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Research Article

Closing the Loop: Greener and Efficient Hydrolytic Depolymerization for the Recycling of Polyesters Using Biobased Eutectic Solvents

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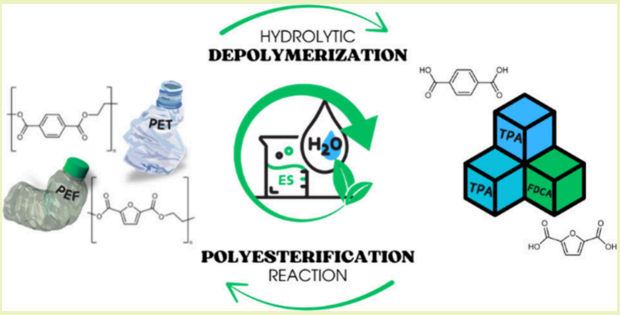

ABSTRACT: The imperative for achieving circularity in the realm of postconsumer polymers predominantly hinges upon the adoption of efficient recycling methodologies with a greener footprint. As such, this study introduces an innovative and eco-friendly depolymerization process for recycling highly consumed poly(ethylene terephthalate) (PET) and innovative bioderived poly(ethylene 2,5-furandicarboxylate) (PEF) which is easily extrapolated to other polyesters. This study demonstrates the pivotal role of eutectic solvents based on biobased phenols with safe design to efficiently mediate the hydrolytic depolymerization, under alkaline conditions, of these recalcitrant polymers into terephthalic acid (TPA) or 2,5-furandicarboxylic acid (FDCA). Additionally, optimization through a design of experiments approach yields TPA and FDCA with over 90% and 80% recovery, respectively, under mild conditions of temperature, below 150 °C, and not exceeding 5 h of reaction time. Structural characterization analyses confirm the chemical nature and the high purity of the recovered products, while eutectic solvent reuse assessments underscore its potential for multiple cycles with minimal loss of catalytic activity, reducing process waste. A proof-of-concept for monomer repolymerization demonstrates feasibility. Green metrics align with the fine chemicals industry, indicating promising market potential for this low-energy eutectic solvent-based approach to enhance circularity in polyester waste management.

KEYWORDS: *polymer chemical recycling, poly(ethylene terephthalate), poly(ethylene 2,5-furandicarboxylate), depolymerization, hydrolysis, eutectic solvents, green chemistry, sustainability*

■ INTRODUCTION

Polymer pollution has emerged as a major global environmental problem, with poly(ethylene terephthalate) (PET) being one of the major contributors to the burgeoning issue of solid waste worldwide.[1,2] PET is a versatile thermoplastic polyester that finds extensive use in various high-consumption applications, including packaging and textile fibers, making it the fourth-largest produced polymer globally,[2−4] accounting for 12% of the world's total solid waste.[1,3−5]

One of the most promising biobased candidates to replace PET is the structurally similar poly(ethylene 2,5-furandicarboxylate) (PEF), produced from the polyesterification of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol (EG),[6] estimated to soon reach the global market as a 5 kton flagship plant in the European Union and a license attributed to Origin in the United States of America for future 100 kton production of FDCA and PEF.[7−9] PEF has several favorable properties compared to PET, including competitive mechanical properties,[10,11] a higher glass transition temperature ($T_g \approx 87-90$ °C vs 80 °C),[12] slightly lower melting point ($T_m \approx 206-212$ °C vs 249−251 °C),[10,13,14] and enhanced gas barrier properties to CO_2, O_2, and water (reduced permeability 19, 11, and 2.1 times, respectively).[13,15]

Efforts to mitigate the environmental impact of polymer waste have primarily focused on recycling strategies, with chemical recycling emerging as a promising approach.[4,5] Chemical recycling entails breaking down polymers into their constituent building-block monomers or related value-added products, such as oligomers. Among the conventional reaction pathways for chemical recycling polyesters, glycolysis and hydrolysis have gained prominence due to their feasibility for industrial-scale applications.[16−18] While glycolysis, with ethylene glycol (EG), yields *bis*(hydroxyethyl)-terephthalate

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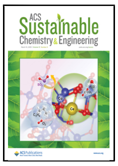

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(BHET) or *bis*(hydroxyethyl)-2,5-furandicarboxylate (BHEFDC) or their oligomeric derivatives,[19,20] the neutral, acidic, or alkaline hydrolysis of these polymers produces instead EG and the dicarboxylic acid (either terephthalic acid (TPA) or FDCA monomers).[19,20]

Despite the potential of glycolysis and hydrolysis, these processes typically face relevant challenges, including slow reaction rates, usage of large quantities of solvent, and high energy consumption during depolymerization processes.[19] To overcome these limitations and promote the development of more sustainable polyester recycling processes, researchers have explored the use of catalysts in depolymerization reactions, striving to convert these polymers into their building-block monomers under milder conditions.[21,22]

In this context, eutectic solvents (ES), typical mixtures of different hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) which allow for tunability, have demonstrated remarkable potential in various organic, analytical, and polymer chemistry fields.[23] Notably, urea and glycol-based ES have exhibited exceptional catalytic capabilities in PET depolymerization reactions through a combination of glycolysis and hydrolysis, offering fast reaction rates and high conversion rates of PET; nonetheless, these approaches are less favored since they ultimately lead to a mixture of different monomers (and oligomers) hard to repolymerize and/or needing intensive purification steps.[24−26] In previous research on PET depolymerization, the synergistic effects of ES and microwave (MW) irradiation led to a remarkable 85% PET conversion within just 92 s of irradiation.[27] However, this study reported only on PET and the ES of choice, which was composed of choline chloride (ChCl) and hazardous *m*-cresol. Also, the greenness of the process in terms of green metrics was not reported.[27]

Furthermore, to the best of our knowledge, the hydrolysis of PEF has not yet been published, only its glycolysis,[28] despite its potential, since the hydrolysis products (i.e., FDCA) are the most industrially relevant for the synthesis of the related polymers and additives.[12,29,30] Therefore, recognizing the need for more environmentally friendly depolymerizing agents for hydrolysis mediated recycling, we present in this study a novel and *greener* approach to PEF and PET depolymerization that is easily extended to other polyester recycling. We propose a versatile method carried out under hydrolytic alkaline conditions, utilizing biobased carvacrol, eugenol- or thymol-derived ES and sodium carbonate as depolymerizing agents. This study also demonstrates the feasibility of recovering the depolymerization products by a simple precipitation and separation steps, also enabling solvent recovery and reuse, in accordance with the Green Chemistry principles as assessed by atom economy and E-factor metrics and aligning with the growing demand for *greener* recycling practices.[31]

