Research on Conversion of Waste Polyethylene Terephthalate into Value-Added Monomer replacing Landfill and Incineration for Environmental Pollution Control

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Abstract. Traditional Polyethylene terephthalate (PET) disposal methods are mainly mechanical recycling, landfill and incineration, which have some problems such as poor quality of recycled products and environmental pollution. By comparison, the products of chemical recycling can be resynthesized into PET, saving petrochemical resources and reducing environmental pollution. In view of this, some recent chemical recycling methods that convert waste PET into value-added monomers are summarized in this paper. For instance, PET can be reduced by hydrogen into terephthalic acid or other valuable products. And it can be decomposed into bis(2-hydroxyethyl) terephthalate in the presence of ethylene glycol and catalysts such as magnetic metal oxides. Also, it can be hydrolyzed into terephthalic acid and ethylene glycol by green catalyst. Besides, it can be pyrolyzed into benzene catalyzed by non-noble metal oxides. Finally, several possible strategies have been proposed to help convert waste PET into value-added monomers.

Keywords: Polyethylene terephthalate, chemical recycling, waste plastics, hydrogenolysis, glycolysis.

1. Introduction
Plastics are present in almost every aspect of daily life. Due to its light weight, high durability, strong adaptability and relatively low production cost, plastics are produced in large quantities and widely used in clothing, packaging, buildings, transportation, toy/furniture manufacture, etc. [1] However, the good properties of plastics also make it difficult for them to degrade naturally. The present estimate suggests that roughly 6300 million metric tons of plastic waste had been generated by 2015, and only about 9% of which had been recycled [2]. Consequently, plastic fragments are accumulating on land, in fresh water, and in the ocean, leading to a series of long-term and deep-seated environmental problems [3-8].

Polyethylene terephthalate (PET) is the most used plastic among polyester plastics. It is produced from ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT). It has excellent toughness, tensile and impact strength, wear resistance and electrical insulation properties, so it is often used in synthetic fibers, soft drink bottles, food containers and films. Its production has gradually increased to about 78 million tons per year. Given the growing consumption of PET and the damage caused by its accumulation after being discarded, it is especially important to take steps to
deal with the PET waste. Traditional PET waste disposal methods mainly include mechanical recycling, landfill, and incineration. Among them, mechanical recycling has high requirements on the category and purity of plastic waste and is also faced with the problems of plastic degradation and heterogeneity, resulting in low quality recycled products [9, 10]. Moreover, PET eventually becomes waste again after the loss of its properties. Landfill will take up a lot of land, and harmful substances can leach from landfill into surface waters and groundwater, which presents potential threats in terrestrial environments [11]. The incineration process can produce a series of toxic compounds such as polycyclic aromatic hydrocarbons and toxic metals [12]. It can also increase carbon emissions, which has become a major environmental problem. In contrast, chemical recycling can effectively deal with mixed dirty plastics without sacrificing the quality of recycled products and is more in line with the requirements of sustainable development. Chemical recycling of PET is one of the promising methods realized by depolymerizing PET into monomers or oligomers. After purification, these products can be turned into raw materials to re-synthesize PET, forming a closed loop of PET recycling. The closed-loop recycling can not only save the petroleum resources for PET production but also avoid the pollution caused by PET waste and pollutants from incineration. Compared with traditional disposal methods, chemical recycling has significant advantages and has become a future trend. This work summarizes four main methods of chemical recycling, namely hydrogenolysis, glycolysis, hydrolysis, and pyrolysis (Figure 1). The merits and limitations of these methods are presented in Table 1.

![Figure 1. Methods of chemical recycling: pyrolysis, hydrogenolysis, glycolysis and hydrolysis.](image-url)
Table 1. The merits and limitations of the above chemical recycling processes.

| Process       | Merits                              | Limitations                                        |
|---------------|-------------------------------------|----------------------------------------------------|
| Hydrogenolysis| suitable for handling mixed plastics waste with additives, without solvents high temperature, high pressure, long time, expensive catalysts, not environmentally friendly |
| Glycolysis    | closed loop between PET and BHET, milder reaction conditions catalyst residues and additives |
| Hydrolysis    | low-cost, eco-friendlier, high purity product high temperature, high pressure, long time, waste acid and alkaline solutions |
| Pyrolysis     | simple to operate, easy to industrialize high temperature, low product selectivity |

