Theoretical insights into chemical recycling of polyethylene terephthalate (PET)

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ABSTRACT

Polyethylene Terephthalate (PET) is one of the most commonly used plastics. Currently, PET waste has been mainly recycled through mechanical methods and alternative effective ways have emerged, such as chemical recycling including ammonolysis, aminolysis, hydrolysis, alcoholysis and glycolysis. However, a precise understanding of the reaction mechanisms and kinetics of these methods is lacking. This paper aims at providing a comprehensive review elucidating the mechanisms and the reaction kinetics of these methods, considering various catalysts, solvents and heating modes. The degradation performance of each method and its suitability towards a circular economy is discussed and compared. It is concluded that novel processes of PET glycolysis stand out as the most promising chemical recycling methods. The degradation process via glycolysis can be significantly enhanced by the increased interactions facilitated by the synergic effect reaction mechanism, and the improved kinetics provided by the advanced heating modes such as microwave-assisted techniques. Heterogeneous catalysts with large surface area were found to promote efficient PET degradation into its monomer, Bis(2-Hydroxyethyl) terephthalate (BHET); these catalysts also offer environmental and economic advantages owing to their ease of separation and reusability. This review provides a guidance for future research aimed at designing an effective PET chemical recycling process. It was identified that to advance PET glycolysis in the near future, research can focus on 1) the utilising novel heterogeneous catalysts and catalyst supports that induce synergic effect reaction mechanisms, and 2) advancing technologies such as microwave heating. Furthermore, the suitability of PET recycling technologies should be considered in the context of high BHET yield/selectivity, mild reaction conditions, short reaction times and reusability, and economical feasibility at an industrial scale.

1. Introduction

The use of plastic materials is ubiquitous in industry and daily life due to their strength, flexibility and low production cost. For example, in fields like packaging and construction, they are completely unparalleled by any other materials [1]. In 2020, a global production of plastics was 367 million metric tonnes [2]. Such a rate of plastic production inevitably leads to huge amounts of plastic waste. Despite the availability of recycling methods, the recycling rate remains low due to various factors such as the expense associated with waste management [3], inadequate infrastructure [4], and insufficient demand for chemically processed plastic [5]. In contrast to the massive production rate, it is estimated that only 9.5 % of all plastic ever produced has been recycled, leaving significant amounts of plastic finding its way to the environment [6]. Once in the environment, plastic waste undergoes partial degradation to form micro- and nanoplastics which are harmful to both human and animal health [7].

One of the most commonly produced synthetic plastics, and the most common thermoplastic resin of the polyester family, is Polyethylene terephthalate (PET). Despite PET’s widespread use, especially in food and drinks packaging and in synthetic fibres for clothing [8], it constitutes a large percentage of plastic waste, contributing to 8 % by weight and 12 % by volume of the world’s solid waste [9]. According to data published by United States Environmental Protection Agency (EPA) [10], 29.1 % of PET bottles and jars were recycled in 2018. While this recycling rate is notably higher than the overall plastic recycling rate of 8.7 %, the large volume of PET production underscores the imperative for a substantial increase in recycling rates.

Numerous recycling methods have been explored, including: primary, secondary, tertiary and quaternary recycling. Primary recycling involves reintroducing plastic scrap into production lines, this requires very low contamination levels so household plastic waste cannot be...
recycled using this method without undergoing significant processing [11]. Secondary recycling is the most common method of plastic recycling and involves the separation and processing of waste plastic using mechanical methods such as grinding and melting [12]. Tertiary recycling, also known as chemical recycling, is a more complicated process where polymer backbones are broken down to produce monomers, oligomers and other valuable intermediates. The main advantage of tertiary recycling lies in its ability to fully close the plastic recycling loop without compromising the material’s desirable properties [13]. Quaternary recycling, or energy recovery, presents a final option for recycling plastic material by burning plastic waste to generate energy in the form of heat or electricity [14].

Various tertiary recycling techniques, including thermo-chemical processes and solvolysis, have been used for PET recycling. Thermo-chemical recycling techniques such as gasification and pyrolysis have been studied extensively for plastics recycling, producing valuable chemicals which can be further refined for applications such as fuels and other high-value products. However, when used with PET plastic, a high concentration of benzoic acid is produced, making the liquid product unsuitable for use as a fuel and causing manufacturing challenges due to its high corrosivity [15,16]. Furthermore, compared to the pyrolysis of other plastics such as polyethylene, PET pyrolysis yields a significantly higher proportion of less valuable gaseous products [17]. In contrast, pyrolysis of polyethylene produces liquid oil comparable to gasoline, kerosene and diesel [18].

Solvolysis stands out as another efficient method for the chemical recycling of PET. Depending on the solvent utilised, there are various types of solvolysis including: aminolysis, ammonolysis, hydrolysis, alcoholysis, and glycolysis. Aminolysis and ammonolysis processes, involving reactions with amines and ammonia respectively, break down the PET chain into monomers such as terephthalamide and bis(2-hydroxy ethylene)terephthalamide (BHETA). Hydrolysis yields terephthalic acid (TPA) from PET using water in an acidic, alkaline or neutral medium. The main advantage of hydrolysis is that TPA is a preferred starting point for PET production compared to its alternative monomer, dimethyl terephthalate (DMT) [13]. Alcohololysis of PET, typically employing methanol, produces DMT monomers which can be directly mixed with ethylene glycol (EG) to reproduce PET. The most common PET solvolysis method is PET glycolysis, which involves the use of glycols to degrade PET into bis(2-hydroxyethyl) terephthlate (BHET). While EG is the primary glycol used, other options such as diethylene glycol (DEG), propylene glycol (PG), and polyethylene glycol (PEG) have also been employed. PET glycolysis is generally considered favourable to other solvolysis methods due to its shorter reaction time, milder reaction conditions, and lower separation and purification costs. Additionally, as BHET serves as an intermediate for both TPA- and DMT-based PET production, it can be entered into the production stream of either process [19].

