Optimization of Reaction Parameters in the Conversion of PET to Produce BHET

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The conversion of poly(ethylene terephthalate) (PET) was analyzed in order to define the optimal conditions for the Bis(2-Hydroxyethyl) terephthalate (BHET) yield as regards catalyst use (zinc acetate), glycol (ethylene glycol), reaction time and temperature. These conditions were optimized so as to decrease the consumption of catalyst and glycolytic agents aiming to extend the analysis to achieve continuous recycling at a greater scale. At the same time, an analysis of the activity of different catalysts (zeolites, acid, and basic resins) was performed; no BHET yields of commercial interest were obtained. The results indicate that a very small catalyst/PET mass ratio and a low glycol/PET ratio are necessary. The reactions were carried out at a temperature of 195°C and a reaction time of 1 h: under these conditions, BHET yield is 30% (starting from pure PET) and up to 88.2% (recycling oligomers plus pure PET). POLYM. ENG. SCI., 00:000–000, 2017. © 2017 Society of Plastics Engineers

INTRODUCTION

At present, everyday life demands the employment of various materials, among which petroleum-based products such as plastics are widely used. The production of polymers has greatly expanded as a consequence of their versatility to be employed in numerous applications and their capacity to replace other materials due to their properties. However, the fact that they are highly resistant to chemical attack represents a serious environmental problem at the time of their disposal.

Therefore, it is of utmost importance to investigate how the degradation of these plastics can be accelerated to minimize environmental problems. It is worth remarking that 40% of plastic waste ends up in landfills, 35% is used as raw material to generate energy and only 25% is recycled [1, 2]. Current legislation promotes the recovery, valorization and recycling of waste in order to stimulate the application of this methodology [3, 4].

Currently, polymer production is focused on LDPE, HDPE, PET, PP, and PS. Numerous studies have been carried out with the goal of converting them into raw materials for other processes, after being discarded. In the case of PET, there are several chemical conversion ways for chemical recycling: hydrolysis, alcoholysis, acidolysis, aminolysis, methanolysis, and glycolysis [5]. The products obtained by each way are: terephthalates, esters, acids, amides, dimethyl terephthalates and bis(2-Hydroxyethyl) terephthalates, respectively. The latter is the most interesting to analyze since it is the monomer of PET, which is formed from the polymer when it reacts with ethylene glycol (EG) [6].

The process of glycolysis is based on the degradation of the polymer in the presence of a transesterification catalyst, generally metallic acetates, and a glycol thus achieving the scission of the ester bonds to be later replaced by hydroxyl terminals [7]. To carry out this reaction, glycol has to be in excess so as to obtain a good quantity in terms of product. In this sense, different authors have reported various mass ratios between EG and PET: 2 [8, 9], 2 to 6 [10], 5 [11], and 16 [12]. Therefore, all the said ratios are between 6 and 49 times higher to the stoichiometric one (0.32). This excess of EG during the reaction generates a high consumption of this reactant which, after the reaction, can be recovered through distillation vacuum (which involves one more process in PET conversion and an important energy expenditure).

Another important factor is the mass ratio between catalyst and PET, which varies according to different authors. Most studies employ zinc acetate ($ZnAc_2$) as catalyst with mass ratio: 0.002 to 0.01 [10], 0.01 [11], 0 to 0.01 [8], or 0.004 [12]. Furthermore, Na_2CO_3, $NaHCO_3$, Na_2SO_4, and K_2SO_4 [9, 13] have also been employed, the most active one being Na_2CO_3 with a mass ratio of Na_2CO_3/PET of 0.0026, even though the conversion obtained (61%) is not better than with $ZnAc_2$ (76%). The reason why $ZnAc_2$ is more effective than the other catalysts maybe lies in the fact that this compound in its cationic part has a strong affinity for the oxygen electron pair of the polymer ester group. The carbon in this group results with an electron-deficient load, and is attacked by the EG oxygen forming a tetrahedral intermediate. The C—O bond cleavage of PET is generated as well as a re-arrangement of atoms and the formation of a new ester group to produce BHET after multiple consecutive reactions [14].

Temperature and time are also important factors. Previous studies [10, 15] indicate that at temperatures below 190°C the transesterification reaction leads to an excess of subproducts, and above 220°C the rate of reaction does not increase significantly with temperature. Most reports [11, 12] employ reaction temperatures between 190 and 200°C. Several studies coincide in pointing out that it is necessary to carry out the transesterification reaction within a period of time no shorter than 45 min [9], period in which equilibrium would be reached, although other studies claim that the time lapse should be between 150 and 210 min [10]. The reaction time under study is ample, covering a range of up to 120 min [9], 150 min [11], 210 min [10], 270 min [16], and 360 min [17], among others.

It is logical to think that, considering the low cost of plastic production from virgin raw materials (products from the petrochemical industry, derived from petroleum), the optimization of resources and costs for plastic recycling plays a fundamental role in the success this process might obtain at industrial level. Therefore, the aim

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of this work is to find optimal parameters for the BHET yield, through PET glycolysis, minimizing the elements employed.

MATERIALS AND METHODS

Materials

Commercial PET chips (~3 mm × 3 mm × 350 μm) were employed. Ethylene glycol (EG) was proanalysis quality (Merck, >99.5%, CAS 107-21-1). The zinc acetate ($ZnAc_2$) employed was dihydrate (Merck, CAS 5970-45-6). In addition, in order to evaluate the activity of different catalytic materials, the following elements were used: basic resins (Purolite A850, Purolite A520), acid resins (Amberlyst 15 Dry, Amberlyst 15 Wet) and a commercial Y zeolite of the FCC process. The variation of the EG/PET and Cat/PET mass ratios was experimentally performed by modifying the mass of glycol and catalysts (the mass of PET being 20 g, constant).

