

Article

Multifactor Optimization of Solvolytic Recycling of Polyethylene Terephthalate in Designer Deep Eutectic Solvents

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Abstract

A circular economy for polyethylene terephthalate (PET) aims to achieve complete material recirculation and reduce dependence on fossil-based feedstocks. Among recycling strategies, depolymerization offers the greatest potential for true circularity. This work investigates deep eutectic solvent (DES)-assisted PET depolymerization using a tetrabutylammonium bromide/sulfolane (TBABr/Sulf) system. A four-factor, three-level Box–Behnken design was employed, where reaction time, NaOH concentration, PET/solvent ratio, and water content were selected as independent variables, with PET weight loss as the response. The optimized conditions of 35 min reaction time, 5.9 wt% NaOH, a PET/solvent ratio (g/g) of 0.061, and a 1:1 water-to-DES ratio achieved 97% PET depolymerization and 93.8% TPA recovery. The process achieved a relatively low PET/DES (g/g) utilization ratio of 0.12 and required at least 40% less NaOH than other DES-based alkaline hydrolysis reported in the literature. The identity and quality of the recovered TPA were confirmed by FTIR, NMR, DSC, and elemental analysis. Under microwave-assisted conditions, TBABr/Sulf was successfully reused over three consecutive cycles while maintaining 100% depolymerization efficiency with consistent TPA quality. Collectively, these results demonstrate the technical potential of the proposed DES-assisted PET depolymerization process, particularly in terms of reduced solvent and alkaline requirements, shortened reaction time, and demonstrated solvent recyclability.

Keywords: Box–Behnken design; deep eutectic solvents; depolymerization; optimization; solvent recovery



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1. Introduction

Plastics have become indispensable materials across modern society because of their versatility, durability, and relatively low production cost [1]. Current advancements endow plastics with many economic and societal advantages; however, post-consumer use becomes a burden mostly due to irresponsible handling. The use of alternative plastics requires the incorporation of plastic additives to enhance strength, and this also complicates end-of-life management [2]. Consequently, current strategies increasingly focus on maintaining the value of plastics within the production cycle through circular economy

approaches, in which materials are retained in use for as long as possible while minimizing waste generation and resource depletion [3,4]. In this context, effective end-of-life recycling technologies are essential for establishing a more circular plastics economy.

The goal of plastic circularity is to ensure that (1) plastic waste and pollution are reduced through product design, (2) resources and products in use are retained, and (3) natural systems are preserved and regenerated [5,6]. One notable approach to achieving circularity is via recycling. Plastic recycling extends into four main types, which are primary or re-extrusion, secondary or mechanical recycling, tertiary or chemical recycling, and quaternary or energy recovery through incineration [7]. Among these approaches, mechanical recycling remains the most established route but is constrained by contamination, polymer degradation, and deterioration of material properties after repeated processing [8–10]. For polyethylene terephthalate (PET), these limitations can result in progressive downcycling and eventual loss of material value. Chemical recycling via depolymerization has therefore attracted increasing attention because it enables material recovery that is comparable to its virgin grade, which is advantageous in longer-cycle retention [11,12].

PET can be chemically depolymerized through several routes, including glycolysis, methanolysis, aminolysis, and hydrolysis. Among these, glycolysis is the most extensively researched and commercially viable route, yielding bis(2-hydroxyethyl) terephthalate (BHET) as a key intermediate [13]. Glycolysis has historically dominated industrial and academic efforts due to its favorable processing conditions [14–16], whereas conventional hydrolysis has faced limitations due to harsh reaction requirements, high energy demand, and issues surrounding catalyst recovery and stoichiometric acid consumption.

Nevertheless, hydrolysis offers a broader market opportunity due to the versatility of the monomer terephthalic acid (TPA) produced. TPA serves as the primary precursor for most PET-based materials such as packaging and textiles, with additional applications in polybutylene terephthalate (PBT) [17] and polyamide plastics [18]. Beyond polymer synthesis, TPA finds utility in several specialized applications including as an organic ligand for metal–organic framework (MOF) synthesis [15] and a raw material for plasticizer production [19]. To leverage these advantages, recent research has increasingly focused on developing innovative, mild hydrolysis strategies to make this route energy-efficient and competitive with glycolysis.

Recent advances have identified deep eutectic solvents (DESs) as a promising and efficient medium for depolymerization of PET [20–24], and they have been utilized in various branches of depolymerization [25–27]. DESs are typically formed by combining two or more components whose intermolecular interactions result in a pronounced depression of the melting point relative to the individual components [28]. Historically their formation was understood to be driven primarily by a dense network of hydrogen bonding between a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD); however, subsequent research has demonstrated that non-hydrogen bonding interactions can also dictate DES behavior. Depending on the chosen constituents, forces such as ion–dipole interactions, ionic forces, complexation, and charge delocalization can assist in the formation of DESs [29,30].

The increasing adoption of DESs in recent processes is primarily due to their ability to be tailored to be used in different types of processes. This is then complemented by their simple preparation process, high stability under ambient conditions, lower cost compared with many ionic-liquid-based designer solvents, and potential for recovery and reuse [31].

For the hydrolytic depolymerization of PET, DESs have been investigated primarily as dissolution media and reaction media to facilitate polymer swelling, enhance mass transfer, and promote the accessibility of reactive species, thereby potentially reducing the severity of the depolymerization process [32,33]. The incorporation of DESs has demonstrated

potential for reducing processing requirements, including reaction temperature, time, and pressure, compared with some conventional hydrolysis systems. However, despite these advantages, the application of DESs in PET hydrolytic depolymerization remains at an early stage, with relatively few studies reported to date [23]. Existing studies have primarily focused on achieving high PET conversion and monomer recovery, while limited attention has been given to the rational selection of DESs, optimization of solvent and reaction conditions, scalable process design, and solvent recovery and reuse [34–36]. These challenges highlight the need for continued development of DES-based hydrolysis systems to improve process efficiency and practical applicability.

Based on previous computational screening using COSMO-RS and subsequent preliminary experimental validation, a tetrabutylammonium bromide (TBABr)-sulfolane DES has been identified as a promising solvent for PET hydrolysis [37]. Building upon these findings, the present study aims to optimize the hydrolysis process using this DES in a four-factor, three-level Box–Behnken design (BBD). The investigated variables comprised reaction time, NaOH concentration, solvent-to-PET ratio, and water content (expressed as water-to-DES ratio), with PET weight loss selected as the response variable. The predictive capability of the developed model was verified by comparing predicted and experimental responses under the optimized conditions. The recovered TPA was subsequently characterized using various analytical techniques to verify its identity and quality. Finally, the optimized conditions obtained under conventional heating were adapted to microwave-assisted depolymerization, and the process was further extended to include DES recovery and reuse.

2. Materials and Methods

2.1. Materials

Post-consumer polyethylene terephthalate (PET) was sourced and prepared (1 cm × 1 cm flakes) according to the procedure reported in our previous work [37]. Tetrabutylammonium bromide (TBABr, 99%), sulfolane (Sulf, 99%), and DMSO-d₆ were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH) pellets and hydrochloric acid (HCl, 37%) were supplied by Chemiz (Shah Alam, Selangor, Malaysia) and RM Chemicals (Mississauga, ON, Canada), respectively. All reagents were analytical grade and used as received.

2.2. Preparation of Deep Eutectic Solvent (DES)

The TBABr/Sulfolane DES was synthesized in a 1:7 molar ratio by stirring at 150 rpm and 90 °C until a homogeneous liquid formed, following the method established earlier [37]. The DES was stored under dark, anhydrous conditions and used within one week.