Regarding chemical recycling of PET, although a number of reviews [20–24] provide summaries of the processes, there remains a notable scarcity of reviews focusing on the reaction mechanisms and kinetics, which are essential to provide a more profound understanding of the processes. Reaction mechanisms provide insight into the molecular level dynamics occurring during a chemical reaction, while reaction kinetics offer clues on the effect of reactants and the conditions on a reaction, allowing for the design of optimised chemical processes. Understanding both the reaction mechanism and kinetics is crucial to make informed decisions regarding catalyst selection and optimal reaction conditions for PET chemical recycling. The review by Ghasemi et al. [25] highlighted the significance of understanding the general mechanisms for each chemical recycling method. However, no details were provided on the variations and complexity of these mechanisms especially when they are influenced by factors such as the choice of catalyst. Similarly, while kinetics has been emphasized in existing reviews [20–24], there is still a gap in literature regarding a comprehensive examination of how kinetics is affected by external factors such as reaction conditions, catalysts, and heating modes.

This review aims to fill the existing gap by providing a comprehensive review into the mechanisms and kinetics of key PET chemical recycling methods (aminolysis, ammonolysis, hydrolysis, alcohololysis and glycolysis). The key influencing factors will be explored, including types of catalyst, novel techniques such as the use of supercritical fluids, microwave heating and co-solvents. Additionally, the detailed reaction mechanism explored using computational chemistry methods such as Density Functional Theory (DFT) will be summarised. It is expected that the findings from this review can be applied to facilitate the development of new, efficient processes, thereby advancing towards a circular economy.

2. Reaction mechanisms of PET degradation

2.1. General reaction pathways of PET degradation

A thorough comprehension of the reaction mechanism is essential for designing an efficient PET degradation process. It provides clarity on understanding the conditions and involved chemicals, resulting in more informed decision making. PET can be chemically recycled through five main processes: aminolysis, ammonolysis, hydrolysis, alcohololysis and glycolysis. Fig. 1 illustrates the general degradation pathways associated with these processes.

2.2. Uncatalysed reaction mechanisms

For the five main PET degradation processes, while their resultant monomer products vary, the mechanisms of each process exhibit similarity in the absence of a catalyst. Generally, the mechanism involves a nucleophilic functional group (X in Fig. 2) attacking the carbonyl ester of PET via its lone pair of electrons, resulting in chain cleavage and modification of the ester group. This sequence recurs until the polymer chain is completely fragmented, producing the final monomer products.

In the chemical recycling of PET, selecting the appropriate nucleophile is crucial as it greatly impacts the reaction products and conditions. Ammonia and its derivatives, such as amines, are capable of breaking down the PET chain. The higher alkalinity of the ammonia or amino group renders it a more effective nucleophile compared to the -OH group used in other degradation techniques. This creates the potential for reduced reaction conditions and increased monomer yields. In ammonolysis, ammonia is used to break the PET chain down into the monomer terephthalamide. Although not inherently valuable, this terephthalamide monomer can be utilised to produce a range of value-added products, including p-xylendiamine and 1, 4-bis (aminoethyl) cyclohexane [26]. For aminolysis, the most commonly used amine is ethanolamine (EA) as it encourages production of the desired product, BHETA, while larger amines such as diethanolamine suffer from greater steric hindrance which can have detrimental effects on the degradation process [27]. The BHETA monomer can be used to produce valuable poly(ester amides), which represents an emerging category within various industries due to their combination of attractive characteristics of both polyesters and polyamides [28]. Within the EA molecule, there are two nucleophilic centres capable of attacking the carbonyl group of PET: the amine group (-NH₂) and the hydroxyl group (-OH). The amine group is more likely to attack the PET chain due to its increased basicity compared to the hydroxyl. Both ammonolysis and aminolysis are still in relative infancy compared to hydrolysis and glycolysis. Nonetheless, significant research has been carried out in recent years due to their potential, with various literature proposing reaction mechanisms for both processes.

Although there are distinctions among the PET degradation processes, the fundamental reaction mechanisms of hydrolysis, alcohololysis, and glycolysis are the same, involving the interaction between a hydroxyl group and the ester group of PET. The key differences lie in how
the whole molecule facilitates the nucleophilic nature of the \(-\text{OH}\) group. Despite their similarities, there are some key structural differences among water, alcohols and polyols that significantly affect the degradation process. The use of water is beneficial due to its small molecular size resulting in reduced steric hindrance, while polyols benefit from their greater number of hydroxyl sites. In a study carried out by Sammon et al. [29] that investigated liquid diffusion in PET using FTIR, it was found out that for methanol diffusion, the PET polymer is more readily affected by swelling which in turn leads to greater diffusion and degradation. Similar to methanol, the use of EG as a solvent is beneficial as it results in significant swelling of the PET molecule following the absorption of EG into the polymer matrix, as reported by numerous
Complexes with the carbonyl oxygen. However, the environmental effects and the challenge of separating metal salts must be considered. Acidic ILs and DESs are particularly effective catalysts as they can simultaneously enhance the nucleophilic attack of the ester bond while also improve the solubility of PET within the system due to their strong solvent properties. Compared to metal salts and ILs, DESs offer a higher concentration of catalytically active sites due to their greater potential for hydrogen bonding owing to their structure. Similarly, Lewis acid catalysts such as quaternary salts have been used for both aminolysis and ammonolysis. Using scanning electron microscopy (SEM), Mittal et al. [38] found that aminolysis of PET was more efficient than ammonolysis, due to the stronger nucleophilic nature of amines, which enables increased selectivity of aminolysis in quickly degrading the amorphous phase of PET as opposed to its crystalline phase that requires more time to break down.