Equipment and Reaction Stages

Reactions were carried out in a Parr batch reactor (300 cm^3) with external heating, continuous stirring (600 rpm) and purge with nitrogen. Reactants were loaded into the reactor, and heating (10°C min^{-1}) was started together with stirring until working temperature. Once reaction time was over, the reactor was quickly cooled down (−15°C min^{-1}) up to room temperature. Products were mixed with water up to boiling temperature, 105–110°C, keeping this condition for 60 min with continuous stirring in order to dissolve the BHET formed during the aqueous phase. After dissolving, a hot filtration was carried out to separate the liquid phase (H_2O, remaining EG, catalyst and formed BHET) from the rest of the solid products (unconverted PET and formed oligomers). The filtered liquid phase was performed at 4°C for at least 10 h in order to achieve BHET crystallization and precipitation. After cold filtration the said product was separated, washed with cold water and dried until constant weight at 60°C. To quantify the mass of the solid products from hot filtration, the samples were dried at 85°C until constant weight.

Analysis of the Product Obtained

The product obtained was characterized by GCMS (Varian Saturn 2000, capillary column VF-17, 0.25 μm, 0.25 mm, 30 m, Helium 1 mL min^{-1}, oven 40°C, 3 min, 12°C min^{-1}, 250°C, 15 min), FTIR (RPrestige-21 Shimadzu spectrometer, sample with KBr, frequency range: 400 to 4000 cm^{-1}), DSC (Mettler Toledo DSC821e, temperature range: 25–140°C with ramp of 10°C min^{-1}) and H MNR (Bruker Avance II 300 MHz with solvent $CDCl_3$).

Mass Balance and BHET Yield

The mass balances obtained in the experiments were, in every case, over 95%. BHET yield was calculated as the ratio between monomer mass produced and PET mass employed affected by the molecular weights of the said compounds:

$$Y_{\mathrm{BHET}}, \% = \frac{w_{\mathrm{BHET}}}{w^0_{\mathrm{PET}}} \frac{MW_{\mathrm{PET}}}{MW_{\mathrm{BHET}}} 100 \tag{1}$$

where w^0_{PET} is the PET mass employed for the reaction (20 g), w_{BHET} is the BHET mass synthesized in each experiment, and MW_{PET} and MW_{BHET} are, respectively, the molecular weights of PET (192 g mol^{-1}, repetitive unit) and BHET (254 g mol^{-1}).

RESULTS AND DISCUSSION

Given the different reaction conditions reported in the literature for BHET synthesis, experiments were performed by varying the wCat/wPET and wEG/wPET ratios, reaction time and temperature to establish optimal working conditions. In addition, analytical determinations were carried out to make sure that the product formed was BHET, and also to determine its purity.

Qualitative and Quantitative Analysis of the Formed BHET Product

Gas Chromatography with Mass Spectrometry. The GCMS spectrum (Fig. 1a) shows a peak (the most important one) at $m/z = 238$, which would correspond to the BHET molecule after having lost a terminal OH group, a significant peak at $m/z = 194$ corresponding to the loss of part of a lateral chain ($HO{-}(CH_2)_2{-}O{-}$), a peak at $m/z = 149$ which coincides with the BHET molecule without a complete lateral chain and without a terminal OH group, and a peak at $m/z = 104$ which corresponds to the C_6H_4-CO structure [18]. From the chromatogram (figure not shown), only two peaks can be observed, one BHET peak at 22.138 min and a solvent peak (acetone) at 1.638 min.

Fourier Transform Infrared Spectroscopy (FTIR). Different transmittance peaks are observed from the FTIR analysis (Fig. 1b): between 3400 and 3200 cm^{-1} (O—H bond stretching of an alcohol), between 3000 and 2900 cm^{-1} (C—H bond stretching of a methyl group), between 1750 and 1700 cm^{-1} (C—O stretching of a carbonyl group of unsaturated alpha-beta esters), at 1400 cm^{-1} (O—H stretching of alcohols), and peaks between 1300 and 1050 cm^{-1} (symmetrical deformation of the C—O bond of esters linked to unsaturated structures and a narrow peak between 800 and 700 cm^{-1}, *para* substitution of the aromatic ring). This analysis coincides with those reported in other publications [19].

Differential Scanning Calorimetry (DSC). This technique was employed during the heating of the three samples (Fig. 2) to identify the fusion point of the samples. A negative peak (heat absorption) can be observed with a minimum at 113° corresponding to the fusion of the sample, in agreement with the information reported in the literature [10, 17, 20] (fusion temperatures are informed for BHET −108°C-, oligomers −150, 170, 210°C- and PET −245°C-). The heat involved in those peaks is 42.05, 41.79, and 41.98 cal g^{-1}; an average fusion heat of 41.94 cal g^{-1} can be adopted.

Hydrogen Nuclear Magnetic Resonance (H NMR). A spectrum was obtained (Fig. 3) which shows signals at 8.13 ppm (4 protons linked to an aromatic ring), at 4.51 ppm (protons of the $COO{-}CH_2{-}$ methyl group) and at 4.00 (protons of the CH_2OH methyl group), signals which match previous reports [18].

By means of these analyses, it can be confirmed that the synthesized and purified product is indeed BHET.