EXPERIMENTAL SECTION

Materials and Reagents. Anhydrous ethylene glycol (EG, 99.8%), choline chloride (ChCl, ≥99%), carvacrol (Car, 99%), eugenol (Eug, 99%), thymol (Thy, ≥98.5%), maleic acid (≥99%, HPLC grade), methanol (MeOH, ≥99.8%), hydrochloric acid (37%), trifluoroacetic acid (TFA, ≥99%), titanium(IV) butoxide (TBT, >99%), and DMSO-d_6 (99.96% atom D) were purchased from Sigma-Aldrich. Anhydrous Na_2CO_3 (99.8%) was acquired from Acros Organics. Chloroform (99.9%) was acquired from Fischer Scientific. Dimethyl furan-2,5-dicarboxylate (DMFDC, 99.9%) was acquired from Sarchem Laboratories. Titanium dioxide (99%) was acquired from Millennium Chemicals. Commercial PET was obtained from postconsumer poly(ethylene terephthalate) (pcPET) bottle-grade waste (cut with a diameter of 4 mm). ChCl was dried in an oven at 105 °C overnight before use. All of the other reagents were used as received.

PEF Synthesis. PEF was synthesized at our lab, following previous reported procedure.[32−34] Briefly, in a first step, *ca.* 2.5 g DMFDC, an excess of EG (1:2.2 mol:mol, *ca.* 1.7 mL), and the TBT catalyst (0.25 wt % in relation to DMFDC) were mixed and heated progressively from 165 up to 200 °C for 4 h and then kept at that maximum temperature under a nitrogen atmosphere for 30 min. Subsequently, in a second step, the reaction was allowed to proceed under a vacuum, and the temperature was progressively increased to approximately 240 °C and finally kept at that maximum temperature for 3 h. The mixture was purified by dissolving it in chloroform, with a few drops of TFA, and pouring the solution into an excess of cold MeOH to precipitate the polymer, which was filtered, dried overnight at 40 °C, and stored for further usage in the depolymerization reactions.

Eutectic Solvent Synthesis. ChCl:Car, ChCl:Eug, and ChCl:Thy eutectic mixtures were synthesized by using a 1:2 (HBA:HBD) molar ratio. ChCl (*ca.* 5−10 g) and the selected HBD were weighted, added to a round-bottom flask, and heated at 50 °C, under stirring, until a homogeneous liquid mixture was achieved.

Polyester Hydrolysis Reaction Experiments. Reactions were carried out mixing *ca.* 1 g of the polyester (either PEF or pcPET) with ES, Na_2CO_3, and water in a 1:1:1:15 ratio by weight, and the temperature was raised to the set temperature, between 120 and 180 °C, measured externally, and kept at that temperature for a variable period of time, between 2 and 8 h, as defined by the Design of Experiments. Subsequently, the reaction mixtures were cooled down to room temperature, approximately 10 mL of distilled water was added for dissolving the sodium salt derivatives of FDCA or TPA, unreacted polymer pieces were taken off, and the water-immiscible ES was recovered from the aqueous media. TPA or FDCA were recovered by neutralizing the solution using concentrated HCl (*ca.* 2 mL) and finally followed by filtration and drying at 40 °C. The polyesters weight loss (weight $\text{loss}_{\text{polyester}}$) and monomers recovery yield (η) percentages were determined following eqs 1 and 2, where $W_{\text{P,i}}$, $W_{\text{P,f}}$, and W_{M} stand for the initial and final weights of the polymer and the weight of the resulting monomers (TPA or FDCA), respectively, and Mw_{M} and Mw_{RU} represent the molecular weights of the monomers and the repeating unit of the pristine polyesters, respectively.

$$\text{weight loss}_{\text{polyester}}\ (\%) = \frac{W_{\text{P,i}} - W_{\text{P,f}}}{W_{\text{P,i}}} \times 100 \tag{1}$$

$$\eta\ (\%) = \frac{W_{\text{M}} \cdot Mw_{\text{RU}}}{W_{\text{P,i}} \cdot Mw_{\text{M}}} \times 100 \tag{2}$$

Single-component depolymerization assays using only one of the two species of which ES was composed, either the HBA or the HBD, with and without the presence of Na_2CO_3, always in the presence of water, were also conducted to assess the synergistic effect of ES components. The ratios were maintained as previously described.

Repolymerization of the Recycled Monomers. PET and PEF synthesis from recovered TPA and FDCA was conducted by adapting extant knowledge in the art.[28,35−42] Briefly, in a first esterification step, recovered TPA or FDCA (*ca.* 2.5 g), an excess of EG in a 1:4 (mol:mol) ratio, and the TiO_2 catalyst (1 wt %, in relation to TPA or FDCA) were mixed and heated progressively from room temperature to 230 °C for 5 h and then kept at that maximum temperature under the nitrogen atmosphere for 30 min. Subsequently, in a second polytransesterifcation step, the reaction was allowed to proceed under vacuum, and the temperature was progressively increased to approximately 260 °C and finally kept at that maximum temperature for 3 h. The mixture (of recycled PET (rPET) or recycled PEF (rPEF)) was purified by dissolving it in chloroform, with a few drops of TFA, and pouring the solution into an excess of cold MeOH to precipitate the polymer, which was filtered, dried in a 40 °C oven overnight, and stored for further characterization.

Optimization of Depolymerization by Design of Experiments. Design of Experiments (DoE) was performed using the Central Composite Design methodology (Design-Expert, version 13.0.5.0, Stat-Ease Inc., Minneapolis, MN), PET as a model system, and the design defined was constituted of four important factors, namely: the reaction time (t), reaction temperature (T), base weight percentage (W_{base}), and eutectic solvent weight percentage (W_{ES}). The selection of specific ranges was guided by the accumulated expertise of the research group, as documented in previous studies.[34,43] Multiple runs were conducted, and the PET weight loss and TPA recovery yield were calculated and presented as responses for each run. The optimum conditions were selected based on the criteria of attaining maximum TPA recovery (η_{TPA}), and wet experiments were carried out in duplicate.

Determination of Green Chemistry Metrics. Atom economy (AE) and E-factor were determined according to eqs 3 and 4, respectively, where $Mw_{\text{desired product}}$ and $Mw_{\text{all species}}$ represents the molecular weight of TPA or FDCA and all reactants in the overall reaction, respectively.

$$\text{AE (\%)} = \frac{Mw_{\text{desired product}}}{Mw_{\text{all species}}} \times 100 \tag{3}$$

$$\text{E-factor} = \frac{\text{total mass of waste}}{\text{total mass of product}} \tag{4}$$

Characterization. *Attenuated Total Reflectance Fourier Transform Infrared (ATR FTIR).* ATR FTIR spectra were obtained using a PARAGON 1000 PerkinElmer FTIR spectrometer equipped with a single-horizontal Golden Gate ATR cell, recorded within the range of 500−4000 cm^{-1} at a resolution of 8 cm^{-1}.