For PET glycolysis, heterogeneous metal-based catalysts are most commonly associated with the Lewis acid reaction mechanism. This includes traditional catalysts such as zinc acetate [39], innovative catalysts such as metal oxide spinels [40], and easily recoverable super-paramagnetic γ-Fe₂O₃ nanoparticles [41]. Additionally, Chaudhary et al. [32] studied PET glycolysis under microwave irradiation in the presence of zinc acetate, finding that the Lewis acid mechanism still applies as it is independent of heating mode. The presence of catalysts containing metal atom centres can significantly affect the reaction due to their coordination ability, facilitating bonds forming between the cation and the ester group of PET [42]. The formation of these ligands can reduce the electron density of the carbonyl group, thereby enhancing the nucleophilic attack of the hydroxyl oxygen. The role of ligands in metal catalysis is significant as they can enhance the Lewis acidity of the metal centre to provide additional coordination sites. This will influence the reaction selectivity, catalyst solubility, and extend the lifetime of metal catalysts by suppressing catalyst deactivation pathways [43, 44]. For example, hard metals such as magnesium can bind strongly to oxygen-based anions such as acetate, thereby reducing their activity, whereas soft metals such as zinc shows an increase in activity when bound to oxygen-based anions as opposed to halogens [45].

The PET hydrolysis process can be conducted within an acidic, alkaline, or neutral medium at high temperature and pressure. Numerous studies [46–48] have proposed mechanisms for acidic hydrolysis. In an acidic medium, a hydrogen proton from the acid catalyst is donated to water molecules to produce positively charged hydronium ions that serve as the Lewis acid catalysts. Yan et al. [49] investigated the hydrolysis of polyester/cotton blends due to the widespread use of PET in textiles. The study uses dispersion-corrected DFT (DFT-D) and various solvation models to provide deeper insights into the hydrolysis mechanism, while comparing with experimental data. Their results showed that cotton is preferentially degraded compared to polyester during the hydrolysis of waste fabrics, which was consistent with experiment. The study shed light on the dual function of catalytic water molecules, serving as both protonation and deprotonation mediums, thereby shortening the required distance for hydrogen transfer. The selection of acid catalyst can depend on various factors, including its state, stability and structure. The presence of Lewis acid sites is crucial for generating hydronium ions, and Bronsted acid sites initiate the degradation reaction, while increased thermal stability of the catalyst can prevent a reduction in acidity due to the dissociation of Lewis acid sites. Solid acid catalysts such as tungsten-promoted metal oxides have demonstrated strong acidity and catalytic activity due to charge imbalances of the lattice structure caused by framework substitution of metal ions [50]. Alternatively, for liquid acids, the most commonly used catalyst is sulfuric acid. However, improved kinetics and recoverability has been found through the use of other acids such as Poly (4-styrenesulfonic acid) (PSSA), attributed to increased surface wetting of PET occurring due to the catalysts’ hydrophobic backbone.

2.3.2. Alkaline catalysis

In alkaline hydrolysis, an alkaline medium such as NaOH is used, however in this case the base is acting as both a reactant and a catalyst. The degradation of esters via alkaline hydrolysis has previously been described as a saponification reaction, as shown in Fig. 4 using NaOH as the base and H₂SO₄ as the acid [51]. The hydroxide ion attacks the carbonyl group as the ester linkages are cleaved. Subsequently, the hydrogen of the hydroxyl group leaves to connect with the severed PET

![Reaction mechanism of PET chemical recycling catalysed by a Lewis acid. LA – Lewis acid.](image)
link. The terephthalate ion then binds with the base’s cation, which can be removed via the addition of acid to form pure TPA and EG. The large amounts of acid required for both acidic and alkaline hydrolysis are a major drawback due to the high risk of corrosion. Zhang et al. used DFT to explore the use of a substituted binuclear zinc complex for catalysing the alkaline hydrolysis of PET [52]. By comparing the charge densities with different alkyl substituents, they found that the optimal substituent should electronically enrich the zinc sites to facilitate the formation of a six-membered ring intermediate. The addition of certain substituents to the PET chain can significantly enhance certain properties of the plastic while keeping other properties unchanged. Liu et al. [53] proposed the addition of simple hydroxyl acids into the polymer chain to provide increased hydrolysis sites, thus enhancing the degradation. DFT calculations were employed to examine the degradation mechanism of these co-polymers, revealing that the presence of hydroxyl acids reduces the energy barrier and accelerates the reaction rate.

2.3.3. Synergic catalysis

As catalytic technologies advanced, efforts were made to improve the efficiency of PET degradation. One such method involved the development of catalysts with a synergic catalytic effect. The mechanism of this effect is similar to the one described in Figure 3, however, it relies more heavily on hydrogen bonding between a nucleophile and the negatively charged part of the catalyst [30, 54, 55]. The term “synergic” comes from the fact that two different moieties (e.g. cation and anion) are working in tandem to interact with PET, acting as Lewis acids and bases, respectively. A hydrogen bond is formed between the negatively charged molecule of the catalyst and the hydrogen of the nucleophile hydroxyl group. Such bonding enhances the electronegativity of the hydroxyl oxygen and the nucleophile attacking ability. Simultaneously, the hydrogen from the hydroxyl group of the positively charged moiety protonates the carbon in the carbonyl group of PET and makes it more electronegative. Subsequently, both the hydroxyl bond and the ester bond of PET are cleaved. A new C–O bond then forms between the carbon of carbonyl in PET and the nucleophilic hydroxyl oxygen, while the hydrogen detached from the hydroxyl is bonded to the oxygen in another part of PET. The catalyst continues to repeat these steps, gradually breaking down PET into oligomers and eventually forming the desired monomers. This mechanism, featuring a general Lewis acid and Lewis base, is shown in Fig. 5.