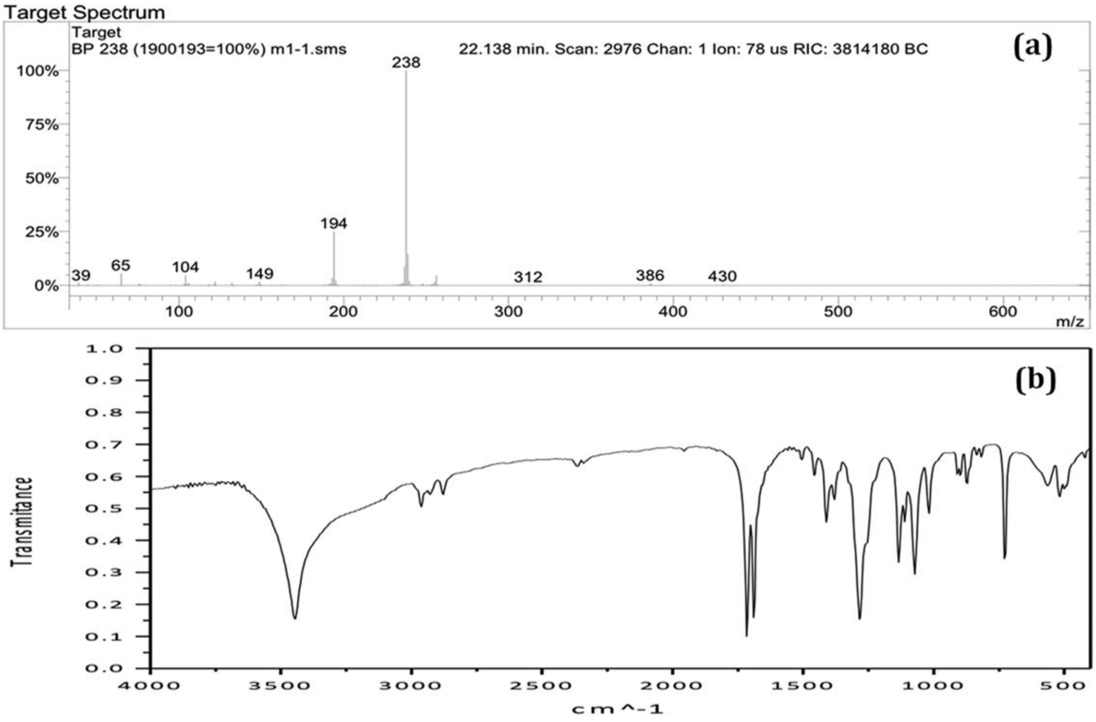

FIG. 1. Mass spectrometry and FTIR of a BHET sample.

Analysis of the Variation in the Mass Ratios Cat/PET and EG/PET and Reaction Time

From literature information, PET conversion experiments were first established at a reaction time of 150 min, employing $ZnAc_2$ as catalyst. For this purpose, a wide range of ratios was covered: $0.75 < wEG/wPET < 5$ and $0 < wCat/wPET < 2$ (Fig. 4, in which dots represent experimental results and surface represents and adjustment as a function of the McLaurin series, taking into account boundary conditions).

As observed, there is negative variation in the BHET yield with the amount of catalysts employed. Besides, the experiments suggest that at a time of 150 min, the reaction has reached equilibrium. This is demonstrated by the fact that without catalyst, the products obtained are practically equal as those obtained with the catalyst, in agreement with other authors: conversion curves as a function of reaction time with sigmoidal form (190°C, $wCat/wPET = 0.117$, $wEG/wPET = 4$) [20], equilibrium reaction time at 60 min (196°C, $wCat/wPET = 0.0096$ and $wEG/wPET = 2.45$) [9], and 150 min (with, diethylene glycol, 240°C, $wCat/wPET = 0.005$, $wDEG/wPET = 0.55$) [21]. Pardal and Tersac [16] analyzed various glycols and found different equilibrium reaction times: 90 min for diethylene glycol and a diethylene glycol/dipropylene glycol mixture, 150 min for dipropylene glycol and a longer time at 300 min for glycol and glycerol-dipropylene glycol and glycerol-diethylene glycol mixtures.

Figure 4 shows that as the wCat/wPET ratio increases, the yield slightly decreases. It can be assumed that even though the reaction reaches equilibrium, the catalyst could be favoring other undesirable reactions towards other products, e.g. oligomerization of the BHET formed. This behavior is evidenced in other reactions analyzed (referred to below). Besides, for wEG/wPET ratios over 2.5, the BHET yield is kept practically constant, being advisable not to employ ratios beyond this value.

Analysis of the Activity of Different Catalysts in Equilibrium Conditions

Because the results obtained at 150 min of reaction showed equilibrium state, different commercial catalysts were analyzed in our laboratory in order to assess their activity in this transesterification reaction. Basic resins (Purolite A850 and Purolite A520), acid resins (Amberlyst 15 Dry and Amberlyst 15 Wet) and a Y zeolite of the FCC process were employed under the same conditions: 195°C, $wCat/wPET = 0.3$, $wEG/wPET = 3$,

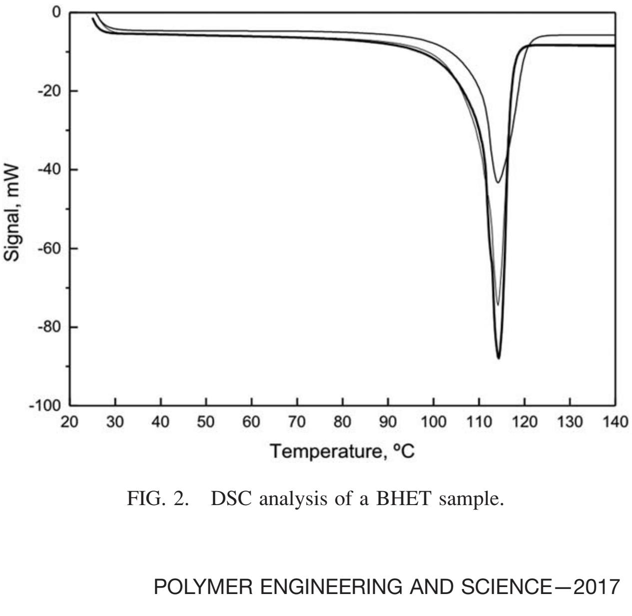

FIG. 2. DSC analysis of a BHET sample.