2.3. PET Hydrolysis and TPA Recovery

The hydrolysis of PET was conducted by introducing PET flakes into a preheated mixture of the DES and aqueous NaOH. Throughout this manuscript, the combined mass of the DES and aqueous NaOH solution is referred to as the total solvent mass. The PET/solvent ratio can be described in Equation (1) below:

$$\text{PET/Solvent ratio} = \frac{\text{mass of PET (g)}}{\text{mass of DES (g) + aqueous NaOH solution}} \quad (1)$$

The reaction was then quenched with cold water upon completion to stop further reaction, and the resulting disodium terephthalate (Na₂TPA) was converted to TPA via acidification with 2 mL of HCl (37%). The precipitated TPA was then filtered, washed with

deionized water, and dried at 60 °C for 6 h. To quantify the process efficiency, the PET weight loss (%) and TPA recovery (%) were calculated using Equations (2) and (3):

$$\text{PET weight loss (\%)} = \frac{W_{p1} - W_{p2}}{W_{p1}} \times 100\% \quad (2)$$

$$\text{TPA recovery (\%)} = \frac{W_{\text{TPA}}}{\text{Theoretical TPA}} \times 100\% \quad (3)$$

where W_{p1} is the initial PET mass, W_{p2} is the residual PET mass, W_{TPA} is the mass of recovered TPA, and Theoretical TPA is calculated based on the stoichiometric relationship between the PET and TPA using their respective molecular weights.

2.4. Optimization Using Box–Behnken Design (BBD)

The chemical recycling of PET via hydrolysis was optimized using a four-factor, three-level Box–Behnken design (BBD) (Design Expert, version 12, Stat-Ease Inc., Minneapolis, MN, USA).

A total of 27 experimental runs, including three centre points, were carried out. The four independent variables studied were reaction time, NaOH concentration (wt%), water content, and PET/solvent ratio (g/g). All experiments were performed in duplicate to ensure reproducibility, and the average PET weight loss (%) was used as the response variable. The ranges for each variable, outlined in Table 1, were established based on preliminary data. Statistical analysis of the BBD data was performed using analysis of variance (ANOVA), with significance set at $p < 0.05$. PET depolymerization was optimized by maximizing PET weight loss.

Table 1. Variables and levels in Box–Behnken experimental design for PET depolymerization.

Independent Variables	Level		
	Lower	Middle	Upper
A: Time (min)	20	40	60
B: NaOH concentration (wt%)	2.5	5	7.5
^a C: PET/solvent ratio (g/g)	0.1	0.075	0.05
^b D: Water content (water to DES ratio)	1 (1:3)	2 (1:1)	3 (3:1)

^a Higher ratio corresponds to a lower solvent requirement. Thus, the lower experimental level represents a ratio of 0.10 g/g (least solvent), while the upper level represents 0.05 g/g (highest solvent loading). ^b Water content is expressed as the ratio of water to DES where 1 is 1:3, 2 is 1:1 and 3 is 3:1. This coding system was designed to maintain proper proportionality, where the 1:1 midpoint accurately reflects the geometric mean of the extreme ratios (1:3 and 3:1).

2.5. Hydrolysis of PET via Microwave Irradiation and DES Recycling Procedure

Microwave-assisted depolymerization was performed using an Anton Paar Monowave 450 microwave reactor (Anton Paar GmbH, Graz, Austria) equipped with a 30 mL wide-neck glass vial. Optimized quantities of TBABr/Sulf (1:7) DES, aqueous NaOH, and post-consumer PET flakes were introduced into the vial and stirred at 600 rpm. The reactor was operated in temperature-control mode. The microwave irradiation protocol featured a rapid ramp to the target temperature of 130 °C, a holding duration of 90 s and a controlled cooling phase to 50 °C prior to the removal of the vial. The 90 s duration was selected based on previous work [38] without further optimization.

The recyclability of the DES was facilitated by the phase-separation behaviour of the TBABr/Sulf system. Due to its dual-polarity nature, the DES remained partially immiscible with the Na₂TPA phase, forming a distinct upper layer that allowed for straightforward mechanical separation from the lower aqueous salt layer. In this section, two recycling strategies were evaluated. In approach 1, residual water was completely removed from

the DES via evaporation. This resulted in the crystallization of any Na_2TPA salt dissolved within the DES/water mixture. In approach 2, the separated DES layer was reused in subsequent reaction cycles without further addition of fresh DES. In both approaches, NaOH was replenished for each cycle to assist in stoichiometric conversion to Na_2TPA . For the final tested cycle, the residual liquid was diluted with distilled water and filtered to recover the fraction of TPA that remained soluble in the DES.

2.6. Analytical Characterizations

2.6.1. Characterization of DES

Density was measured at ambient temperature using a Mettler Toledo DM40 digital density meter (Mettler Toledo, Greifensee, Switzerland). Viscosity was determined with a HAAKE Viscotester VT550 (Thermo Fisher Scientific, Karlsruhe, Germany) at room temperature under constant shear rate conditions. Temperature was regulated using an external water bath, with viscosity measurements exhibiting an estimated uncertainty of 3–5% (in cP). The viscosity values were derived from the slope of the linear regression plot of shear stress (Pa) versus shear rate (s^{-1}). pH measurements of the DES were conducted at room temperature using a calibrated Milwaukee Mi 151 pH meter (Milwaukee Instruments, Gallarate, Italy), (typical deviation: ± 0.02 pH units). Calibration was performed with standard buffer solutions (pH 1.68, 4.01, 6.86, 7.01, 9.18, 10.01, and 12.45). The thermal stabilities of the DES were determined by STA under a nitrogen atmosphere using a PerkinElmer (STA-6000) instrument (PerkinElmer Inc., Waltham, MA, USA). The temperature ranged from 30 to 500 °C with a 10 °C/min, and a 20 mL/min nitrogen gas flow rate was used to determine the onset decomposition temperature. For structural characterization, freshly prepared DES samples were analyzed using a PerkinElmer Spectrum 400 FTIR-ATR spectrometer (PerkinElmer Inc., Waltham, MA, USA). Spectra were recorded from 400 to 4000 cm^{-1} at a resolution of 1 cm^{-1} .

2.6.2. Identity and Quality of Recovered TPA

The identity and quality of the recycled TPA obtained from PET depolymerization were confirmed using FTIR-ATR spectroscopy and nuclear magnetic resonance (NMR) analyses with the corresponding spectra compared directly with those of a commercial TPA. FTIR-ATR spectra were recorded on a PerkinElmer Spectrum 400 FTIR-ATR system, covering the wavenumber range of 4000–650 cm^{-1} .

NMR characterization was performed using a Bruker Avance III HD 400 MHz spectrometer (Bruker Corp., Billerica, MA, USA) for both ^1H and ^{13}C analyses.

Differential scanning calorimetry (DSC) was performed using a PerkinElmer instrument under a nitrogen atmosphere to analyze the thermal behavior of the recovered TPA. This value was then compared with reported literature values for commercial TPA. Briefly, samples weighing approximately 5–6 mg were sealed in aluminum pans and subjected to DSC scans. The temperature program involved heating from 30 to 500 °C at a rate of 10 °C/min, and then cooled back to 30 °C.

Elemental analysis (CHNS/O) was performed using a Thermo Scientific FlashSmart CHNS/O elemental analyser (Thermo Fisher Scientific, Waltham, MA, USA), and the measured elemental composition was compared with reported literature values for TPA.

