of 21.5% (69.31%) in case of 2 w/w. This excessive use of EG has its drawback in the economy of the process. Increasing the EG/PET mass ratio from 4 to 6 means that the cost of producing 1 kg of BHET increases by 28% (Aguado et al. 2014). Therefore, it is necessary to recover the remaining EG of the process and reuse it for consecutive reactions, in order to optimise the glycolysis of PET making it economical and more environmentally.

The filtrate obtained from BHET crystallization contains mainly unreacted EG, water and catalyst but at very low levels. A distillation of this solution is carried out recovering

the EG which vary from 70 to 85% of the initial amount. So, for comparison purposes, the EG used for each new glycolysis cycle is 70% of recovered EG and 30% of fresh EG. The aim is to determine the number of cycles conduct with this mixture of recovered and fresh EG and evaluate the evolution of the BHET yield and purity. These global cycles are repeated 10 times. Figure 3 illustrates the evolution of the BHET yield using recovered EG, along the 10 consecutive glycolysis reactions for the different PET wastes evaluated. It is found that yield is maintaining constant at around 71–81% depending the type of PET waste. In general, BHET yield decreased up to 6.6–7.4% from the glycolysis carried out with fresh EG to the glycolysis carried out with 10 times recovered EG and with the same behaviour all types of PET waste studied. Although this observation could lead to assume that recovered EG is as reactive as fresh EG, it has to be pointed out that these results may be affected by increased catalyst concentration during the consecutive reactions (López-Fonseca et al. 2010).

Analysis of products

In order to check the purity of the BHET recovered after different PET waste glycolysis, this was analysed by means of a number of analytical techniques, and the results were