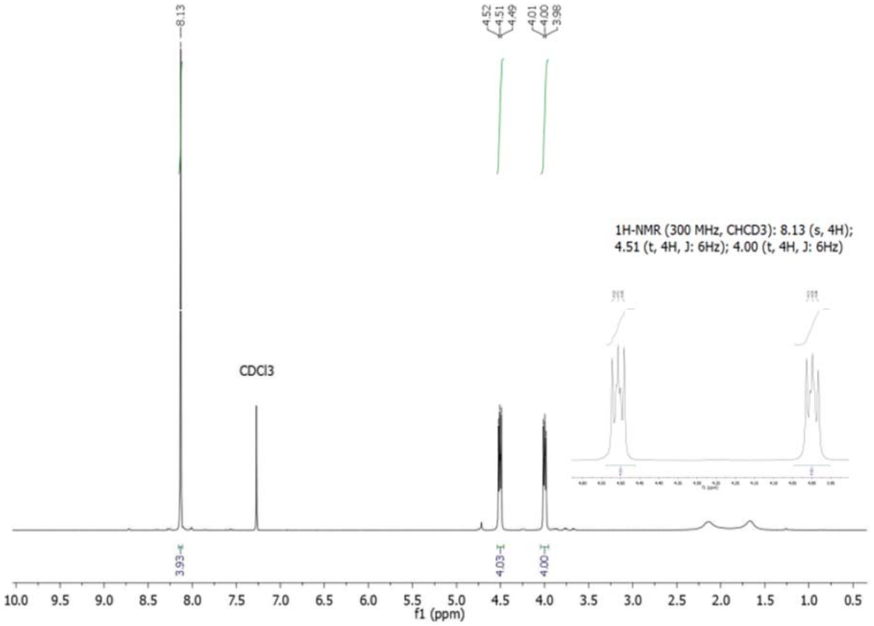

FIG. 3. H NMR of BHET dissolved in CHCD3. [Color figure can be viewed at wileyonlinelibrary.com]

150 min. The results (Fig. 5) demonstrate that the best catalyst for this type of reactions is zinc acetate, presenting a net negative effect when using the other catalysts, thus obtaining yields lower than 5% in these cases.

Optimization of the Reaction Parameters to Maximize Ratios wBHET/wCat and wBHET/wEG

From the above results, $ZnAc_2$ was adopted as the most adequate catalyst to evaluate the effect of the different parameters in this reaction: temperature, time and ratios wCat/wPET and wEG/wPET. This led to establish optimal working conditions to maximize BHET yield with a minimal use of $ZnAc_2$ and EG. This analysis considered an important number of experiments which are summarized below, analyzing the dependence of the BHET yield on each parameter.

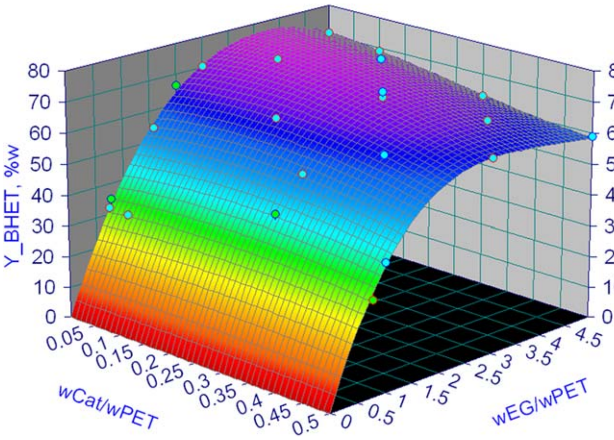

FIG. 4. BHET yield as a function of ratios wCat/wPET and wEG/wPET. $T = 195°C$, $t = 150$ min. Symbols: experimental data; surface: McLaurin modeling. [Color figure can be viewed at wileyonlinelibrary.com]

Analysis of the BHET Yield with Time of Reaction. Performing an analysis as a function of time of reaction, the BHET yield was studied under two conditions: in the absence of catalyst and with zinc acetate in a ratio wCat/wPET = 0.0008, and a ratio wEG/wPET = 0.75 (optimal according to the subsequent analysis). The results obtained are shown in Fig. 6.

It can be observed that in the experiments with catalyst, up to 60 min of reaction the BHET yield increases considerably, and after this time it remains practically constant. Without catalyst, the equilibrium yield is achieved at over 150 min (Fig. 4), yields of interest appearing only after 100 min of reaction.

Analysis of the BHET Yield With Temperature. As mentioned in the Introduction section, several studies [10, 15] report that below 190°C, the transesterification reaction does not lead to BHET formation quantitatively while at temperatures over 220°C the reaction rate does not increase significantly. Different experiments between 165 and 250°C were performed keeping the wEG/wPET = 0.75 and wCat/wPET = 0.0008 ratios constant as well as the reaction time (60 min), obtaining the results presented in Fig. 6.

The yield increases significantly with temperature, obtaining values of interest in the range of $195 < T$, $°C < 210$. At higher thermal values, the polymerization of the product of interest (BHET) would be favored, decreasing the yield for temperatures higher than 210°C.

