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Research Paper

Integrating experimental and computational approaches for deep eutectic solvent-catalyzed glycolysis of post-consumer polyethylene terephthalate

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ABSTRACT

To achieve a sustainable and circular economy, developing effective plastic recycling methods is essential. Despite advances in the chemical recycling of plastic waste, modern industries require highly efficient and sustainable solutions to address environmental problems. In this study, we propose an efficient glycolysis strategy for post-consumer polyethylene terephthalate (PET) using deep eutectic solvents (DESs) to produce bis (2-hydroxyethyl) terephthalate (BHET) with high selectivity. Choline chloride (ChCl)- and urea-based DESs were synthesized using various metal salts and were tested for the glycolysis of PET waste; ChCl–Zn(OAc)$_2$ exhibited the best performance. The DES-containing solvent system afforded a complete PET conversion, producing BHET at a high yield (91.6%) under optimal reaction conditions. The degradation mechanism of PET and its interaction with DESs were systematically investigated using density functional theory-based calculations. Furthermore, an intuitive machine learning model was developed to predict the PET conversion and BHET selectivity for different DES compositions. Our findings demonstrate that the DES-catalyzed glycolysis of post-consumer PET could enable the development of a sustainable chemical recycling process, providing insights to identify the new design of DESs for plastic decomposition.

1. Introduction

Single-use plastics are prevalent in modern life owing to their low manufacturing costs and multifaceted uses. However, the increasing volume of plastic production makes plastic pollution one of the most pressing environmental problems. The exponentially growing production of disposable plastic products has surpassed their management capacity worldwide. Although global efforts have been made to reduce plastic pollution, only 10% of the total plastic waste is recycled, and the rest is either incinerated or disposed of in landfills (Huang et al., 2022; OECD, 2022). Therefore, the development of sustainable recycling processes for plastic waste is imperative for preventing detrimental social and environmental impacts (Ellis et al., 2021).

Polyethylene terephthalate (PET) is a thermoplastic polymer belonging to polyester group and widely used in packaging, drinking bottles, and textile fibers (Pudack et al., 2020). Due to its water resistance, high strength-to-weight ratio, and wide availability, PET has been used to manufacture a wide range of products. However, the chemical stability and recalcitrant nature of PET against atmospheric and biological degradation lead to its environmental persistence (Wang et al., 2020). The chemical recycling of PET has been viewed as a promising strategy to address this problem, which mainly involves the decomposition of polymers into monomeric compounds that can be reused to produce new polymers. Several processes have been proposed, including glycolysis, hydrolysis, aminolysis, and methanolysis, depending on the specific reagents used for the chemical degradation (Thomas et al.,

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2018).

Among the various chemical recycling methods, the glycolysis of PET to *bis*(2-hydroxyethyl terephthalate) (BHET) using ethylene glycol (EG) is the most preferred approach because BHET can be directly reinserted into the polymerization process (Carta et al., 2003). However, PET glycolysis is slow reaction when it is conducted without a catalyst (Campanelli et al., 1994). Therefore, recent studies focus on finding an effective catalyst for this reaction. Examples include sodium bicarbonate ($NaHCO_3$) (Van-Pham et al., 2020), 1,3-dimethylimidazolium-2-carboxylate (Wang et al., 2020), zinc acetate (López-Fonseca et al., 2010), and zinc sulfate (Ghaemy and Mossaddegh, 2005). While various catalysts have been identified to improve PET glycolysis, the yield of the final product (*i.e.*, BHET) is often low, and harsh reaction conditions (>300 °C) are often required (Imran et al., 2010). Therefore, developing an efficient chemical recycling process that can convert PET into BHET in high yields under mild reaction conditions is necessary.

Deep eutectic solvents (DESs) are cost-effective green solvents that exhibit high thermal stability, low toxicity, and tunability (Hansen et al., 2020). Chemical reactions, including PET glycolysis, are catalyzed by hydrogen bonds or coordination interactions, which are readily provided by DESs. Previously, urea-based DESs with metallic salts were found to exhibit high catalytic activity for PET degradation (Zhou et al., 2019). PET glycolysis at 170 °C using urea–$ZnCl_2$ DES afforded complete conversion of PET with 83% of BHET selectivity. Strong hydrogen and metal coordination bonds were the primary interactions between PET, EG, and the DES catalyst. Potassium carbonate–EG DES was found to facilitate the decomposition of PET, yielding 88% BHET at 180 °C (Sert et al., 2019). Considering that DESs are "designer solvents" that possess tunable properties, they exhibit significant potential for further development as catalysts. However, urea- or potassium carbonate-based DESs showed insufficient BHET selectivity and require high process volumes for high yields. Instead, recent studies revealed that choline chloride (ChCl)-based DES exhibits higher thermal stability and strong catalytic activity for plastic depolymerization, enabling the production of high monomer yields with a low process volume (Wang et al., 2022).

Computational approaches, including density functional theory (DFT) and machine learning (ML), play pivotal roles in chemistry and materials science due to their high predictability, efficiency, and scalability (Huang et al., 2023). An approach that combines both simulation and experimental data is essential for understanding the complex hydrogen bonding network in the reaction. This computational analysis can provide the fundamental framework required for a deeper understanding of DES and its performance in PET glycolysis (Hansen et al., 2020). Furthermore, ML models have the capability to unearth intricate insights and establish correlations that might not be immediately discernible through traditional computational methods. ML can rapidly achieve maximum efficiency, minimize unnecessary energy consumption, and scale up to industrial levels for process optimization based on predictive modeling using experimental data (Nagai et al., 2020). This computational approach can facilitate catalyst design and the development of sustainable chemical recycling processes for efficient depolymerization, thereby contributing to the circular economy.

In this study, we developed an effective PET glycolysis process using DESs as organocatalysts, to achieve high BHET yields. Various DESs were synthesized and screened and the final product was analyzed using nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC). In addition, a ML-based model was developed to predict PET conversion and BHET selectivity. The key parameters were optimized and used to develop a kinetic model. Furthermore, the mechanism of PET glycolysis with the DESs was studied using density functional theory (DFT) calculations.