Several studies have also investigated the methanolysis of PET through a synergic mechanism. Du et al. [56], Pham et al. [57] and Jiang et al. [58] proposed similar mechanisms for the catalysed methanolysis process. Pham et al. [57], using potassium carbonate as a catalyst alongside an aprotic co-solvent, proposed that the synergistic mechanism is more selective to DMT as a product, as the scission process is more likely to occur at either side of the benzene ring. This renders this mechanism, along with the processes that induce it, more favourable as DMT is the most desirable product produced by methanolysis. The successful use of potassium carbonate as a catalyst was attributed to its high rate of surface-controlled dissolution into the surrounding co-solvent, implying that solubility of the solid catalyst benefits the

![Fig. 4. Reaction mechanism of alkaline hydrolysis saponification process of PET.](image)

![Fig. 5. – Synergistic reaction mechanism of PET chemical recycling using a Lewis acid-base catalyst. LB – Lewis base.](image)
process. DFT has been used to investigate the influence of co-solvents on the DES-catalysed methanolysis of PET [59]. Theoretical calculations were used to establish a previously unclear reaction mechanism for co-solvent promotion of PET degradation. It was found that, based on the calculation of PET-co solvent interaction energies, effective co-solvents should be selected based on their polarity, with the most polar solvent producing a greater degree of PET degradation. Furthermore, the findings showed that strong interactions between the solvent and methanol also contributed to enhanced degradation.

Catalysts that facilitate the synergic catalytic effect are highly encouraged for PET glycolysis. One such catalyst is ionic liquids (ILs), which stand out as novel green catalysts known for their attractive properties such as non-toxicity, non-flammability, and recoverability. The synergic catalytic effect has been reported in PET glycolysis processes catalysed by various types of ILs, including metal acetate ILs [30, 54], halometallate ILs [55,60,61], and non-metal ILs [62]. This synergic effect arises through the co-catalysis caused by both cations and anions such as deep eutectic solvents (DESs) [63] and polyoxometallates (POMs) [42]. An important balance to strike when using Lewis acid-base catalysts is the strength of interactions between the two moieties. If the interactions are too strong, there may be insufficient “free” acid or base within the system to enhance the degradation. Conversely, if the interactions are too weak, the catalyst will be too unstable, leading to decomposition at reaction conditions [45,64].

The addition of catalyst supports has been successfully used to realise the synergic mechanism. Carbon nanotubes (CNT), graphene and zeolites have all demonstrated the ability to produce high BHET yields during PET glycolysis when used in conjunction with metal-based catalysts [65-67]. For instance, Jin et al. [68] used MnO2 supported by graphene oxide (GO) nanosheets to achieve excellent PET degradation. In certain instances, the catalyst supports have been observed to act both as supports and catalysts, thereby creating an additional synergic effect. Given that glycolysis is the most common chemical recycling method for PET, DFT calculations of glycolysis have been extensively researched. The synergic mechanism described in literature is commonly validated by investigating the interactions employing DFT between PET/EG and various catalysts including DESs [69-71], ILs [62,72,73], nanocatalysts [31] and organocatalysts [74]. By analysing the interaction energies between neighbouring molecules, DFT can validate the synergic mechanism by proving cation-PET and anion-EG interactions. This is useful for high throughput screening of potential catalysts, as they are more likely to be successful if they induce this mechanism. The use of a protic IL produced from the combination of triazabicyclocdecene (TBD) and methanesulfonylic acid (MSA) was studied by Jehanno et al. [75]. The study revealed that the metal-free catalyst could achieve BHET yields comparable to those of a metallic nature, while being significantly more environmentally friendly and easier to recycle. The success of this catalyst was attributed to the unusually high thermal stability within the IL, resulting from strong H-bonding and protonation between the two moieties.

Alternatively, DFT can be used to explore more specific properties and effects of potential catalysts, providing valuable insights for future catalytic design. Yao et al. investigated a series of amino acid IL catalysts with varying anions [76]. To quantify the influence of the anion, electrostatic potential fit charges were applied using the Merz-Kollmann (MK) approach and the electronegativity of the carboxyl oxygen atom was assessed. The results, which were validated by experiment, found that the catalyst’s effectiveness increased with the electronegativity of the O atom. Another study, by Wang et al., used DFT to investigate the immobilisation of metal ions atop polymer-ILs [77]. Through combined FTIR characterisation and DFT calculation, the study demonstrated that the interactions between metal ions and IL were stronger than those between the ions and EG, suggesting the feasibility of using polymer IL as support for metal ions. Another heterogeneous catalyst, Ni2+-doped MgO, was identified as a potential accelerator for PET glycolysis [78]. Employing DFT, the adsorption of oxygen onto MgO doped by various transition metals and the subsequent generation of monoatomic oxygen as an active species was investigated. The study revealed that the free oxygen atom could act as a Bronsted base to effectively produce an E- anion via proton donation and activate the glycolysis process.

When designing a novel PET glycolysis process, it is recommended that catalysts are selected such that the synergic mechanism is induced. Due to the additional interaction caused by the presence of a negatively charged moiety, the catalysis of the process is more effective. Additionally, important catalytic properties such as thermal stability and solubility are extremely important to enhancing the process.

3. Kinetics of PET degradation

The kinetics of each PET degradation process are heavily influenced by external factors such as catalyst choice and reaction conditions. Developing a deeper understanding of these kinetics allow for more efficient processes to be designed. Two main kinetics models are commonly employed regarding PET solvolysis: the shrinking core model and the “bulk” model.

3.1. Shrinking core model

Yoshioka et al. [79] described the kinetics of heterogeneous PET hydrolysis using sulphuric acid with a modified shrinking core kinetic model, where the reaction occurs at the surface of the PET particle. As the reaction progresses, cracks and pores appear on the surface of the PET and result in an increase in reaction rate. This process is shown in Fig. 6. The apparent rate constant was found to be directly proportional to the concentration of sulphuric acid and inversely proportional to the initial size of the PET particles.