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR). NMR spectra were recorded using a Bruker AMX 300 spectrometer, operating at 300.13 and 75.47 MHz, respectively. The chemical shift (δ) is expressed in parts per million (ppm), downfield from tetramethylsilane. DMSO-d_6 or $CDCl_3$ were used to dissolve the samples. Maleic acid was used as the internal standard to perform quantitative ^{1}H NMR analyses (Figures S7 and S8), and the purity of the recovered monomers was calculated following eq 5, where m represents the mass of the weighted sample (recovered TPA of FDCA), I the integral value of the selected resonance ($H_{2,3,5,6}$ viz. $\delta \approx 8.0$ ppm for TPA, $H_{3,4}$ viz. $\delta \approx 7.3$ ppm for FDCA, and $H_{2',3'}$ viz. $\delta \approx 6.3$ ppm for maleic acid), Mw the molecular weight of the species, N the number of protons represented by the selected peak ($N = 4$ for TPA, $N = 2$ for FDCA, and $N = 2$ for maleic acid), P the purity, and subscript IS for internal standard.

$$\%\ \text{purity} = \frac{m_{\text{IS}}}{m_{\text{monomer}}} \cdot \frac{I_{\text{aromatic protons, monomer}}}{I_{H_{2\prime,3\prime},\text{IS}}} \cdot \frac{Mw_{\text{monomer}}}{Mw_{\text{IS}}} \cdot \frac{N_{H_{2\prime,3\prime},\text{IS}}}{N_{\text{aromatic protons, monomer}}} \cdot P_{\text{IS}} \tag{5}$$

^{13}C Cross-Polarization−Magic-Angle Spinning (CP-MAS) NMR. ^{13}C CP-MAS NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer equipped with a Bruker 400 MHz (9.4 T), UltraShieldTM, wide-bore magnet, and a 4 mm, 9 kHz, with respect to MAS, probe. The chemical shift (δ) is expressed in parts per million (ppm) downfield from glycine (used as the internal standard).

Elemental Analyses (C and H). Analyses were carried out in duplicate using a LECO TruSpec analyzer by infrared absorption, with the combustion furnace operating at 1075 °C and afterburner operating at 850 °C.

Differential Scanning Calorimetry (DSC). DSC was carried out in Netzsch Caliris 300 equipment, and the thermograms were recorded following a heating rate of 10 °C min^{-1} and cooling of 50 °C min^{-1} under a nitrogen flow of 40 mL min^{-1} in a temperature range from 25 to 300 °C.

Intrinsic Viscosity Measurements. Measurements were carried out on an Ubbelohde type viscometer maintained at 25 °C using a 1:1 mixture of phenol/TCE (w/w). rPET and rPEF samples were dissolved in the solvent mixture (0.1 g per 20 mL) and the intrinsic viscosity was determined by the ratio of specific viscosity and sample solution concentration following eq 6, where [η] represents the intrinsic viscosity, η_{sp} represents the specific viscosity, C represents the solution concentration, and t_0 and t_1 are the solvent mixture elution time of the solvent mixture and polyester solution, respectively.

$$[\eta]\ (\text{dLg}^{-1}) = \eta_{\text{sp}} \cdot C, \text{ where } \eta_{\text{sp}} = \frac{t_1 - t_0}{t_0} \tag{6}$$

Reuse of ES Reaction Media. In order to develop a more sustainable depolymerization process, 10 successive cycles of the hydrolysis reaction using the same ES were applied. In each cycle, the ES was separated from the reaction mixture and used in the next cycle with the addition of water and sodium carbonate under optimal conditions, until a relevant loss in catalytic activity was observed.

Discrete *Ab Initio* Calculations. Geometry optimizations and vibrational frequency calculations of the BHET and the phenolic compounds (thymol and carvacrol), as model compounds, were computed using the Gaussian 16 software at the M06-2X level of theory with the 6-311+G(d,p) basis set.[44] All of the optimized structures were found to be real minima, with no imaginary frequencies. Molecular geometries were rendered by using the GaussView6 software. The energy values mentioned throughout the text refer to the electronic energy without a zero-point correction.

RESULTS AND DISCUSSION

ES Screening. In the quest for *greener* approaches to advanced chemical recycling of overused polyesters such as PET and their spotlighted biobased alternative, PEF, in this work it was explored, for the first time, the full potential of ES based on natural-occurring phenols with safe design and low viscosities to safeguard good heat and mass transport, namely carvacrol, thymol, and eugenol (Figure 1). Besides their renewable origin, their known hydrophobic nature,[45,46] favoring interacting with PET or PEF, also supported their choice.[46]

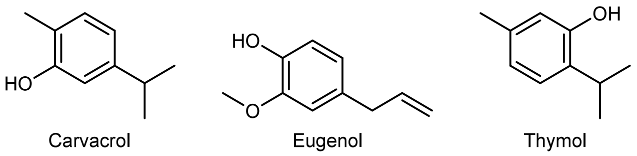


Figure 1. Chemical structures of the selected HBDs.

The screening of the best ES based on choline chloride as the HBA and carvacrol, thymol, or eugenol as the HBD to prompt the depolymerization reaction of polyesters was performed following the general reactional scheme below (Scheme 1), under a temperature of 180 °C for a period of 2 h with PET, Na_2CO_3, water, and ES at a 1:1:1:15 ratio (wt.), based on our previous experience.[28]

Considering that the primary objective at this initial step was to evaluate the capability of the biobased ES to enable the hydrolysis of polyesters, the experiments were carried out using only PET as a model system and thereafter extended to PEF. Results (Table 1) revealed the successful depolymerization of postconsumer PET, reaching weight loss percentages as high as *ca.* 100% when using ChCl:Eug or ChCl:Tym as ES, and TPA was isolated in 91.7% yield for the latter.