2. Materials and methods

2.1. Materials

Post-consumer PET bottles were collected from a local recycling center (Seoul, Republic of Korea). The collected PET samples were thoroughly washed with deionized water (DI water) and ethanol to remove any impurities. The washed PET samples were air-dried and cut into 5 × 1 mm pieces. Zinc acetate ($Zn(OAc)_2$), zinc chloride ($ZnCl_2$), manganese acetate ($Mn(OAc)_2$), manganese chloride ($MnCl_2$), cobalt acetate ($Co(OAc)_2$), cobalt chloride ($CoCl_2$), iron chloride ($FeCl_3$), glycerol, urea, choline chloride (ChCl), EG, and BHET were purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade PET was purchased from Goodfellow Cambridge Ltd. (Huntingdon, UK). All chemicals were used without further purification.

2.2. DES synthesis

As listed in Table S1, 14 DESs were synthesized: ChCl–$Zn(OAc)_2$, ChCl–$Mn(OAc)_2$, ChCl–$Co(OAc)_2$, ChCl–$ZnCl_2$, ChCl–$CoCl_2$, ChCl–Urea, ChCl–glycerol, urea–$Zn(OAc)_2$, urea–$Mn(OAc)_2$, urea–$Co(OAc)_2$, urea–$ZnCl_2$, urea–$MnCl_2$, urea–$CoCl_2$, and urea/$FeCl_3$. In the present study, ChCl- and urea-based DESs, which had previously exhibited good performance in PET degradation, were initially screened to identify and select the most suitable DES for optimizing the PET glycolysis process. DES synthesis involved heating the mixture of a certain molar ratio at 80-120 °C under stirring until a homogenous liquid phase formed. The synthesized DESs were then tested to identify the optimal catalyst for PET decomposition.

2.3. Glycolysis of PET

An initial screening test was performed by mixing 0.2 g of PET samples with 0.8 g of EG and 0.01 g of each DES in a 60 mL pressure tube (Ace Glss Inc., NJ, USA). The reaction was conducted in an oil bath at 180 °C for 3 h. After reaction, the reactor was immersed in an ice bath to stop the reaction. The resulting mixture was vacuum-filtered and washed with acetone. The PET conversion was determined gravimetrically after drying in an oven at 105 °C for 24 h. The filtrate was diluted 1000-fold with acetone, and the amount of BHET was quantified by gas chromatograph.

After the screening, in-depth glycolysis reactions were conducted using the best DES catalyst (*i.e.*, ChCl–$Zn(OAc)_2$) to optimize the reaction conditions including varying DES concentrations (0–20 wt%), temperatures (170–190 °C), durations (0–6 h), and solid/solvent ratios (1:4–1:10, w/w). PET glycolysis and filtration were also performed in the same manner. BHET was precipitated by adding DI water to the filtrate (2:1 ratio, v/v) and stored in a refrigerator at 4 °C for 12 h. The resulting solution was then filtered and washed with DI water; white crystalline BHET flakes were obtained by drying in a vacuum oven at 60 °C for 12 h. The conversion of PET and selectivity of BHET were calculated using Equations (1) and (2). The molecular weights of PET and BHET were 192 and 254 g mol^{-1}, respectively.

$$\text{Conversion of PET}\ (\%) = \frac{\text{Initial weight of PET} - \text{weight of residual PET}}{\text{Initial weight of PET}} \times 100 \tag{1}$$

$$\text{Selectivity of BHET}\ (\%) = \frac{\text{Mole of BHET produced}}{\text{Moles of depolymerized PET}} \times 100 \tag{2}$$

2.4. Analytical methods

The produced BHET was analyzed using an Agilent 7820A GC system equipped with an Agilent 5975 mass spectrometry detector (Agilent Technologies Inc., Santa Clara, CA, USA) and an Agilent DB-5 column

(30 m × 0.25 mm × 0.25 μm). The injection temperature was 300 °C, and the oven temperature was programmed to hold at 70 °C for 5 min, ramp to 300 °C at 10 °C min^{-1}, and hold for an additional 5 min. Analytical-grade BHET was used for peak identification and for constructing a calibration curve for quantification.

The structural characteristics of the purified BHET were analyzed using ^1H NMR spectroscopy on a Bruker Advance HD 800 MHz spectrometer equipped with a TCI cryogenic probe (Bruker Corp., Billerica, MA, USA). The NMR spectra were processed with a Bruker Topspin 3.5pl7 and analyzed using Mnova 14.1.2 (Mestrelab Research, Compostela, Spain). The samples were dissolved in DMSO-d_6 and the spectra were acquired at 298 K.

Inspect F scanning electron microscopy (SEM, Thermo Fisher Scientific, Waltham, MA, USA) was used to study the morphological changes during PET glycolysis. The PET samples were coated with a thin layer of platinum using an E-1045 vacuum-ion sputter coater (Hitachi, Ibaraki, Japan). The SEM images were acquired at an accelerating voltage of 5.0–10.0 kV.

2.5. Computational analysis

All calculations were performed using the Gaussian 16 software (Frisch et al., 2016) and the M06X (*meta*-GGA functional) method (Zhao and Truhlar, 2006), reported to be successful in computing the alcoholysis of PET in ChCl-based DES system (Zhou et al., 2019). The *meta*-GGA functional method includes implicit parameterization of non-covalent interaction energies and enables reliable computations for open-shell 3d metal systems (Luo et al., 2014). In addition, two basis sets, 6-31G(d, p) and LanL2DZ, were employed for the C, H, O, N, and Cl atoms (Blaudeau et al., 1997) and Co, Mn, and Zn atoms (Hay and Wadt, 1985), respectively. Regarding calculations, the effective core potential and associated pseudopotentials were included along with Grimme correction (Grimme et al., 2010), while integrals were evaluated via density-fitting schemes that were automatically generated to improve the computational efficiency. Furthermore, auto-fitting was implemented for the basis sets, whereas an ultrafine grid was exploited for the two electron integrals, with the symmetry being turned off via an external command. Geometry optimizations of all the reactants and intermediates was performed using DFT throughout the study. To ensure that the computed geometries featured minimum energies, subsequent harmonic frequency calculations were performed at the same level of theory using the same basis sets. All stationary points on the potential energy surface were proven to be global minima (no imaginary frequencies were found in the frequency calculation).