Analysis of the BHET Yield With Ratio wCat/wPET. At 60-min reaction time (minimum time to reach equilibrium, Fig. 6) and two ratios wEG/wPET (0.75 and 2.5), the wCat/wPET ratio was varied from 0 to 0.35, obtaining the results shown in Fig. 7. As the amount of catalyst increases, for a constant PET mass, BHET yield decreases. In the case of ratio wEG/wPET = 0.75, a constant BHET yield can be established for $0.005 < \text{wCat/wPET} < 0.0375$. For higher ratios, the oligomerization of the BHET formed is probably being favored. Therefore, it should be

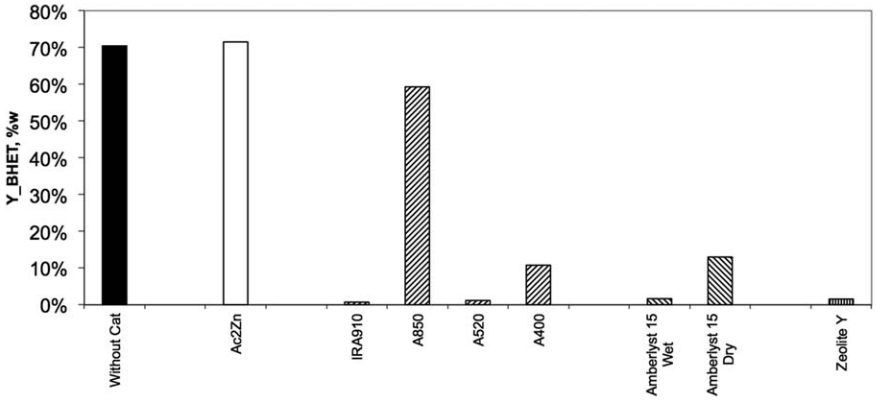

FIG. 5. BHET yield as a function of different catalysts employed.

considered that the wCat/wPET ratio must be low to avoid a decrease in the BHET yield formed.

By analyzing the wBHET/wCat ratio, it can be observed that the trend is inversely proportional to the catalyst mass employed. To maximize the BHET yield and minimize the amount of catalyst employed, it is necessary to employ 0.016 g of ZnAc$_2$ for each 20 g of PET.

Analysis of the BHET Yield With Ratio wEG/wPET. Considering that glycol is used in excess and its subsequent recovery implies an energy expenditure, experiments were performed varying the amount of EG, and keeping constant the remaining experimental variables (195°C, 60 min, ratio wCat/wPET = 0.0008). In Fig. 8, it can be seen that the highest BHET yield by EG mass is given for a ratio wEG/wPET = 0.75. The decreasing trend for ratios wEG/wPET higher than 0.75 is in agreement with previous reports [10, 11]. The value adopted for ratio wEG/wPET is considerably low compared to what has been reported in previous studies (5 [11], 6 [10], or 16 [12]), and much closer to the value established in the stoichiometric ratio (0.32).

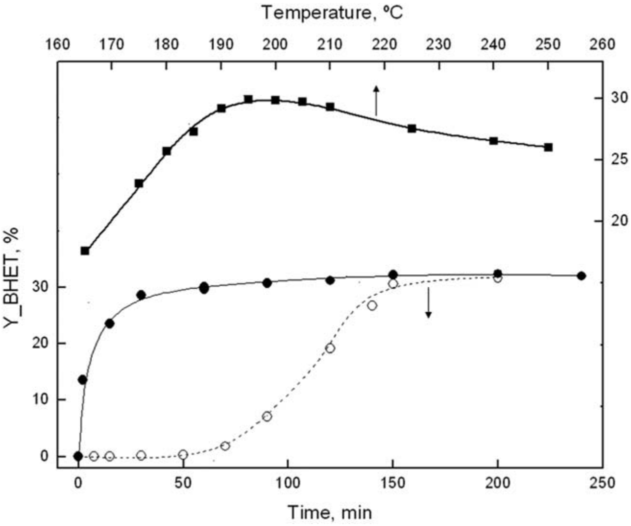

FIG. 6. BHET yield as a function of temperature ($t = 60$ min, wEG/wPET = 0.75, wCat/wPET = 0.0008) and as a function of reaction time (wEG/wPET = 0.75, (○) without catalyst, (•) Cat/wPET = 0.0008).

It is concluded that the optimal conditions to maximize ratios wBHET/wEG and wBHET/wCat are: 195°C, 60 min, wEG/wPET = 0.75 and wCat/wPET = 0.0008. Under these conditions, wBHET/wEG = 0.553 and wBHET/wCat = 518 are obtained (both higher than those obtained in other studies; see Table 1).

Recycling of the Oligomers Obtained in the PET Glycolysis Reaction

Having defined the optimal conditions for the BHET yield from pure PET, the monomer production was analyzed reusing the reaction products composed of oligomers and unconverted PET. A set of simultaneous experiments was established (six under each condition) to assess the real behavior of the process, decreasing the error. A statistical analysis of the results obtained in the described process was performed (Table 2).