Nevertheless, in the case ChCl:Car ES substantially lower results were achieved (*ca.* 50% weight weight$_{\text{loss,PET}}$ and η_{TPA}). To shed some light into the observed differences in the catalytic capacity between the two phenolic isomers, namely

Scheme 1. Reaction Scheme for the Hydrolysis of PET and PEF

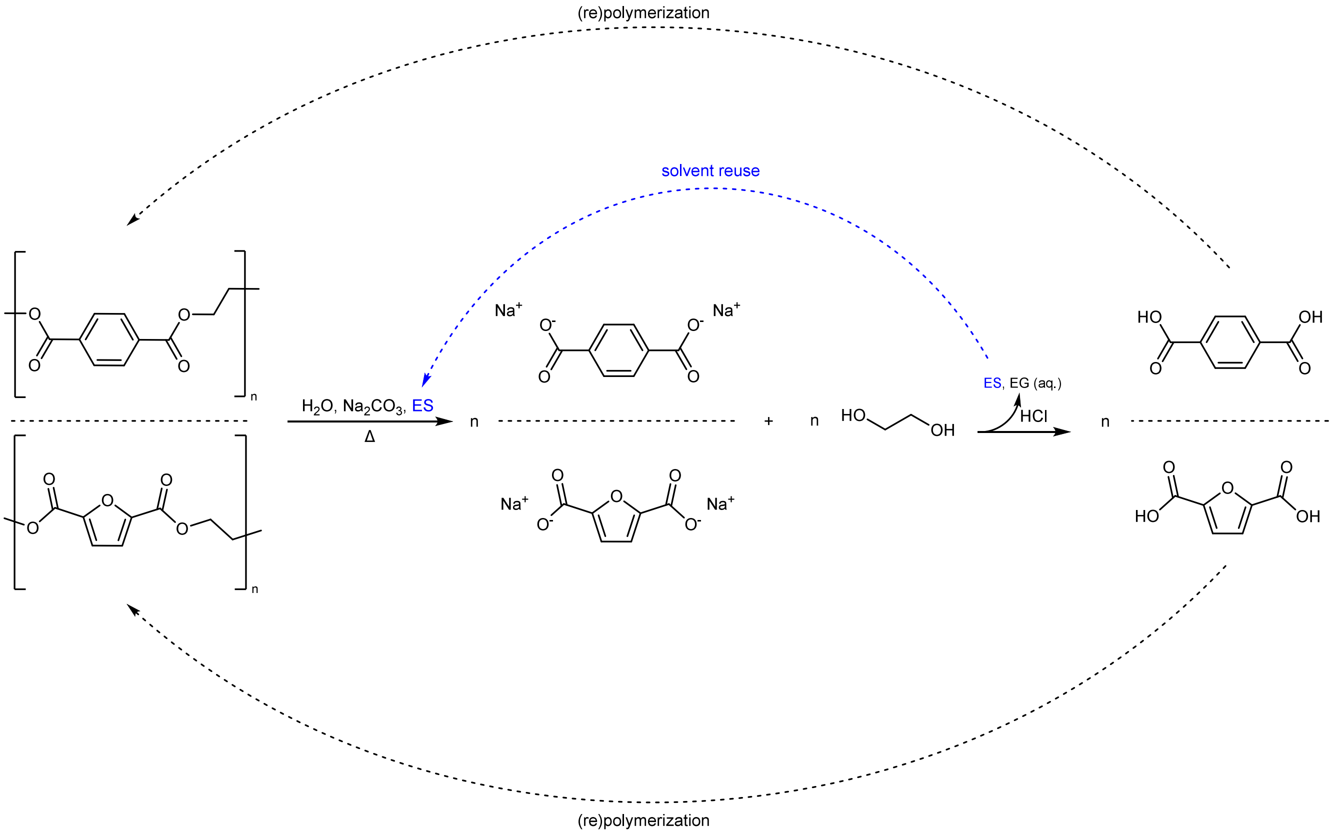


Table 1. Results of the Screening Efficiency of ES for PET Hydrolysis under the Standard Reaction Conditions

	$weight_{loss,PET}$ (%)	η_{TPA} (%)
ChCl:Car	50.9	50.3
ChCl:Eug	100	82.6
ChCl:Thy	99.2	91.7

carvacrol or thymol, an initial computational study, laid on the foundations of the basilar work of Atallah et al.,[27,47] was conducted to study the potential interactions established between each phenolic compound and BHET. Preliminary results show that for any of the evaluated conformations, the interaction energies of carvacrol−BHET are higher than the interaction energies of thymol−BHET (Table S9 and Figure S15), which can be associated with the greater catalytic capacity of thymol over the isomer carvacrol when used as the HBD component of the eutectic solvent.[48]

The chemical nature of the hydrolysis reaction product isolated from these preliminary depolymerization essays was confirmed to be TPA based on ATR FTIR and NMR (^{1}H and ^{13}C) spectroscopic data (Figures S1−S3). The purity was also demonstrated through ^{1}H NMR as high as 97.0%. These features are also in accordance with the spectrum of available literature.[49,50]

The essential and synergetic role played by the combination of the individual components of the selected phenol-based ES, ChCl:Car, ChCl:Eug, and ChCl:Thy, sodium carbonate, and water in the hydrolysis of the model polyester was assessed. In this regard, experiments using only the HBA or the HBD ES component, with or without Na_2CO_3, as well as using only the ES, always in the presence of water, were conducted under the conditions of 180 °C for 2 h.

Results show the essential need to have the triple component system, ES, Na_2CO_3, and H_2O, to prompt hydrolysis. Indeed, when exclusively using an aqueous solution of ChCl, with or without Na_2CO_3, no depolymerization of pcPET occurred. A similar result was observed for Car, Eug, or Thy, although they dissolved pcPET, it still could be fully recovered by a salting out approach. Additionally, the runs using only ES in the presence of water were not able to dissolve or depolymerize pcPET. Overall, these results confirm the essential role played by combining natural occurring phenol-based ESs, sodium carbonate, and water in the hydrolytic depolymerization of pcPET.

Optimization of PET Depolymerization Conditions. In this work, the hydrolysis depolymerization reaction conditions were optimized to efficiently catalyze the depolymerization reaction of abundant postconsumed PET into the starting building-block monomers using a Box−Wilson Central Composite Design (CCD) methodology, and then the optimum conditions were extrapolated to biobased PEF recycling (Scheme 1). Only Eug- and Thy-based systems were considered since the previous ES screening results indicated a substantially lower efficiency for carvacrol-based ones.

The reaction time and temperature were considered as independent variables, and PET weight loss and the TPA depolymerization yield are critical factors to evaluate the reaction and recycling performance of the studied approach. After each run, these factors ($weight_{loss,PET}$ and η_{TPA}) were calculated and presented as contour plots, as depicted in Figure 2. The complete data and statistical analyses for these