2.6. Machine learning model analysis

The PET conversion and BHET selectivity values of 19 different DESs were used as raw data to develop a ML model. Each DES structure was classified into three components, indexed as Component1, Component2, and Component3. If a DES contained fewer than three components, it was denoted as “None”. The dataset included a total of 17 unique components.

To preprocess the data for ML, we used one-hot encoding (Scikit-learn) to convert the categorical component variables into numerical data. The “None” components were excluded from the encoding process. Next, the dataset was divided into training and testing sets in a 70:30 ratio. A ML model was then developed using the Random Forest Regressor algorithm, an ensemble method that constructs multiple decision trees and averages their outputs to enhance accuracy while reducing overfitting. The model was trained using the training set, and its performance was evaluated using both the training and testing sets. The root mean squared error (RMSE) was calculated for both PET conversion and BHET selectivity. Finally, the feature importance was computed to identify the most important factors in predicting PET conversion and BHET selectivity.

2.7. Kinetic of PET glycolysis

The kinetic parameters of PET glycolysis were investigated using a first-order model described in Equation (3) integrated over time, and rearranged as Equation (4) (Anggo Krisbiantoro et al., 2022).

$$\frac{dX}{dt} = k(1 - X) \tag{3}$$

$$\ln\frac{1}{1 - X} = kt \tag{4}$$

where k is the rate constant and X is the conversion of PET.

The activation energy (E_a) was calculated using the Arrhenius equation (Eq. (5)), which was applied to describe the relationship between the rate constant of the first-order model and temperatures (Zhou et al., 2019).

$$\ln k = \frac{-Ea}{RT} + \ln A \tag{5}$$

where A is a pre-exponential factor, R is the universal gas constant, and T is the temperature (K).

3. Results and discussion

3.1. DES screening for PET glycolysis

The glycolysis of post-consumer PET samples using various DESs was conducted at 180 °C for 3 h, at a 1:4 ratio of PET:EG in the presence of 5 wt% DES. The aforementioned conditions were previously reported as the optimal conditions for PET alcoholysis (Wang et al., 2015; Zhou et al., 2019). Table 1 presents the conversion of PET and BHET selectivity after the different glycolysis reactions. The DES screening test revealed that the conversion of PET and production of BHET were highly dependent on the type of DES used. For example, urea–$Zn(OAc)_2$, urea–$Mn(OAc)_2$, urea–$MnCl_2$, ChCl–$Zn(OAc)_2$, and ChCl–$ZnCl_2$ achieved over 90% PET conversion with decent BHET selectivity (Entry 1–3, and 8–9), whereas urea–$FeCl_3$ and ChCl–Gly showed relatively poor catalytic activities (Entry 7 and 14).

Notably, the $Zn(OAc)_2$-containing DES resulted in high PET conversion and BHET selectivity. As shown in Table 1, high PET conversions of 96.1% and 98.4% were achieved when urea–$Zn(OAc)_2$ and ChCl–Zn$(OAc)_2$ were used, respectively, yielding high BHET selectivity. Zn^{2+} reportedly interacts strongly with the carbonyl O_{PET}, resulting in positively charged carbocation. Subsequently, the carbocations are readily attacked by hydroxyl O_{EG}, and the PET chain is finally cleaved (Wang

Table 1
Averaged data of PET glycolysis using various ChCl and urea-based DES.[a]

Entry	DES	PET conversion (%)	BHET selectivity (%)
1	Urea–$Zn(OAc)_2$	96.1	76.2
2	Urea–$Mn(OAc)_2$	94.2	71.1
3	Urea–$MnCl_2$	90.1	63.1
4	Urea–$CoCl_2$	82.8	56.0
5	Urea–$ZnCl_2$	75.2	76.6
6	Urea–$Co(OAc)_2$	77.2	7.0
7	Urea–$FeCl_3$	0.7	0.4
8	ChCl–$Zn(OAc)_2$	98.4	83.5
9	ChCl–$ZnCl_2$	91.1	86.2
10	ChCl–$Mn(OAc)_2$	85.9	75.9
11	ChCl–$CoCl_2$	66.9	55.9
12	ChCl–$Co(OAc)_2$	51.0	25.5
13	ChCl–Urea	30.3	5.1
14	ChCl–Gly	7.9	0.4
15	$Zn(OAc)_2$	72.3	60.3
16	$ZnCl_2$	38.2	33.4
17	Urea	17.7	13.2
18	ChCl	0.8	0.4

[a] Reaction conditions. 0.2 g PET, 0.8 g EG, 0.01 g DES, 180 ℃, 3 h.

et al., 2021).

Furthermore, ChCl-containing DESs evidently outperform urea-based DESs. For example, the use of ChCl–Zn(OAc)$_2$ and ChCl–ZnCl$_2$ resulted in high PET conversions of 91–98% and BHET selectivities of 83–85%, which were higher than those obtained with urea–Zn(OAc)$_2$ and urea–ZnCl$_2$. As previously demonstrated, the stable structures formed through the H-bond between the carbonyl $O_{Zn(OAc)2}$ and hydroxyl H_{ChCl}, and the coordination bond between Cl–Zn, facilitating the chemical reaction of PET degradation (Wang et al., 2015).

The effect of metal ions on the catalytic performance of DESs was also studied. When urea–Zn(OAc)$_2$, urea–Mn(OAc)$_2$, and urea–Co(OAc)$_2$ were used, the PET conversions were 96%, 94%, and 77%, respectively, and the BHET selectivities were 76%, 71%, and 7%, respectively. In the case of ChCl–Zn(OAc)$_2$, ChCl–Mn(OAc)$_2$, and ChCl–Co(OAc)$_2$, the PET conversions were 98%, 86%, and 51%, respectively, and the BHET selectivities were 84%, 76%, and 26%, respectively. These results indicate that Zn has the highest catalytic activity for PET glycolysis, followed by Mn and Co, which is consistent with previous findings (Zhou et al., 2019).