The modified shrinking core model has been applied extensively to characterise the kinetics of both acid [47] and alkaline [80,81] hydrolysis of PET. Alternatively, some studies have used a first-order reaction model to describe the same process [48,82]. Using these models, reaction kinetics were found to be heavily dependent on temperature, PET-to-acid/alkali ratio, and stirring rate. The process often requires high temperatures (>200 °C), high pressure (1.4–2 MPa) and long reaction times (3–5 h) [11]. Likewise, such a model has also been used to elucidate the surface reaction of PET glycolysis [62,83].

A common approach for making the reaction conditions milder is the use of phase transfer catalysts (PTCs) [84,85]. These catalysts play a crucial role in efficiently transferring hydroxide ions from the aqueous phase to the surface of the PET particles. They require a high enough lipophilicity to allow them to be soluble in non-polar solvents, while also being small enough molecularly to avoid any steric hindrance [86]. Lopez-Fonseca et al. [87], using quaternary salts as PTCs, achieved 96 % PET conversion at 80 °C, compared to <2 % conversion reported by Kosmidis et al. [88] at the same temperature. Although the intrinsic reaction mechanism, and therefore the activation energy, is unchanged, the use of PTCs can amplify the reaction rate by 2–9 times greater.

3.2. Bulk model

An alternative kinetic model is known as the “bulk” model. The bulk model is usually induced by the use of supercritical CO2 (sCO2) in acidic hydrolysis. For this model to be applicable, the hydrolysis reaction must occur at both the interfacial surface and within the bulk of the PET particle. Fig. 7 shows the two potential paths for PET hydrolysis can simultaneously follow when sCO2 is used. In the first stage of the process, sCO2 diffuses into the PET matrix and simultaneously swells the PET to create bulk spaces, while a solid powder catalyst adheres to the surface of PET. Water is carried through the acid medium to the PET/ catalyst surface by sCO2, where it is able to form hydronium ions. Simultaneously, some water molecules and hydronium ions are carried
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Fig. 6. Schematic of modified shrinking core model commonly used to describe PET hydrolysis kinetics.

Fig. 7. Schematic showing the kinetic model described when PET acid hydrolysis is carried out using sCCO₂ combined with a catalyst.

into the bulk by the sCCO₂. This allows for hydronium ions to attack the surface of PET while also diffusing into the bulk, creating two paths for the hydrolysis of PET. In Path 1, only sCCO₂ and water are able to penetrate the amorphous regions of the PET, while the hydronium ions remain on the surface. In this case, the reaction follows the shrinking core model previously described in Figure 6, as the hydrolysis occurs on the surface of PET. In Path 2, both water molecules and hydronium ions are able to penetrate the PET particle, allowing for the hydrolysis reaction to occur simultaneously on the surface and within the bulk of PET. Using this model, the reaction kinetics including activation energy and frequency factor were found to improve with increasing temperature and pressure, with the optimum conditions being at 160 °C and 15 MPa [46,50]. It should be noted that this temperature is lower than in some other hydrolysis studies due to the introduction of CO₂, which can still provide access to the PET bulk at low temperatures. Therefore, it was concluded that CO₂ both allows for reduced reaction conditions as well as improving reaction kinetics by swelling the PET particles.

In a similar process, Kim et al. [89] investigated the use of supercritical methanol as a means of improving reaction kinetics during methanolysis, through a similar effect. They found that the total conversion and the yield of DMT increased with temperature, with 300 °C and 310 °C producing the optimal results while the methanol density also had a significant impact. This was attributed to the increased diffusivity of the methanol induced by its ability to act as a gas. By applying a kinetic model based on the scission of one ester linkage in PET by a methanol molecule resulting in the formation of one carboxymethyl group and one hydroxyl group, an activation energy of 44.9 kJ/mol was found. This compares favourably to the activation energy calculated when lead acetate is used as a catalyst under milder conditions (95.31 kJ/mol) [90]. Another study, employing potassium carbonate as a catalyst alongside an additional co-solvent, formulated their kinetic model based on two steps: the first step was featured by intermediate polymer matrices, which exhibited delayed decomposition behaviour. The second step provided a depolymerisation process with a relatively low activation energy of 66.5 kJ/mol [57]. The use of a co-solvent was found to relax the amorphous PET matrix at a lower temperature, restricting the mobility of the ester bonds and thus creating a more stable attack site for potassium carbonate. While the activation energy is still greater than when supercritical methanol is used, the reaction temperature is significantly lower (25 °C) and the yields are
Therefore, although the kinetics are improved when supercritical methanol is used, this should be balanced against the milder reaction conditions achieved by effective catalysts and co-solvents such as potassium carbonate and dichloromethane. Moreover, the process is significantly impacted by factors including reaction time and PET particle size.

The swelling of the polymer matrix can also be induced by certain catalysts. Zheng et al. [91], using [Ch][OAc] IL as a catalyst, found that at elevated temperatures, the catalyst dramatically enhanced the swelling of the polymer matrix through its excellent solvent properties, thus facilitating the nucleophilic attack by EG. There are fewer studies of the dissolution mechanism, however a study by Liu et al. [92] investigated the solvent-assisted glycolysis of PET using solvents such as aniline, nitrobenzene, 1-methyl-2-pyrrolidinone (NMP), or dimethyl sulfoxide (DMSO). They found that, as the use of solvents results in a homogeneous system, the reaction no longer takes place on the solid surface of PET, with it instead taking place within the solution. They concluded that the π-π interaction between the aromatic solvents and the benzene ring of PET plays an important role in this process. For many of the solvents used, distances between the PET and solvent was too large for hydrogen bonding to come into effect, hence the π-π interaction was considered to be the dominant factor. Similarly, Huang et al. [93] tested a DES-catalysed glycolysis process using acetonitrile as a co-solvent. The results showed that efficient production of BHET could be achieved under mild conditions due to the increased swelling of PET by the co-solvent. This swelling effect led to cracks and defects on the surface of PET particles which can significantly accelerate degradation. The swelling effects induced by various non-aqueous solvents can be pre-screened through molecular dynamics (MD) methods, allowing for high-throughput testing without the need for initial experiments. Various studies have been carried out testing the free volume of a modelled PET polymer chain, allowing for an estimation of the swelling effects [94,95].