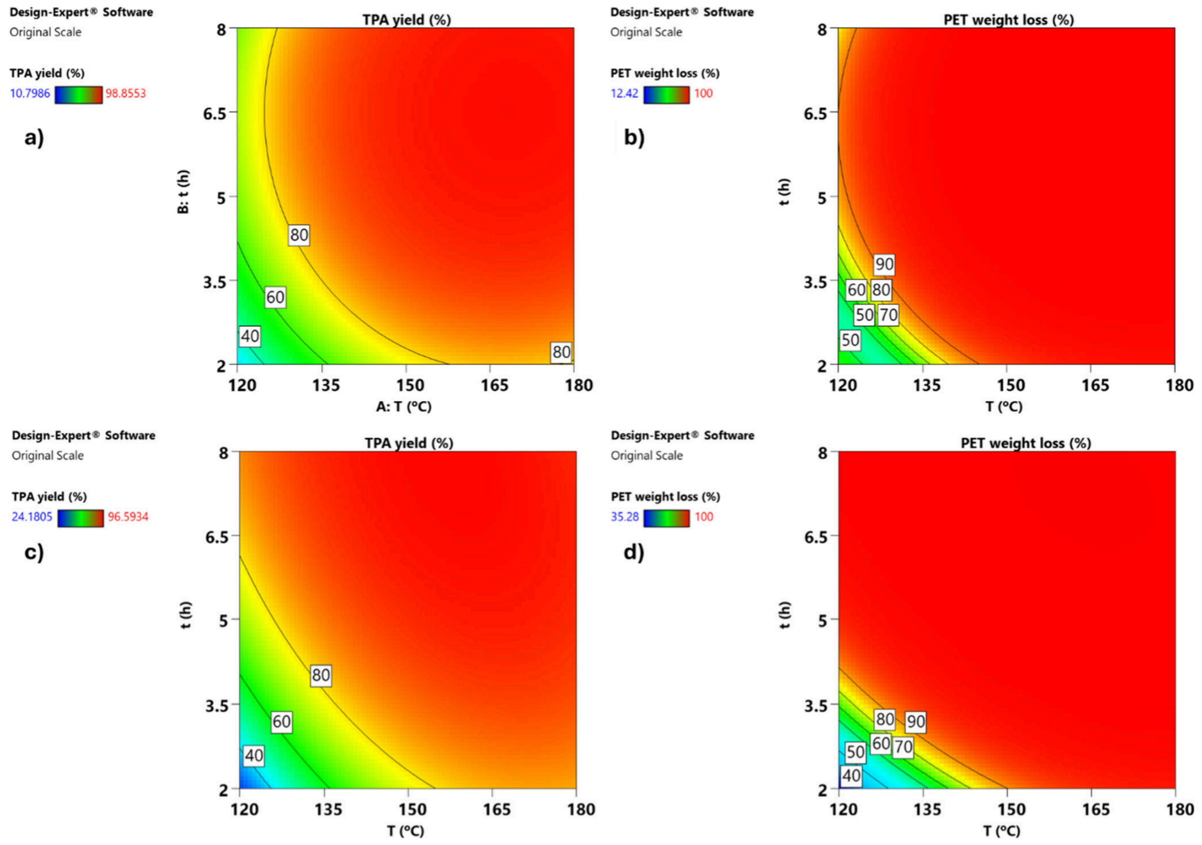


Figure 2. Contour plot of the effects of temperature and reaction time on TPA yield (a) and PET weight loss (b) for the Eug-based process and on TPA yield (c) and PET weight loss (d) for the Thy-based process.

experimental runs (Tables S1−S4 and Figure S11) and the respective response surfaces (Figure S12) are available in the Supporting Information.

Observing the plots of Figure 2, it becomes evident that for the Thy-based systems, the regions where both η_{TPA} and weight$_{\text{loss,PET}}$ exceed 90% emerges at relatively slightly lower values of T and shorter reaction times t, compared with Eug-based ones. Nonetheless, both Eug- and Thy-based ES depolymerization systems achieve complete weight$_{\text{loss,PET}}$ and over 90% η_{TPA} under predicted optimal conditions (Table 2), indicating the high potential of these ES-based depolymerization systems. Wet experiment results confirmed the trends observed in the predicted optimal values and indicate that both selected ES based on eugenol and thymol moieties are effective to mediate hydrolysis reactions under the experimental conditions.

Table 2. Predicted and Experimental Results under Optimal Conditions of Temperature and Time of Reaction for the Biobased Alkaline PET Depolymerization Experiments[a]

			predicted		experimental	
system	T (°C)	t (h)	$W_{\text{loss,PET}}$ (%)	η_{TPA} (%)	$W_{\text{loss,PET}}$ (%)	η_{TPA} (%)
ChCl:Eug	148	4.3	100	91	100	97.5 (±2.2)
ChCl:Thy	147	4.5	100	93	100	94.7 (±1.4)

[a] Standard deviations are presented in parentheses.

After determining the optimal depolymerization time and temperature conditions, a subsequent set of experiments was conducted to refine the base solid:solid ($w_{\text{base}}/w_{\text{PET}}$) and ES liquid:solid ($v_{\text{ES}}/w_{\text{PET}}$) ratios in relation to the added amount of PET, while still maximizing PET weight loss and TPA isolation yield, as maximizing the polyester weight loss amount in the process can reduce the overall cost and contribute to a more sustainable approach by reducing the consumption of materials and potentially also minimizing process waste. Therefore, optimizing these parameters would not only enhance the depolymerization process but also have broader implications for cost-effectiveness, *greenness*, and environmental impact of the novel approach.

An important result from the analysis of the statistical significance of the factors reveals that the volume of ES in relation to the weight of PET does not exert a significant influence on the output variables (Tables S5 and S8). Nevertheless, considering the significant nature of the models, all terms were retained to ensure an optimized fit and develop an empirical model capable of accurately predicting the response under given conditions. Contour plots depicting the TPA yield and PET weight loss were generated to visually represent these effects and are illustrated in Figure 3. The respective experimental data and response surfaces are available as supporting materials (Figures S13 and S14).

According to the response surfaces, it can be observed that variations in the base solid:solid and ES liquid:solid ratios greatly influence the depolymerization of PET when employing different HBDs. Importantly, for a fixed base:PET weight ratio, an increase in the added amount of ES promotes the depolymerization reaction when utilizing thymol as the HBD. In contrast, when eugenol is employed as the HBD, an increase in the amount of ES added to the reaction media hinders the depolymerization process, decreasing the weight$_{\text{loss,PET}}$ and