Compared to DES catalysts, non-DES or single-component catalysts, including Zn(OAc)$_2$, ZnCl$_2$, urea, and ChCl, afforded lower PET conversions and BHET selectivities (Entry 15–18). Evidently, eutectic mixtures (*i.e.*, ChCl/urea–metal salts) exhibit high catalytic activity, which is possibly due to the synergistic effect between the DES components.

3.2. Optimization of PET glycolysis catalyzed by ChCl–Zn(OAc)$_2$

Among the tested DESs, ChCl–Zn(OAc)$_2$ was selected for further experiments because of its high catalytic activity toward PET glycolysis. In a previous study, comprehensive the characterization of ChCl–Zn(OAc)$_2$, including its structural and thermal properties, was thoroughly conducted (Zhou et al., 2019). In the present work, the reaction conditions, including temperature, time, EG dosage, and DES quantity, were optimized to maximize both PET conversion and BHET selectivity.

Fig. 1 shows the results of PET glycolysis under varying reaction conditions. As shown in Fig. 1A, high PET conversions of 98–99% were obtained over a wide range of DES concentrations (1–20 wt%). Remarkably, even when small amounts of ChCl–Zn(OAc)$_2$ were used, the conversion of PET was significantly enhanced. When no DES was used, the conversion of PET was considerably low, indicating that the addition of a catalyst is necessary for effective PET glycolysis. When the amount of DES was increased to 7 wt%, BHET selectivity increased to 87.5%, followed by a slight decrease to 75% when the DES concentration was further increased. The presence of an excessively large number of hydrogen atoms and coordinating binding sites can lead to the competitive binding of the reactants, reducing the selectivity of BHET (Roagna et al., 2020). This result suggests that an appropriate amount of DES is required to achieve high selectivity for the BHET monomer.

The degree of PET glycolysis was also affected by the reaction temperature. As shown in Fig. 1B, a high PET conversion of 98% was obtained at 180–190 °C. BHET selectivity reached 87.5% at 180 °C, and decreased significantly to 66.0% at 190 °C. At higher temperatures, further thermal depolymerization of the reaction products occurred, leading to a decrease in BHET yield (Wang et al., 2015). It is also noteworthy that ChCl–Zn(OAc)$_2$ remains stable during the PET glycolysis reaction. In a prior study, thermogravimetric analysis of ChCl-Zn(OAc)$_2$ revealed a substantial weight reduction within the temperature interval of 214–478 ℃, notably surpassing the reaction temperature tested in the present study (Zhou et al., 2019).

Fig. 1C shows the increase in PET conversion and BHET selectivity upon increase in the reaction time. Approximately 80% of the samples were decomposed within 1 h under the aforementioned reaction conditions. When the reaction time was extended to 2 h, complete PET conversion was achieved, whereas BHET selectivity continuously increased to 91.6 % after 6 h. To understand the thermal behavior of macromolecular PET over time, a PET sample was collected during glycolysis (0.5 h), and morphological analysis was conducted using SEM. The SEM images of the partially decomposed PET sample showed

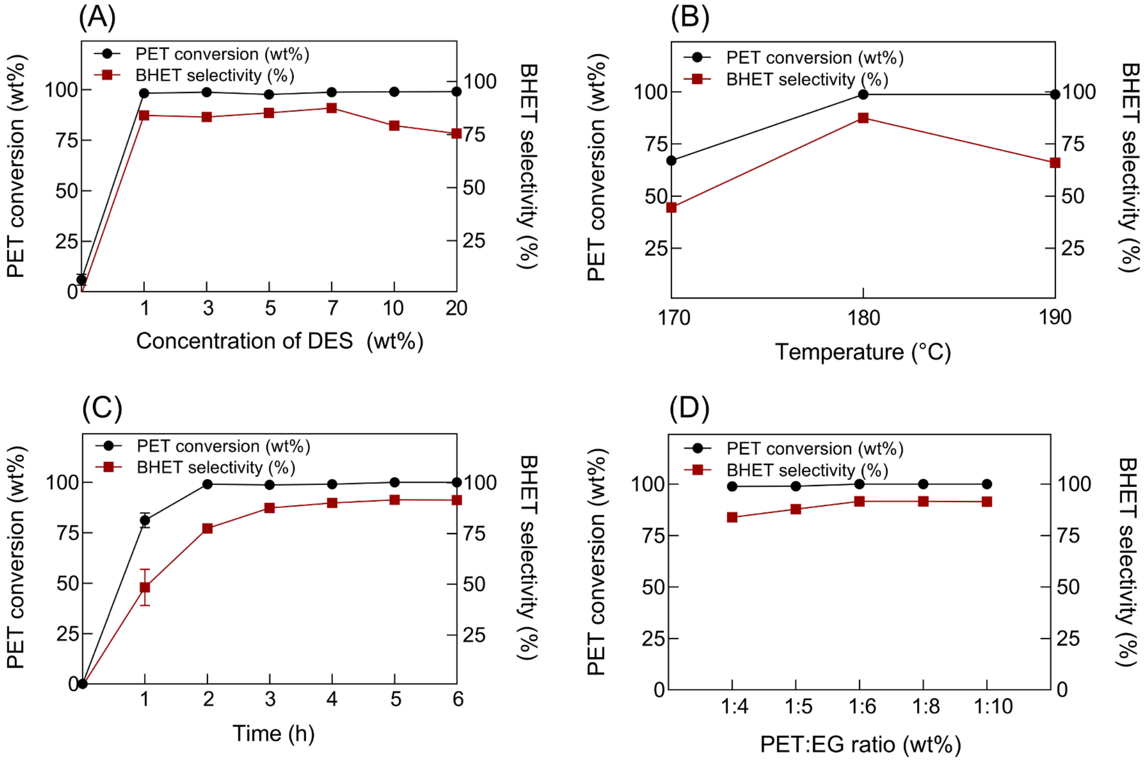

Fig. 1. Optimization of PET glycolysis using ChCl–Zn(OAc)$_2$. Effect of (A) DES concentration (PET:EG = 1:8, T = 180 °C, t = 3 h), (B) reaction temperature (PET:EG = 1:8, C_{DES} = 7 wt%, t = 3 h), (C) reaction time (PET:EG = 1:8, C_{DES} = 7 wt%, T = 180 °C), and (D) EG dosage (C_{DES} = 7 wt%, T = 180 °C, t = 5 h) on PET conversion and BHET selectivity.