3. Results

3.1. Properties of Synthesized DES

The general properties of TBABr/Sulf (1:7) measured at room temperature are shown in Table 2.

Table 2. Properties of TBABr/Sulf DES at room temperature.

Properties	Value
pH	5.45
Density (g/cm ³)	1.21
Viscosity (mPa·s)	35.3
Onset degradation temperature (°C)	204

The tunable nature of DESs makes their physicochemical characterization essential for optimizing performance in different types of reactions and processes. As shown in Table 2, the TBABr/Sulf (1:7) DES exhibited a relatively low viscosity of 35.3 mPa·s at room temperature. This low viscosity is primarily due to the absence of hydroxyl groups in its structure, as confirmed by the FTIR analysis in Figure 1. For comparison with a typical hydrogen-bonded DES, Reline, a widely studied and commonly used DES composed of choline chloride and urea, has been reported to exhibit a viscosity of approximately 1571 mPa·s at 25 °C [39]. The relatively low viscosity of TBABr/Sulf can be understood to facilitate improved mass transfer and contact between the DES and the PET substrate during depolymerization.

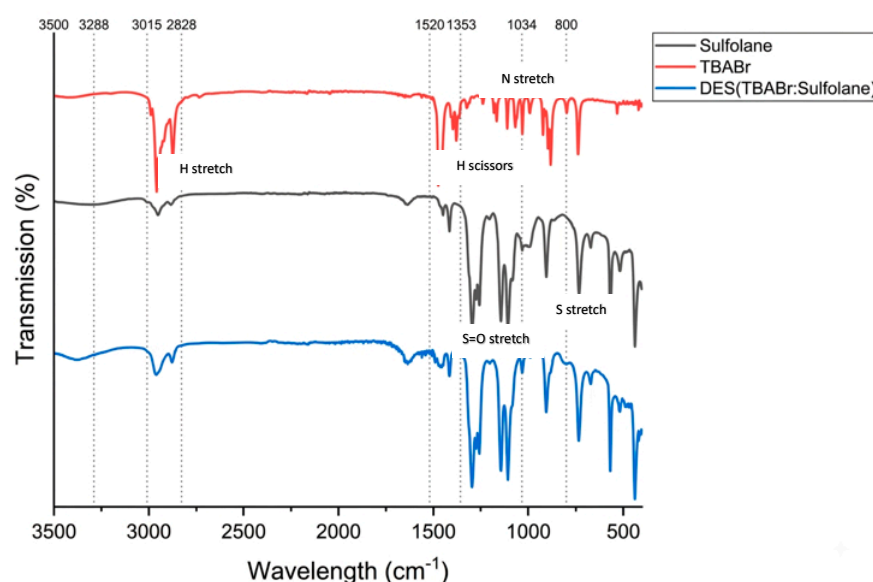


Figure 1. FTIR spectra of TBABr/Sulf (1:7).

The stabilization of TBABr-based DESs containing various HBDs has been previously reported in the literature [40,41]. In these systems, TBABr primarily acts as the HBA, facilitating hydrogen-bonding interactions with HBDs containing suitable donor functionalities. However, hydrogen-bonding interactions may be weakened or disrupted when sufficient HBD functionality is unavailable, there is high water content within the DES system, TBABr is present in excess relative to the HBD, or HBD is present in excess relative to TBABr. Given the absence of conventional HBD functionality in sulfolane, it is therefore plausible that the stability of TBABr/Sulf (1:7) is influenced by van der Waals interactions since the conventional hydrogen-bonding spectra is not visible.

The FTIR spectra of TBABr, sulfolane, and the synthesized TBABr/Sulf (1:7) DES are presented in Figure 1. The FTIR spectrum indicates that the characteristic functional groups of both components are retained, with no evidence of major chemical transformation. Strong absorption bands within 1300–1100 cm^{−1} are assigned to the asymmetric and symmetric stretching vibrations of the sulfolane SO₂ group. The bands observed between 2800 and

3000 cm^{-1} correspond to aliphatic C–H stretching vibrations arising from the methylene and methyl groups of both TBABr and sulfolane. No broad absorption band is observed in the 3200–3600 cm^{-1} region, consistent with the absence of hydroxyl functionalities in either component and indicating that conventional O–H hydrogen bonding is not involved in DES formation. Characteristic vibrational bands associated with TBABr appear attenuated in the DES spectrum due to its lower molar proportion relative to sulfolane (1:7). When compared against the individual FTIR spectra of the starting materials, the DES spectrum is heavily dominated by the absorption features of sulfolane. Fundamentally, this type of DES possesses the combination of low viscosity and high thermal stability, with degradation onset temperatures of 204 °C, which makes it ideal for depolymerization applications.

3.2. Experimental Design Results

The depolymerization of PET was investigated using response surface methodology (RSM) to evaluate and optimize key process parameters. A designed experimental matrix was employed to study four critical variables: (A) reaction time (20–60 min), (B) NaOH concentration (2.5–7.5 wt%), (C) PET/solvent ratio (0.05–0.10 g/g), and (D) water content (coded 1–3, corresponding to water/DES ratios of 1:3, 1:1, and 3:1, respectively). Following each experimental run, the extent of depolymerization was quantitatively assessed through PET weight loss, with the results compiled in Table 3. The individual replicate measurements and their corresponding standard deviations are provided in Appendix A Table A1.

Table 3. Experimental design matrix and observed responses for PET depolymerization.

Run	Independent Variables				Dependent Variable
	A (min)	B (wt%)	C (g/g)	D	Average PET Weight Loss (%)
1	20	7.5	0.075	2	91.22
2	20	5	0.05	2	88.80
3	40	5	0.075	2	95.85
4	40	7.5	0.075	1	92.50
5	60	5	0.05	2	93.83
6	60	7.5	0.075	2	98.20
7	40	7.5	0.1	2	92.75
8	40	2.5	0.075	3	64.21
9	20	2.5	0.075	2	55.93
10	60	5	0.1	2	94.30
11	20	5	0.075	1	73.98
12	20	5	0.1	2	70.13
13	40	5	0.075	2	93.74
14	40	5	0.075	2	96.12
15	40	7.5	0.075	3	97.70
16	60	5	0.075	1	91.59
17	40	2.5	0.1	2	42.46
18	40	5	0.05	1	95.87
19	60	5	0.075	3	97.85
20	40	5	0.1	1	79.95
21	40	2.5	0.05	2	65.87
22	20	5	0.075	3	77.78
23	40	5	0.1	3	90.51
24	40	7.5	0.05	2	96.27
25	60	2.5	0.075	2	62.00
26	40	2.5	0.075	1	61.48
27	40	5	0.05	3	96.63

3.2.1. Statistical Analysis

The analysis of variance (ANOVA) demonstrated in Table 4 showed that the quadratic model developed for PET weight loss was highly significant, with an F-value of 27.77 and a *p*-value of less than 0.0001, indicating that the selected process variables adequately explained the variation in PET depolymerization. The model exhibited a high coefficient of determination, R^2 of 0.9701. The predicted R^2 of 0.8295 was reasonably close to the adjusted R^2 of 0.9351, with a difference of 0.1056, which is less than 0.2. The coefficient of variation of 4.82% indicated good experimental precision and reproducibility, as values below 10% reflect acceptable experimental reliability.

Table 4. Statistical analysis of measured responses for PET depolymerization.