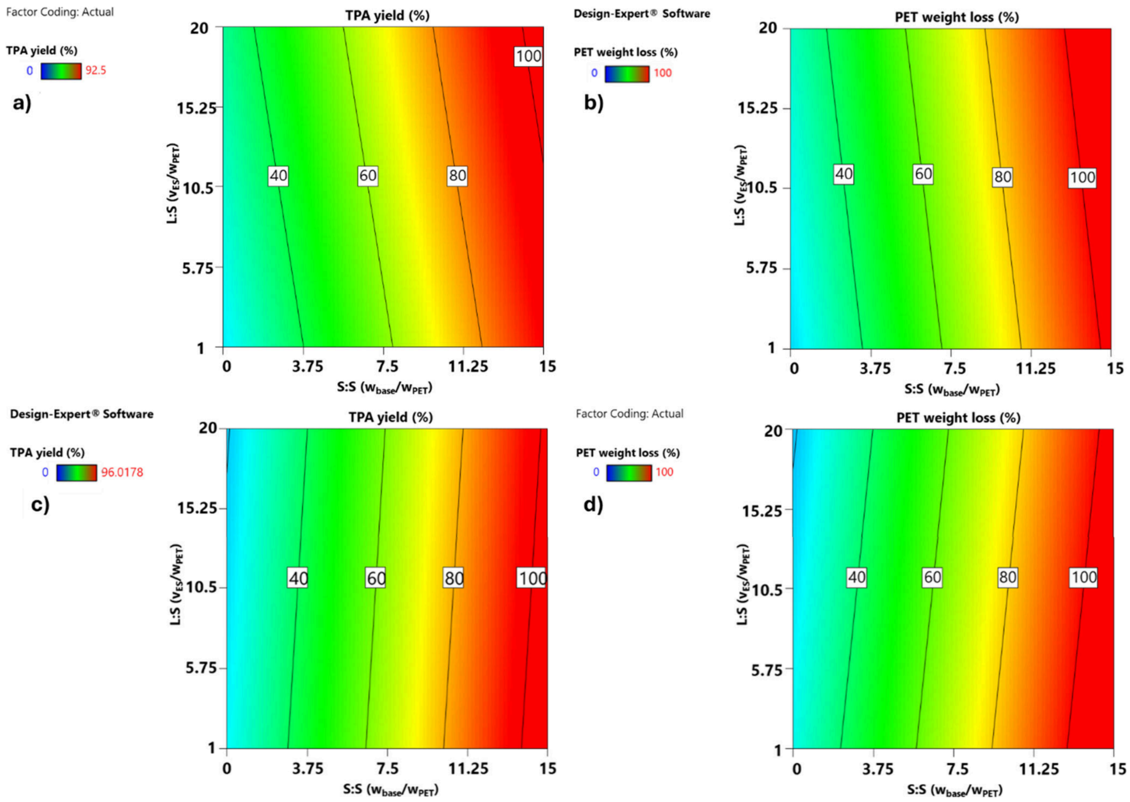


Figure 3. Contour plot of the effects of base and ES on TPA yield (a) and PET weight loss (b) for the Eug-based process and on TPA yield (c) and PET weight loss (d) for the Thy-based process.

Table 3. Predicted and Experimental Results under Optimal Conditions of the Solid:Solid Ratio (w_{base}/w_{PET}) and Liquid:Solid Ratio (v_{ES}/w_{PET}) for the Biobased Alkaline PET Depolymerization Experiments

			predicted		experimental	
system	w_{base}/w_{PET}	v_{ES}/w_{PET}	$W_{loss,PET}$ (%)	η_{TPA} (%)	$W_{loss,PET}$ (%)	η_{TPA} (%)
ChCl:Eug	1.23	13	94	88	96.8 (±4.1)	88.6 (±1.1)
ChCl:Thy	1.24	4	97	92	95.8 (±3.6)	91.8 (±0.3)

η_{TPA}. This indicates that a lower volume of ES is needed in the case of Thy:ChCl. Validation experiments were also performed to corroborate the optimal conditions determined previously.

A duplicate set of runs was carried out, and the predicted optimal values, as well as the experimental validation results and corresponding standard deviations, are presented in Table 3.

Upon initial examination, the predicted optimal conditions for the two systems seemed closely aligned. However, it is noteworthy that achieving comparable results would require the eugenol-based system to employ more than three times the quantity of ES in comparison with the thymol-based system.

Based on the predicted results, it was expected that the ChCl:Eug system would yield an η_{TPA} of 88% and a weight$_{loss,PET}$ of 94%. The actual experimental results yielded an η_{TPA} of 88.6% and a weight$_{loss,PET}$ of 96.8%. For the ChCl:Thy system, the actual experimental values η_{TPA} equal to 91.8% and a weight$_{loss,PET}$ of 95.8% compare with the predicted η_{TPA} of 92% and a weight$_{loss,PET}$ of 97%. From these data, it can be concluded that the actual experimental results closely align with the predicted optimal values. Both the ChCl:Eug and ChCl:Thy systems demonstrated high η_{TPA} and weight$_{loss,PET}$ values, indicating the effectiveness of these systems in depolymerizing PET.

These results further support the earlier conclusions regarding thymol-based systems in terms of higher η_{TPA}. Additionally, the experimental data demonstrate the potential for achieving even higher weight$_{loss,PET}$ and η_{TPA} values while reducing the amount of reagents required to achieve those results, implying a potential reduction in process waste, highlighting the potential cost-effectiveness, *greenness*, and environmental benefits of the biobased ES alkaline hydrolytic depolymerization approach with further optimization.

Depolymerization of PEF. Taking into account the imminent market introduction of biobased PEF,[6] there is an even more pressing need to breakthrough recycling approaches suitable for different polyesters. Nevertheless, to the best of our knowledge, there is no report on PEF hydrolytic depolymerization; therefore, in this study, the optimal conditions developed for PET using either thymol or eugenol were extended to PEF. Them being, briefly, a 1:1.23:1:13 ratio (*w*:*w*:*w*:*v*, PEF:Na_2CO_3:H_2O:ES) at 148 °C and 4.3 h of reaction for the eugenol system, and 1:1.24:1:4 ratio (*w*:*w*:*w*:*v*, PEF:Na_2CO_3:H_2O:ES) at 147 °C and 4.5 h of reaction for the thymol-based one.

The isolated solid material was confirmed to be FDCA. In fact, the ATR FTIR spectra of the isolated solids, shown in Figure 4, exhibited the typical FDCA features, *viz.*: a very

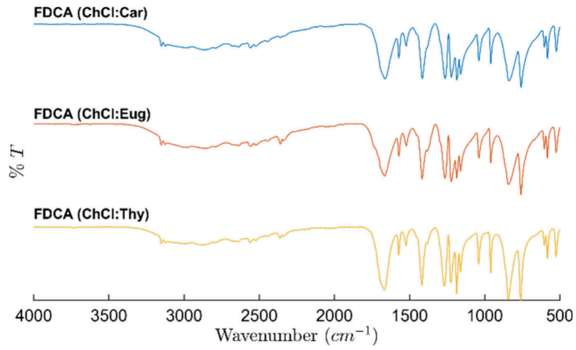


Figure 4. ATR FTIR spectra of the FDCA obtained after the depolymerization reactions mediated by ChCl:Car/Na_2CO_3, ChCl:Eug/Na_2CO_3, and ChCl:Thy/Na_2CO_3 systems.

