RSC Sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Petrovski, H. Q. Araujo, D. Martins, J. Gonçalves, I. Matos, M. Ventura, M. E. Dinis, D. Fonseca Tomazio, L. C. Branco and N. Lapa, *RSC Sustainability*, 2026, DOI: 10.1039/D6SU00314A.

ROYAL SOCIETY OF CHEMISTRY

Sustainability Spotlight Statement

View Article Online
DOI: 10.1039/D6SU00314A

This work contributes to sustainable plastic waste management by presenting a low-energy and resource-efficient method for the depolymerisation of polyethylene terephthalate (PET) under mild conditions. The process operates at ambient temperature during the depolymerisation stage, reducing energy requirements compared with many conventional PET recycling approaches.

A key sustainability achievement is the replacement of dichloromethane with dimethoxymethane as a greener co-solvent while maintaining effective PET conversion. In addition, the process provides high atom economy, minimises waste generation, and enables recovery of terephthalate-based products suitable for further valorisation within a circular economy framework.

The work supports the principles of green chemistry by improving energy efficiency, reducing the use of hazardous substances, and promoting chemical recycling pathways that can contribute to more sustainable management of plastic waste streams.

View Article Online
DOI: 10.1039/D6SU00314A

ARTICLE

High Atom-Economy Low-Temperature Depolymerization of Polyethylene Terephthalate Using Choline Hydroxide

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Hugo Q. Araújo,[a,b] Diogo Martins,[a] João Gonçalves,[a] Inês Matos,[a] Márcia Ventura,[a,c], Mário Diniz,[d] Diana Tomázio,[b] Luís C. Branco,[a] Nuno Lapa,*[a] Željko Petrovski,*[a,e]

This study investigates the low-temperature depolymerization of polyethylene terephthalate (PET) using near-stoichiometric choline hydroxide (ChOH) in methanol, assisted by dichloromethane (DCM) or dimethoxymethane (DMM) as co-solvents. The DCM-assisted system enables rapid apparent PET depolymerization within 30 min under mild conditions, whereas the DMM-assisted system achieves hydrolysis within 20 h at room temperature, yielding choline terephthalate and ethylene glycol. Although slower, the DMM-assisted process proceeds more smoothly, as supported by spectroscopic and microscopic analyses, while the DCM-assisted route leads to accumulation of partially hydrolysed intermediates and transient micro/nanoplastic residues during the early stages of hydrolysis. The studied processes exhibit high atom economy due to the near-stoichiometric use of choline hydroxide and simplified product isolation without acid neutralization or extensive purification steps. In addition, benchmarking based on energy and environmental metrics was extended to account for multistage operations such as solvent removal, drying, and metathesis processes, enabling more comprehensive comparison with previously reported PET depolymerization methods. The results highlight the importance of balanced benchmarking when evaluating sustainability claims in chemical plastic recycling and demonstrate the potential of choline hydroxide-mediated PET hydrolysis as a low-temperature and resource-efficient depolymerization strategy.

Introduction

Human society has become increasingly reliant on plastic. However, plastic pollution is a significant issue, as current plastic recycling rates are low. This means that most of the plastic waste ends up in landfills or the ocean. Approximately 90% of the solid waste found in the oceans is plastic, and around 10% of all manufactured plastic enters the hydrosphere. Increasing recycling and upcycling rates is currently a critical strategy for developing novel technologies and addressing the issue of plastic pollution, recent research has focused on improving the degradation of more labile polymer systems, including biodegradable plastics, often in combination with the pre-treatment strategies to enhance efficiency [1,2].

Polyethylene terephthalate (PET), a polyester plastic, is one of the most widely used packaging materials for beverages, accounting for 44.7% of single-serve beverage packaging in the US alone [3]. It also represents 12% of global solid waste and 10.8% of all conventional plastics. [4] While the biodegradation of PET, which belongs to the polyester group of polymers, is conceptually attractive, it is also challenging without modification or engineering of the involved enzymes or microorganisms. Most PET-hydrolysing enzymes exhibit significant degradation efficiency only at elevated temperatures, approximately 70 °C, and preserving the thermal stability of the enzyme is difficult. [5] Consequently, chemical PET depolymerization processes have attracted considerable attention. However, these methods often require high temperatures (above 70 °C) and/or long reaction times. Some successful methods involve stoichiometric or catalytic reactions with bases [6–14] and ionic liquids/deep eutectics [15–18]. Recent developments also include the integration of computational approaches and advances in sustainable materials, which constitutes significant scientific progress [19–21]. Machine Learning (ML) has been crucial, accelerating the optimization of Deep Eutectic Solvents (DES) and Ionic Liquid (IL)-catalysed glycolysis, with models developed to predict essential physicochemical properties (such as viscosity and eutectic temperature), facilitating the rational design of improved and greener solvents [19,21,22]. In terms of catalytic and chemical innovation, new classes of catalysts have been introduced, such as tetra-cationic imidazolium ionic liquids for CO_2 capture and conversion [23] and bis-phosphonium terephthalate catalysts for neutral PET hydrolysis, designed to circumvent product inhibition [24]. More eco-friendly processes include PET degradation via neutral hydrolysis using deionized water [25] and multifunctional

[a] LAQV REQUIMTE, NOVA School of Science and Technology | NOVA FCT, Portugal
[b] VALORSUL S.A., 2650-262, Amadora, Portugal
[c] Escola Superior de Tecnologia do Barreiro - Instituto Politécnico de Setúbal
[d] UCIBIO, NOVA School of Science and Technology | NOVA FCT, Portugal
[e] GILAB DOO Beograd, 11050 Belgrade, Serbia

*Corresponding authors: z_petrovski@yahoo.com ; ncsn@fct.unl.pt

systems employing bio-based solvents (Cyrene) for flexible conversion into polymeric products [26], alongside the capability to promote polymerization from monomers and oligomers, with antimony being an efficient catalyst in this upcycling process [27]. Finally, reaction and monitoring techniques have technically advanced, with the full valorisation of mixed textile waste into methyl benzoate [28] and the use of a Fused Silica Capillary Reactor coupled with Raman spectroscopy for in situ kinetic studies of PET hydrolysis at high temperature [29].

The most efficient low- or room-temperature chemical PET transformation procedures described in the literature are transesterification [6] and hydrolysis methods employing dichloromethane (DCM) as a co-solvent. Thus, selective PET depolymerization procedure with the KOH/EtOH/DCM, recently applied to waste plastic blends and composites containing PET [8], as well as with KOH/MeOH/DCM [30], provide rapid hydrolysis under relatively mild conditions. These reactions were reported to reach high PET conversions within 30 min at temperatures as low as 35 and 50 °C. According to the reported yields and process characteristics, such systems may exhibit favorable energy and environmental performance due to the combination of high conversion efficiency, low operating temperature and short reaction times. Furthermore, the degradation solution can reportedly be recycled through relatively simple solvent recovery and distillation.

The hydrolysis products are alkali metals salts (K, Na). If not used directly, conversion to terephthalic acid requires neutralization with sulfuric acid, generating significant salt byproducts, and reducing overall environmental performance. Moreover, organic terephthalate salts themselves may constitute useful intermediates or functional media for further transformations, potentially avoiding additional neutralization steps, particularly in the context of choline-based ionic liquids and deep eutectic systems discussed below [31–33]. Furthermore, if the organic cation is biodegradable, such as the choline cation, the environmental impact could be further reduced as choline is an essential nutrient for living cells and easily biodegraded [34]. Additionally, choline hydroxide solution in methanol (approximately 45%) is readily available as an industrial reagent and sold by the Sigma-Aldrich Company, so it can be used instead of KOH or NaOH in similar PET depolymerization procedures.

Due to choline's rapid biodegradability, non-toxicity, and large-scale availability of choline chloride, there has been a growing interest in the synthesis and application of biocompatible choline cation-based compounds, such as choline-based ionic liquids (ILs) and deep eutectic solvents (DES), particularly in industrial applications and even in food packaging [31,35]. Thus, the use of choline hydroxide in PET hydrolysis may contribute to more sustainable and environmentally friendly processes in PET transformations [32]. Rapid and efficient alkaline PET hydrolysis typically requires a significant excess of base, concentrated base solutions, elevated temperatures, and large volumes of solvents [8,9,11,13]. Accordingly, considerable effort has been devoted to finding to reduce reaction time, energy demand and material usage in this process. Herein, we described a laboratory-scale method enabling rapid PET flake hydrolysis under mild conditions with favourable atom economy.

Despite the increasing number of reported PET depolymerization methods, direct comparison of their sustainability remains challenging due to differences in reaction conditions, solvent systems, and post-treatment requirements. In particular, metrics such as reaction temperature or time alone do not capture the full energy, and material demands of multistage processes, including solvent removal and product isolation. In this context, the present study aims to evaluate a choline hydroxide-mediated PET depolymerization system under mild conditions using different co-solvents, with a focus on identifying performance-sustainability trade-offs rather than claiming a universally optimal solution.

Results and discussion

PET flakes from plastic water bottles from Caldas de Penacova were used as a plastic PET source. They are virtually pure polymer (for details, see the experimental part in the SI). The bottles, except for the contaminated and coloured parts around caps and labels, were cut into approximately 5 × 5 mm square flakes and used without any additional treatment.

First, the reaction with dichloromethane (DCM) was studied, which had already been used as a co-solvent for PET hydrolysis [8]. Additionally, we also searched for an alternative co-solvent and found that dimethoxymethane (DMM) can be successfully used instead of DCM. Although slower, due to DMM's far lower toxicity and environmental impact, we find the alternative process far more interesting, although, due to the longer reaction time, it is more energy demanding. Thus, while the DCM route is operationally faster, the DMM route represents the greener alternative considered in this work. Finally, we monitored the hydrolysis process by NMR, FTIR and optical microscopy, revealing an additional advantage to the DMM-supported process compared to the DCM-supported one: it is smoother and free of undesirable and possibly harmful intermediates. The results of this investigation are summarised in **Figure 1**.

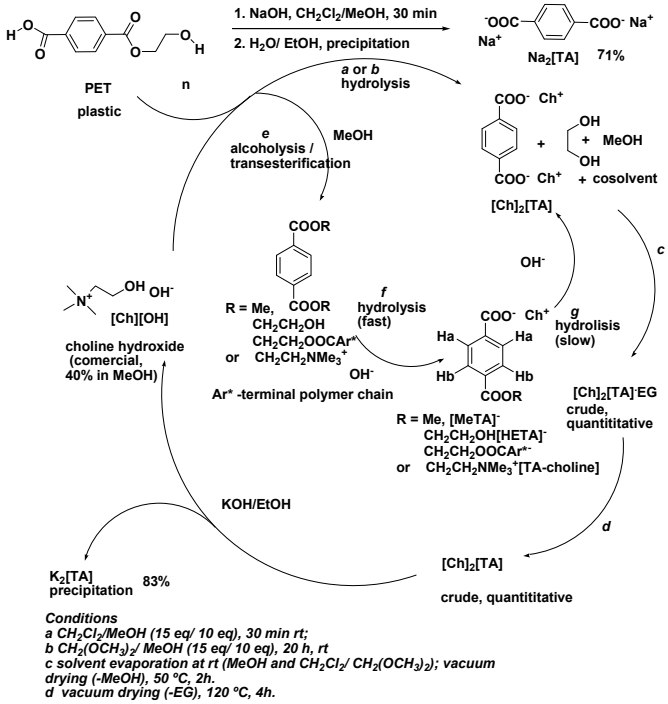

Fig. 1 PET dissolution cycle with use of commercial concentrated ChOH in MeOH and base recovery in ethanol.