Source	Sum of Squares	Coefficient	Mean Square	F-Value	<i>p</i> -Value
Model	6317.16	95.24	451.23	27.77	<0.0001
A-Time	533.16	6.67	533.16	32.82	<0.0001
B-NaOH	3913.10	18.06	3913.10	240.86	<0.0001
C-PET/solvent	376.02	−5.60	376.02	23.14	0.0004
D-Water content	71.77	2.45	71.77	4.42	0.0574
AB	0.2107	0.2295	0.2107	0.0130	0.9112
AC	91.63	4.79	91.63	5.64	0.0351
AD	1.58	0.6290	1.58	0.0974	0.7603
BC	98.95	4.97	98.95	6.09	0.0296
BD	1.53	0.6188	1.53	0.0943	0.7641
CD	23.99	2.45	23.99	1.48	0.2477
A ²	151.18	−5.32	151.18	9.31	0.0101
B ²	1153.68	−14.71	1153.68	71.01	<0.0001
C ²	79.46	−3.86	79.46	4.89	0.0472
D ²	27.41	−2.27	27.41	1.69	0.2184
Fit statistics					
Standard deviation	4.03				
Mean	83.61				
Coefficient of variation (%)	4.82				
R^2	0.9701				
Adjusted R^2	0.9351				
Predicted R^2	0.8295				
Adequate precision	17.3480				

Among the linear terms, NaOH concentration accounted for approximately 80% of the total sum of squares associated with the linear effects. Reaction time was the second most influential factor. Extending the reaction time increased the degree of depolymerization by allowing sufficient time for hydroxide ions to diffuse into the polymer matrix and continuously cleave the ester linkages. The PET/solvent ratio also significantly affected PET weight loss. At higher PET loadings, the available solvent and hydroxide ions are distributed over a larger quantity of polymer, reducing solvent accessibility and limiting mass transfer between the reactive medium and PET. Consequently, the hydrolysis reaction becomes diffusion-limited, resulting in lower PET weight loss. In contrast, the water content did not significantly influence PET weight loss within the investigated experimental range. This observation suggests that the investigated range of water used in this experimental design does not significantly affect the strength of DES in the dissolution process of PET. Among the interaction terms, only the interactions between reaction time and PET/solvent ratio, and between NaOH concentration and PET/solvent ratio, were statistically significant. This is further discussed in Section 3.2.2.

3.2.2. Response Surface Analysis

The BBD design was employed within the Design Expert software (version 12.0.0, Stat-Ease Inc., Minneapolis, MN, USA) to establish the relationship between the PET weight loss (%) via hydrolysis and its corresponding process parameters to optimize performance. Through the analysis, quadratic regression models were derived to describe the relationships between PET weight loss % and each studied parameter. The coded equation is described in Equation (4) below.

$$\text{PET weight loss (\%)} = 95.24 + 6.67A + 18.06B - 5.60C + 2.45D + 0.2295AB + 4.79AC + 0.6290AD + 4.97BC + 0.6188BD + 2.45CD - 5.32A^2 - 14.71B^2 - 3.86C^2 - 2.27D^2 \quad (4)$$

where A is the reaction time, B is the NaOH concentration (wt%), C is PET/solvent ratio, and D is the water content.

Subsequent analysis using RSM produced three-dimensional response surface plots that visually represent the relationships between the process parameters and PET weight loss, as shown in Figure 2a–f. The color gradients in these plots serve as clear indicators of degradation efficiency, with red zones representing the highest weight loss percentages, followed by progressively lower values in yellow, green, and blue regions. Figure 2a illustrates the interaction between NaOH concentration and reaction time, while Figure 2b demonstrates how the PET/solvent ratio varies with time. The influence of water content over time is depicted in Figure 2c, while Figure 2d shows the combined effect of the PET/solvent ratio and the NaOH concentration. Figure 2e examines the relationship between the water content and the NaOH concentration, with Figure 2f completing the analysis by showing the interaction between the water content and the PET/solvent ratio.

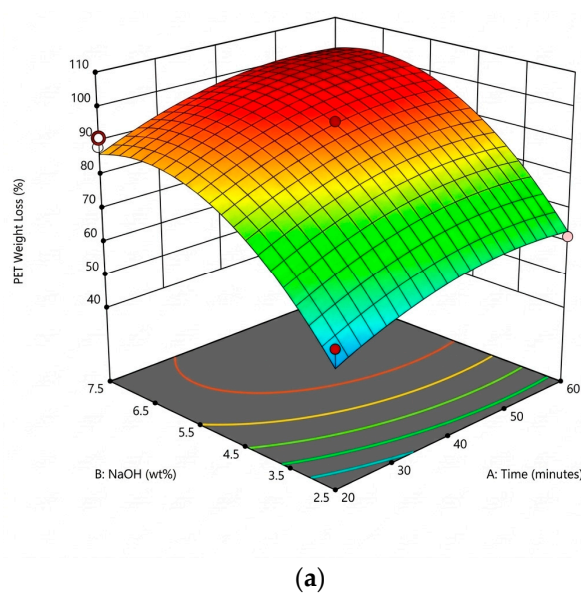
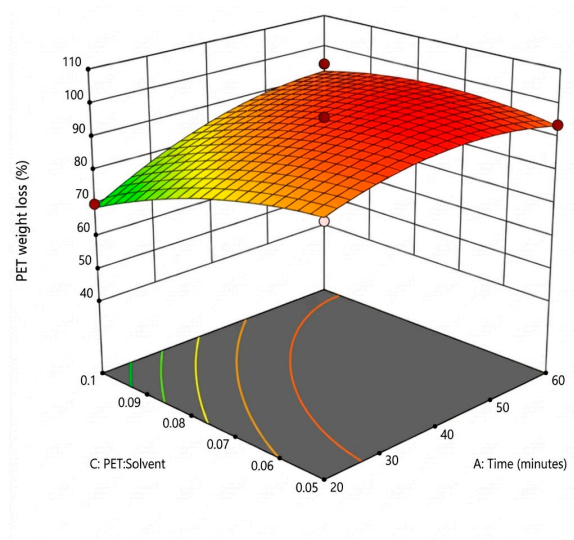
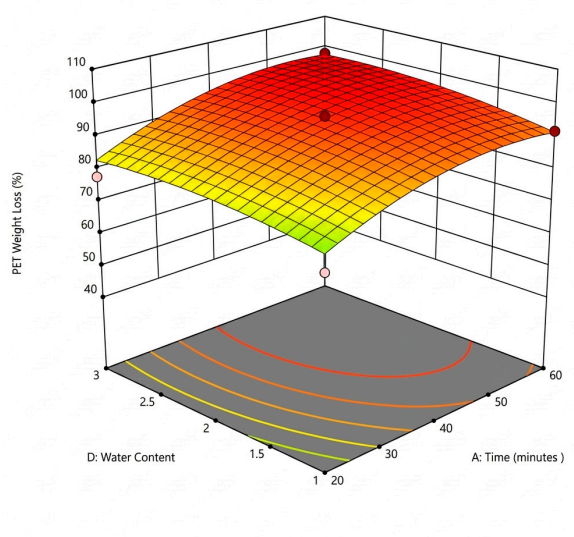


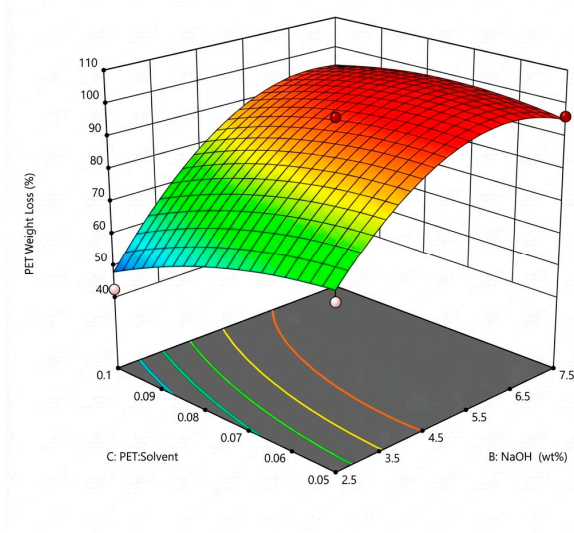
Figure 2. Cont.