multiple cracks and an irregular surface, indicating that glycolysis mainly occurred on the surface of the PET particles (Fig. 2).

One question is whether a decrease in the PET particle size can reduce the reaction time and achieve high PET conversion and BHET selectivity. To answer this question, PET powder with a particle size of 300 μm was subjected to the optimized glycolysis reaction. As shown in Fig. S1, the glycolysis reaction of PET powder proceeded rapidly within 0.5 h, yielding a high PET conversion of 91.2% and BHET selectivity of 71.2%. PET samples of small particle size are expected to exhibit enhanced mass transfer related to the diffusion of EG at the liquid–solid interface, resulting in a fast glycolysis reaction (Zheng et al., 2023). Considering that BHET flakes and powder showed similar BHET selectivity after the reaction, PET glycolysis was found to be particle size-dependent. This also implies that the reaction time can be reduced by changing the particle size of PET. However, to prepare samples with small particle sizes, energy-intensive mechanical pre-processing is required (Qin et al., 2022).

Fig. 1D shows the effect of PET:EG ratio on PET conversion and BHET selectivity. A higher PET:EG ratio resulted in enhanced BHET selectivity. The highest BHET selectivity was 91.6% at a 1:6 of PET/EG ratio and remained unchanged at higher molar ratios. The low BHET selectivities afforded by reduced PET/EG molar ratios may be attributed to the lack of catalytic activity. A PEG/EG ratio of less than 1:6 reportedly results in incomplete coordination with Zn^{2+}, leading to a decrease in BHET selectivity and increase in the production of dimers and oligomers (Liu et al., 2019). Consequently, reaction temperature, duration, PET/EG ratios, and DES concentration were revealed to significantly affect PET glycolysis. A high PET conversion of >99 wt% and BHET selectivity of 91.6 % were obtained under optimal reaction conditions.

3.3. Characterization of recrystallized BHET

BHET, a primary glycolysis product of PET, was recovered, and its structure was confirmed by ^{1}H NMR and GC–MS analysis. Fig. 3A displays the ^{1}H NMR spectra of authentic BHET and BHET recovered after DES-mediated glycolysis. The signals at 3.73 and 4.32 ppm are characteristic of the methylene groups (–CH_2–) of EG. The signals at 4.97 and 8.11 ppm represent the protons of the hydroxyl group and four aromatic protons, respectively. In addition to the NMR analysis, gas chromatography (Fig. 3B) confirmed that the recovered crystals were BHET monomers of high purity (>99%).

3.4. Reaction mechanism of PET glycolysis with ChCl–Zn(OAc)$_2$

The screening test revealed that Zn-containing DESs outperform other metal-containing DESs (*i.e.*, Mn and Co). DFT-based computational analyses were conducted to elucidate the interactions among the reaction components. The optimized intermediate complex structures of DESs (ChCl–M(OAc)$_2$, M = Zn, Mn, and Co), EG, and PET are shown in Fig. 4; various H-bonds and coordination bonds were formed among the molecules of the intermediates (Ju et al., 2018). The optimized intermediate structure of the ChCl–Zn(OAc)$_2$-containing system (Fig. 4A) exhibited five H-bond networks, including hydroxyl $H_{choline}$–O_{EG}, hydroxyl H_{EG}–carbonyl $O_{acetate}$, O_{EG}–H_{PET}, carboxylate $O_{acetate}$–H_{EG}, and Cl–$N_{choline}$. In addition, two coordination bonds, Zn–Cl and Zn–carbonyl O_{PET}, were observed.

Regarding ChCl–Mn(OAc)$_2$, four H-bonds were formed: hydroxyl H_{EG}–carboyl $O_{acetate}$, H_{EG}–carboxylate $O_{acetate}$, hydroxyl $H_{choline}$–hydroxyl O_{EG}, and Cl–$N_{choline}$. Two coordination bonds, Mn–Cl and Mn–carbonyl O_{PET} were observed in the stable intermediate complexes (Fig. 4B). Similarly, the ChCl–Co(OAc)$_2$-containing reaction system contained H-bonds, including hydroxyl H_{EG}–hydroxyl $O_{choline}$, hydroxyl H_{EG}–carboxylate $O_{acetate}$, hydroxyl $H_{choline}$–carbonyl $O_{acetate}$, and carbonyl O_{PET}–Co. Only one coordination bond was formed between Co and Cl.