DCM as a cosolvent for efficient and fast choline assisted PET hydrolysis

The reaction with DCM as cosolvent is very fast, and after a few minutes of vigorous magnetic stirring, the flakes turn milky-turbid and dissipate light. After 10–15 min, large pieces completely break down, and after 30 min, the reaction appears complete, yielding a turbid brownish suspension. A minimum of 1.1 equivalents of hydroxide (or 2.2 equivalents per two ester groups of the repeating polymer unit) is necessary, as slightly smaller quantities of base (1.05 equivalents) result in incomplete hydrolysis under the studied conditions. A partial reason for this could be the concentration fluctuation of commercial ChOH in MeOH, which is approximately 45% and can vary slightly over time. Therefore, the base concentration and reagent quality were estimated by titration and qNMR. The progress of the hydrolysis can be easily monitored by the presence of unsymmetrical terephthalate intermediates, and eventually microplastic particles and ethylene glycol (EG) species, as detected by NMR and IR spectroscopy and optical microscopy. Hydrolysis, unfortunately, did not proceed as smoothly.

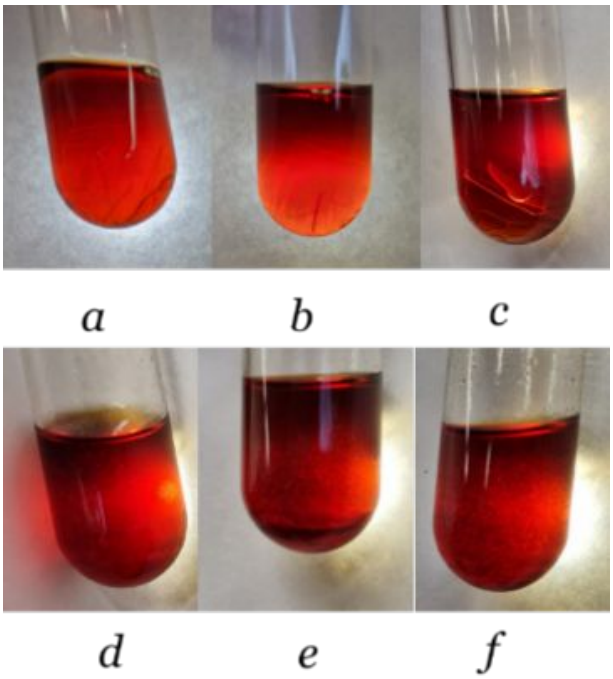

Fig. 2 Reaction mixture aspect for PET pellets hydrolysis in ChOH /MeOH/DCM mixture after: a) 2 min; b) 3 min; c) 5 min; d) 15 min; e) 20 min and f) 30 min.

The crude residue was obtained after evaporation on the vacuum line at room temperature, with almost complete recovery of dichloromethane and methanol (18 g, 91% out of approximately 19.7 g total CH_2Cl_2-MeOH mixture) in a nitrogen-cooled pre-trap. Complete recovery of the remaining solvent, mainly methanol, was achieved by vacuum drying at 50 °C for 4 h, resulting in the crude choline terephthalate and ethylene glycol mixture (crude Ch_2TA·EG) with a 1:1 proportion of the components, as indicated by ^{1}H NMR. Interestingly, the full disappearance of signals from intermediates, as well as crystalline intermediates and possibly microplastic (see Chapter 2.3), was only possible after exposure to 50 °C, proving that exposure to this temperature is not only necessary for complete solvent removal but also for the completion of the reaction. Ethylene glycol (EG) was subsequently removed through vacuum drying at 120 °C for 4 h, yielding crude Ch_2TA in quantitative yield as a hygroscopic yellow-brown powder. The ^{1}H NMR indicates a slight excess of choline cation in relation to terephthalate and the presence of some water. The EG only appears in traces (0.06 eq), visible as a singlet at 3.66 ppm. The EG, being a high boiling point liquid (bp 195 °C), is difficult to evaporate, and its mixture with choline salts has recently been described as an alternative for greener eutectic mixtures [36]. Thus, strong hydrogen-bond interactions between EG and Ch_2TA may also be responsible for the additional difficulty in removing EG from Ch_2TA·EG. The elemental analysis of a crude sample confirms the composition and points to the most accurate empirical chemical formula of Ch_2TA:0.3ChOH:H_2O. The near-equimolar use of the reagent (titrated commercial concentrated choline hydroxide) and a simple workup procedure—consisting solely of evaporation and recovery of the used solvent and EG formed, without the need for additional solvents, extraction procedures, or separation—ensures quantitative transformation with 100% atom economy for the described reaction.

For academic research, X-ray quality single crystals of pure choline terephthalate (Ch_2TA) were obtained by slow crystallization from anhydrous tetrahydrofuran [37]. We attempted to get a pure compound through precipitation/crystallization. However, the distinct ionic components (hydrophilic choline and hydrophobic terephthalate) hindered successful bulk crystallization, at least in protic solvents (the only ones showing satisfying solubility), resulting always in the separation of choline (which preferred to remain in solution) and terephthalic acid (which preferred to precipitate).

Attempting to substitute ChOH with NaOH in a MeOH-DCM for hydrolysis proved also troublesome. Incomplete hydrolysis and recovery of unhydrolyzed PET flakes were seen due to the formation of a very viscous reaction mixture containing insoluble salts clogging the reaction. Adding more solvent did not improve agitation, and a significant quantity of flakes remained intact. The isolated yield of pure sodium terephthalate (Na_2TA) was 71% and it was achieved with precipitation from EtOH. Since hydrolysis of PET flakes appears to be more sustainable using choline hydroxide (which requires a much smaller quantity of solvent), we attempted to prepare Na_2TA by precipitation in a subsequent ion metathesis reaction with sodium chloride (48 h after the hydrolysis reaction) while simultaneously recovering choline chloride and an ethylene glycol solution in MeOH-CH_2Cl_2. The precipitated salt was filtered off, washed with cold methanol, and dried under a vacuum. However, the ^{1}H NMR analysis indicated that, at least in this solvent mixture, the attempt at a metathesis reaction appeared incomplete, leading to the precipitation of impure sodium terephthalate along with some choline, ethylene glycol, and methanol.

As reported in recent literature, hydrolysis of PET with KOH in ethanol/dichloromethane seems to be very effective [8]. However much higher solvent loads were used in this process, and the prepared salt was washed out with water, requiring additional energy input for salt recovery by evaporation. Therefore, another approach was tested here. Unlike sodium and potassium hydroxides which are very soluble in methanol and ethanol their salts are very insoluble (particularly potassium salts in ethanol) [38]. In the present system, choline-containing species were observed to be considerably more soluble in ethanol, making metathesis reaction between KOH and crude Ch_2TA suitable for obtaining pure potassium terephthalate (K_2TA) salt, by simple precipitation and filtration without any additional purification. Recycled and concentrated alcoholic solutions of choline hydroxide can thus potentially be reused in a continuous process for transforming waste PET and preparing pure sodium and potassium terephthalate salts by precipitation from

alcoholic solution without the use of water and without the need for evaporation of aqueous solutions. This method proved very successful on laboratory scale providing high-purity K_2TA, confirmed by ^1H NMR and elemental analysis (83% yield).

Search for alternative co-solvent for hydrolysis

Accordingly, DCM was retained as an efficiency benchmark, whereas DMM was investigated as the greener alternative. According to the CHEM21 solvent guide, substituting methanol with ethanol in the studied reaction can improve both health and environmental scores (health score: 7 vs. 3; environmental score: 5 vs. 3, for methanol and ethanol, respectively). Additionally, our experiments indicated that choline hydroxide (ChOH) is more easily recovered in an ethanol solution with KOH. Thus, concentrating ChOH in ethanol and using recycled ChOH in ethanol for hydrolysis could provide even better alternative for the reaction, enhancing probably both efficiency and recyclability of ChOH (see Figure 1). This approach was not explored further in this work (although can serve as basis for further investigations) due to the readily available commercially concentrated ChOH in methanol and the general positive recommendation for methanol use in comparison to ethanol. Unlike methanol, however, dichloromethane (DCM) is classified as a hazardous solvent with high health (7) and environmental (7) scores [39]. DCM hepatotoxicity has been observed in oral and inhalation exposure studies in animals. Additionally, neurologic effects, including long-term neurological impacts persisting after chronic exposure, have been reported. DCM is also classified as "likely to be carcinogenic to humans", based on evidence of carcinogenicity at two sites: the liver and lungs [40]. Therefore, despite its ease of recovery from our mixture, replacing DCM is strongly advisable. Thus, except for being greener, alternative solvents to dichloromethane (DCM) were screened based on two main additional criteria: to enable the reaction at room temperature (maintain low energy requirements), and to be easily removable, ideally through evaporation. To test this, PET flakes (approximately 200 mg) were placed in test tubes, followed by the addition of around 0.65 mL of a commercial ChOH/MeOH solution and 1–2 mL of the tested cosolvent. For comparison, a parallel experiment was conducted using DCM as the cosolvent. Several commercial laboratory solvents were tested first: water, methanol, THF, acetonitrile, 1,4-dioxane, isopropanol, diethyl ether, and petroleum ether (bp 30–60 °C). Among these, water and methanol, like DCM, formed a single-liquid phase, while less polar solvents formed two liquid phases with the reagent (ChOH in MeOH). PET flakes at the beginning of the reaction appear as separate solid chunks in contact with liquid phase(s). They eventually change and break down as the reaction proceeds but seem never to completely dissolve forming some partially crystalline precipitates. Since methanol is fully miscible with most organic solvents (except highly non-polar hydrocarbons), the formation of two liquid phases from methanol and less polar solvents mixture is due to salting-out effect of ionic compounds, a phenomenon recently also documented with choline salts solutions [33,41].

Interestingly, in the case of THF and 1,4-dioxane, visible changes to the PET pellets (such as pellet opacity) were observed after a few hours of exposure to the mixture and seemed somewhat similar to the changes seen with DCM after just a few minutes. As expected, the complete breaking of the pellets occurred after 30 min with DCM in test tube but took 20 h with THF and 1,4-dioxane. In contrast, no visible changes were noted with any other tested solvent mixtures, even after prolonged exposure and observation (several days). In a separate experiment conducted in a flask with methanol as the sole solvent and with magnetic stirring, deterioration of the PET pellets was observed only after nearly two weeks. Similarly, though not precisely tracked, an even slower room-temperature process appeared to occur in aqueous solutions and with solid (solventless) ChOH obtained by evaporation of the methanol from the reagent and exposure of the surface of PET pellets to the pure choline base.

Since the dissolution process appeared to benefit from polar ethers (as demonstrated by the effectiveness of THF and 1,4-dioxane compared to diethyl ether), it was hypothesized that some compounds possessing similar alkoxy functionalities but with higher polarity than ethers—such as acetals, orthoesters, aminals, and orthoester amides—might exhibit a comparable effect. This hypothesis seemed reasonable, as these compounds share structural similarities with DCM, featuring a carbon atom substituted with two or more oxygen or nitrogen atoms instead of chlorine. To our knowledge, these compounds do not appear to have been previously tested for this purpose and could be interesting alternatives to halogenated solvents in general. Additionally, although THF and 1,4-dioxane showed potential as alternatives to DCM and are commonly used solvents, they are expensive and considered problematic and hazardous by the CHEM21 solvent guide [27].