(b)



(c)



(d)

Figure 2. Cont.

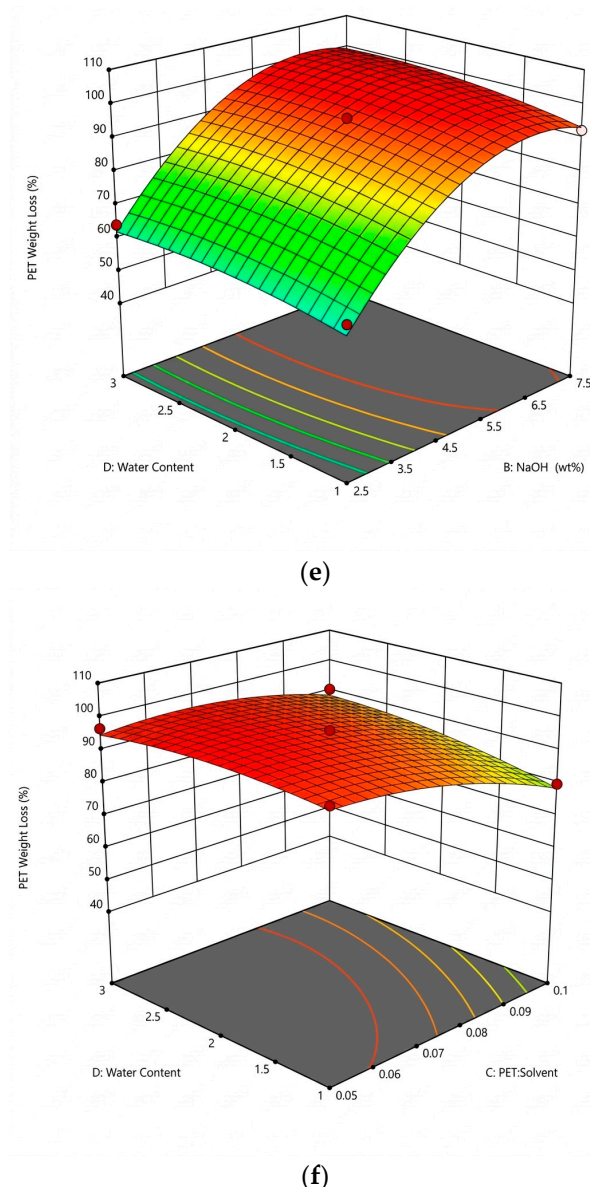


Figure 2. Response surface plots showing the interactive effects of process parameters on PET weight loss: (a) reaction time and NaOH concentration, (b) reaction time and PET/solvent ratio, (c) reaction time and water content, (d) NaOH concentration and PET/solvent ratio, (e) NaOH concentration and water content, and (f) PET/solvent ratio and water content.

Figure 2a shows the combined effect of reaction time and NaOH wt%. Increasing the NaOH concentration enhanced PET depolymerization, while reaction time had a comparatively smaller influence but still significant positive influence. The curvature of the surface indicates diminishing effects at higher concentrations, supported by the significant negative quadratic term for NaOH. In Figure 2b, the reaction time positively contributed to PET weight loss; however, the main effect of the PET/solvent ratio was significantly negative. Their interaction (AC) was positive and significant, indicating that longer reaction times partially offset the negative impact of a higher PET/solvent ratio. Figure 2c illustrates the effect of the reaction time and the water content. Increasing the reaction time consistently increased depolymerization, whereas higher water content showed a slight positive coefficient, but this effect was not statistically significant, suggesting a largely neutral influence.

The most pronounced interaction was observed between the NaOH wt% and the PET/solvent ratio in Figure 2d. PET depolymerization increased sharply when both factors were elevated, consistent with the ANOVA results that identified this interaction as statistically significant. This demonstrates the strong synergistic role of solvent availability in enhancing the hydrolytic action of NaOH. Figure 2e depicts the interaction between NaOH wt% and water content. Increasing the NaOH concentration consistently improved PET weight loss, but the interaction with water content (BD) was not significant and showed a negligible positive coefficient. Therefore, the data does not support the claim that water suppresses NaOH activity as dilution does not appear to be a limiting factor within the tested range. Finally, Figure 2f shows the effect of the PET/solvent ratio and water content. The PET/solvent ratio demonstrated a significant negative main effect while water content again exerted a minimal, non-significant positive influence. The weak interaction between these two factors suggests they act independently, with the PET/solvent ratio being the more statistically dominant, although individually it is a negative parameter compared to water content.

Process optimization was achieved by employing sufficiently high NaOH concentrations and lower PET/solvent ratios, along with reasonable timing, while minimizing excess water content. Based on these observations, the reaction time was fixed at 35 min, and several parameter combinations with a desirability value of 1 were identified. Three optimized conditions were selected for validation and the predicted versus actual outcomes are summarized in Table 5.

Table 5. Optimized PET depolymerization parameters with observed and predicted value with the amount of TPA produced.

Solution	Independent Variable	Optimized Level	Expected (%)	Observed (%)	TPA Produced (%)
1	A: Time (min)	35	98.58	94.6	98.26
	B: NaOH (wt%)	6.4			
	C: PET/solvent ratio (g/g)	0.06			
	D: Water content	1.5			
2	A: Time (min)	35	99.4	97.25	93.8
	B: NaOH (wt%)	5.9			
	C: PET/solvent ratio (g/g)	0.061			
	D: Water content	2			
3	A: Time (min)	35	99.10	95.2	90
	B: NaOH (wt%)	5.8			
	C: PET/solvent ratio (g/g)	0.066			
	D: Water content	2.4			

3.3. MW-Assisted Hydrolysis and Solvent Reuse

Microwave-assisted hydrolysis was carried out using the parameters optimized under conventional heating. A reaction time of 90 s was selected based on a previous study employing choline chloride and m-cresol DES for microwave-assisted alkaline PET hydrolysis [38], which was used as a benchmark for comparison with the present TBABr/Sulf system. This 90 s duration represents one of the fastest reported times for MW-assisted PET hydrolysis in a DES medium, which helps to directly provide a comparative baseline to evaluate the efficiency of the present TBABr/Sulf system without requiring further optimization.

In the first approach, the used DES was fully separated from its mixture, yielding a purer recovered form. However, this method leads to significant solvent loss of more than 50% due to retention on equipment surfaces, salt residues, and filters. Consequently, each cycle requires replenishment with fresh DES to maintain performance. The first method

achieved PET depolymerization and TPA recovery similar to those obtained using the second method.

In the second approach, the DES-containing phase was retained in the reaction system and directly reused for the subsequent depolymerization cycle, eliminating an additional solvent-separation step between cycles. Fresh aqueous NaOH was added for each subsequent cycle, whereas the retained DES phase was not regenerated or restored to its initial composition. Therefore, residual water and dissolved reaction species from the preceding cycle remained in the recycled DES-containing phase. The PET depolymerization performance remained relatively consistent over the three consecutive cycles depicted in Figure 3, indicating that the retained DES phase maintained sufficient functional performance under the conditions investigated.