Because the wCat/wPET ratio to maximize wBHET/wPET was very low, three different ratios were established to analyze if there is an important dependence on the latter when recycling the oligomers formed in the glycolysis of PET. wCat/wPET ratios of 0.0008 (optimal in the previous analysis), 0.0016 (twice the former) and 0.0375 (maximum one, keeping the BHET yield at the highest value, Fig. 7) were assumed. This analysis also considered the performance of consecutive experiments (6) until achieving a constant accumulated BHET yield, defined as:

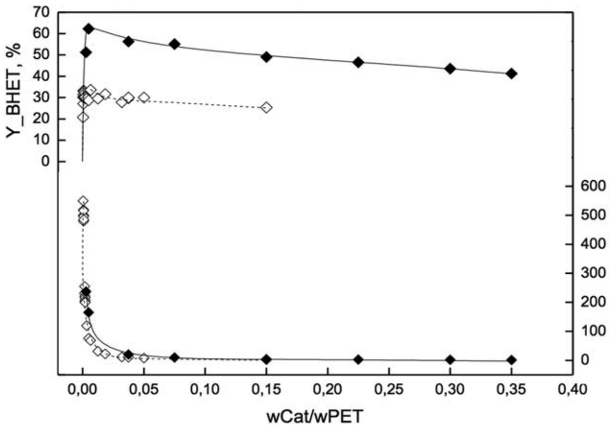

FIG. 7. BHET yield and wBHET/wCat ratio, as a function of the wCat/wPET ratio. Symbols: (◇) wEG/wPET = 0.75; (•) wEG/wPET =2.5.

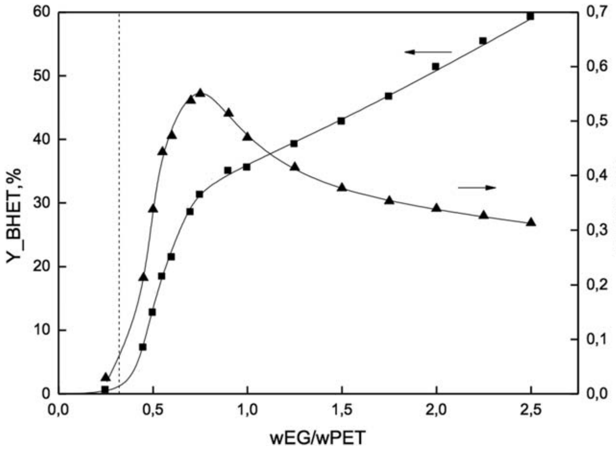

FIG. 8. BHET yield and ratio wBHET/wEG as a function of ratio wEG/wPET (dashed line: stoichiometric wEG/wPET ratio).

$$Y_{\mathrm{BHET}}, i, \% = \frac{\sum_{j=1}^{i} w_{\mathrm{BHET,j}}}{\sum_{j=1}^{i} w^{0}_{\mathrm{PET,j}}} \frac{MW_{\mathrm{PET}}}{MW_{\mathrm{BHET}}} 100 \qquad (2)$$

where $Y_{\mathrm{BHET}}, i, \%$ is percent accumulated yield of BHET in stage i, $w_{\mathrm{BHET,j}}$ is the BHET mass produced in each stage, and $w^{0}_{\mathrm{PET,j}}$ is the PET mass employed in each stage.

In all cases, a mass of reactants was employed (pure PET for the first stage, solid subproducts of the previous stage plus pure PET, in order to complete the mass needed, in the following stages) constant and equal to 20 g, a mass of EG of 15 g and an amount of catalysts equal to 0.016, 0.032 for 0.75 g for ratios wCat/wAlim 0.0008, 0.0016, and 0.0375, respectively. Temperature and reaction time was 195°C and 1 h, respectively. This methodology determines that the ratio between total reactants (pure PET plus subproducts of the previous stage) and EG remain constant (wEG/wAlim, accum = constant), but not ratio wEG/wPET, accum, which will increase with respect to the initial one resulting that in each stage the addition of pure PET is lower than at the beginning. At the end of the sixth stage (with constant BHET yield), having as subproduct a mass of solids composed of oligomers and unconverted PET of the 6 runs, this mass was employed to carry out the seventh and eighth stages (with no PET addition).

Oligomer Recycling Experiments with an Optimal Ratio wCat/wAlim = 0.0008. In Fig. 9 it can be observed that the accumulated BHET yield increases as the number of stages proceeds, from 31.3% (stage 1) to 60% (stage 5) remaining constant in subsequent stages. Afterwards, without adding PET (stages 7 and 8), conversion increases up to values of 70.5 and 82.5% for the said stages. It is important to remark that even though in an initial stage the yield is low (in the order of 30%), at the end conversions of about 80% are achieved, comparable with experiments that employ a higher ratio catalyst and/or glycolysing agent. By means of the analysis of ratios wBHET/wEG and wBHET/wCat it can be seen that in both cases the behavior is similar: an increase of those ratios up to stage 2 and then a small decrease as the number of stages increases, presenting a slight increase in stages 7 and 8 (without pure PET). It can be established for the first 6 stages that ratios can be constant, with values of 0.57 and 533 for wBHET/wEG and wBHET/wCat, respectively, reaching 0.576 and 540 in stage 8. Ratio wEG/wPET, accum, which in stage 1 is 0.75, increases up to stage 6 at 1.42, and 1.89 in stage 8. In this case, even though ratio wEG/wPET, accum considerably increases, it is still lower than the minimum ratio employed in other studies [8] (see Table 1).

Oligomer Recycling Experiments With a Ratio wCat/wAlim = 0.0016. According to the reaction stages analyzed, the accumulated BHET yield shows a sustained increase similar to that of the previous case: up to stage 3 the increase is more noticeable (reaching a value of 50.8%) and then the growth rate is somewhat slower until reaching a value of 57.9% in stage 6. For the last two stages (7 and 8, without pure PET), the accumulated yield shows values of up to 80.5%. The wBHET/wEG and wBHET/wCat accumulated ratios show a slight growth with linear trends as the number of stages increases (different from the previous case). These ratios go from 0.539 and 253 (wBHET/wEG and wBHET/wCat, respectively) for stage 1 up to 0.586 and 275 for stage 8. Ratio wEG/wPET, accum shows an increase from 0.75 in stage 1 to 1.36 in stage 6, and to 1.82 at the end of stage 8. These values are somewhat lower than those in the previous case and, consequently, better than the values reported in the literature.