To test our hypothesis, we selected compounds from those available in our lab that met additional criteria and were liquid at room temperature. The following compounds were tested in tube experiments as co-solvents: 2,2-dimethoxypropane, dimethoxymethane (DMM), triethyl orthoformate, dimethoxy-*N,N*-dimethylmethaneamine (dimethyl acetal of DMF), and bis(dimethylamino)methane. All of these formed a liquid two-phase system with the reagent (ChOH/MeOH). However, after 20 h, only DMM provided PET dissolution similar to THF and 1,4-dioxane. Besides always forming two liquid phases (unlike the mixture in DCM), the DMM reaction mixture shows some similarities with the DCM system. Thus, PET pellets turn whitish but much more slowly and completely disappear after 20 h.

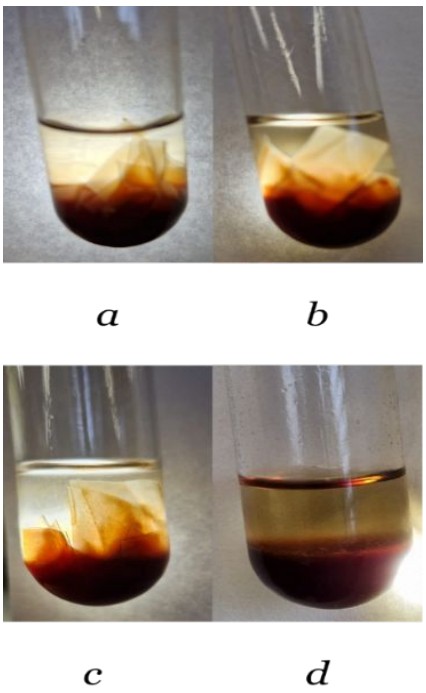

Fig. 3 Reaction mixture aspect for PET pellets hydrolysis in ChOH (1.1 eq)/MeOH/DMM after: a) 2 min; b) 15 min; c) 30 min; d) 20 h.

The preparation of crude choline terephthalate from PET bottle flakes using DMM instead of DCM was conducted on a 10 g scale (see Procedure B in the experimental section). The main difference was the reaction time (20 h instead of 30 min) while the simple consecutive treatment, consisting only of solvent evaporation, remained practically the same. The DMM and MeOH mixture was evaporated, followed by vacuum drying at 50 °C for 4 h to completely remove methanol and obtain crude $Ch_2TA{\cdot}EG$. Further drying at 120 °C for 4 h removed EG, yielding crude Ch_2TA. The respective products (Ch_2TA EG and Ch_2TA) were thus prepared in quantitative yields also, and their spectral characterization by ^{1}H NMR was identical to products obtained in DCM procedure (see the spectra in supporting Information).

The most noticeable difference with reaction promoted by DMM and DCM was the reaction time required for the breaking of PET pellets (30 min for DCM vs 20 h for DMM). The slower process with DMM may be attributed to presence of two liquid phases during the reaction. Thus, to clarify how exactly DMM affects the hydrolysis, a series of ^{1}H NMR experiments were conducted on neat liquid phases isolated from: the upper phase (a) obtained after mixing DMM and ChOH in MeOH and allowing it to settle for 20 h; the lower phase (b) of the same mixture; (c) 1:1 volume mixture of DMM and MeOH; (d) The pure reagent (ChOH in MeOH); (e) pure MeOH; pure DMM (f).

For all samples, 500 µL were taken and analysed by ^{1}H NMR in their neat form in 5 mm tubes, containing also capillary (external solution of TSP in D_2O for lock and calibration as external standard). To samples (b) and (d), a small quantity of maleic acid was added too, to serve as an internal standard in order to estimate the quantity of components present by qNMR [42] (see **Figure 4** and **SI table 1** and **SI table 2**).

The ^{1}H NMR spectrum of the mixture of DMM/MeOH (sample c, see also **SI spectrum 7**) was notably different from those of pure MeOH (e, **SI spectrum 9**). While position of DMM signals in mixture (c) is not different or shifted in respect to pure DMM (f, **SI spectrum 8**) in pure MeOH (e), the CH_3 and OH group signals appeared as broad singlets. However, in the 1:1 DMM:MeOH mixture (c), these singlets are transformed into distinct doublet and quartet, indicating slower proton exchange due to the lower polarity of the mixture. The ^{1}H NMR spectra analysis revealed no significant differences between samples a (**SI spectrum 10**) and f, confirming that the upper phase in the DMM/ChOH/MeOH mixture consists primarily of DMM. In contrast, lower phase (sample b, **SI spectrum 11**) and pure reagent (sample d, **SI spectrum 6**) are not so similar. The proportion of ChOH and MeOH in both is essentially similar and as expected from reagent concentration (1: 4.7 vs 1:4.5), but sample d was somewhat more hygroscopic – accumulated more water during sample preparation and NMR analysis (see also **SI table 1** and **2** for calculations) with the molar proportion ChOH:MeOH: H_2O approximately 1:4.5:3.6 while the lower phase of the mixture (sample b) is less hygroscopic and displayed additional signals attributed to DMM with overall ChOH:DMM:MeOH:H_2O proportion 1:1:4.7:2.6. Moreover, the spectra of both samples b and d were significantly distinct from those of the pure solvents and their simple mixture (c, e, and f). Notably, both the methyl signals of both DMM and MeOH as well to lesser degree methylene signals from DMM were shielded/shifted downfield to up to 0.5 ppm. Upper DMM phase thus seems to serve as a DMM reservoir and saturate the reactive (lower) methanolic phase changing its polarity and reactivity and making it less hygroscopic. If this hypothesis is true, further reduction in DMM quantity is possible as it is just necessary to saturate ChOH/MeOH phase. This can be particularly advantageous for larger scale applications.

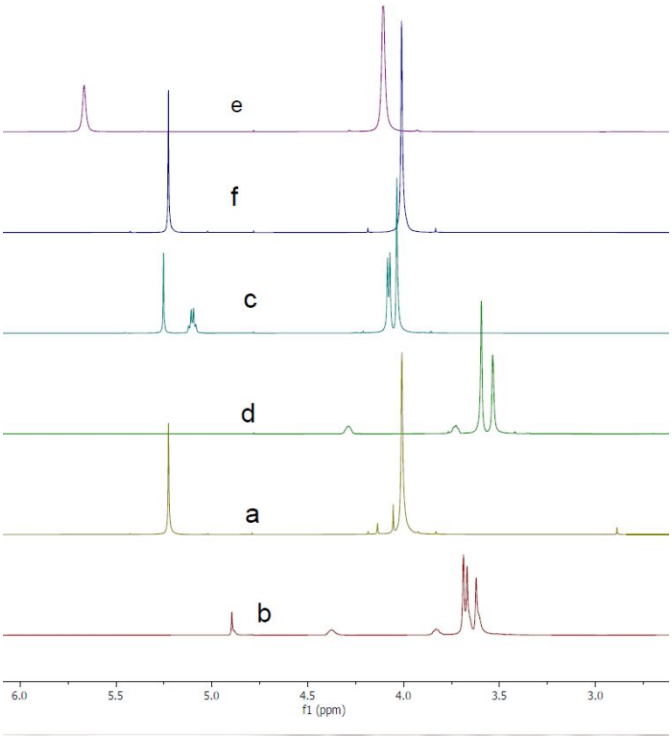

Fig. 4 Neat ^{1}H NMR spectra of the samples: (a) the upper phase obtained after mixing DMM and ChOH in MeOH and allowing it to settle for 20 h; (b) the lower phase of the same mixture; (c) a 1:1 volume mixture of DMM and MeOH; (d) the pure reagent (ChOH in MeOH); (e) pure MeOH and (f) pure DMM. ^{1}H NMR accumulation and

calibration in the presence of external TSP in D_2O. Maleic acid was also used as internal standard in b and d (see SI table 1 and 2).

Slow aqueous and methanolic alkaline hydrolysis of PET is typically described by the "shrinking core model" [6,43]. However, in alcohols (MeOH/EtOH) saturated with less polar co-solvents, additional effects contribute to low energy requirement. These include PET dissolution, swelling, and pore formation [6,8,30]. Decreased solvent polarity facilitate nucleophilic attack on the polyester carbonyl group by hydroxide and methoxide ions [30]. Additionally, the high concentration of choline cations, as observed in ionic liquids and deep eutectic solvents, helps in PET glycolysis and hydrolysis unlike other cations, due to interaction between polyester carbonyl groups and choline hydroxide [44–46] All these processes likely contribute to hydrolysis in DMM/ChOH/MeOH system too, but further kinetic and thermodynamic explorations are required to confirm their exact contribution.

To our knowledge, DMM has already been identified as a greener alternative solvent, albeit infrequently used, and is often absent from solvent selection tables [47,48]. DMM is a liquid with a chloroform-like odour, easily recovered by distillation (boiling point: 42 °C). Although flammable, it is significantly less hazardous unlike ether solvents. Thus, unlike THF and diethyl ether, DMM does not readily form peroxides due to its acetal structure. It is stable under neutral and alkaline conditions and has relatively low toxicity compared to many conventional solvents (LDLo Guinea pig SC: 3013 mg/kg; LC_{50} Guinea pig SC: 5 g/kg; LC_{50} Mouse inhalation: 18,000 ppm/7 hr). Environmentally, DMM is advantageous as it degrades rapidly in the atmosphere through reaction with photochemically produced hydroxyl radicals, with an estimated half-life of just 2.3 days. Overall, it is a far safer and more environmentally friendly alternative to DCM as well as to ether solvents [49]

Monitoring of hydrolytic process

The breaking down of PET flakes appears to proceed very quickly, particularly when DCM is used as a co-solvent. However, visual inspection of the reaction mixture suggests the formation of some crystalline solid. As mentioned earlier, attempts to isolate choline terephthalate through crystallization were unsuccessful, so it was unlikely that those crystals are, in fact, Ch_2TA. Consequently, an experimental setup was prepared to screen the hydrolysis process with DCM and DMM as co-solvents in order to investigate mechanism, intermediates and possible presence of microplastics in process of hydrolysis using optical microscopy and NMR spectroscopy.

In a typical monitoring procedure, hydrolysis was setup at, heterogeneous liquid samples were taken from vigorously agitated reaction mixtures and quenched with saturated ammonium bicarbonate at specific intervals: after 10, 20, 30 min from DCM containing reaction mixtures (samples 1-3) and after 30 min and 20 h from the DMM containing mixtures (samples 7 and 8). Additional solid samples were collected and quenched after solvent evaporation after 30 min and drying for 4 h at 50 °C and 120 °C (samples 4-6 for DCM, and samples 9-11 for DMM, respectively). Sample 3 (quenched after 30 min) was also analysed by ^{13}C NMR, HSQC and IR spectroscopy to elucidate presence of additional intermediates. All samples were evaporated to remove excess solvents and ammonium bicarbonate and dried under vacuum. The samples were dissolved in D_2O and analysed by NMR, IR as well as under optical microscope.