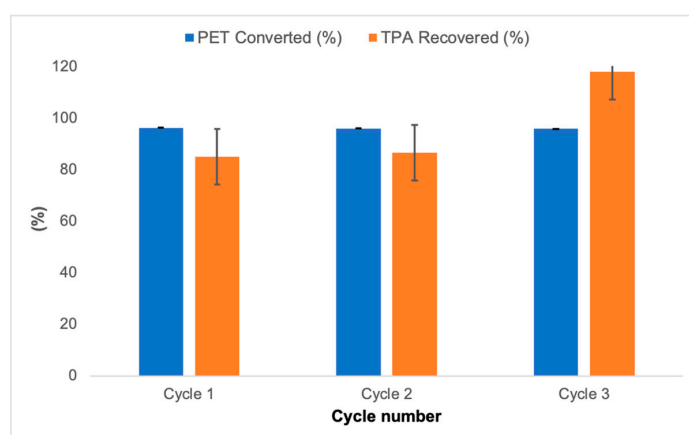


Figure 3. PET converted vs. TPA recovered using method 2.

The performance of the TBABr/Sulf (1:7) can be attributed to its dual-polarity and unique phase behavior. Unlike the Thymol/Phenol (1:2) system which was also utilized in our previous work [37], the optimal theoretical efficiency in computational and experimental validations shown comes with significant challenges in post-reaction processing. The TBABr/Sulf (1:7) structure exhibits a dual functionality. Specifically, the polar part comprising the quaternary ammonium–bromide ion pair of TBABr and the highly polar sulfone group of sulfolane provides solvating power for PET, while the non-polar network from the butyl alkyl chains of the tetrabutylammonium cation maintains the structural integrity of DES. A distinct advantage of this system is the formation of a visible separation layer post depolymerization, which greatly simplifies solvent recovery. Also, due to its dual-polar nature, there will be a partial solubilization of polar species such as Na₂TPA and water, but this does not compromise the overall performance of this solvent.

For depolymerization using MW-assisted heating, 100% depolymerization was achieved for all three cycles, with 85% TPA recovered in the first and second cycles. Because the TBABr/Sulf system exhibits partial solubility toward polar species, including Na₂TPA, a fraction of the Na₂TPA generated during each cycle remained associated with the retained DES phase rather than being recovered during the corresponding acidification step. The retained Na₂TPA was therefore carried over into the subsequent cycles. During the third cycle, the DES was no longer recycled and the accumulated Na₂TPA in the DES-containing phase was recovered together with the Na₂TPA generated during the third depolymerization cycle. Consequently, the calculated TPA recovery relative only to the PET introduced in the third cycle reached an apparent value of 118%. Consequently, this DES showed an ideal balance between depolymerization efficiency and ease of downstream separation, which helps to overcome the hurdles associated with more traditional, highly hydrophobic or hydrophilic eutectic mixtures.

3.4. Identity and Quality of TPA

The quality and stability of recycled monomers are important considerations. High-quality TPA ensures suitability for high-demand applications, which helps to effectively close the loop by reducing reliance on virgin feedstocks and lowering the overall carbon footprint across the life cycle of PET. The identity of the recovered TPA was verified through three analytical techniques: structural identification via FTIR and NMR spectroscopy; elemental analysis for carbon, hydrogen, nitrogen, and sulfur composition; and DSC for thermal transition.

3.4.1. FTIR and NMR Analysis

FTIR analysis is an important characterization technique for confirming the identity of TPA. The obtained spectra were compared with those of virgin TPA powder (99% purity) purchased from Chemiz Malaysia, Shah Alam, Malaysia. The FTIR and NMR spectra of the obtained product were identical to those reported in our earlier study [37].

Additionally, FTIR analysis of TPA recovered over three consecutive DES reuse cycles (Figures A1–A3) revealed no significant variations, which confirms that the recovered TPA quality remained consistent throughout the recycling study.

3.4.2. Elemental Analysis

The elemental composition (CHNS) analysis of the recycled TPA obtained from the recycling of PET using the TBABr/Sulf (1:7)-based DES revealed a carbon content of 58.6%, closely matching both the theoretical value of 57.5% for pure TPA and reported values for virgin TPA of $58.0 \pm 0.37\%$ [42]. The hydrogen content of recycled TPA, at 3.752%, also aligns well with the expected theoretical value of 3.6% and literature data for virgin TPA at $3.7 \pm 0.12\%$ [42]. Notably, a trace amount of nitrogen (0.2%) was detected, likely due to residual TBABr from the DES. The absence of sulfur confirms the complete removal of sulfolane during purification.

3.4.3. DSC

The recycled TPA exhibited a major endothermic sublimation peak at 362 °C (Figure 4), which falls within the broad range reported in the literature for TPA [43,44]. No thermal peaks were observed in the 200 °C region that would indicate residual DES contamination.

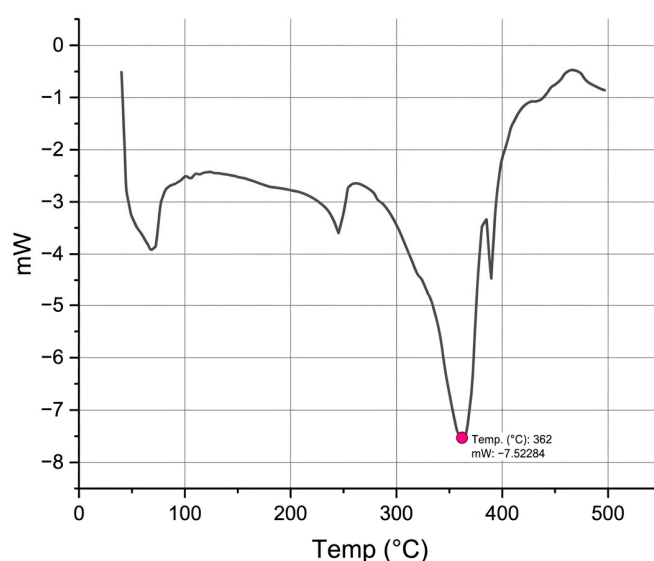


Figure 4. DSC spectra of recycled TPA.

4. Discussion

The RSM results demonstrate that PET depolymerization in the TBABr/Sulf system is primarily governed by the NaOH concentration, followed by the reaction time and PET/solvent ratio, whereas water content exerted a comparatively limited effect within the investigated range. The strong influence of NaOH concentration is consistent with the role of hydroxide ions as the principal reactive species responsible for hydrolytic cleavage of the ester bonds in PET. Regarding the interaction terms, two factor pairs were found to be statistically significant: reaction time with PET/solvent ratio, and NaOH concentration with PET/solvent ratio. Based on the desirability analysis, an optimum condition was selected at 35 min reaction time, 5.9 wt% NaOH, a PET/solvent ratio of 0.061 g/g, and a 1:1 water-to-DES ratio. Under these conditions, approximately 97% PET depolymerization and 93.8% TPA recovery were achieved during validation. The agreement between the predicted and experimental responses confirms that the developed model can be used to identify suitable operating conditions within the investigated experimental parameters.

PET weight loss was adopted as the primary response variable, since the extent of depolymerization offers a convenient proxy of estimating TPA recovery, especially at higher conversion levels, while avoiding the acidification step. As acidification introduces its own set of optimization parameters, it is more meaningful to optimize this step independently to prevent the confounding of variables between depolymerization and product recovery.