The interaction energy of the stable intermediates are shown in Fig. 5. The intermediate complex with Co(OAc)$_2$ showed the highest intermediate interaction energy, whereas the complex containing Zn

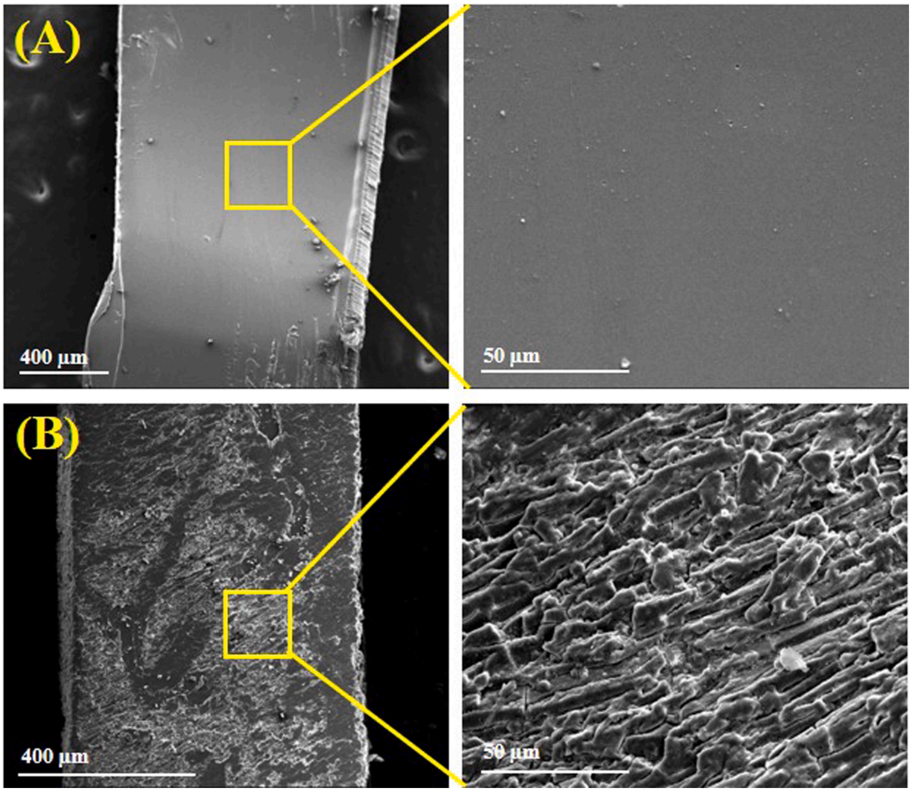

Fig. 2. SEM images of untreated PET fragment (A), partially degraded PET fragment after glycolysis at 180 °C for 30 min with ChCl–Zn(OAc)$_2$ (B).

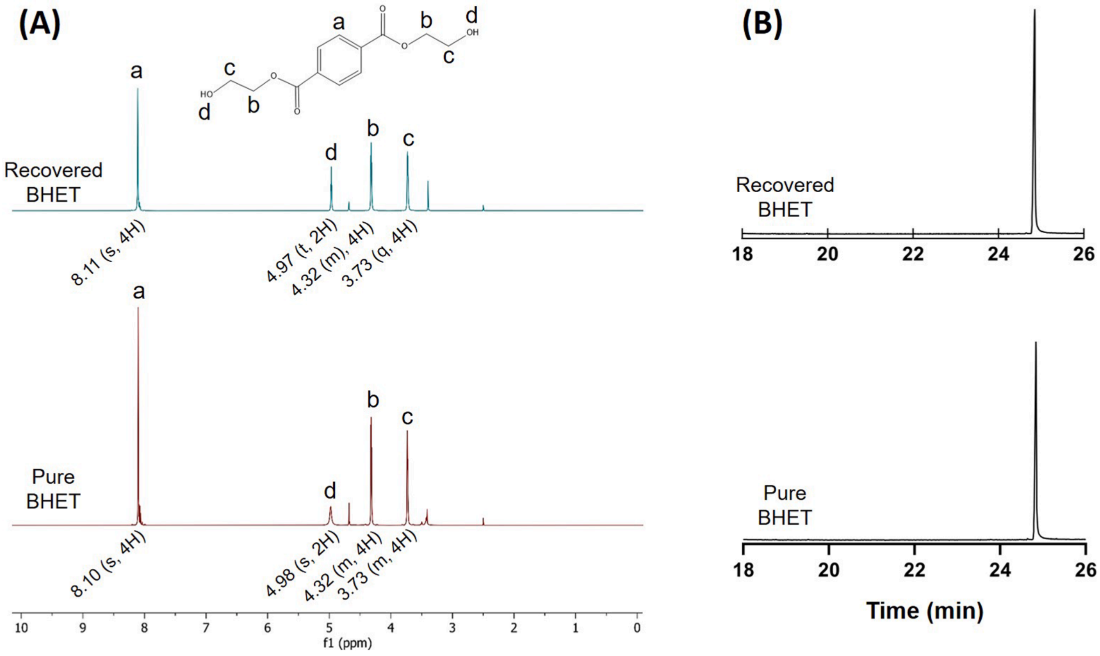

Fig. 3. ^{1}H NMR spectra (A) and gas chromatogram (B) of BHET monomer.

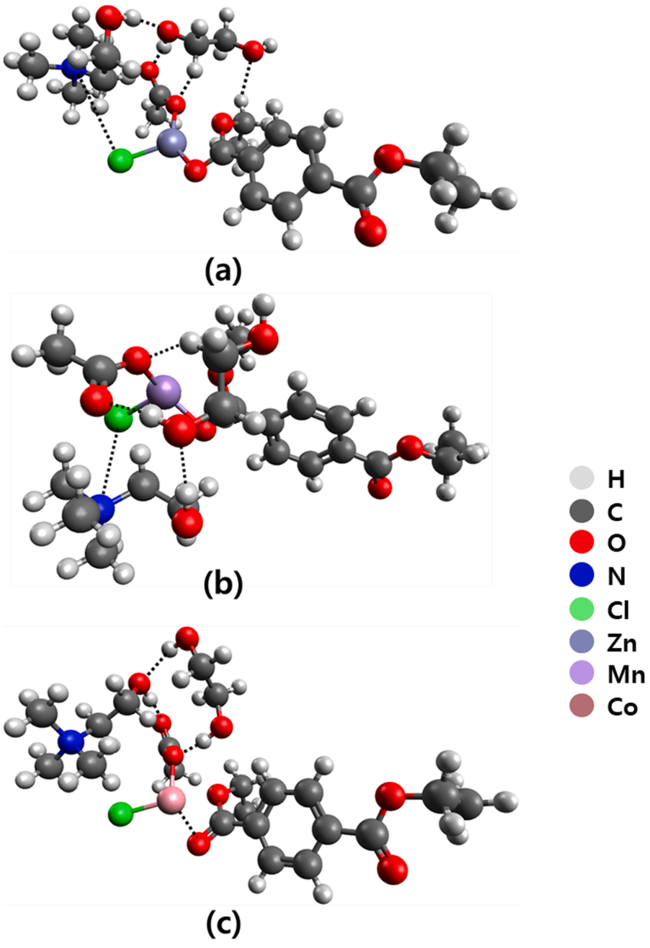

Fig. 4. Optimized structures for the intermediate complexes between ChCl, EG, PET, and metal acetate: (A) $Zn(OAc)_2$, (B) $Mn(OAc)_2$, and (C) $Co(OAc)_2$. Dashed black lines represent H-bonds.