Breaking down of PET flakes appears to proceed very quickly, particularly when DCM is used as co-solvent (see **figure 2** and **SI figure 1**). Within a few minutes PET pellets turn milky whitish and after 30 min they seem completely reduced into powder. Interestingly the ^1H NMR spectra after 10, 20 and 30 min (sample 1-3, **SI spectra 12, 13** and **14**) and after 30 min and evaporation (sample 4 **SI spectra 15**) are quite similar in content Immediately after 10 min, a peak of terephthalate anion (TA) is present (singlet at 7.88 ppm) with growing prominence as time passes (it increases its intensity relative to other signals after 20 and 30 min – spectra 13 and 14). A notable feature in all these spectra is presence of two sets of doublet signals H_a and H_b (at 7.93 and 8.08 ppm) with coupling constant J=8.0 Hz, together with singlet signal at 3.96 ppm attributable all to aromatic hydrogen atoms and methyl group of monomethyl ester of terephthalate anion (MeTA) (see **Figure 1**). These signals are practically identical to those reported in literature [50]. Alcoholysis (i.e. PET transesterification with alcohol) is a prominent competitive reaction to PET hydrolysis which is subsequently completed by diester hydrolysis to terephthalate [8]. The diester hydrolysis proceeds rapidly due to its solubility and reactivity (reaction f, **Figure 1**) so this intermediate does not seem to accumulate enough to be visible in the NMR spectra. DCM does not appear to participate directly in the process, although alcoholysis pathway seems to stall at the monoester stage, likely due to precipitation of the monoester as a salt with choline in the very apolar solvent mixture (methanol and DCM). As a result, a strong, nearly unchanged MeTA signal remains even after the reaction is supposedly finished (after 30 min, see sample 4, **spectrum 15**) and only disappears after heating the evaporated residue for 4h at 50 °C (**spectrum 16**, see reaction g, **Figure 1**).

Another prominent feature in the early-stage hydrolysis spectra is a smaller peak at 8.12 ppm (J= 8.0 Hz). This signal can be attributed to H_a/H_b protons (**Figure 1**, **SI spectrum 14** and **15**) of the other monoester analogue of terephthalic acid–hydroxyethylterephthalate (HETA) as described in recent literature [51]. In addition, signals from some oligomers with terminal polymer chains ending in a TA monoester may overlap with this intermediate signal ($Ar^*COOCH_2CH_2TA$) or potentially even with signals from microplastics. Another aromatic signal of this compound overlaps with MeTA signal at 8.07 ppm and yet another aliphatic signal overlaps with the methyl ester at 3.96 ppm. A small but distinct signal attributable to a -$COO\underline{CH_2}CH_2OH$ of hydroxyethylterephathalate anion (HETA) and oligomers is visible at 4.45 ppm. The presence of this intermediate (HETA) is further confirmed by identical signals in ^{13}C and HSQC (peak at 4.44 and 69.8 ppm in ^1H and ^{13}C NMR spectra respectively) of sample 3 (**SI spectrum 14 – ^{13}C NMR/HSQC**) (see also for comparison SI from [51]).

The ^{13}C and HSQC NMR revealed also a small signal at 4.79 ppm (^1H NMR) and 62.0 ppm (^{13}C NMR). This signal is barely noticeable in ^1H NMR spectrum due to its proximity to the intense HOD at 4.70 ppm. It can be attributed to methylene group of zwitterionic intermediate $ArCOO\underline{CH_2}CH_2N^+Me_3$ intermediate (TA-choline, see **Scheme 1**). If present, the concentration of TA-choline is even lower than that of HETA, based on the signal intensity in the ^1H NMR spectrum. The highlighted methylene signal is the only distinguishable feature attributable to TA-choline, as all other signals likely overlap with those of compounds present at much higher concentration in the mixture. To our knowledge the TA-choline has not been described or characterized in the literature. Closest reported spectral analogue is choline benzoate, whose methylene signal ($PhCOO_2\underline{CH_2}CH_2N^+Me_3$) appears iat 4.70 ppm [52]. Chemdraw prediction for the methylene group of TA-choline intermediate place it at 4.69 ppm (^1H) and 58.2 ppm (^{13}C NMR). Small deviations in chemical shift may arise due to experimental conditions; however, in the absence of exact

experimental data for TA-choline, we cannot completely rule out its possible presence (see also the discussion on microplastics below). Interestingly, after exposure to elevated temperature (4h vacuum drying at 50 °C) all these minor signals are eliminated presumably due to hydrolysis providing final product (terephthalate dianion).

Unlike transient signals of the previously mentioned intermediates (MeTA, HETA), there is another small aromatic signal at 8.46 ppm that also appear in early stages of hydrolysis but does not disappear in the later stages. Its intensity fades over time, so it is most likely related to the hydrolysis product of some plasticizer (e.g isophthalates esters). These compounds, like terephthalate diesters intermediates and unlike polymeric PET are more soluble and therefore more readily hydrolysed in the early stages. However, due to their very low concentration, the signal intensity of the hydrolysed product (isophthalate) diminishes as large quantities of terephthalate are formed through PET hydrolysis, resulting in a relative increase in the intensity of the singlet at 7.88 ppm. Other accompanying aromatic signals of iso phthalate (at 7.66, 8.28 ppm) are very weak and sometimes go undetected by NMR. They appear only as minor impurities in the ^{1}H NMR spectrum of the final product (see spectrum 1). The presence of isophthalate in PET plastic hydrolysis was already confirmed by NMR [42].

Finally, from all these spectral data another interesting feature of the hydrolysis/alcoholysis process can be deduced. The process may occur randomly along the PET chain, as also postulated by DFT calculations [53]. Our spectra provide no evidence for the presence of oligomeric units in significant quantities. Thus, once PET chains are broken by alcoholysis or hydrolysis, they seem to continue degrading most rapidly from the terminal end, which is more exposed to the solution. Alternatively, fast hydrolysis of oligomers as well as diesters (see reaction f), compared to the monoanionic species MeTA, HETA and $ArCOOCH_2CH_2TA$ (see reaction g) renders these intermediates virtually undetectable in the NMR spectra of samples collected during the reaction. Monoanionic species may hydrolyse slowly due to electrostatic repulsion between the anion and the nucleophile (OH^-) or more likely (see mechanistic discussion with DMM below) due to lower solubility and precipitation of these compounds from highly apolar solvent mixtures (MeOH/DCM). This results in the formation of some unidentified crystalline precipitate.

When dimethoxymethane (DMM) is used as a co-solvent in the hydrolysis of PET flakes, the reaction exhibits a markedly different progression. The heterogenous reaction mixture forms two liquid phases resulting in a significantly slower hydrolysis process. Consequently, the first sample was collected for analysis only after 30 min. from a well agitated system to ensure both liquid phases were included.

The ^{1}H NMR spectrum of this sample (SI **spectrum 18**) differs notably from those obtained using DCM as a co-solvent. The hydrolysis appears to proceed smoothly, with signals corresponding to fully hydrolysed terephthalate (singlet at 7.89 ppm) and ethylene glycol (EG) (singlet at 3.67 ppm). Notably, no intermediates such as methyl terephthalate (MeTA), hydroxyethyl terephthalate (HETA), or suspected TA-choline monoesters are detected. This pattern remains consistent after 20 h (SI **spectrum 19**). In contrast to reactions with as a co-solvent, aside from the signals of reagent and solvents, only a very small isophthalate peak is observed at 8.46 ppm (see SI **spectra 18** and **19**). Similar to observations with DCM, evaporation of the reaction mixture yields a residue containing methanol and EG signals (singlet sat 3.46 and 3.67 ppm, respectively). Vacuum drying at 50 °C produces methanol free $Ch_2TA \cdot EG$, while drying at 120 °C yields Ch_2TA. The spectra of both products are identical to those obtained when DCM is used as a co-solvent.

In contrast to the monophasic DCM/ChOH/MeOH system, hydrolysis in the biphasic DMM/ChOH/MeOH system proceeds more slowly but more smoothly. This is likely due to the limited concentration of DMM in the saturated methanolic phase (approximately 1:1:4.7 ChOH:DMM:MeOH molar ratio). This concentration is sufficient to accelerate PET hydrolysis, achieving apparent completion of hydrolysis after 20 h, without significantly decreasing the polarity to the point of precipitating ionic intermediates and thereby slowing their hydrolysis.

Microplastic identification

As previously mentioned, certain signals observed in ^{1}H and ^{13}C NMR spectra during hydrolysis with DCM as a co-solvent cannot be definitively attributed to small molecular intermediates such as TA-choline. These signals may also indicate the presence of microplastic particles (MPs). Recent advancements have introduced high-resolution NMR (qNMR) techniques for the reliable identification and precise quantification of PET microplastic[54,55]. Notably, two characteristic singlet signals for PET MPs have been identified in NMR spectra - for aromatic CH groups: ^{1}H at 8.11 ppm / ^{13}C at 130.1 ppm and for methylene ($-CH_2-$) groups: ^{1}H at 4.78 ppm / ^{13}C at 63.8 ppm. These signals were observed in a $CDCl_3$-TFA (5:1 v/v) medium. To further investigate, sample 3 was examined using ^{1}H and HSQC NMR spectroscopy in both $CDCl_3$ and $CDCl_3$-TFA (5:1 v/v) solvents. Unlike the spectra recorded in $CDCl_3$ (see **spectra 14a**, SI), the spectra obtained in $CDCl_3$-TFA revealed signals attributable to PET microplastics- aromatic C-H: ^{1}H at 8.12 ppm / ^{13}C 130.35 ppm and methylene ($-CH_2-$) groups: ^{1}H at 4.81 ppm/ ^{13}C 60.79 ppm. The chemical shifts of these signals are within the typical variability range for high resolution NMR spectra acquired under consistent conditions (solvent and temperature). Specifically, the variability is approximately ±0.05 ppm for ^{1}H NMR and ±0.2 ppm for ^{13}C NMR. However, the observed difference of approximately 3.0 ppm for the aliphatic CH_2 signal exceeds this typical range [56] This discrepancy may be acceptable given the poor resolution of the spectra in question, characterized by broad and low intensity signals in both ^{1}H and ^{13}C NMR spectra. Such factors likely result from the low concentration of microplastics in the complex sample matrix. Additionally, the CH_2 group is adjacent to an oxygen atom, and its chemical shift may therefore be sensitive to solvent effects, concentration variations, aggregation, hydrogen bonding, and the presence of other compounds [56].

Different techniques for separation combined with visual observation by optical microscopy and FTIR-ATR IR spectroscopy are also commonly employed analytical techniques for identification and quantification of microplastic and nanoplastic particles (MPs/NPs) [57]. According to standard protocols for samples derived from aquatic ecosystems, they are typically filtered using polycarbonate membranes or glass microfiber filters – often following several pretreatment steps. To bypass these procedures, we performed a direct FTIT-ATR IR analysis of crude sample form the hydrolysis to obtain rapid qualitative insight. The IR spectrum of the sample – taken from the reaction mixture of the ChOH/MeOH/DCM system and quenched after 30 min indeed displayed all but one five strongest bands characteristic of PET water bottle pellets (1714, 1095, 1241, 1023 and 1016 ±4 cm^{-1}), in agreement with reported ATR-FTIR data [58,59]. The 1241 cm^{-1} band was not observed, likely to overlap with another strong and broad band at 1276 cm^{-1}. In contrast, the final product - free of any residual MPs only two remaining bands at 1095 and 1014 cm^{-1}, which are unrelated to PET (see Fig. 4). The strongest ester PET carbonyl band at 1714 cm^{-1}

View Article Online
DOI: 10.1039/D6SU00314A

completely disappeared and was replaced by the strongest 1579 cm^{-1} carboxylate anion band [60]. These findings strongly support the presence of non-hydrolysed PET MPs/NPs in the sample taken after 30 min reaction with DCM as co-solvent.