In a summary, while the solvolysis of PET can be effectively carried out through the shrinking core kinetic model, studies have shown that by introducing factors such as supercritical fluids, co-solvents and catalysts with excellent solvation properties, the PET polymer can be swelled to allow for significantly improved diffusion of reactants. Such techniques have been found to enhance the rate and extent of PET degradation.

4. Performance evaluation and circular economy consideration

The concept of circular economy of PET describes materials being fully recirculated back into various industries, thus negating the need for the production of virgin PET. Achieving this aim would provide a synergistic positive effect as less PET waste is sent to landfill and less pollution is created through the process of PET production from petrochemicals [96]. Although there is huge scope for the chemical recycling of PET to be implemented on an industrial scale, many challenges must be addressed beforehand. A life-cycle assessment carried out by Shen et al. [97] showed that while mechanical recycling results in lower CO₂ emissions compared to chemical recycling, the superior quality of chemically recycled PET means it can replace virgin PET production and therefore have a net reduction on CO₂ emissions [98]. For chemical recycling to be implemented worldwide, substantial efforts must be put into improving the collection and separation of waste PET. This can be achieved through regulations introduced by the likes of the EU and the Chinese Government which enforce the need for consumers to recycle [99,100]. Before it can be chemically recycled, PET often has to be effectively separated from other plastics so as not to disturb the process. This process is easier for PET than for other plastics as it is rarely used in multilayer products [101]. Although PET is more widely recycled compared to other plastics, there is a discrepancy between PET recycling in developed and developing countries. It is estimated that 16 of the top 20 global producers of plastic are middle-income countries with unsatisfactory waste management infrastructure, leading to considerable mismanagement of plastic waste [4]. This can only be solved by the design and implementation of economically efficient chemical recycling processes [100].

Although the challenge to achieve the PET circular economy is formidable, notable progress has been made, and areas for continued research and efforts have been identified. The hydrolysis of PET has been utilised in industry by Infinia, while BP has outlined plans to start a pilot plant using this method [102]. Methanolysis of PET is already being used by Loop Industries [103], with Eastman currently developing their own process [104]. Regarding the glycolysis of PET, many global companies such as DuPont, Goodyear, Shell Polyester, Zimmer and Eastman Kodak have already employed this process at an industrial scale [105]. Notably, chemical recycling has demonstrated a positive impact on addressing issues related to the strength and quality of recycled materials. However, challenges still remain regarding the economics and scalability of these processes, restricting most to the laboratory level. By designing processes which economically achieve high yields of PET monomer while minimizing environmental impact, the demand for virgin material can be significantly reduced. Table 1 provides details regarding selected chemical recycling process. Comparisons can be made between different processes, catalysts, and conditions to establish which process is most suitable for PET recycling. Monomer yields and selectivity are clearly of high importance to a successful process, however, kinetics and reaction conditions also have a great effect on the economics and scalability of a process.

Table 1 provides insights into the wide variety of chemical processes in which PET waste can be degraded. Due to the toxicity of methanol and the difficult and costly post-processing involved in PET hydrolysis, glycolysis has long been identified as the most promising chemical recycling method. In recent years, there has been increased research focus on the aminolysis of PET, with numerous studies providing promising results. However, this method is limited to the production of value-added polymers as opposed to the more economically attractive reproduction of virgin PET [33].

Microwave heating is a promising method for streamlining the PET glycolysis process, without influencing the reaction mechanism directly. As illustrated in Table 1, when compared to conventional heating methods, microwave-assisted reactions can significantly reduce the reaction time by several hours through the dielectric heating mode. Through this heating mode, reactive systems can be heated much more rapidly through non-contact heating as heat is generated inside the materials rather than relying on thermal conductivities like in a conventionally heated process [115]. Such improvements vastly reduce the energy demands and enhance the scalability of the process. When microwave-assisted glycolysis is being considered, it is vital that catalysts are selected with their dielectric constants in mind. A high dielectric constant allows for selective heating and the generation of hotspots within the system, providing a much more efficient method of heating than can be obtained in conventional heating [116]. One such form of catalyst which can provide such heating are heterogeneous catalysts. Table 1 shows that heterogeneous catalysts (rows 31–36) offer excellent catalytic properties for PET glycolysis. Invariably metal-based, they offer both cationic and anionic interactions with PET and EG which induce the synergic reaction mechanism, resulting in full PET conversion and extremely high BHET yields. These catalysts have very high surface areas which allow for increased reaction with reagents, while the immobilisation of reactive molecules such as metal oxides and ILs provides chemical stability. The low solubility of heterogeneous catalysts allows for simple removal from product mixtures and studies have shown that they are often reusable, making them economically attractive. Traditionally used catalysts such as heavy metal salts require a much more laborious and costly separation process. Additionally, the use of techniques which induce a swelling effect on the polymer matrix have been shown to significantly improve glycolysis kinetics (row 38). This can significantly reduce operating costs of the process by reducing
### Table 1

Summary of monomer yields, kinetics, and reaction conditions of various PET chemical recycling techniques. Products of ammonolysis, aminolysis, hydrolysis, alcoholysis, and glycolysis are terephthalamide, BHETA, TPA, DMT, and BHET, respectively, unless stated otherwise. Reaction rate constants are at the temperature specified in the same row. (* denotes reaction rate constants graphically determined for this review).