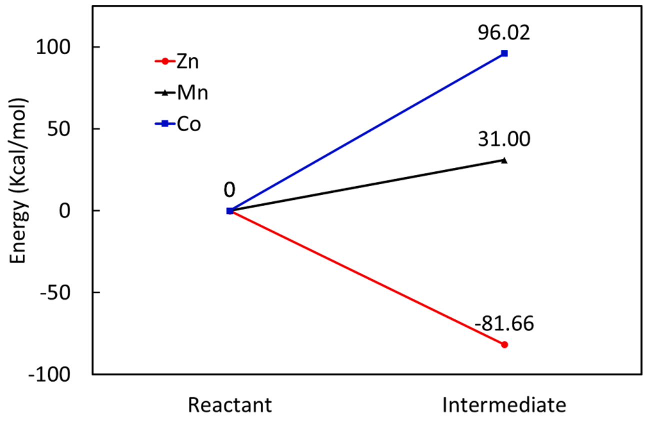

Fig. 5. Interaction energy of the complexes with different metals ions.

$(OAc)_2$ showed the lowest. Obviously, the ChCl–$Zn(OAc)_2$ DES complex was the most stable intermediate, followed by Mn- and Co-containing complexes. Considering the occurrence of strong interactions when ChCl–$Zn(OAc)_2$ was employed, the lowest interaction energy was expected, which is in good agreement with the experimental results observed above.

In the present work, we employed DFT-based calculations to reveal a critical mechanistic insights. The formation of H-bonds and coordination bonds between EG, PET, choline, and metal acetate play a key role in accelerating the degradation of PET, supporting our hypothesis. Notably, among the various DESs assessed, it was evident that the Zn-containing DES system was the most promising catalyst for facilitating the glycolysis of PET.

3.5. Random forest model to predict PET conversion and BHET selectivity

In our research, a Machine Learning (ML) model was developed using experimental data to predict both PET conversion and BHET selectivity, as shown in Fig. 6. An important limitation of this study was the relatively small dataset size, comprising 54 data points (see Table S2 for all the data used). Despite this constraint, the random forest method

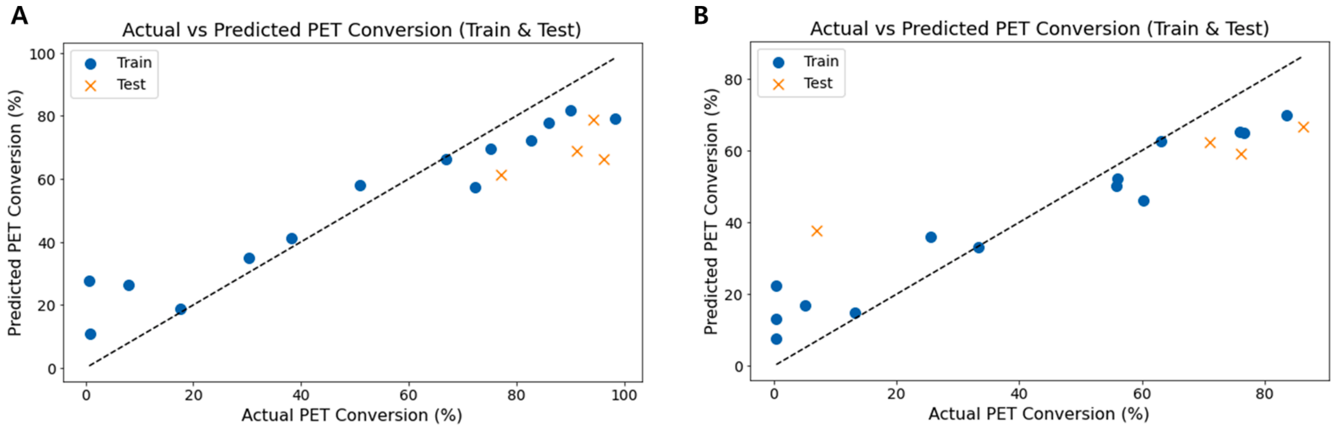

Fig. 6. Comparison of actual and predicted PET Conversion (a) and BHET Selectivity (b) using Random Forest Regression Model on Train and Test Sets (averaged data).

was selected due to its proven effectiveness in handling small datasets. To mitigate the risk of overfitting, a portion of the data was set aside as a test set, allowing for a robust validation of our ML model's performance.

The dataset for the present study 18 different conditions, each represented by three experimental values. We employed two different methodological approach to analyze the data. Initially, each data point was averaged per condition to generate an average model. Subsequently, all 54 individual data points were utilized to construct a full data model. Both approaches were implemented using the random forest regression method.

In the performance evaluation of the average model, the Root Mean Squared Error (RMSE) for PET conversion was 12.3% in the training set, which exhibited an increase to 21.6% in the test set. For BHET selectivity, the RMSE was 10.8% in training and rose to 20.6% in testing. This substantial increase in RMSE from training to testing could raise concerns about potential overfitting, particularly with the average model where the discrepancy between training and testing errors was more evident. In contrast, the full data model demonstrated a markedly enhanced performance with significantly lower RMSE values, suggesting a more robust predictive capability. The RMSE for PET conversion was only 2.8% in training and 4.9% in testing, while for BHET selectivity, it was 2.3% and 3.9%, respectively (Fig. S2).