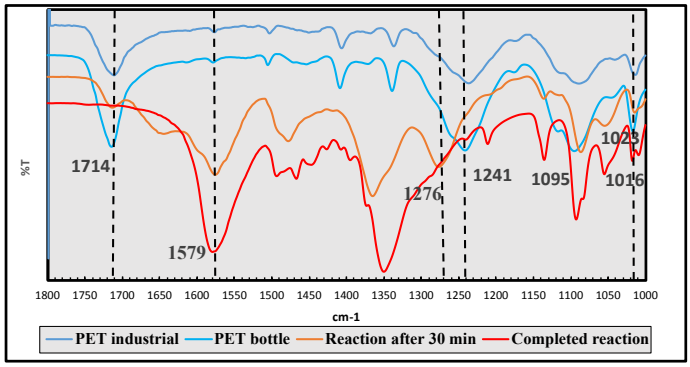

Fig. 5 FTIR-ATR spectra comparison of industrial and water bottles PET pellets and follow up of water bottles PET pellets hydrolysis in the presence of DCM.

Optical microscopy analysis revealed, at certain stages of the hydrolysis process, the presence of microscopic particles with irregular morphology alongside small, well-defined crystalline aggregates. Some particles exhibited partial transparency, whitish coloration, and, in some cases, birefringence under polarized light—features consistent with PET-derived microplastic fragments (figure 5). Conversely, the occurrence of well-formed crystals with uniform geometry and high refraction suggests the possible formation of crystalline monoester intermediates during the reaction. Taken together, these observations indicate that, throughout hydrolysis, solid residues arise from both the physical breakdown of the polymer and the chemical conversion into intermediate products.

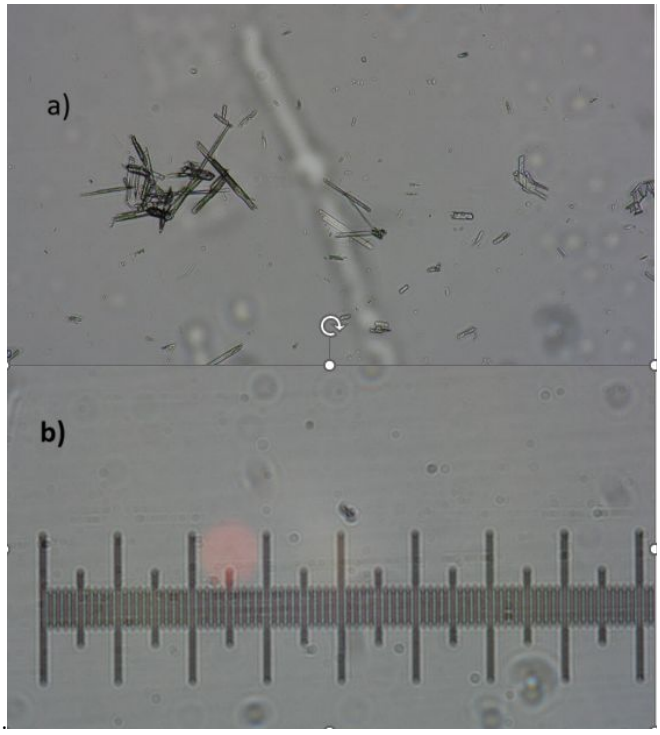

Fig. 6 a) Optical microscopy of the sample of PET flakes hydrolyzed for 20 min with ChOH/MeOH-DCM, b) scale 1 mm.

Energy and Environmental Metrics for PET Hydrolysis

In the chemical depolymerization of PET, researchers are continuously working to improve processes to meet industrial scale standards, reduce energy consumption, increase the yield of highly pure products, and minimize environmental impact. To enable objective comparison, specific energy and environmental metrics were recently introduced by Barnard, E. et al. [61] for easier quantification and assessment of PET transformation processes. These include the energy economy coefficient (ε), environmental factor (E_{factor}) and environmental energy impact (ξ). Together, these metrics provide a comprehensive evaluation of the sustainability and efficiency of chemical processes, considering both resource utilization and environmental impact. These formulae were also slightly modified by Kumar, G. et al. [62] to incorporate additional parameters such as solvent to PET mass ratio, due to its contribution to energy consumption. In this context, the modified metrics are presented here as first derivatives (eg ε ', E'_{factor}, ξ'). However, both proposed metric systems proved inadequate for the present work, as they appear incomplete and fail to account for the significant energy and time demands require for the complete removal of the solvent (MeOH) and secondary product (EG) from the reaction mixture, as previously discussed. Therefore, in this study, it was necessary to develop new equations that consider the requirements of the entire multistep process – from PET flakes to the final product ($Ch_2TA/K_2TA/Na_2TA$) – even though some stages may not involve direct chemical transformation. For simplicity the total multistep process is broken down into a series of individual transformation steps (stages), each defined by specific conditions (time, temperature, reagent and solvent quantities; see eqs. 1-4). Formulae are then derived to calculate the energy and environmental metric parameters for each individual stage, as well as for any sequence of consecutive stages or the entire multistage transformation. These derived metrics are proposed here as practical extensions of the previously reported parameters, intended to facilitate exploratory comparison of multistep depolymerization processes that include work-up and solvent-removal stages.

Stage 1: PET (flakes) $\rightarrow Ch_2TA{\cdot}EG{\cdot}MeOH$ (cosolvent) (eq. 1)
T= 25 °C, t = 30 min for DCM or 1200 min for DMM cosolvent respectively.
Stage 2: $Ch_2TA{\cdot}EG{\cdot}MeOH \rightarrow Ch_2TA{\cdot}EG{\cdot}$ (eq. 2)
T= 50 °C, t= 240 min.
Stage 3: $Ch_2TA{\cdot}EG{\cdot} \rightarrow Ch_2TA$ (eq. 3)
T= 120 °C; t= 240 min.
There is also a unique and final stage 4 corresponding to closing loop in (Scheme 2).
Stage 4: $Ch_2TA + 2KOH\ (EtOH){\cdot} \rightarrow K_2TA + 2ChOH{\cdot}$ (eq. 4)

Thus, modified formulae from Barnard, E. et al. are [61] designated as second derivatives (ε'', E''_{factor}, ξ'') and those from Kumar, G. et al. as third derivative formulae (ε''', E'''_{factor}, ξ'''). They provide two additional (derived) sets of formulae (for comparison of all four systems see table 1). The derived formulae thus enable the calculation of energy and environmental parameter for any consecutive multistep process. In addition, they provide simplified

formulae based on the equations suggested by Barnard et al and Kumar et al, when the calculation is limited to a single chemical transformation step. By doing so the derived formulae thus provide a more comprehensive tool for the evaluation of energy and environmental parameters for any multistep process. The full explanation and details of the formulae derivation are described in supporting information.

The graphical data presented in **Figure 7** for the original formulae by Barnard E. et al. and the first derivative modification by Kumar G. et al. (see also **table 3 and 4 in the SI**) show that parameters calculated for the basic chemical transformations studied here do not significantly differ from the values of some of the most efficient processes described in the literature. See and compare Stage 1, entries 1a and 2a vs. 8a in **Figure 7a**, and entries 1b and 2b vs 4b in **Figure 7b.** The energy economy coefficient (ε and ε') for all these reactions is generally of the same order and among the highest recorded (entries 1a/b, $\varepsilon=5.73\cdot10^{-4}$, $\varepsilon'=6.86\cdot10^{-5}$; entry 2a/b, $\varepsilon=3.33\cdot10^{-5}$, $\varepsilon'=4.41\cdot10^{-6}$ vs entry 8a $\varepsilon=8.25\cdot10^{-4}$ and entry 4b $\varepsilon'=2.55\cdot10^{-5}$ °C^{-1}·min^{-1}), while environmental factors (E_{factor} and E'_{factor}) are among the lowest recorded in the literature (entry 1a/b, E_{factor} =2.61 and E'_{factor} = 1.16 ; entry 2a/b, E_{factor} = 1.08 and E'_{factor} = 0.46; vs entry 8a, E_{factor} = 3.05 and entry 4b, E'_{factor} =0.56). This results in some of the lowest recorded Environmental Energy Impact parameters in literature ranging from 1860 to 32300 for ξ and 16980 to 104 035 °C·min for ξ'.

Table 1: Energy and Environmental Metrics by Barnard, E. formulae [61] its derivation by Kumar, G. et al. (1st derivation) [62] and 2nd and 3rd derivation formulae (this work)

System	Energy Economy Coefficient [°C^{-1}·min^{-1}]	Environmental Factor	Environmental Energy Impact [°C min]
Barnard, E. et al. Formulae	$\varepsilon=\frac{Y}{Tt}$	$E_{\text{factor}}=\frac{[0.1\times(\frac{m(solvent)}{m(PET)})+(\frac{m(catalyst)}{m(PET)})+(\frac{m(other\ substances)}{m(PET)})]}{Y(product)\times\frac{MW(product)}{MW(PET\ monomer-unit)}}$	$\xi=\frac{E(factor)}{\varepsilon}$
Modification of Barnard E. et al. (2nd derivation formulae), this work	$\varepsilon''=\frac{\prod Y(n)}{[\sum T(n)t(n)]}$	$E''_{\text{factor}}=\frac{[0.1\times(\frac{\Sigma m(solvent)}{m(PET)})+(\frac{\Sigma m(catalyst)}{m(PET)})+(\frac{\Sigma m(other\ substances)}{m(PET)})]}{\Pi Y(n)\times\frac{MW(product)}{MW(PET\ monomer-unit)}}$	$\xi''=\frac{E''(factor)}{\varepsilon''}$
Kumar G. et al. formulae (1st derivation of Barnard E. et al.)	$\varepsilon'=\frac{Y}{Tt(\frac{m(solvent)}{m(PET)}ratio)}$	$E'_{\text{factor}}=\frac{[0.1\times(\frac{m(solvent)}{m(PET)})+0.1\times(\frac{m(catalyst)}{m(PET)})]}{Y(product)\times\frac{MW(product)}{MW(PET\ monomer-unit)}}$	$\xi'=\frac{E'(factor)}{\varepsilon'}$
Modification of Kumar, G. et al formulae (3rd derivation), this work	$\varepsilon'''=\frac{\prod Y(n)}{[\sum T(n)t(n)]_{\chi}(\frac{\sum m(solvent)}{m(PET)})}$	$E'''_{\text{factor}}=\frac{[0.1\times(\frac{\Sigma m(solvent)}{m(PET)})+0.1\times(\frac{\Sigma m(catalyst/other)}{m(PET)})]}{\Pi Y(products\ of\ distinct\ stages)\times\frac{MW(product)}{MW(PET\ monomer-unit)}}$	$\xi'''=\frac{E'''(factor)}{\varepsilon'''}$

Y- yield of a particular reaction or stage; *T*-reaction or stage temperature; *t*- reaction or stage time; *m(solvent)* – mass of solvent used in the reaction; *m(catalyst/other substance)* – mass of catalysts or other substances (excluding solvent) used in the reaction (Note that, unlike the original formula by Barnard E. et al.[61] which includes *m(catalyst)* and *m(other substances)* separately, the first derivative formulae by Kumar G. et al [62]. only use *m(catalysts)* applied indiscriminately. However, in many cases the reaction studied is in fact stoichiometric. We decided to avoid this ambivalence in 2nd and 3rd derivative formulae to facilitate possible further discrimination in the future.); *MW (product*) – molecular weight of product and *MW (PET monomer unit)* = 192.04 g/mol for -[OOC(C_6H_4)COOCH_2CH_2]- unit (see also experimental part).