2. Chemical recycling

2.1. Hydrogenolysis

In the hydrogenolysis process, polyesters are depolymerized by breaking the C-O bond with hydrogen or other reducing agents, and value-added products such as diols or arenes are obtained. Klankermayer and coworkers performed the application of the molecular ruthenium complex in the transformation of waste polyesters and polycarbonates to value-added diols respectively [13]. PET was depolymerized to 1,4-benzene dimethanol and EG with full conversion and excellent selectivity (>99%) by 1mol% [Ru(triphos-xyl) tmm] in 1,4-dioxane, under H₂ (100 bar), 140°C, and after 16 h. They also tested commercially available PET sources like water bottles under the same reaction conditions and even lower catalyst loading, and got the result that all of the tested products were converted to diols with excellent conversion and selectivity. Marks and coworkers reported the use of a carbon-supported single-site molybdenum-dioxo complex (C/MoO₂) in the depolymerization of PET [14]. This process could be carried out under low pressure and solvent-free conditions, and the catalyst is abundant, stable, non-toxic and recyclable. Under 1 atmosphere of H₂, 260°C and 24 h, PET was depolymerized with C/MoO₂ and 87% yields of terephthalic acid, ethylene, and trace acetaldehyde (<5%) were obtained (Figure 2A). The mechanism of the reaction was studied by using 1,2-ethanediol dibenzoate model. The results indicated that β-C-O scission occurred initially, followed by hydrogenolysis of vinyl benzoate intermediate (Figure 2B). Recently, Yan and coworkers demonstrated that aromatic plastic wastes with C-O and/or C-C linkages could be hydrogenolyzed to arenes with Ru/Nb₂O₅ as catalyst [15]. PET was effectively converted in octane with Ru/Nb₂O₅ under 0.5 MPa H₂ and 280°C, and the yield of arenes was 83.6% after 8 h. The practicality of this process has been proven with Coca-Cola bottle, and a high monomer yield (90.9%) and arene selectivity (78.4%) were achieved. They also used mixture (containing PET, PS, PC and PPO) as the feedstock and achieved an arene yield of 78.9%, which provided a new way to convert mixed aromatic plastics into arenes at the same time, eliminating the need for sorting.

To avoid the limitation of high temperature conditions in most hydrogenolysis processes, Cantat and Feghali developed an alternative approach [16]. They used hydrosilanes as reductants and metal-free catalysts to depolymerize polyethers, polyesters, and polycarbonates to functional chemicals at room temperature. With tetramethylidisiloxane, 5mol% B(C₆F₅)₃, and CH₂Cl₂, PET is converted into p-xylene and ethane at room temperature, and the yield of p-xylene is 82% after 16 h. Although hydrogenolysis is an effective way to recycle PET, the catalysts (such as Ru) used in most processes are costly, potentially toxic, and have poor recyclability. Furthermore, there remains a need for an efficient method that can lower the temperature, reduce the pressure, and shorten the reaction time. Meanwhile, it is also a good choice to develop a better renewable hydrogen source instead of hydrogen to simplify the process and reduce costs.
Figure 2. A. Tentative diester hydrogenolysis pathway. B. C/MoO$_2$-catalyzed hydrogenolysis of PET to TPA and ethylene.

2.2. Glycolysis

Glycolysis is an important chemical recycling method of PET widely used in industry. It is a transesterification reaction in which the ester linkages of PET are broken by a glycol in the presence of catalysts to generate bis(2-hydroxyethyl) terephthalate (BHET). EG is the most commonly used glycol. The catalysts mainly include metal salts, metal oxides and various ionic liquids (ILs).

Kim and coworkers presented superparamagnetic $\gamma$-Fe$_2$O$_3$ nanoparticles as an efficient, environment-friendly and reusable catalyst for PET glycolysis [17]. The glycolysis reaction took only 60 min to achieve maximum BHET monomer yield more than 90% at 300°C, approximately 1.1 MPa, and a 0.05 catalyst/PET weight ratio. Due to its superparamagnetic property, the catalyst could be easily recovered up to 10 times by simple magnetic decantation, and the yield was almost the same each time. Rinaldi and coworkers applied ultrasmall cobalt nanoparticles (~3nm) as the catalyst for the glycolysis of PET at relatively low temperature and pressure [18]. The conversion of PET is up to 96% and the yield of BHET is 77% within 3 h at 180°C and 1 atm. An optimization for product separation is to obtain pure BHET precipitates without the need for water. The ultrasmall cobalt nanoparticle catalyst in the remaining EG solution could be directly reused for at least 5 times without significant reduction in BHET yield. Pedro and coworkers devised Fe$_3$O$_4$@SiO$_2$@mim)[FeCl$_4$] (mim: methylimidazolium) magnetic nanoparticles as a magnetically recoverable nanocatalyst [19]. The catalyst provided almost 100% yield and selectivity of BHET in the glycolysis of PET in EG at 180°C. In addition, it could be easily recovered in the presence of an external magnetic field and reused up to 12 times with no significant loss of the catalytic activity. At the 12th run, the yield of BHET could reach 84%. The purity of the product is also very high with no residual Fe found in the purified BHET.

Traditional catalysts usually contain heavy metals, which are efficient but expensive and not environmentally friendly. ILs and deep eutectic solvents are considered as promising green solvents because of their easy synthesis, low price, environmental friendliness, thermal stability, low volatility, and designable structure. Zhang and coworkers developed a series of metal-free choline-based ILs catalysts as alternatives to conventional imidazolium metal-based ILs catalysts for the glycolysis of PET [20]. Using this catalyst is more economical, environmentally friendly and efficient. The conversion of PET and the yield of BHET reached up to 98.2% and 85.2% respectively catalyzed by [Ch][OAc] at 180°C in 4 h. The possible mechanism of this reaction is shown in Figure 3, and the key
is the synergic interaction between the cation and anion of the IL. The choline cation in the IL interacts with the oxygen of carbonyl in PET and makes the carbon of carbonyl more electrophilic, while the acetate anion in the IL interacts with the hydrogen of hydroxyl in EG and enhances the nucleophilic attack ability of hydroxyl oxygen.