An important result of the optimized process is the relatively low DES requirement. The optimized PET/solvent ratio of 0.061 g/g, together with the 1:1 water-to-DES composition, corresponds to approximately 0.12 g PET per g DES, or approximately 8.3 g DES per gram of PET. This represents a marked reduction compared to earlier studies, which reported DES requirements of 13.3 g/g PET [20] and 20 g/g PET [45]. The lower DES requirement observed in the present system indicates that effective PET depolymerization can be achieved without relying on a large excess of DES.

The optimized process also required 5.9 wt% NaOH, representing at least a 40% reduction relative to DES-assisted alkaline hydrolysis systems employing NaOH concentrations above 10 wt% [38]. The optimized reaction time of 35 min is also within the lower range of reaction times reported for several DES-based PET hydrolysis processes, which commonly require approximately 1–4 h to achieve comparable conversion [36,46].

The thermal stability of TBABr/Sulf (1:7) was also evaluated to determine its suitability as the reaction medium. The onset degradation temperature was approximately 204 °C, substantially higher than the reaction temperature of 130 °C. Thus, the reaction was conducted approximately 74 °C below the measured onset temperature. This temperature difference indicates that no major thermal decomposition of the DES would be expected under the investigated reaction conditions. The observation is further supported by the absence of substantial changes in the characteristic FTIR features of the recovered DES after reuse (Figure A4).

The TBABr/Sulf (1:7) system primarily functions as a reaction medium that facilitates contact between PET and the reactive hydroxide species. In our previous study [37], PET dissolution in TBABr/Sulf was experimentally demonstrated, establishing the ability of this medium to solubilize PET. In the present alkaline system, the addition of NaOH further accelerates the transformation of PET into the solvated or softened state, thereby facilitating interaction between the polymer and hydroxide ions. Hydroxide ions supplied by NaOH are considered the principal reactive species responsible for hydrolytic cleavage of ester bonds and formation of Na₂TPA. The role of the DES is therefore considered primarily to provide a medium that promotes PET solubilization and facilitates interaction between the polymer substrate and the reactive aqueous phase. The unchanged characteristic FTIR

features of the recovered DES (Figure A4) indicate that no major chemical transformation of the DES components was detected after reaction.

The ability to retain the DES-containing phase for subsequent reaction cycles represents an important feature of the present system. In contrast to some DES-assisted PET hydrolysis systems where solvent recovery can be complicated by miscibility with aqueous products or retention of dissolved terephthalate species [35,36], the TBABr/Sulf system exhibited phase separation that enabled the DES-containing phase to be retained for subsequent reactions. Over three consecutive cycles, the PET showed 100% depolymerization efficiency, and FTIR analysis showed no evident changes in the characteristic spectral features of the recovered DES. No fresh DES was added between cycles in this approach; only the aqueous NaOH component was replenished according to the experimental procedure. Therefore, the results demonstrate the feasibility of retaining the DES-containing reaction medium over three consecutive cycles under the conditions investigated.

Building on the optimized conventional-heating conditions, microwave-assisted depolymerization was subsequently evaluated using a 90 s reaction period adopted from a previously reported microwave-assisted PET hydrolysis study [38]. The contribution of microwave irradiation to the observed depolymerization performance should, however, be interpreted with caution, as the observed performance cannot be unambiguously attributed to microwave irradiation alone or to a synergistic combination with the DES. Several studies have reported exceptional PET depolymerization using a DES under microwave irradiation [38,47,48]. However, another contradictory study emphasizes that choline-based DES does not perform competitively in conventional depolymerization [37]. In the present study, however, conventional heating already confirmed the solubilization capacity of the TBABr/Sulf DES. Microwave irradiation can therefore be regarded as a complementary intensification tool, primarily to accelerate processing and enhance solvent recovery.

5. Conclusions

This study demonstrates the application of TBABr/Sulf (1:7) as a DES-assisted medium for PET hydrolysis and establishes the key process–response relationships governing PET depolymerization. RSM using a Box–Behnken design identified NaOH concentration as the dominant process variable, followed by reaction time and PET/solvent ratio, while significant interactions were observed between reaction time–PET/solvent ratio and NaOH concentration–PET/solvent ratio. The optimized condition of 35 min reaction time, 5.9 wt% NaOH, a PET/solvent ratio of 0.061 g/g, and a 1:1 water-to-DES ratio achieved 97% PET depolymerization and 93.8% TPA recovery. A key contribution of this work is the demonstration that high PET depolymerization can be achieved using a relatively low NaOH concentration and solvent loading compared with previously reported DES-assisted alkaline hydrolysis systems. Under the optimized conditions, the PET/DES utilization ratio was only 0.12 g/g. The recovered TPA exhibited chemical and thermal characteristics comparable to commercial TPA, as confirmed by FTIR, NMR, elemental analysis, and DSC. Furthermore, the TBABr/Sulf was directly reused over three consecutive cycles without detectable structural degradation or loss of performance, addressing the solvent recovery challenge associated with DES-based PET hydrolysis. The observed recyclability also demonstrates the potential advantage of the phase behavior of the TBABr/Sulf system for separating the DES from the aqueous product phase. Finally, the optimized process was transferred to microwave-assisted operation, with reaction time of 90 s, achieving 100% PET depolymerization with efficient TPA recovery. Collectively, the findings establish TBABr/Sulf as a recoverable reaction medium for PET depolymerization and provide quantitative process conditions for reducing NaOH and DES requirements. Further assessment of long-term DES recyclability, energy consumption, economic performance, and

environmental impacts is required to establish the broader sustainability advantages of the process.

Author Contributions: Conceptualization, Formal analysis, Investigation, Writing—original draft, visualization, N.A.F.; data curation, validation, writing—review and editing, supervision, methodology, project administration, M.Z.M.S.; Supervision, project administration, funding acquisition, N.Y.Y.; writing—review and editing, methodology, validation, M.A.H.; writing—review and editing, resources, validation, visualization, funding acquisition, M.K.H.-K. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DES Deep eutectic solvent
Na₂TPA Disodium terephthalate
TPA Terephthalic acid

Appendix A

Table A1 presents the PET depolymerization percentages obtained from two replicate runs, along with the corresponding average and standard deviation.

Table A1. PET depolymerization percentages, mean, and standard deviation from duplicate runs.

Run	A: Time (min)	B: NaOH (wt%)	C: PET/Solvent (g/g)	D: Water	Weight Loss 1 (%)	Weight Loss 2 (%)	Average Weight Loss (%)	Standard Deviation
1	20	7.5	0.075	2	90.07	92.363	91.217	1.621
2	20	5	0.05	2	90.33	87.27	88.800	2.164
3	40	5	0.075	2	95.20	96.5	95.850	0.919
4	40	7.5	0.075	1	92.783	92.22	92.502	0.398
5	60	5	0.05	2	94.35	93.3	93.825	0.742
6	60	7.5	0.075	2	98.20	98.2	98.200	0.000
7	40	7.5	0.1	2	91.93	93.57	92.750	1.160
8	40	2.5	0.075	3	66.667	61.75	64.209	3.477
9	20	2.5	0.075	2	54.783	57.07	55.927	1.617
10	60	5	0.1	2	94.067	94.533	94.300	0.330
11	20	5	0.075	1	71.617	76.35	73.984	3.347
12	20	5	0.1	2	72.97	67.28	70.125	4.023
13	40	5	0.075	2	93.7	93.78	93.740	0.057
14	40	5	0.075	2	96.98	95.25	96.115	1.223
15	40	7.5	0.075	3	97.70	97.7	97.700	0.000
16	60	5	0.075	1	90.767	92.42	91.594	1.169
17	40	2.5	0.1	2	42.233	42.68	42.457	0.316
18	40	5	0.05	1	95.85	95.88	95.865	0.021
19	60	5	0.075	3	97.60	98.1	97.850	0.354
20	40	5	0.1	1	77.35	82.55	79.950	3.677

Table A1. Cont.