Oligomer Recycling Experiments With a Ratio wCat/wAlim = 0.0375. In this case, the accumulated yield of BHET as a function of the stages presents a similar behavior, reaching a value of 50.3% in stage 4 (lower than in the previous cases). For the two final stages (7 and 8), an increase in the yield of the monomer is observed reaching accumulated yields of 70.7%. An increase in the BHET formed/EG employed accumulated ratio as a function of stages is observed, up to stage 3, then remaining constant at a value of 0.536 up to stage 8. A similar behavior is observed when the ratio between monomer formed and catalyst employed is analyzed, in which this ratio increases from a value of 10.04 in the first stage up to 10.49 in the third stage, then becoming stabilized at a value of 10.68 in the

TABLE 1. Mass ratio catalyst/PET and EG/PET according to the different authors cited above.

			Ratios employed		Ratios obtained	
Authors	Temp (°C)	Time (min)	wEG/wPET	wCat/wPET	wBHET/wCat	wBHET/wEG
Aguado et al. [5]	208	150	6	0.002	440	0.147
Moral et al. [12]	190 a 195	150	5	0.01	101	0.201
Campanelli et al. [13]	> 245	40	2	0 a 0.01	s.d.	s.d.
López-Fonseca et al. [14]	165 a 196	60	7.6	0.01	106	0.139
Lituma and Koniyoshi [15]	190 a 200	120	16	0.004	231	0.058
Stoichiometry			0.32			

TABLE 2. Statistical analysis of the PET recycling experiments.

Stage number	wCat/ wPET = 0.0008 X	SD	SD/X	wCat/ wPet = 0.0016 X	SD	SD/X	wCat/ wPET = 0.0375 X	SD	SD/X
1	0.313	0.015	**4.7%**	0.306	0.011	**3.6%**	0.286	0.011	**3.7%**
2	0.349	0.010	**2.8%**	0.319	0.011	**3.4%**	0.301	0.005	**1.7%**
3	0.321	0.008	**2.6%**	0.313	0.012	**3.7%**	0.302	0.009	**3.1%**
4	0.312	0.008	**2.6%**	0.334	0.012	**3.4%**	0.310	0.005	**1.7%**
5	0.304	0.008	**2.7%**	0.315	0.010	**3.0%**	0.307	0.008	**2.5%**
6	0.302	0.011	**3.6%**	0.322	0.009	**2.7%**	0.306	0.011	**3.7%**

X: average yield of each stage; SD: standard deviation.

subsequent stages. For this third case, the analysis of wEG/wPET, accum indicates that at the end of stage 6, the ratio has a value of 1.29 and after stage 8, a value of 1.73, both lower than in previous cases.

Comparison Between the Three wCat/wPET Ratios. The accumulated BHET yield shows, at each reaction stage, a decrease in values as ratio wCat/wAlim increases (which coincides with what was previously observed, Fig. 4). In this case, the average BHET yield in stage 6 presents values of 60.1, 57.9, and 52.3% for ratios wCat/wAlim 0.0008, 0.0016, and 0.0375, respectively. Concerning ratio wBHET/wEG, different behaviors were observed in the three cases under analysis: ratio wBHET/wEG = 0.0008 presents an increase up to stage 2 and then a decrease up to stage 6 (obtaining practically the same value in stage 1 and 6). Then, in stages 7 and 8 (recycling without PET), there is an increase up to a value of 0.576 even though it is not higher than in stage 2 (0.584). In the case of ratio 0.0016, the increase is sustained, from 0.539 in stage 1 up to 0.561 in stage 6, trend that continues up to a value of 0.586 in stage 8. Finally, in the case of the highest mass ratio, the ratio increases at a higher rate from 0.502 (stage 1) up to 0.530 (stage 4) and then, with a slower growth rate, up to 0.534 in stage 6, remaining constant in stage 7 and increasing in stage 8 (0.542).

It is clear that the best wCat/wAlim ratio to improve the accumulated wBHET/wEG ratio is the one adopted as optimal (0.0008), performing only stages 1 and 2. Taking into account that since PET is not recycled in the successive stages (as in stages 7 and 8), this ratio could improve even more if after stage 2 the two stages mentioned above are carried out. For this reason, this experimental analysis is presented below.

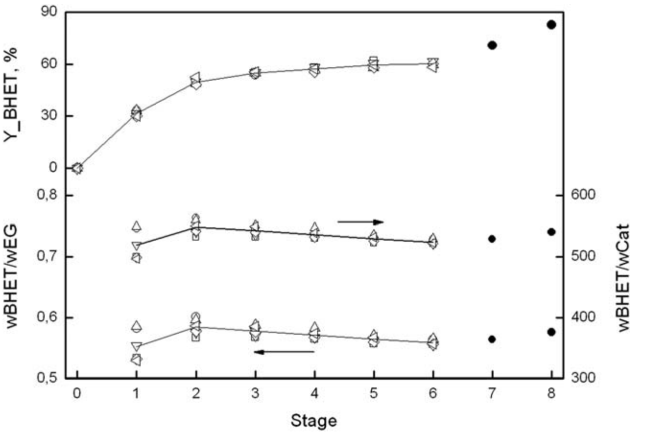

FIG. 9. Accumulated BHET yield, accumulated wBHET/wEG and accumulated wBHET/wCat as a function of the reaction stages. Ratio wCat/wPET = 0.0008. Open symbols: runs 1–6 in stages 1 to 6; closed symbol: average yields without PET addition in stages 7 and 8; dashed line: average.