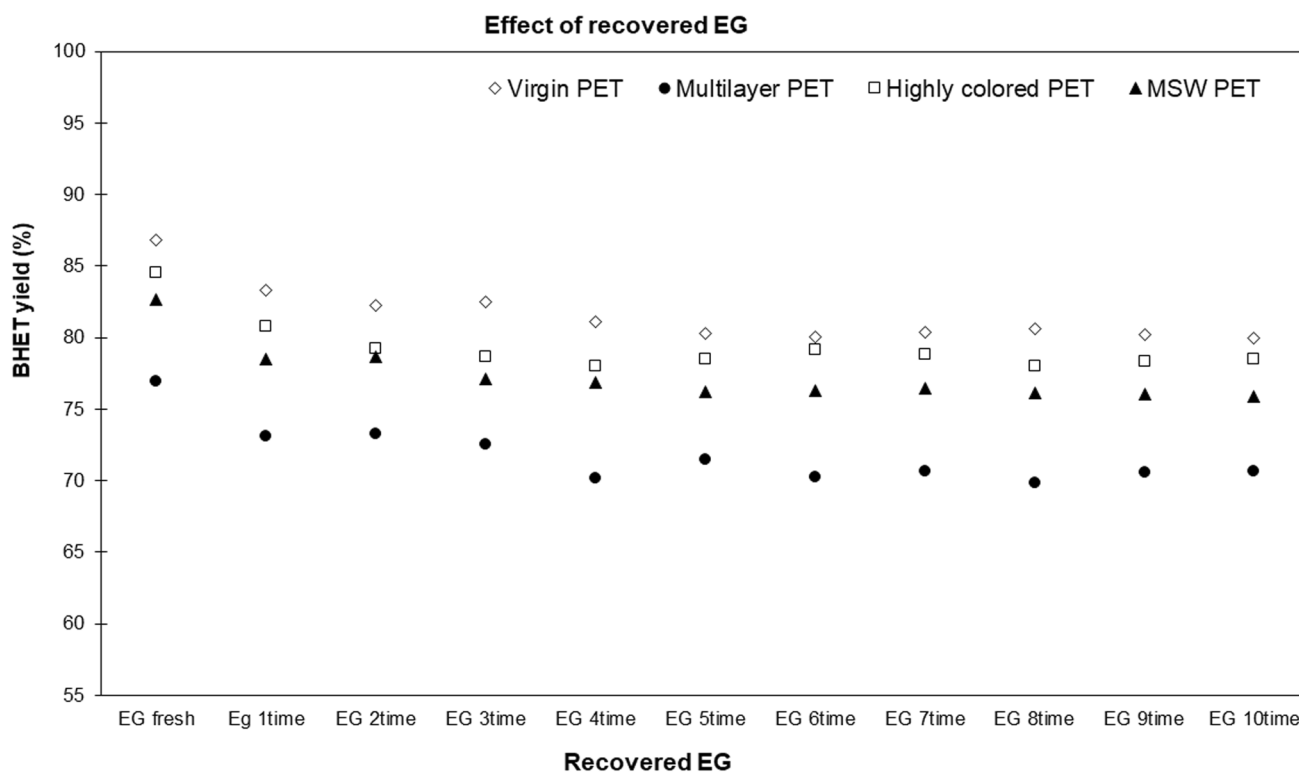


Fig. 3 BHET yield obtained with 70% recovered EG and 30% fresh EG and optimal conditions (195 °C, 150 min, 6 w/w EG/PET and 0.2%w/w ZnAc₂/PET)

compared with those corresponding to a commercial BHET sample.

Figure 4 shows characteristic signals of BHET molecule through FTIR spectrum. Bands at 2867 and 2960 cm^{-1} correspond to the stretching vibrations, asymmetric and symmetric, of the methyl and methylene groups (aliphatic CH_2 group) which indicate a depolymerization reaction. Bands at 3434 and 3281 cm^{-1} confirm the presence of O–H bond vibrations at chain terminations. The peak at 1132 cm^{-1} confirms the presence of hydroxyl groups related to C–OH alcohol bonds, whilst the peaks between 1282 and 1020 cm^{-1} are originated from the stretching vibrations of the C–O ester bonds. A transmission band at 1721 cm^{-1} confirms the presence of ester carbonyl group (C=O). Bands at 1509–1404 and 720 cm^{-1} correspond to the C=C bonds of the aromatic rings. All these results are according to the literature (Duque-Ingunza et al. 2014; Palhano Zanela et al. 2018; Park et al. 2020; Stoski et al. 2016; Ovalle-Sánchez et al. 2017). From all these observations, it can be confirmed that the glycolysis products correspond with BHET, regardless of the type of PET waste and the use of recovered EG.

Figure 5 shows the DSC thermal analysis of the different BHET obtained from the glycolysis recorded by heating sample 250 °C at 10 °C·min⁻¹. All the samples show only one sharp endothermic peak at 110 °C which agrees with the known melting point of commercial BHET (at 112 °C)

(Duque-Ingunza et al. 2014; Ghaemy and Mossaddegh 2005; Imran et al. 2013; Wang et al. 2015; Park et al. 2020; Ovalle-Sánchez et al. 2017; Kratofil Krehula et al. 2009). Besides, it can be confirmed that the product is BHET with a high purity due to does not appear any other peak. For example, according to the literature, BHET dimers, trimers and oligomers appear at 151 °C, 170 °C and 210 °C, and a peak in the region of 250 °C is attributed to the melting of the remaining solid PET (Imran et al. 2013; Wang et al. 2015; Viana et al. 2011). So, DSC chromatogram also demonstrates high level of purity of the monomers produced by glycolysis process of different PET waste and by the addition of recovered EG to the process.

Conclusions

In this work, a set of glycolysis process of virgin PET and different complex PET waste (highly coloured PET, multilayer PET and sorting municipal waste PET) with EG as diol and ZnAc_2 as catalyst has been studied to optimise the process. The effect of various operation parameters has been investigated through Taguchi methodology in order to optimise glycolysis and efficiently recover its purified monomer, BHET. The sequence of the main effects with higher influence on the glycolysis to increase yield of monomer,