intense and broad band centered around 2750 cm^{-1}, ascribed to the O−H stretching typical of carboxylic acids, superimposed to the CH stretching modes of the benzyl group; a very intense band near 1672 cm^{-1}, arising from the C=O stretching vibration of carboxylic acids; and the CO−H bending vibration mode around 1420, also typical of carboxylic acid groups. These features are also in accordance with the spectrum of available literature.[51]

The ^{1}H NMR spectroscopic analyses (Figure 5) unambiguously corroborated the previous FTIR features and the purity

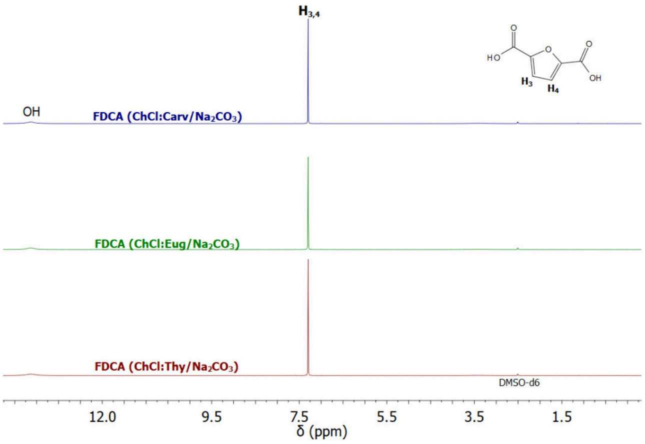


Figure 5. ^{1}H NMR spectra of the recycled FDCA obtained after the depolymerization essays conducted with ChCl:Car/Na_2CO_3, ChCl:Eug/Na_2CO_3, and ChCl:Thy/Na_2CO_3.

of the attained product (94.5%, determined by ^{1}H NMR), *viz.*: $\delta \approx 7.30$ ppm, arising from $H_{3,4}$ furanic protons and $\delta \approx 13.62$ ppm, assigned to COOH proton resonance.[28] The ^{13}C NMR spectrum also corroborated the chemical nature of FDCA and agreed with a high purity monomer (Figure S4).

Alkaline hydrolysis experiments conducted under the optimal conditions of *T* and *t* for PEF followed the predicted values reaching a 100% weight loss for the two ES systems studied (Table 4), as already observed for PET. In terms of isolation yield, the *in silico* results were also in agreement with the experimental ones. FDCA monomer was isolated with a η_{FDCA} value as high as 82%. Importantly, similarly to PET, the Thy-based ES enabled slightly higher weight$_{loss,PEF}$ and η_{FDCA}.

Regarding the results for the optimal conditions for solid:solid ratio (w_{base}/w_{PET}) and liquid:solid ratio (v_{ES}/w_{PET}), summarized in Table 5, the experimental weight$_{loss,PEF}$ values were 100% for both systems, suggesting that the depolymerization conditions optimized for PET are also suitable for PEF. This also enables us to hypothesize that the optimum conditions optimized here could easily serve as a benchmark to investigate the feasibility of depolymerizing other aromatic polyesters, including biobased ones.

Table 4. Experimental Results under Optimal Conditions of Temperature and Time of Reaction for the Biobased Alkaline PEF Depolymerization Experiments

system	*T* (°C)	*t* (h)	$W_{loss,PEF}$ (%)	η_{FDCA} (%)
ChCl:Eug	148	4.3	100	70.8 (±2.1)
ChCl:Thy	147	4.5	100	82.1 (±0.4)

Table 5. Experimental Results under Optimal Conditions of the Solid:Solid Ratio (w_{base}/w_{PET}) and Liquid:Solid Ratio (v_{ES}/w_{PET}) for the Biobased Alkaline PEF Depolymerization Experiments

system	w_{base}/w_{PEF}	v_{ES}/w_{PEF}	$W_{loss,PEF}$ (%)	η_{FDCA} (%)
ChCl:Eug	1.23	13	100	87.4 (±1.2)
ChCl:Thy	1.24	4	100	81.3 (±0.9)

Interestingly, the eugenol-based system, under optimal conditions of solid:solid ratio (w_{base}/w_{PET}) and liquid:solid ratio (v_{ES}/w_{PET}), shows a slightly higher η_{FDCA} than for ChCl:Thy mediated hydrolytic depolymerization (87.4 vs 81.3%). However, this entails employing more than three times the quantity of ES in comparison to the thymol-based system, which would impact the process *greenness*, increasing the environmental impact and ultimately leading to less cost-effectiveness. Thus, these results further corroborate the earlier conclusions regarding thymol-based systems in terms of overall enhanced prospects.

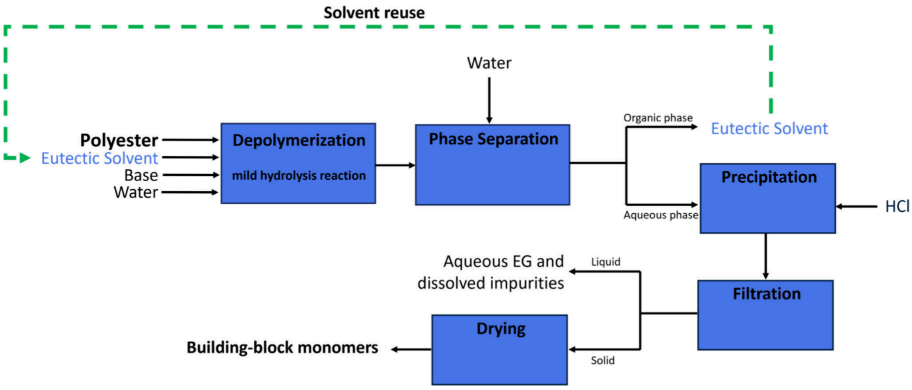
Eutectic Solvent Reuse. The reuse of the eutectic solvents selected is of upmost importance for the *greenness* of the process herein proposed, in addition to its efficiency and safe design. Therefore, the reuse of ChCl:Thy reaction media was assessed for the depolymerization of PEF by recovering the ES (Scheme 2), as previously described, and using it in subsequent reactions under optimal conditions, 147 and 148 °C for 4.7 and 4.5 h for the thymol and eugenol systems, respectively, adding the optimal amount of base in each run, 1.24 and 1.23 (w_{base}/w_{PEF}) for thymol and eugenol, respectively. The reuse was accessed along 10 cycles, and the resulting η_{FDCA} is plotted against the number of cycles (Figure 6).

The results show that both systems can be reused up to seven times with an η_{FDCA} of over 80%, and after the eighth cycle this variable, although it decreases, is still 72.4% and 82.6% for ChCl:Thy and ChCl:Eug, respectively.

These results clearly highlight the potential to reuse the ES several times, minimizing the solvent consumption and improving cost-effectiveness and *greenness* of the process. Furthermore, the aqueous effluent from the separation and purification steps can also be reused in the same process after being neutralized, which means that only the base needs to be replenished in each cycle.