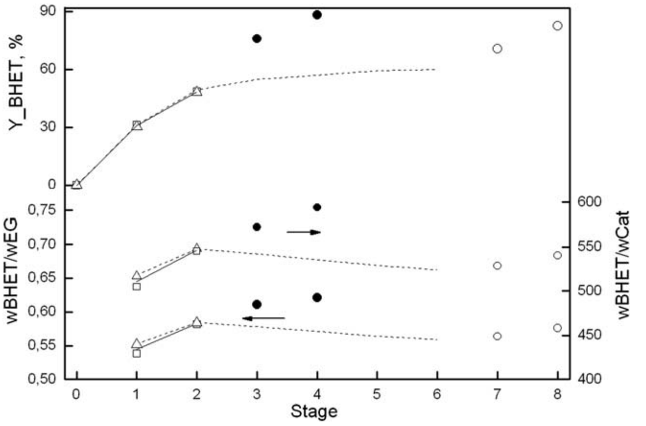

FIG. 10. Accumulated BHET yield, accumulated wBHET/wEG and accumulated wBHET/wCat as a function of the reaction stages. Ratio wCat/wPET = 0.0008. Open symbols (△) and (□): runs 1 and 2 in stages 1 and 2; closed symbol: recycling without addition of PET in stage 3 and 4; solid line: average; dashed line and symbol (○): experimental data in stages 1–8.

Oligomer Recycling Experiments with Ratio wCat/wAlim = 0.0008 With Fewer Reaction Stages

From the results obtained, a set of experiments was performed taking into account the optimal wCat/wPET ratio and considering the trend of ratio wBHET/wEG, accum. It was decided to perform PET recycling in two stages, and in the third stage not to add PET but recycle the oligomer products obtained in stage 2 to be compared with the result previously shown. A priori, in this way, ratio wBHET/wEG could be further improved. For that purpose, and taking into account the behavior so far observed in the reactor, it was decided to carry out two experiments, maintaining ratios wCat/wAlim and wEG/wAlim, but triplicating the masses of reactants and catalyst. The results obtained in the said experiments are shown in Fig. 10.

The experiments corresponding to stages 1 and 2 were practically equal to those included in Oligomer Recycling Experiments with an Optimal Ratio wCat/wAlim = 0.0008 subheading, (the experimental results are independent of the total mass employed in the reactor). When the oligomers and unconverted PET of the second stage were employed as feed in the third stage, an accumulated yield of 76.0% was obtained, higher than that achieved in stage 6 of Oligomer Recycling Experiments with an Optimal Ratio wCat/wAlim = 0.0008 subheading (61.0%). When stage 4 was performed (in which only 25 g were employed), a conversion of 88.2% was achieved, thus improving the BHET yield obtained in the 8 stages previously studied.

The analysis of ratio wBHET/wEG shows an increasing behavior for the 4 stages studied, manifesting the same trend as in the eight-stage case. Here, the ratio is 0.545 for stage 1 reaching 0.621 for stage 4, thus increasing 14%. A similar situation is observed in the same figure for ratio wBHET/wCat in which a ratio of 549 is achieved in stage 4 against 511 in the first stage (increase of 16%). The analysis of ratio wEG/wPET, accum shows an increase from 0.75 in the first stage to 1.10 in the second stage, being 1.65 and 1.87 in the third and fourth stage (without addition of pure PET), respectively. Again, as in the previous case, the values obtained are lower than those reported in the literature (Table 1).

Statistical Analysis of the Results Obtained

A statistical analysis can be carried out as a function of the results obtained in the set of experiments of six stages with six runs for each one for the three wCat/wPET ratios (108 experiments). Each one of the percent BHET yields is taken as a representative parameter. The average value of each set of experiments was calculated as well as its standard deviation and percentage error (calculated as standard deviation divided by average), which are shown in Table 2. In every case, the average error of the experiments is not higher than 4.7% with respect to the average value of each one of them, which reflects the accuracy of the results.

CONCLUSIONS

From the experimental results in the glycolytic and catalytic PET conversion, it was possible to establish the optimal reaction conditions minimizing the use of catalyst (zinc acetate) and glycol (ethylene glycol): $T = 195°C$, $t = 60$ min, and ratios wEG/wPET = 0.75 and wCat/wPET = 0.0008. A BHET yield of 31.3% could be achieved. In parallel, an analysis was performed with catalysts of a different nature in order to verify their activity in the esterification reaction: in every case, their catalytic activity was not the expected one. This evidence opens up an important research line (reaction mechanisms, microscopic structure of the catalyst employed, etc.) to elucidate this behavior, which is beyond the scope of the present work.

The results obtained in optimization were later employed to analyze the recycling of the reaction oligomers with which, through a process of eight stages, the BHET yield was increased up to 82.5% (value similar to those reported by other authors using greater amounts of catalyst and/or glycol). Performing the same analysis, this time in four stages (the last two ones without addition of PET), the yield attained reached 88.2%, which was significantly higher than that previously obtained. It should be remarked that the initial wEG/wPET = 0.75 ratio was significantly closer to the stoichiometric ratio (0.32), even though as expected in recycling, ratio wEG/wPET, accum showed an important increase, reaching 1.87 in the case of four-stage recycling (Oligomer Recycling Experiments with Ratio wCat/wAlim = 0.0008 With Fewer Reaction Stages subheading). However, in no case were these values higher than the minimum reported in other publications, with which the ratio between the reactants employed substantially improves. The mass ratios between the product of interest obtained and glycol and catalyst showed values that are quite higher than those so far reported in the literature. Average values of wBHET/wEG = 0.569 and wBHET/wCat = 533.2 were obtained.

A statistical analysis of the results obtained indicates that the reacting system employed is very accurate (with a standard deviation lower than 5% in every case).

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