<table>
<thead>
<tr>
<th>Catalyst used/Special conditions</th>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>Time (min)</th>
<th>Ea (kJ/mol)</th>
<th>Reaction rate constant (h⁻¹)</th>
<th>Product yield/Selectivity (%)</th>
<th>No. times Recycled</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonolysis</td>
<td>120-180</td>
<td>0.862</td>
<td>–</td>
<td>–</td>
<td>90/ -</td>
<td>–</td>
<td>–</td>
<td>[26]</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>160</td>
<td>–</td>
<td>120</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Ethanolamine/microwave heating</td>
<td>180</td>
<td>60</td>
<td>–</td>
<td>–</td>
<td>98/ -</td>
<td>–</td>
<td>–</td>
<td>[107]</td>
</tr>
<tr>
<td>Ethanolamine/microwave heating</td>
<td>200</td>
<td>0.101</td>
<td>10</td>
<td>–</td>
<td>91/ -</td>
<td>–</td>
<td>–</td>
<td>[108]</td>
</tr>
<tr>
<td>Ethanolamine/[Hmim][TFO]</td>
<td>196</td>
<td>0.101</td>
<td>60</td>
<td>–</td>
<td>89/ -</td>
<td>–</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>Diethanolamine/[Zn][Cl2]</td>
<td>196</td>
<td>0.101</td>
<td>30</td>
<td>–</td>
<td>95/ -</td>
<td>–</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td>Alkaline/PTC</td>
<td>90</td>
<td>8.106</td>
<td>61</td>
<td>3.5</td>
<td>- / -</td>
<td>-</td>
<td>-</td>
<td>[87]</td>
</tr>
<tr>
<td>Alkaline/Ultrasound assisted</td>
<td>60</td>
<td>5.066</td>
<td>1</td>
<td>55.42</td>
<td>1.794 *</td>
<td>NA (TA produced)/</td>
<td>–</td>
<td>[81]</td>
</tr>
<tr>
<td>Alkaline</td>
<td>NA</td>
<td>–25.331</td>
<td>–110</td>
<td>–</td>
<td>NA (TP salts produced)/</td>
<td>–</td>
<td>–</td>
<td>[109]</td>
</tr>
<tr>
<td>Alkaline/PTC (triethylmethyllummonium bromide)</td>
<td>300 9.626</td>
<td>1</td>
<td>83</td>
<td>1.371 *</td>
<td>98/ -</td>
<td>–</td>
<td>–</td>
<td>[88]</td>
</tr>
<tr>
<td>Acidic</td>
<td>300</td>
<td>13.679</td>
<td>1</td>
<td>99.7</td>
<td>90/ -</td>
<td>–</td>
<td>–</td>
<td>[84]</td>
</tr>
<tr>
<td>Alcoholysis</td>
<td>70</td>
<td>30.398</td>
<td>81.5</td>
<td>49.9</td>
<td>0.322</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Zn(OAc)₂/127.5 μm PET particle size</td>
<td>120 14.186</td>
<td>10.3</td>
<td>95.31</td>
<td>0.0014</td>
<td>97.7 % (DMT and EG)/</td>
<td>2</td>
<td>[90]</td>
<td></td>
</tr>
<tr>
<td>16 K₂CO₃ / dichloromethane co-solvent</td>
<td>25</td>
<td>–</td>
<td>1</td>
<td>66.5</td>
<td>93.1/ -</td>
<td>–</td>
<td>–</td>
<td>[57]</td>
</tr>
<tr>
<td>17 Ph-Zn²⁺</td>
<td>170</td>
<td>–</td>
<td>1</td>
<td>107.6</td>
<td>2.580</td>
<td>89.1/ -</td>
<td>6</td>
<td>[58]</td>
</tr>
<tr>
<td>Glycolysis</td>
<td>18 [Ch][OAc]</td>
<td>180 0.101</td>
<td>240</td>
<td>131.31</td>
<td>0.552*</td>
<td>85.2/-</td>
<td>–</td>
<td>[62]</td>
</tr>
<tr>
<td>19 Zn(OAc)₂ in DMSO solvent</td>
<td>190</td>
<td>0.101</td>
<td>1</td>
<td>75.2</td>
<td>13.68*</td>
<td>82/-</td>
<td>–</td>
<td>[92]</td>
</tr>
<tr>
<td>20 Zn(OAc)₂ with microwave heating</td>
<td>196</td>
<td>0.101</td>
<td>35</td>
<td>36.5</td>
<td>1.716*</td>
<td>78/-</td>
<td>–</td>
<td>[110]</td>
</tr>
<tr>
<td>21 [Bimino][OAc]</td>
<td>190</td>
<td>0.101</td>
<td>180</td>
<td>58.53</td>
<td>0.884</td>
<td>58.2/8.52</td>
<td>6</td>
<td>[111]</td>
</tr>
<tr>
<td>22 Cu(OAc)²⁺/ [Bimino][OAc]</td>
<td>190</td>
<td>0.101</td>
<td>180</td>
<td>56.4</td>
<td>0.748</td>
<td>53.9/33.9</td>
<td>6</td>
<td>[30]</td>
</tr>
<tr>
<td>23 (n=1,3-DMU)/n(Zn(OAc)₃)</td>
<td>190</td>
<td>0.101</td>
<td>20</td>
<td>148.89</td>
<td>2.796*</td>
<td>82/-</td>
<td>6</td>
<td>[63]</td>
</tr>
<tr>
<td>24 Zn(OAc)₃</td>
<td>265</td>
<td>–</td>
<td>–10</td>
<td>85</td>
<td>- / -</td>
<td>-</td>
<td>-</td>
<td>[112]</td>
</tr>
<tr>
<td>25 Nano ZnO</td>
<td>190</td>
<td>–</td>
<td>80</td>
<td>–</td>
<td>90/ -</td>
<td>–</td>
<td>–</td>
<td>[113]</td>
</tr>
<tr>
<td>26 Zn(OAc)₂ with microwave heating</td>
<td>190</td>
<td>–</td>
<td>30</td>
<td>–</td>
<td>98/-</td>
<td>–</td>
<td>–</td>
<td>[32]</td>
</tr>
<tr>
<td>27 [Bimino][Pro]</td>
<td>190</td>
<td>–</td>
<td>120</td>
<td>142.5</td>
<td>75.5/ -</td>
<td>–</td>
<td>–</td>
<td>[76]</td>
</tr>
<tr>
<td>28 [TBD]/[MSA]</td>
<td>180</td>
<td>0.101</td>
<td>120</td>
<td>–</td>
<td>91/-</td>
<td>5</td>
<td>75/ -</td>
<td>[75]</td>
</tr>
<tr>
<td>29 [C₇TMD]/[ZnCl₂]</td>
<td>195</td>
<td>–</td>
<td>70</td>
<td>–</td>
<td>92.7/-</td>
<td>6</td>
<td>114/ -</td>
<td>[114]</td>
</tr>
<tr>
<td>30 Fe₃O₄-boosted MWNT</td>
<td>190</td>
<td>0.101</td>
<td>120</td>
<td>–</td>
<td>100/-</td>
<td>5</td>
<td>6</td>
<td>[65]</td>
</tr>
<tr>
<td>31 MnO₂@HGO</td>
<td>200</td>
<td>–</td>
<td>10</td>
<td>–</td>
<td>100/-</td>
<td>5</td>
<td>6</td>
<td>[64]</td>
</tr>
<tr>
<td>32 ZnO/SBA-15</td>
<td>197</td>
<td>–</td>
<td>60</td>
<td>215.91</td>
<td>91/ -</td>
<td>6</td>
<td>67/ -</td>
<td>[67]</td>
</tr>
<tr>
<td>33 (rGO)[TSPM][Cu₃O₄]</td>
<td>190</td>
<td>0.101</td>
<td>180</td>
<td>–</td>
<td>95.2/-</td>
<td>5</td>
<td>66/ -</td>
<td>[66]</td>
</tr>
<tr>
<td>34 Tetragonal ZnMnO₄ spinel</td>
<td>260</td>
<td>0.507</td>
<td>60</td>
<td>–</td>
<td>92.2/-</td>
<td>-</td>
<td>40/ -</td>
<td>[40]</td>
</tr>
<tr>
<td>35 Magnetic γ-Fe₂O₃</td>
<td>300</td>
<td>–</td>
<td>60</td>
<td>–</td>
<td>90/-</td>
<td>10</td>
<td>41/ -</td>
<td>[41]</td>
</tr>
<tr>
<td>36 Magnetic ZnO-Fe₃O₄ hollow micro-sized nanoneggregates</td>
<td>190</td>
<td>0.101</td>
<td>30</td>
<td>161.6</td>
<td>5.160</td>
<td>92.3/ -</td>
<td>5</td>
<td>[31]</td>
</tr>
<tr>
<td>37 [Ch][Zn(OAc)₂]/acetanilide</td>
<td>90</td>
<td>–</td>
<td>12</td>
<td>–</td>
<td>90/-</td>
<td>–</td>
<td>5</td>
<td>[93]</td>
</tr>
</tbody>
</table>