This study further involved a feature importance analysis, which yielded consistent results across both models. This analysis revealed the substantial influence of metal ions (e.g., Component_Fe/Co/Mn/Zn) in the DES structure on both PET conversion and BHET selectivity (Figs. 7 and S3). This finding aligns with our initial hypothesis that metal ions play a crucial role in DES composition, significantly impacting the glycolysis process.

To statistically validate our models, we employed Pearson correlation coefficients and t-tests. The correlation coefficients for PET conversion and BHET selectivity were −0.0104 ($p = 0.9405$) and −0.0430 ($p = 0.7575$), respectively. These values indicate a high degree of similarity in the predictions generated by both models. Additionally, *t*-test results demonstrated no significant statistical difference between the predictions of the two models for both PET conversion and BHET selectivity.

Furthermore, we conducted an AIC (Akaike Information Criterion) and BIC (Bayesian Information Criterion) analysis for both models. The AIC and BIC values for the average model in PET conversion were 116.7 and 124.4, respectively, while for the full data model, they were 331.8 and 352.9. In the case of BHET selectivity, the average model's AIC and BIC were 101.5 and 109.1, compared to 308.1 and 329.2 for the full data model. These results suggest that while the average model exhibited lower complexity, the full data model provided a more precise and efficient explanation of the data.

The utilization of ML was showcased in predicting the performance of DES catalyst for PET glycolysis. Specifically, our study revealed that the random forest algorithm yielded notably improved predictive capabilities, even with a limited dataset. More importantly, the ML model can serve as a potent tool for facilitating the exploration of novel DES compositions within the research community of chemical PET recycling. By reliably forecasting the performance of various DES catalysts, this ML-based with feature importance analysis approach has the potential to substantially reduce the time and resource required for the discovery of optimal DES compositions.

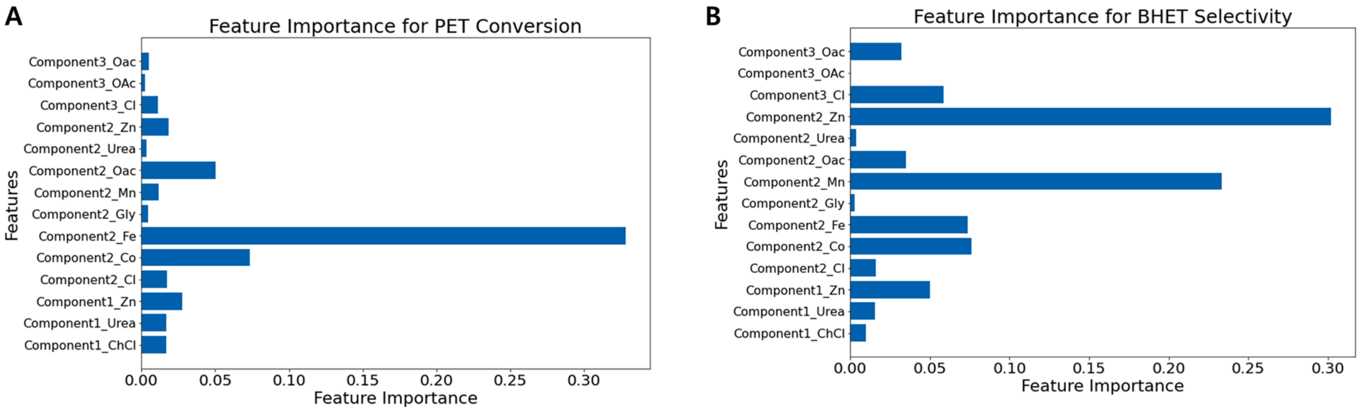

Fig. 7. Feature importance comparison for PET Conversion and BHET Selectivity for the generated Random Forest model.

3.6. Kinetics of PET glycolysis

Various parameters, such as the DES concentration, reaction temperature, time, and PET/EG ratio, affect the kinetics of PET glycolysis. Temperature was found to be an important factor for the selectivity of the BHET monomer. Therefore, the kinetics of the reaction were investigated according to temperature by analyzing the experimental results using a first-order model and the Arrhenius equation. Fig. S4 shows the effect of reaction temperature on the glycolysis rate of PET in the presence of ChCl–$Zn(OAc)_2$ and the activation energy for PET depolymerization through Arrhenius plots. A high linear correlation coefficient (0.9512–0.9964) was observed in the tested temperature range (140–180 °C). The rate constant of the reaction increased rapidly with increasing temperature, indicating that temperature had a significant effect on the decomposition of PET, and a high reaction rate constant of 0.03926 was obtained at 140 °C. Based on these rate constants, the activation energy calculated from the slope of the Arrhenius plot was 162 kJ mol^{-1} (Table S3). The activation energy is expected to be significantly reduced when microwave- and co-solvent-assisted glycolysis is used (Anggo Krisbiantoro et al., 2022; Chiao et al., 2023; López-Fonseca et al., 2011). These estimated parameters can be useful for enhancing PET glycolysis and catalyst performance to improve the efficiency of the process.

4. Conclusions

This study demonstrated the catalytic efficiency of ChCl-containing DESs with metal salts for PET glycolysis under mild reaction conditions. Among the tested DESs, ChCl–$Zn(OAc)_2$ was the best catalyst, resulting in complete PET degradation and a high selectivity for BHET monomers (91.6%). DFT calculations suggested a mechanism in which H-bonds and coordination bonds formed between the PET, EG, and DES components played an essential role in PET conversion. Specifically, the synergistic effect of Zn^{2+} and acetate significantly enhanced the catalytic activity of DES. Also, a ML model developed in this work successfully predicted PET conversion and BHET selectivity for various DESs with low RMSE values. The ML model combined with theoretical calculation can provide insights toward developing a new class of DESs for plastic depolymerization. Although further studies on DES recycling and techno-economic analyses are necessary to make the proposed strategy more sustainable and scalable, this study sets the basis for the development of an effective chemical recycling process for PET.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2023.12.028.

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