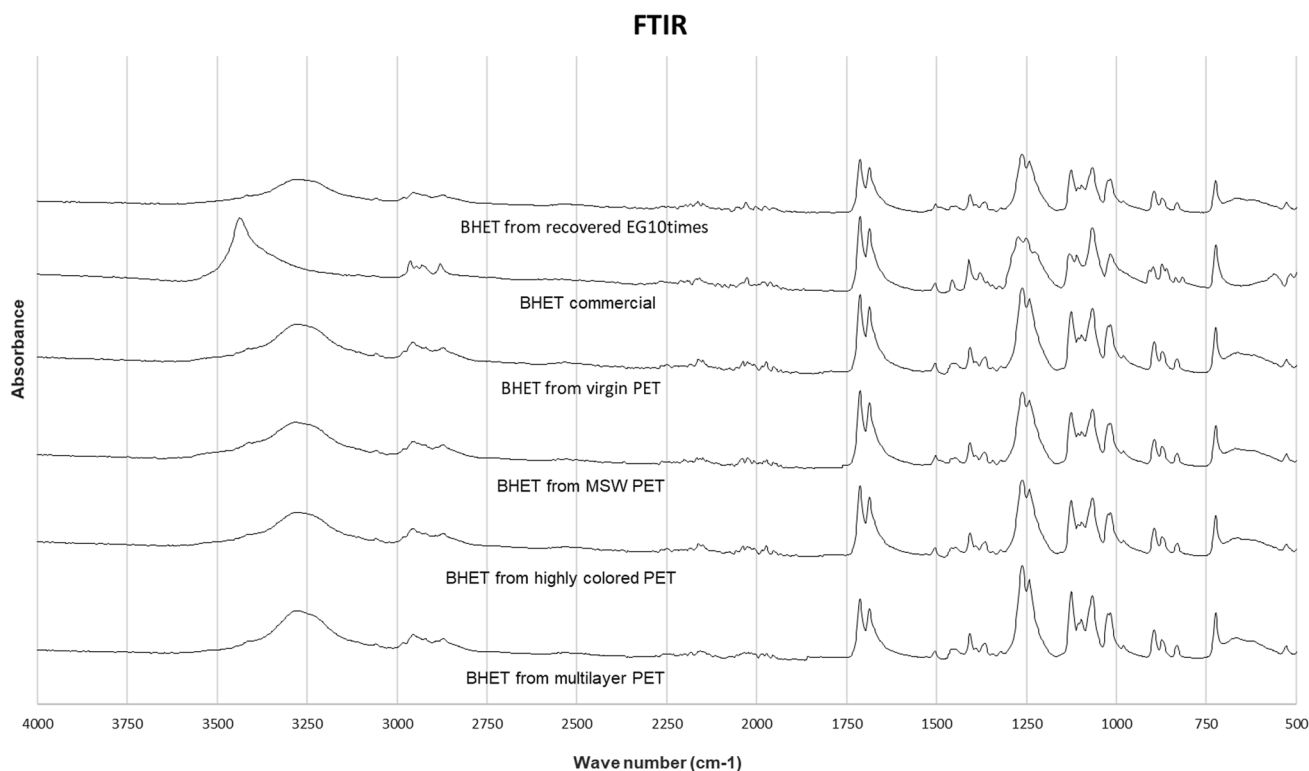


Fig. 4 FTIR spectra of BHET products obtained in optimal conditions

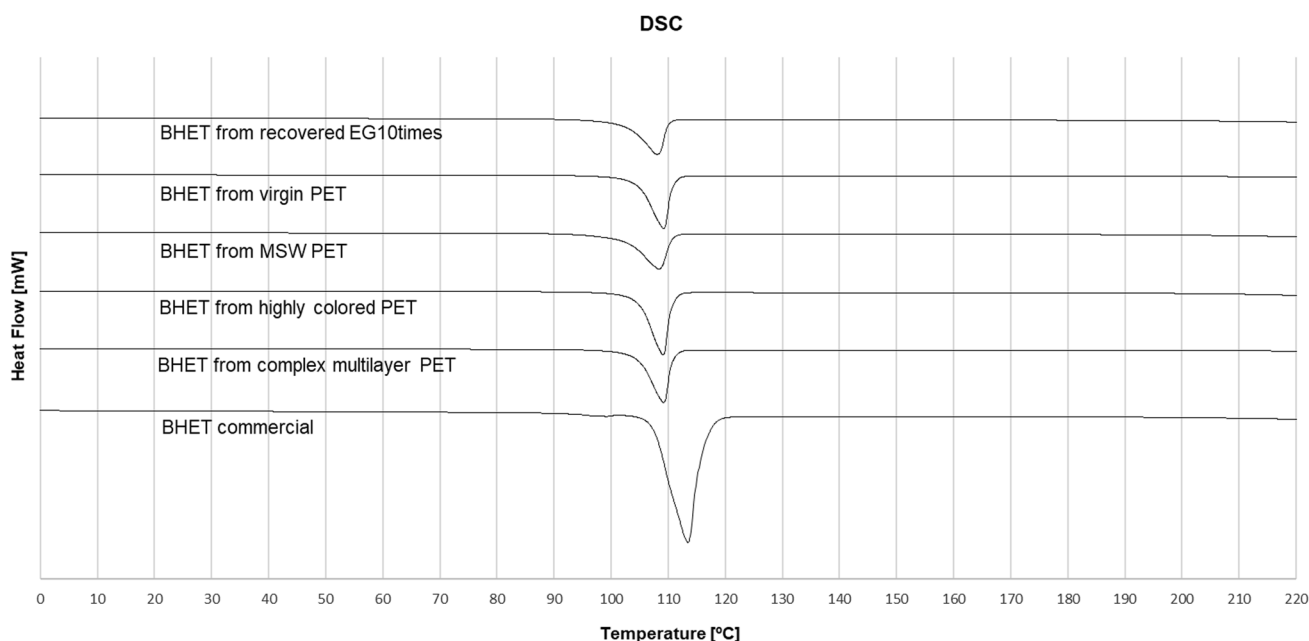


Fig. 5 DSC chromatograms of BHET products obtained in optimal conditions

in ascending order, is EG/PET mass ratio, reaction time, ZnAc_2 /PET mass percentage ratio and temperature. EG/PET mass ratio has the highest influence on the BHET yield, achieving a growth of 27.4% increasing the mass ratio from 2 to 6 w/w. However, the BHET yield does not vary as much with the rest of the factors, less than 1%. Applying the best conditions chosen (195 °C, 150 min, 6 w/w EG/PET and 0.2%w/w ZnAc_2 /PET), gives yields of 86.82%, 84.52%, 82.65% and 76.93% corresponding to virgin PET, highly coloured PET, MSW PET and multilayer PET, showing that all of them have similar yield to the one coming from virgin PET, being the multilayer PET the one with the greatest decrease respect virgin PET, 11.4%, due to has more impurities in its composition, demonstrating that PET nature and colour has little influence on BHET yield.

Other point studied on this work is the recovery of EG due to the excessive use of solvent to achieve high yield of BHET, damaging the economics of the process and the environment. Through distillation, a 70% of EG is recovered which is used adding 30% of fresh EG in new glycolysis cycles. This gives very good results, showing that the use of recovered EG does not affect the yield and quality of BHET, maintaining constant at around 71–81% and decreasing only about 7% during 10 times glycolysis cycles. This trend has been observed in all the different PET waste evaluated.

Finally, the DSC and FTIR results have verified that the BHET products derived from all types of PET waste, with the use of recovered EG, have been equivalent to the one derived from virgin PET with high purity and

similitude with commercial BHET, so PET nature and colour also have no influence on the quality and purity of the monomer obtained.

Thus, it has been demonstrated that glycolysis with EG and ZnAc_2 is suitable for chemical recycling of PET waste with more complex nature and characteristics (highly coloured PET, multilayer PET and MSW PET) than virgin PET, used as a reference waste in this study. Therefore, glycolysis has been verified as a process with a great relevance given the increased presence of this type of complex waste and a promising and efficient option for the recycling of these non-mechanically recoverable PET waste that currently ending up in landfill or incinerated.

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Data availability All data generated or analysed during this study are included in this published article.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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