5. Conclusions

This review summarised the overall understanding of the reaction mechanism and kinetics of the key techniques of PET chemical recycling together with each technique’s merits and limitations. Such an understanding leads to better decision making in designing efficient chemical recycling processes to address the PET waste issue. Hydrolysis and alcoholysis processes have demonstrated the capability to yield higher monomer yield; however, their implementation at an industrial scale is hindered by the associated economic issues. Aminolysis has emerging as a promising degradation method, with very high BHETA yields in short reaction times, however, it is limited to the production of value-added polymers. Glycolysis processes using more traditional catalysts are a more feasible option due to the milder reaction conditions compared to hydrolysis and methanolysis, as well as its simple integration into PET production streams. However, the technology still needs to overcome several challenges before it can be implemented on an industrial scale. The potential of the glycolysis route for establishing a circular PET production stream. However, the use of organic solvents in industry is being somewhat phased out so the reusability and environmental effects must be considered.

Despite significant advancements in the glycolysis process, further improvements in economics are imperative for its widespread implementation on an industrial scale. Heterogeneous catalysts show promising potential for producing high BHET yields while retaining their catalytic effects after numerous runs, however, their production costs pose a significant challenge. Therefore, for their implementation to be feasible, it is crucial to streamline the process to be reasonably possible. For future research, it is recommended to explore the use of novel heterogeneous catalysts capable of inducing the synergic reaction mechanism for PET glycolysis. Further insight into the interactions and reaction kinetics on a molecular level, potentially provided by DFT calculations, could be invaluable in the design of efficient new catalysts. Furthermore, combining these catalysts with microwave heating holds the potential to significantly enhance the economic feasibility of the process.
production and recycling system is underscored by the advantages it offers. If novel catalysts and methods can be developed to affordably enhance yields through the synergic effect mechanism, the glycolysis process holds considerable promise. Heterogeneous catalysts inducing the synergic mechanism in PET glycolysis have demonstrated the ability to produce extremely high yields while being easily separated and highly reusable. Therefore, it is recommended that further research can be carried out to design and test such catalysts. Additionally, microwave heating shows great promise in improving the economics and industrial feasibility by vastly reducing reaction times. This, in conjunction with an effective heterogeneous catalyst, shows great potential for significantly improving the glycolysis process. Mechanistic and kinetic data, obtained through experiment or computational methods, could provide valuable insight into the efficiency of such novel processes and guide future design.

CRediT authorship contribution statement

Stuart Conway: Writing – original draft, Investigation. Xiaolei Zhang: Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

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

No data was used for the research described in the article.

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