View Article Online
DOI: 10.1039/D6SU00314A

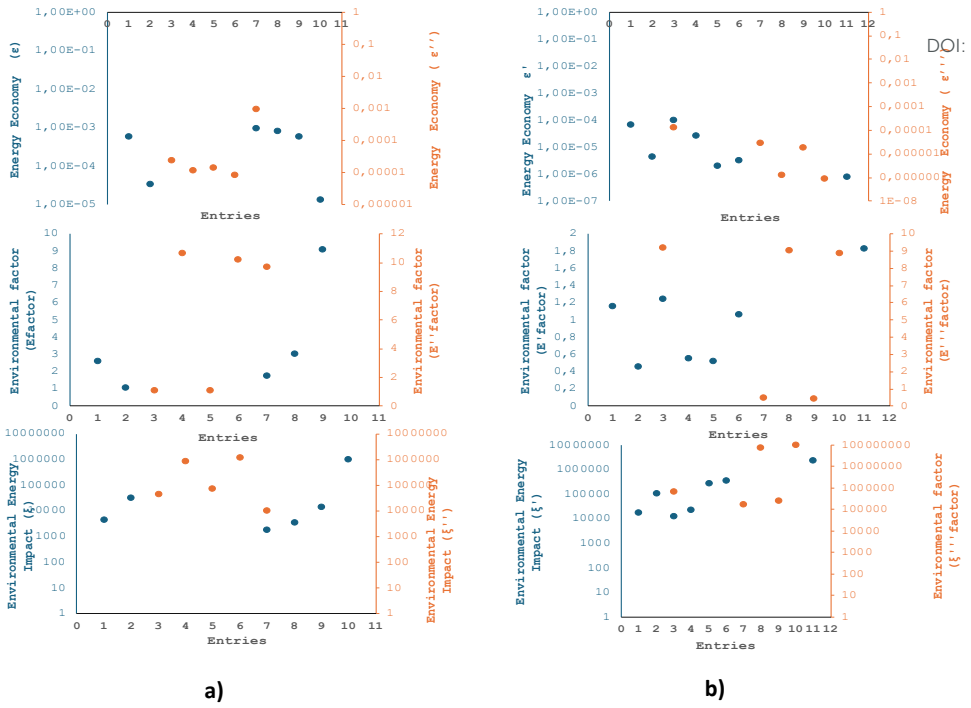

Fig. 7 Graphical presentation of: a) environmental energy impact (ξ), energy economy factor (ε) and environmental factor (E_{fac}) and their 2nd derivatives as well as b) their 1st and 3rd derivatives for some o PET transformation processes [8,61,62](see also **Table 2**)

Table 2: Summary of Entries from Figure 7 *		
Entry No.	**Reaction summary**	**Ref.**
1a,1b	PET+ ChOH→ Ch_2TA-EG-MeOH /DCM-MeOH	this work
2a, 2b	PET+ChOH→C h_2TA-EG-MeOH /DMM-MeOH	this work
3a, 7b	PET→→ Ch_2TA (DCM-MeOH)	this work
4a, 8b	PET→→ K_2TA (DCM-MeOH/EtOH)	this work
5a, 9b	PET→→ Ch_2TA (DMM-MeOH)	this work
6a, 10b	PET→→ K_2TA (DMM-MeOH/EtOH)	this work
7a, 3b	PET+ NaOH→ Na_2TA (DCM/MeOH)	this work
8a	PET+ KOH→ K_2TA/DCM-EtOH	8
9a	PET+ NaOH→ Na_2TA/EtOH-H_2O	8,11
10a	PET+ diols→ PET-polyols	8
4b	PET→BHET (DBU+4-MePhOH)	62
5b	PET→BHET([BMIM]Cl)	62
6b	PET→BHET([BMIM]OH)	62
11b	PET→BHET(ChOH)	62

*Table 2 presents a condensed summary of the data shown in Figure 7. Complete datasets for the "a" (Barnard-derived) and "b" (Kumar-derived) entries are provided in SI Tables 3 and 4 of the Supporting Information, respectively.

However, calculation of 2nd and 3rd derivative parameters for consecutive transformations across various stages - including not only chemical transformations but also additional processes such as drying (entries 3a, 5a, 7b, 9b), as well as crystallization (entries 7a, 3b) – generally shows a decrease in the energy economy coefficient by one order of magnitude. Compare ε'' vs ε and ε'''vs ε' for these processes with those of simpler, single-stage reactions (entries 1 and 2), where the drop is due to additional time, temperature and solvent requirements being factored in. In the case of metathesis reactions involving large quantities of organic solvent (entries 4a, 6a, 8b, 10b) the decrease is even more pronounced – by two orders of magnitude. Interestingly, the environmental factor parameters also increase by approximately one order of magnitude, except in the case of drying process (entries 3a, 5a, 7b and 9b). This is reasonable, as no additional solvent is used – only vacuum treatment over time- and thus the environmental factor parameters remain unaffected. The outcome is that the resulting Environmental Energy Impact is even more elevated as it is a quotient of these two parameters. Thus, particularly in the case of ionic metathesis reaction (entries 4a, 6a, 8b and 10b) the resulting environmental energy impact parameters reach values on the order of millions (up to 99,400,000 °C·min). These findings clearly indicate that the type of ionic metathesis reaction used for the preparation of K_2TA, involving large quantities of organic solvent, is utterly impractical for large-scale applications.

The stage equations presented here (eqs. 1-4) can be further extended to include any additional processes as required. For example, in an industrial process a mechanical step such as the transformation of PET bottles into PET flakes can also contribute to the calculation of the derived formulae, or even steps involving simple solvent (DCM, DMM, MeOH) evaporation from the reaction mixture. As our exploration was conducted at the laboratory scale these calculations are not particularly meaningful in our specific case. However, the idea is that the derived formulae can serve as basis and be applied to any multistep PET transformation process, including consecutive chemical reactions as well as other essential steps, thus providing an ideal tool for the numerical comparison of different processes.

View Article Online
DOI: 10.1039/D6SU00314A

Comparative Benchmarking and Sustainability Analysis of PET Depolymerization Methods

To contextualize the performance of the investigated ChOH-based systems, a comparative benchmarking analysis of representative PET depolymerization methods was performed (Table 3). The comparison includes alkaline hydrolysis, glycolysis, and enzymatic depolymerization approaches reported in the literature [8,61–63]. In addition to reaction temperature and time, the analysis also considers isolation requirements, solvent systems, and approximate practical atom-economy estimates. These values were calculated comparatively by considering the stoichiometric reaction equation together with the reported use of excess reactive reagents (eg NaOH, KOH, ChOH, or ethylene glycol) and reactive solvents where applicable.

The ChOH/MeOH/DCM system showed rapid bulk PET depolymerization under mild conditions, while the ChOH/MeOH/DMM biphasic system proceeded more slowly but in a controlled manner without pronounced accumulation of partially hydrolysed intermediates. In comparison with conventional alkaline hydrolysis using NaOH or KOH [8], the stoichiometric use of choline hydroxide resulted in higher estimated atom-economy values and avoided the large excesses of inorganic base commonly associated with salt-generating neutralization steps. Glycolysis systems employing excess ethylene glycol and ionic-liquid-based catalysts [61,62] exhibited efficient BHET production but lower effective material utilization due to the large excess of glycolysis medium and elevated reaction temperatures. Enzymatic PET hydrolysis [63] provides highly selective depolymerization under aqueous conditions but still suffers from limitations related to enzyme stability, PET crystallinity, and reaction times.

Table 3: Comparative Benchmarking of PET Depolymerization Methods

Entry	Method	System	Reaction temperature (°C)	Reaction Time	Isolation conditions	Yield	Atom Economy*	Solvent	Energy/ advantage	Limitations	Ref.
1	Hydrolysis	ChOH/MeOH/ DCM	25-50	30 min (4 h to complete)	120 °C, ~4h	quant.	~100%	MeOH/ DCM	Moderate/ fast bulk depolymerization; stoichiometric ChOH	Toxic solvent; microplastics/ intermediates accumulation	This work
2	Hydrolysis	ChOH/MeOH/ DMM	25	~ 20 h	120 °C, ~4h	quant.	~100%	MeOH/ DMM	Low-moderate/ controlled biphasic hydrolysis; stoichiometric ChOH	Slow reaction, isolation still energy-intensive	This work
3	Hydrolysis	KOH/EtOH/ DCM	25-35	10-30 min	RT filtration	~99%	~60%	EtOH/ DCM	Fast selective depolymerization	Toxic solvent; KOH excess	[8]
4	Hydrolysis	NaOH/EtOH/ H_2O	80	20 min	Acidification/ crystallisation	~95%	~40%	EtOH/ H_2O	Fast hydrolysis	Large NaOH excess; aqueous salt waste	[8]
5	Glycolysis	EG/$Zn(OAc)_2$	180-200	1-4 h	Crystallisation	80-90%	~30%	EG	High/Industrial maturity; BHET recovery	High temperature; excess EG required	[61]
6	Enzymatic hydrolysis	Engineered PET Hydrolase	72	10 h	Aqueous purification/ concentration	>90%	High theoretical	Aqueous buffer	Selective biocatalytic Depolymerization	Enzyme cost/ Stability; pretreated PET required	[63]
7	Glycolysis	[BMIM]$ZnCl_3$ IL	190	1-4 h	Crystallisation	84.9%	~10%	EG	High/Complete conversion; high BHET selectivity	Large EG excess; IL cost/toxicity	[62]
8	Glycolysis	EG/ChCl-urea (DES)		180 min	Crystallisation	84.5%	~30%	EG	High/ Metal free	Large EG excess	[62]

*Atom-economy values are approximate comparative process estimates and not rigorous theoretical atom-economy calculations. [64,65] Values were rounded to one significant figure and estimated considering reagent stoichiometry, useful isolated products, and the reported use of excess reactive reagent or solvent. For literature hydrolysis methods employing excess NaOH or KOH, the excess inorganic base was included in the calculation, resulting in lower effective atom-economy values compared to the stoichiometric ChOH systems investigated in this work. For glycolysis entries, excess ethylene glycol was included because it functions both as reagent and solvent. For detailed explanation and justification of calculations see the SI.