Green Chemistry Metrics. After gaining insight into the optimal conditions, the green chemistry metrics, atom economy, and E-factor were determined. These important concepts were assessed to confirm the *greenness*[52] of the PEF and PET recycling strategy breakthrough in this study.

Scheme 2. Generic Process Flow for the Mild Hydrolytic Depolymerization of Polyester and Solvent Reuse



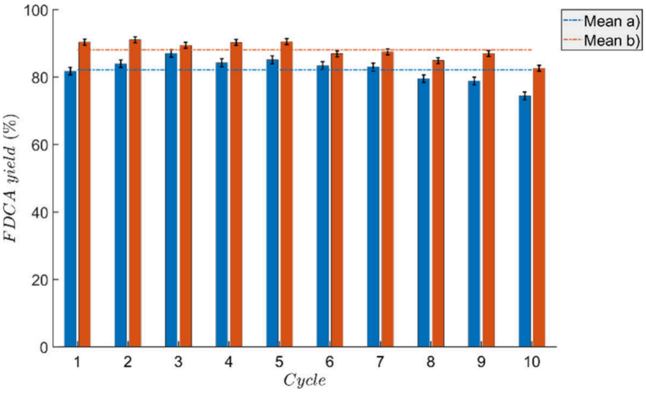


Figure 6. FDCA yield as a function of the number of (a) ChCl:Thy (blue) and (b) ChCl:Eug (orange) ES reuse cycles.

When TPA is the desired product, the AE amounts to 50.24%, compared to 48.69% when the calculations are performed for FDCA. These results show that the conversion efficiency of the PET and PEF hydrolysis is, as expected, almost equivalent. When compared to well established processes, these reactions still show a moderately efficient AE. However, AE does not give any information about reaction yield, selectivity, or the nature of the waste.

Roger A. Sheldon's E-factor can provide a more complete vision of the process and was therefore calculated. Water is not often included in the E-factor calculations;[53] however, to show a more accurate picture of the processes herein initiated, the calculations were also performed considering the water used in the purification step as waste, henceforth denoted the 'complete E-factor'. In the present work, it is considered total waste over seven cycles of usage, based on the ES recyclability tests described previously. For the best performing ES, ChCl:Thy, under optimal conditions, the E-factor amounts to *ca.* 6 and the complete E-factor amounts to approximately 11 for the recovery of TPA and marginally higher to FDCA isolation (*ca.* 7 for the E-factor and 13 for the complete E-factor). More importantly, the obtained complete E-factors align with those observed in well-established processes across various industries, particularly on the lower limit of the fine chemicals, where E-factors typically range from 5 to 50.[53]

Proof-of-Concept: PET and PEF Syntheses from Recycled Monomers. To foster the effective *greener* recycling of polyesters, such as PET and PEF, the use of the recovered TPA and FDCA monomers in polymer synthesis was also assessed in this work. Both PET and PEF were successfully synthesized through a well-established polyesterification procedure[28,35−42] and isolated in a yield as high as 89.4%. The spectroscopic characterization caried out using ATR FTIR and ^{13}C CP-MAS NMR (Figures S5 and S6) confirmed the rPET and rPEF chemical nature and were in accordance with the literature.[50,54] DSC analyses moreover corroborated these findings, where the obtained T_g appeared at 74.8 and 79.0 °C and the T_m at 253.2 and 207.7 °C for PET and PEF, respectively, which is closely aligned with literature data for these polymers.[10,14] The complete thermograms are available as Supporting Information (Figures S9 and S10). Furthermore, the high intrinsic viscosity values obtained (0.35 and 0.69 for rPET and rPEF, respectively) further support the high purity of the recycled monomers and their suitability for polymer synthesis, showcasing the success of the herein proposed advanced *greener* recycling approach.

CONCLUSIONS

The present study has made relevant contributions to the breakthrough of a more sustainable and solvent-efficient hydrolysis process suitable for both PET and PEF, verifying the versatility of the process for different polyesters.

Exceptional yields exceeding 90% for TPA and 80% for FDCA, accompanied by complete weight loss of original polymer and high purity (97.0% and 94.5% for TPA and FDCA, respectively), have been achieved, with empirical models providing valuable insights into the critical variables and paving the way for advancements in chemical recycling.

The reuse of the ES was thoroughly assessed, demonstrating its potential for reuse in multiple cycles of depolymerization. The ES showed consistent performance and maintained its catalytic activity throughout seven cycles, contributing to the *greenness* of the process.

Additionally in line with the principles of green chemistry, various metrics were determined to evaluate the environmental impact of the hydrolysis processes. The results revealed that the processes exhibited favorable green chemistry metrics, achieving an E-factor of *ca.* 6−7 and a complete E-factor of 11−13, achieving results comparable to those observed on the lower limit of the fine chemicals, where E-factors typically range from 5 to 50.[53] This underscores the potential of the proposed methods for sustainable and environmentally conscious chemical recycling practices.

Moreover, a notable milestone was achieved in this study by proving the feasibility of repolymerizing the obtained monomers from the hydrolysis process, thereby completing the recycling loop. This accomplishment marks a crucial step toward a closed-loop system where PET and PEF can be efficiently recycled into high-quality polymers for various applications.

Overall, this study not only achieved remarkable yields and purity in the depolymerization products of PET and PEF but also shed light on the efficient hydrolysis of the polyester family of polymers, contributing to scientific progress in chemical recycling. Future research efforts would benefit from scaling up these findings and exploring their practical application in various industrial settings, facilitating the transition toward a green and more sustainable circular economy.

■ ASSOCIATED CONTENT

Data Availability Statement

All data generated or analyzed during this study are included in this article (and its Supporting Information).

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c09545.

> Additional experimental details, including FTIR and ^{1}H and ^{13}C NMR characterization figures of depolymerization products (Figures S1−S8); ^{13}C CP-MAS NMR spectra and DSC thermogram of repolymerization products (Figures S9−S10); statistical analyses and 3D surface plots of response surface analysis of the DoE of PET depolymerization reactions (Tables S1−S8 and Figures S11−S14); and DFT calculations and evaluation of carvacrol−PET and thymol−PET interactions (Table S9 and Figure S15) (PDF)

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A.F.S. contributed to the conceptualization, investigation, supervision, validation, and writing and reviewing the original draft. A.J.D.S. contributed to the supervision, validation, and writing and reviewing of the original draft. P.R.C. contributed to the data validation and curation. V.P. contributed to practical experimenting, data curation, investigation, and writing and reviewing the original draft. S.V.P. contributed to the formal analysis. All authors have read and contributed to the reviewing of the original draft.

Notes

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