Run	A: Time (min)	B: NaOH (wt%)	C: PET/Solvent (g/g)	D: Water	Weight Loss 1 (%)	Weight Loss 2 (%)	Average Weight Loss (%)	Standard Deviation
21	40	2.5	0.05	2	67.86	63.88	65.870	2.814
22	20	5	0.075	3	77.00	78.55	77.775	1.096
23	40	5	0.1	3	87.683	93.33	90.507	3.993
24	40	7.5	0.05	2	97.25	95.29	96.270	1.386
25	60	2.5	0.075	2	60.55	63.45	62.000	2.051
26	40	2.5	0.075	1	61.76	61.2	61.480	0.396
27	40	5	0.05	3	96.00	97.25	96.625	0.884

The FTIR spectra of TPA obtained from three consecutive cycles employing recycled DES are presented in Figures A1–A3. The spectrum of the DES recovered at the end of the third cycle is shown in Figure A4. Apart from a broad O–H stretching band ($3200\text{--}3600\text{ cm}^{-1}$), which is attributed to residual water retained within the DES, the spectrum shows no additional peaks or shifts. This confirms the absence of any structural degradation of the DES throughout the three reuse cycles.

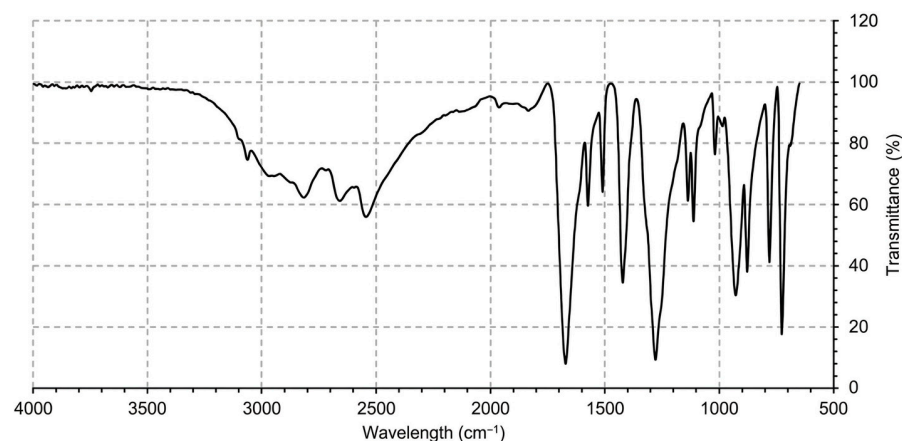


Figure A1. Spectra of TPA formed in DES recycling study (cycle 1).

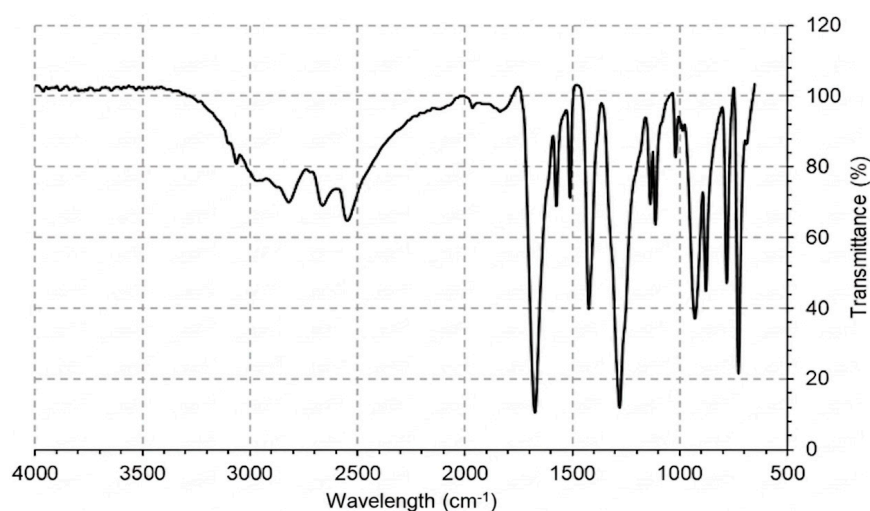


Figure A2. Spectra of TPA formed using recovered DES (cycle 2).

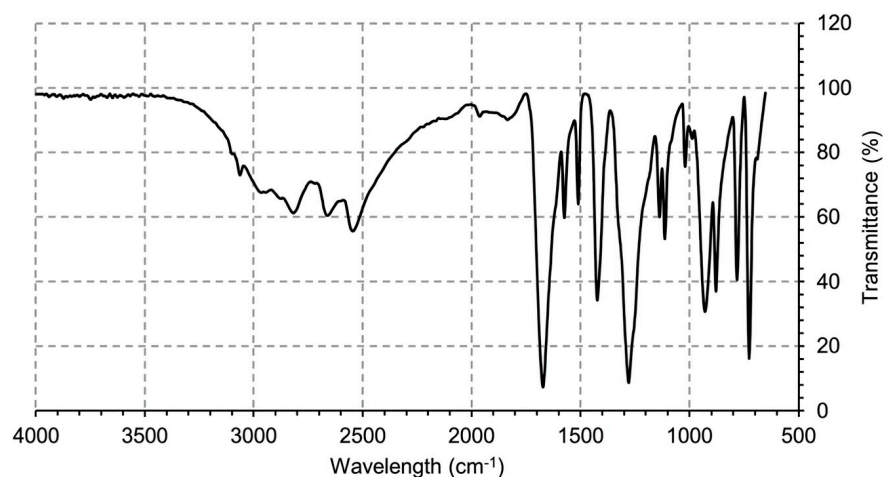


Figure A3. Spectra of TPA formed using recovered DES (cycle 3).

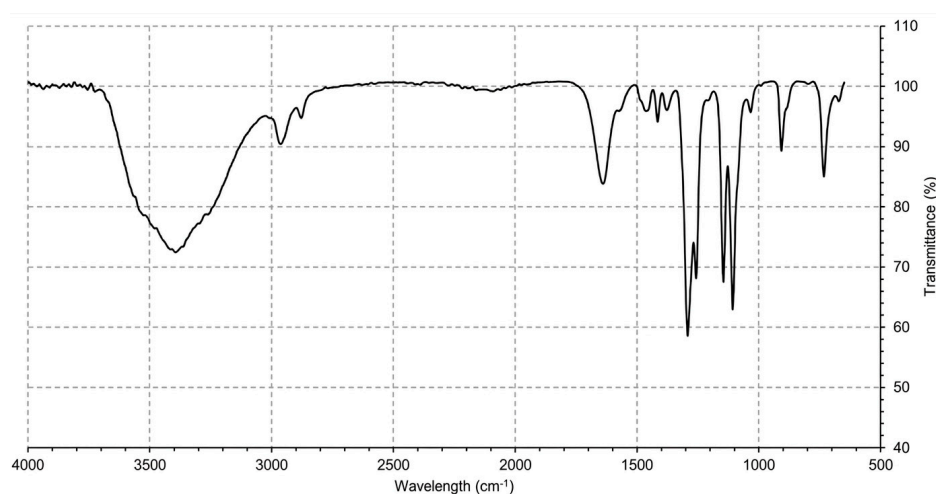


Figure A4. Spectra of recovered DES after 3rd cycle.

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