View Article Online
DOI: 10.1039/D6SU00314A

ARTICLE

Experimental

Experimental details, characterization data, NMR spectra, PET flake analysis, and microscopy studies are provided in the Supporting Information. The post-consumer PET bottle composition and polymer purity considerations are discussed therein. [66] Detailed NMR assignments and supporting spectroscopic analysis are also included. [67]

Conclusions

In conclusion, we have described a high atom economy PET hydrolysis methodology based on the near-stoichiometric use of choline hydroxide under relatively mild conditions using limited solvent quantities und simplified product isolation. Comparison of DCM- and DMM-assisted systems revealed an important trade-off between operational speed and sustainability considerations. While DCM promoted faster depolymerization in a monophasic system, the process was associated with formation of intermediate species and signals attributable to PET microplastic residues. In contrast, the DMM-supported biphasic system proceeded more smoothly and without accumulation of such intermediates, although requiring longer reaction times.

The study additionally demonstrates that evaluation of PET depolymerisation processes based solely on reaction temperature and reaction time may be insufficient. Expanded energy and environmental assessment metrics incorporating solvent recovery, drying, crystallization, and downstream processing steps revealed significant contributions of these stages to the overall process efficiency. The presented results therefore highlight the importance of integrated benchmarking approaches for realistic sustainability assessment of plastic depolymerization methodologies and indicate that further optimization of solvent management and product isolation remains necessary for future process development [61,62].

Author contributions

Conceptualization: Željko Petrovski; **Investigation:** Hugo Araujo, Diogo Martins, João Gonçalves; **Methodology:** Željko Petrovski , Luís C. Branco; **Resources :**Luís C. Branco, Nuno Lapa; **Supervision:** Nuno Lapa, Željko Petrovski, Diana Tomázio; Luís C. Branco; **Validation:**, Inês Matos, Marcia Ventura, Mário Diniz; **Visualization**: Hugo Araujo, Diogo Martins; **Writing – original draft:** Željko Petrovski, Hugo Araujo; **Writing-review & editing:** Luís C. Branco, Nuno Lapa, Mário Diniz, Inês Matos, Marcia Ventura.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. Additional data are available from the corresponding authors on reasonable request.

Acknowledgements

The NMR spectrometer at NOVA-FCT is part of the National NMR Network (PTNMR) and is supported by national funds from financed by national funds from FCT - Fundação para a Ciência e a Tecnologia, I.P. through the scope of projects UIDB/04378/ 2020 of the Research Unit on Applied Molecular Biosciences (UCIBIO) and the project UID/50006/2023 of the Associate Laboratory for Green Chemistry-LAQV REQUIMTE. Elemental analysis data was obtained in the Analytical Laboratory - LAQV-REQUIMTE (Ref. 10.54499/UIDB/50006/2020) at the Department of Chemistry of NOVA School of Science and Technology.

HA acknowledges **FCT - Fundação para a Ciência e a Tecnologia, I.P.** for **the** financial support from grant **with the reference 2023.03925.BDANA.**

The authors acknowledge the use of Google's Gemini (Large Language Model) during the preparation of this work to improve language and readability. The authors also used NotebookLM (Google, with access to 2025 literature feeds) to generate a concise summary paragraph related to recent literature on PET hydrolysis. All final scientific interpretations, conclusions, and the development of the formula model for Energy and Environmental Metrics remain the sole responsibility of the authors.

References

1. Lu J, Qiu Y, Muhmood A, Zhang L, Wang P, Ren L. Appraising co-composting efficiency of biodegradable plastic bags and food wastes: Assessment microplastics morphology, greenhouse gas emissions, and changes in microbial community. Science of the Total Environment. 2023 Jun 1;875. doi:10.1016/j.scitotenv.2023.162356 PubMed PMID: 36822427.

2. Mat Yasin N, Akkermans S, Van Impe JFM. Enhancing the biodegradation of (bio)plastic through pretreatments: A critical review. Waste Management. 2022 Aug;150:1–12. doi:10.1016/j.wasman.2022.06.004

3. Benyathiar P, Kumar P, Carpenter G, Brace J, Mishra DK. Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: A Review. Polymers. MDPI; 2022. doi:10.3390/polym14122366

4. Oliveira J, Belchior A, da Silva VD, Rotter A, Petrovski Ž, Almeida PL, et al. Marine Environmental Plastic Pollution: Mitigation by Microorganism Degradation and Recycling Valorization. Frontiers in Marine Science. Frontiers Media S.A.; 2020. doi:10.3389/fmars.2020.567126

5. Jung H, Shin G, Kwak H, Hao LT, Jegal J, Kim HJ, et al. Review of polymer technologies for improving the recycling and upcycling efficiency of plastic waste. Chemosphere. 2023 Apr;320:138089. doi:10.1016/j.chemosphere.2023.138089

6. Pham DD, Cho J. Low-energy catalytic methanolysis of poly(ethyleneterephthalate). Green Chemistry. 2021 Jan 7;23(1):511–25. doi:10.1039/d0gc03536j

7. Štrukil V. Highly Efficient Solid-State Hydrolysis of Waste Polyethylene Terephthalate by Mechanochemical Milling and Vapor-Assisted Aging. ChemSusChem. 2021 Jan 7;14(1):330–8. doi:10.1002/cssc.202002124 PubMed PMID: 32986929.

8. Zhang S, Xu W, Du R, An W, Liu X, Xu S, et al. Selective depolymerization of PET to monomers from its waste blends and composites at ambient temperature. Chemical Engineering Journal. 2023 Aug 15;470:144032. doi:10.1016/j.cej.2023.144032

9. Rubio Arias JJ, Barnard E, Thielemans W. Ultrafast Simultaneous and Selective Depolymerization of Heterogeneous Streams of Polyethylene Terephthalate and Polycarbonate: Towards Industrially Feasible Chemical Recycling. ChemSusChem. 2022 Aug 5;15(15). doi:10.1002/cssc.202200625 PubMed PMID: 35699250.

10. Lalhmangaihzuala S, Laldinpuii ZT, Khiangte V, Lallawmzuali G, Thanhmingliana, Vanlaldinpuia K. Orange peel ash coated Fe3O4 nanoparticles as a magnetically retrievable catalyst for glycolysis and methanolysis of PET waste. Advanced Powder Technology. 2023 Jul 1;34(7). doi:10.1016/j.apt.2023.104076

11. Zhang S, Xu W, Du R, Zhou X, Liu X, Xu S, et al. Cosolvent-promoted selective non-aqueous hydrolysis of PET wastes and facile product separation. Green Chemistry. 2022 Apr 1;24(8):3284–92. doi:10.1039/d2gc00328g

12. Le NH, Van Ngoc TT, Shong B, Cho J. Low-Temperature Glycolysis of Polyethylene Terephthalate. ACS Sustain Chem Eng. 2022 Dec 26;10(51):17261–73. doi:10.1021/acssuschemeng.2c05570

13. Ügdüler S, Van Geem KM, Denolf R, Roosen M, Mys N, Ragaert K, et al. Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis. Green Chemistry. 2020 Aug 21;22(16):5376–94. doi:10.1039/d0gc00894j

14. Rubio Arias JJ, Thielemans W. Instantaneous hydrolysis of PET bottles: An efficient pathway for the chemical recycling of condensation polymers. Green Chemistry. 2021 Dec 21;23(24):9945–56. doi:10.1039/d1gc02896k

15. Li M, Chen W, Chen W, Chen S. Degradation of Poly(ethylene terephthalate) Using Metal-Free 1,8-Diazabicyclo[5.4.0]undec-7-ene-Based Deep Eutectic Solvents as Efficient Catalysts. Ind Eng Chem Res. 2023 Jul 5;62(26):10040–50. doi:10.1021/acs.iecr.3c01071

16. Marullo S, Rizzo C, Dintcheva NT, D'Anna F. Amino Acid-Based Cholinium Ionic Liquids as Sustainable Catalysts for PET Depolymerization. ACS Sustain Chem Eng. 2021 Nov 15;9(45):15157–65. doi:10.1021/acssuschemeng.1c04060

17. Zhang Y, Tian F, Wu Z, Li X, Liu X, He Y. Chemical conversion of waste PET to valued-added bis(2-hydroxyethyl) terephthalamide through aminolysis. Mater Today Commun. 2022 Aug 1;32. doi:10.1016/j.mtcomm.2022.104045

18. Radadiya R, Shahabuddin S, Gaur R. A facile approach toward the synthesis of terephthalic acid via aminolytic depolymerization of PET waste and studies on the kinetics of depolymerization. Journal of Polymer Science. 2023 Jun 15;61(12):1241–51. doi:10.1002/pol.20220727

19. Gao J, Peng W, Galindo A, Slaton E, Perez Martinez J, Lan G, et al. Machine learning-guided optimization for ionic liquid-based polyethylene terephthalate waste recycling. Green Chemistry. 2025 May 20;27(24):7357–67. doi:10.1039/d5gc01998b

20. Kushwaha A, Goswami L, Kim BS. Advancement in innovative strategies for poly (ethylene terephthalate) biodegradation. Current Opinion in Chemical Engineering. Elsevier Ltd; 2025. doi:10.1016/j.coche.2025.101121

21. Saini S, Sharma A, Saini N, Kaur N, Singh N. Machine learning-driven optimization of Deep Eutectic Solvents: Accelerating physicochemical properties modeling. Sustainable Materials and Technologies. Elsevier B.V.; 2025. doi:10.1016/j.susmat.2025.e01536

22. Indoria S, Kaur G, Singh V. Unveiling the Potential of Deep Eutectic Solvents: Catalysis Through Solvent Innovation. Chemistry Africa. 2025 Aug 1;8(6):2573–85. doi:10.1007/s42250-025-01278-0

23. Atta AM, Melegy AA, El-hoshoudy AN. New recycled polyethylene terephthalate imidazolium ionic liquids and their applications for co2 exhaust capture. Sci Rep. 2025 Dec 1;15(1). doi:10.1038/s41598-025-15433-7 PubMed PMID: 40830636.

24. Martin IL, Anderson LB, McAdams DA, Molloy C, Dunne PW, Connon SJ. Neutral hydrolysis of poly(ethylene terephthalate) catalysed by highly active terephthalate-based ionic liquids at low loadings. Chemical Communications. 2025 Jan 21;61(13):2750–3. doi:10.1039/d4cc05909c PubMed PMID: 39835936.

25. Thulasiraman AV, Vuppaladadiyam AK, Hakeem IG, Nahar K, Jena MK, Shah K. Ecofriendly Degradation of PET via Neutral Hydrolysis: Degradation Mechanism and Green Chemistry Metrics. Environments - MDPI. 2025 Apr 1;12(4). doi:10.3390/environments12040127

26. Deng L, He H, Chen Z, Meng Y, Wang L. Efficient Recovery and Fast Hydrolysis of Polyethylene Terephthalate by Dihydrolevoglucosenone (Cyrene). ChemSusChem. 2025 Oct 23. doi:10.1002/cssc.202501352

27. Celestre V, Madsen J, Siracusa C, Burkart L, Quartinello F, Herres-Pawlis S, et al. Microwave-Assisted Synthesis of Polyethylene Terephthalate as a Fast Screening Method for Catalyst Evaluation and for Evaluating Polymerizability of Monomers Recovered From Degraded Polyesters. J Appl Polym Sci. 2025 Nov 20. doi:10.1002/app.57688

28. Zhu Y, Tang J, Zhu S, Liu Y, Lou L, Mei Q. Facile upcycling of color-mixed polyethylene terephthalate-based textile waste via mild solvolysis with a natural aromatic solvent. Chemical Engineering Journal. 2025 Nov 1;523. doi:10.1016/j.cej.2025.168217

29. Zhao X, Zheng Z, Chou IM, Xiong M, Mei S. In Situ Experimental Study on High-Temperature Hydrolysis of Polyethylene Terephthalate. Polym Eng Sci. 2025 Sep 1;65(9):4644–52. doi:10.1002/pen.27296

30. Razote BJ, Saabome SM, Hong JS, Ahn KH. Integrating thermodynamic and kinetic approaches for the design of effective and sustainable PET chemical upcycling systems. Chemical Engineering Journal. 2024 Nov 1;499. doi:10.1016/j.cej.2024.156438

31. Usmani Z, Sharma M, Tripathi M, Lukk T, Karpichev Y, Gathergood N, et al. Biobased natural deep eutectic system as versatile solvents: Structure, interaction and advanced applications. Science of the Total Environment. Elsevier B.V.; 2023. doi:10.1016/j.scitotenv.2023.163002 PubMed PMID: 37003333.