Figure 3. Mechanism of [Ch][OAC] catalytic PET glycolysis process.

2.3. Hydrolysis
PET can be hydrolyzed into the original feedstock monomers (TPA and EG) under acid, base or neutral catalysis. Hydrolysis is relatively an ecologically sound and sustainable method to recycle waste PET materials. However, the reaction usually requires high temperature, high pressure and a long time. Acidic and alkaline hydrolysis will also produce waste acid and alkaline solutions. To optimize this process, Hou and coworkers used high concentration ZnCl₂/H₂O system as catalyst for hydrolysis of PET [21]. This system is more environmentally friendly and due to the coordination catalysis of Zn²⁺, it has showed excellent catalytic performance. The yield of TPA was reached up to 98.31% with 70% ZnCl₂/H₂O at 180°C for 8 h, and the purity of TPA was up to 97.14%. The main reaction process is shown in Figure 4. In addition, the ZnCl₂ solution was is easily separated and could be reused 3 times with a degradation ratio of 100%.

Figure 4. PET hydrolysis process using ZnCl₂ as catalyst.

2.4. Pyrolysis
Pyrolysis is the thermal degradation in inert atmospheres of long chain organic materials. It is one of the attractive methods to convert PET waste to useful chemicals. The principal products of PET pyrolysis are organic acids, such as TPA and benzoic acid, which can not only cause corrosion and blockages in the processing facilities, but also decrease the quality of the products. Much research in recent years has focused on optimizing this process by using catalysts to convert the organic acids into arenes.
Bollas and coworkers investigated the influence of heating rate, catalysts and co-feeding steam on the distribution of PET-based waste carpets pyrolysis products [22]. The results showed that higher temperature and slow pyrolysis could promote the conversion of PET to arenes. Catalytic pyrolysis (using ZSM-5 or CaO) could decarboxylated benzoic acid and acetylbenzoic acid produced in relatively large quantities during thermal pyrolysis. They also performed steam catalytic slow pyrolysis of carpet waste with CaO, and the yield and selectivity of benzene in the organic phase of the liquid product were about 54 C% and 98 C% respectively (face fiber). Kumagai and coworkers used a tandem μ-reactor gas chromatography–mass spectrometry system (TR-GC/MS) to investigate the catalytic effects of several different metal oxides (ZnO, MgO, TiO$_2$, and ZrO$_2$) on the conversion of PET pyrolysis products to arenes [23]. Among them, ZnO selectively accelerated the decarboxylation of TPA and benzoic acid at a lower temperature (490℃), and the area percentage under the MS peaks of benzene reached the maximum (88.8 area%).

3. Conclusion and Prospect

In this review, we summarize several common chemical recycling methods of PET waste. These methods have given new life to discarded plastics, turning them back into a variety of valuable chemical raw materials. Furthermore, chemical recycling can solve the problem of plastic waste pollution and reduce the dependence on petrochemical resources. We overview that PET can be efficiently hydrogenolyzed by ruthenium-containing catalysts to produce value-added substances such as diols and arenes. Some more environmentally friendly, recyclable and efficient catalysts such as C/MoO$_2$ have been gradually studied and applied to PET hydrogenolysis. Then we survey that catalysts such as γ-Fe$_2$O$_3$, cobalt and various ILs enable efficient glycolysis of PET into BHET monomer. The use of nanoparticles makes the catalysts more efficient and easier to recycle. In terms of hydrolysis, high concentration ZnCl$_2$/H$_2$O system was used to catalyze the hydrolysis of PET into TPA and EG, and a high yield of TPA was obtained. We also outline that PET can be pyrolyzed to TPA and then further converted to benzene by catalysts such as CaO and ZnO under high temperature conditions.

Many studies have made efforts to improve the reaction rate and product yield, reduce costs and pollution, and optimize the reaction conditions to make it as mild as possible. Catalysts for chemical recycling are also being developed to be eco-friendly, recyclable, highly active and low-cost. These research results have made the chemical recycling of PET increasingly competitive, but there is still room for improvement. For example, considering that glycolysis generally requires a large number of solvents, a more economical solvent-free process can be achieved by passing EG vapor into the reaction vessel. In addition, high efficiency catalysts suitable for hydrolysis can be selected from catalysts used for glycolysis, such as Al$_2$O$_3$, Fe$_2$O$_3$ and other metal oxides. Furthermore, new alkali-resistant and high-temperature resistant bacteria can also be isolated and cultivated, which can be combined with hydrolysis to accelerate PET decomposition. Moreover, in the pyrolysis, commonly used alkaline earth metal oxides such as MgO and transition metal oxides such as ZnO can be combined to make a composite catalyst with higher activity. Thus, green and efficient PET recycling strategies are expected to be implemented in the near future.

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