32. El Darai T, Ter-Halle A, Blanzat M, Despras G, Sartor V, Bordeau G, et al. Chemical recycling of polyester textile wastes: shifting towards sustainability. Green Chemistry. Royal Society of Chemistry; 2024. p. 6857–85. doi:10.1039/d4gc00911h

33. Barroca LR, Velho P, Macedo EA. Novel Green Aqueous Two-Phase Systems (ATPSs) based on choline salts and application to the removal of pharmaceutical pollutants from water. Fluid Phase Equilib. 2024 Nov 1;586. doi:10.1016/j.fluid.2024.114193

34. Gallo M, Gámiz F. Choline: An Essential Nutrient for Human Health. Nutrients. Multidisciplinary Digital Publishing Institute (MDPI); 2023. doi:10.3390/nu15132900 PubMed PMID: 37447226.

35. Yu J, Liu X, Xu S, Shao P, Li J, Chen Z, et al. Advances in green solvents for production of polysaccharide-based packaging films: Insights of ionic liquids and deep eutectic solvents. Comprehensive Reviews in Food Science and Food Safety. John Wiley and Sons Inc; 2023. p. 1030–57. doi:10.1111/1541-4337.13099

36. Abbott AP, Abolibda TZ, Davis SJ, Emmerling F, Lourdin D, Leroy E, et al. Glycol based plasticisers for salt modified starch. RSC Adv. 2014;4(76):40421–7. doi:10.1039/c4ra06220e

37. Xu Z, Lee S, Lobkovsky EB, Kiang YH. Structure rationalization and topology prediction of two-distinct-component organic crystals: The role of volume fraction and interface topology. J Am Chem Soc. 2002 Jan 9;124(1):121–35. doi:10.1021/ja0115518 PubMed PMID: 11772069.

38. Pinho SP, Macedo EA. Solubility of NaCl, NaBr, and KCl in water, methanol, ethanol, and their mixed solvents. J Chem Eng Data. 2005 Jan;50(1):29–32. doi:10.1021/je049922y

39. Prat D, Wells A, Hayler J, Sneddon H, McElroy CR, Abou-Shehada S, et al. CHEM21 selection guide of classical- and less classical-solvents. Green Chemistry. 2015 Aug 13;18(1):288–96. doi:10.1039/c5gc01008j

40. Schlosser PM, Bale AS, Gibbons CF, Wilkins A, Cooper GS. Human health effects of dichloromethane: Key findings and scientific issues. Environ Health Perspect. 2015;123(2):114–9. doi:10.1289/ehp.1308030 PubMed PMID: 25325283.

41. Kamalanathan I, Petrovski Z, Branco LC, Najdanovic-Visak V. Novel aqueous biphasic system based on ethyl lactate for sustainable separations: Phase splitting mechanism. J Mol Liq. 2018 Jul 15;262:37–45. doi:10.1016/j.molliq.2018.03.119

42. Westwood S, Stoppacher N, Garrido B, Huang T, Saito T, Un I, et al. qNMR Internal Standard Reference Data (ISRD) Maleic Acid (MA) [ISRD-01]. 2018 Sep.

43. Bhogle CS, Pandit AB. Ultrasound-Assisted Alkaline Hydrolysis of Waste Poly(Ethylene Terephthalate) in Aqueous and Non-aqueous Media at Low Temperature. Indian Chemical Engineer. 2018 Apr 3;60(2):122–40. doi:10.1080/00194506.2017.1310634

44. Liu Y, Yao X, Yao H, Zhou Q, Xin J, Lu X, et al. Degradation of poly(ethylene terephthalate) catalyzed by metal-free choline-based ionic liquids. Green Chemistry. 2020 May 21;22(10):3122–31. doi:10.1039/d0gc00327a

45. Zheng W, Liu C, Wei X, Sun W, Zhao L. Molecular-level swelling behaviors of poly (ethylene terephthalate) glycolysis using ionic liquids as catalyst. Chem Eng Sci. 2023 Mar 5;267. doi:10.1016/j.ces.2022.118329

46. Attallah OA, Janssens A, Azeem M, Fournet MB. Fast, High Monomer Yield from Post-consumer Polyethylene Terephthalate via Combined Microwave and Deep Eutectic Solvent Hydrolytic Depolymerization. ACS Sustain Chem Eng. 2021 Dec 20;9(50):17174–85. doi:10.1021/acssuschemeng.1c07159

47. Gornay J, Secordel X, Capron M, Tesquet G, Fongarland P, Payen E, et al. Direct synthesis of 1,1-dimethoxymethane from methanol by minor modification of the formaldehyde production process over FeMo catalysts. Oil and Gas Science and Technology. 2010;65(5):751–62. doi:10.2516/ogst/2009087

48. Luderer MR, Bailey WF, Luderer MR, Fair JD, Dancer RJ, Sommer MB. Asymmetric addition of achiral organomagnesium reagents or organolithiums to achiral aldehydes or ketones: a review. Tetrahedron Asymmetry. 2009. p. 981–98. doi:10.1016/j.tetasy.2009.03.015

49. PubChem. Dimethoxymethane | C3H8O2 | CID 8020 - PubChem [Internet]. 2025 [cited 2025 Sep 17]. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/8020#section=Information-Sources

50. Luo HK. A process for preparing a monoester of terephthalic acid and its derivatives. Singapore: WIPO; WIPO WO150016 A1, 2022.

51. Jaime-Azuara A, Pedersen TH, Wimmer R. Process optimization by NMR-assisted investigation of chemical pathways during depolymerization of PET in subcritical water. Green Chemistry. 2023 Mar 9;25(7):2711–22. doi:10.1039/d2gc04831k

52. Sinha AK, Vigalok A, Rawat V. Catalytic application of zinc complex of oxygen depleted 1,3-bis(pyrazole)-p-tert-butylcalix[4]arene. Tetrahedron Lett. 2019 Mar 14;60(11):796–9. doi:10.1016/j.tetlet.2019.02.017

53. Huang J, Xu W, Long Y, Zhu Y, Chen S, Duan W, et al. Studies on hydrolysis/alcoholysis/ammonolysis mechanisms of ethylene terephthalate dimer using DFT method. Arabian Journal of Chemistry. Elsevier B.V.; 2024. doi:10.1016/j.arabjc.2024.105719

54. Dukek P, Schleheck D, Kovermann M. High-resolution NMR spectroscopic approaches to quantify PET microplastics pollution in environmental freshwater samples. Chemosphere. 2024 Nov 1;367. doi:10.1016/j.chemosphere.2024.143657 PubMed PMID: 39486629.

55. Peez N, Janiska MC, Imhof W. The first application of quantitative 1H NMR spectroscopy as a simple and fast method of identification and quantification of microplastic particles (PE, PET, and PS). Anal Bioanal Chem. 2019 Feb 1;411(4):823–33. doi:10.1007/s00216-018-1510-z PubMed PMID: 30552493.

56. Claridge TDW. High-Resolution NMR Techniques in Organic Chemistry (Third Edition). Elsevier Science; 2016.

57. Kalaronis D, Ainali NM, Evgenidou E, Kyzas GZ, Yang X, Bikiaris DN, et al. Microscopic techniques as means for the determination of microplastics and nanoplastics in the aquatic environment: A concise review. Green Analytical Chemistry. 2022 Dec 1;3. doi:10.1016/j.greeac.2022.100036

58. Yang J, Xia Z, Kong F, Ma X. The effect of metal catalyst on the discoloration of poly(ethylene terephthalate) in thermo-oxidative degradation. Polym Degrad Stab. 2010 Jan;95(1):53–8. doi:10.1016/j.polymdegradstab.2009.10.009

59. Ioakeimidis C, Fotopoulou KN, Karapanagioti HK, Geraga M, Zeri C, Papathanassiou E, et al. The degradation potential of PET bottles in the marine environment: An ATR-FTIR based approach. Sci Rep. 2016 Mar 22;6. doi:10.1038/srep23501 PubMed PMID: 27000994.

60. Pretsch E, Clerc T, Seibl J, Simon W. Tables of Spectral Data for Structure Determination of Organic Compounds [Internet]. Berlin, Heidelberg: Springer Berlin Heidelberg;

View Article Online
DOI: 10.1039/D6SU00314A

1989. (Chemical Laboratory Practice). Available from: http://link.springer.com/10.1007/978-3-662-10207-7 doi:10.1007/978-3-662-10207-7

61. Barnard E, Rubio Arias JJ, Thielemans W. Chemolytic depolymerisation of PET: A review. Green Chemistry. Royal Society of Chemistry; 2021. p. 3765–89. doi:10.1039/d1gc00887k

62. Kumar G, Kumar K, Bharti A. Energy and Environmental Metrics-Based Comparison of Ionic Liquids/Deep Eutectic Solvents-Assisted Chemical Recycling of Waste Poly(ethylene terephthalate). Industrial and Engineering Chemistry Research. American Chemical Society; 2024. p. 6024–46. doi:10.1021/acs.iecr.3c04481

63. Tournier V, Topham CM, Gilles A, David B, Folgoas C, Moya-Leclair E, et al. An engineered PET depolymerase to break down and recycle plastic bottles. Nature. 2020 Apr 9;580(7802):216–9. doi:10.1038/s41586-020-2149-4 PubMed PMID: 32269349.

64. Trost BM. The atom economy - A search for synthetic efficiency. Science (1979). 1991 Dec 6;254(5037):1471–7. doi:10.1126/science.1962206 PubMed PMID: 1962206.

65. Constable DJC, Curzons AD, Cunningham VL. Metrics to “green” chemistry - Which are the best? Green Chemistry. 2002;4(6):521–7. doi:10.1039/b206169b

66. Roosen M, Mys N, Kusenberg M, Billen P, Dumoulin A, Dewulf J, et al. Detailed Analysis of the Composition of Selected Plastic Packaging Waste Products and Its Implications for Mechanical and Thermochemical Recycling. Environ Sci Technol. 2020 Oct 20;54(20):13282–93. doi:10.1021/acs.est.0c03371 PubMed PMID: 32985869.

67. Kil YS, Han AR, Hong MJ, Kim JB, Park PH, Choi H, et al. 1H NMR-Based Chemometrics to Gain Insights Into the Bran of Radiation-Induced Colored Wheat Mutant. Front Nutr. 2022 Jan 4;8. doi:10.3389/fnut.2021.806744

The data supporting this article have been included as part of the Supplementary Information. Additional data are available from the corresponding authors on reasonable request.