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Chemical upcycling of PET: A mini-review of converting PET into value-added molecules

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Abstract. With the increasing consumption of single-use plastics, a large number of petrochemical resources are used as raw materials, and hundreds of thousands of tons of plastic waste are produced every year. Although there are lots of methods that have been developed to solve this issue by recycling plastic waste, none of them can recover the value of the waste in an efficient way that is less economical cost and less harmful to the environment. Polyethylene terephthalate (PET) is one of the most widely produced single-use polymers. It is challenging to recover the value through mechanical recycling due to the degrading of properties during reprocessing. Chemical upcycling/recycling is an alternative to convert the polymer back to the monomer with less environmental effect, which has lower energy demand. Hydrolysis is one of the common methods in chemical upcycling; it can convert PET waste into value-added materials such as H2 fuel. This paper mainly focuses on the method that converts PET to value-added chemicals through hydrolysis in recent years, so as to offer some references for future researches.

Keywords: Chemical Upcycling, Polyethylene terephthalate, Value-added Molecules.

1. Introduction

Polyethylene terephthalate (PET) is a polyester which is made from ethylene glycol and terephthalic acid. The resulting strands of PET are cut into small resin pellets after compressed and cooled. Heat will then be applied to those pellets and allowed to turn to liquid form, which can be poured into a mould with a particular shape [1].

PET is widely used in food and drinks packaging due to it has properties of strong, lightweight, non-reactive, economical, and shatterproof [2]. It was first synthesized by DuPont chemists during the mid-1940s while searching for polymers to make textile fibers [3]. Until the early 1970s, a technology was developed to mould PET into bottles. PET bottles have all the features to be the perfect container, including lightweight, safe, cheap and recyclable [4].

With time, the demand for plastic has increased, which has led to an increase in the production of plastics. Around 70 million tons of polyethylene terephthalate (PET) is produced annually around the world to make beverage bottles, packaging and clothing. Research shows that about 1.1 million tons of plastic bottle waste end up in the ocean [5]. Although there are several different chemical processes and mechanical methods that can be used to deconstruct the PET into monomers, the resulting poor quality and less profitable products, lead to low recycling rates. There are only 30% in average of PET bottles can be recycled around the world. Research shows that no more than 15% of PET bottles find a second life [6].

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As the products reproduced through mechanical recycling suffer from the loss of properties during reprocessing, chemical upcycling is found to be the feasible alternative to reclaim the monomers. It is an approach to convert plastic trash directly into value-added molecules with lower-energy paths and less environmental effect than traditional chemical recycling [7].

Chemical recycling has several benefits, including a decrease in the consumption of oil as a feedstock, versatility in producing high-value materials, the ability to create new polymers which has the same properties as those created using petrochemical feedstock, and comparatively simple removal of onerous additives and colorants [8]. Based on the quality of the products that can be used directly to produce virgin-like materials, previous life cycle analyses of plastic recycling have shown that chemical recycling has a higher potential for reducing CO_2 emissions than mechanical recycling. Mechanical recycling, on the other hand, typically offers downgraded pellets that perform worse than the original materials, necessitating a constant input of new petroleum-based monomers [8]. Additionally, it is anticipated that a chemical recycling process using little to no organic solvents will improve the process' energy efficiency and hence lessen the environmental effect of a recycling facility [9].

Although there is a number of chemical recycling strategies have been developed to recycle PET, including hydrolysis, aminolysis and alcoholysis, none of those methods can convert a mixture of aromatic plastics directly without pre-classification or have a 100% conversion rate [10]. A brief introduction of two promising procedures for PET upcycling is given in this paper, and finds the possibility to form a complete life cycle for PET plastics, such as producing and recycling the PET by using the same catalyst or procedures.

2. Methods of converting PET into value-added molecules

2.1. PET into BTX

Wang and her research group have developed a process that can convert the PET waste back to BTX (benzene, toluene and xylene) by using Ru/Nb_2O_5 as the multifunctional catalyst to unlock the hidden hydrogen in ethylene glycol. There are three tandem steps involved in the process, which including hydrolysis, reforming and C-O/C-C cleavage. The parallel hydrogenolysis and decarboxylation involved in the cleavage of the C-O/C-C bond were identified to be the rate-determining step [11].

Due to the appropriate hydrogenation ability of Ru, Ru was used as the metal catalyst, which makes Ru the most selective metal site. Nb_2O_5 was employed to promote the hydrogenolysis activity of the Ru catalyst, which allows the Ru/Nb_2O_5 to lower the competitiveness of the undesired decarboxylation reaction and make the desired hydrogenolysis reaction feasible. The gas products H_2 and CO_2 were captured after the reaction, which proves that the reaction undergoes the aqueous-phase reforming of ethylene glycol.

The result of the catalyst recycling test showed that some activity was lost during the first and the second run. They suspect that this loss could be caused by the partial oxidation of the Ru during the posttreatment. However, the catalytic activity was recovered with BTX yield of 84.5% after the reduction using H_2 under 400 ℃ for 4h.

The applicability of Ru/Nb_2O_5 towards prevalent PET products was investigated by using Coca-Cola bottles, polyester film and polyester clothes. The high PET purity of those commercial PET plastics was confirmed by elemental analysis at the beginning, which allows a believable product's yield can be calculated. Both Coca-Cola bottles and polyester film show a total yield of 88.7% and 93.3% for the BTX stream respectively and 74.5% and 72.7% for alkyl aromatics selectivity under the same reaction conditions (220℃, 12h). For polyester clothes, a BTX yield of 81.6% was only achieved at 280℃ in 16h.

As the Ru clusters are small on Nb_2O_5, the high selectivity for aromatics is achieved by preventing the saturation of the aromatic ring, which is achieved by the inhibited co-adsorption of the aromatic ring and hydrogen, the NbO_x species acts as a Brønsted acid to activate the C-C bond and the strong affinity of this species allows it to activate the C-O. With further research done by Wang and her

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research group, it was found that Ru/Nb_2O_5 can act as a catalyst for various aromatic plastic waste conversion (upcycling) and resulting in a high yield (75%-85%) of arenes produced. More importantly, Ru/Nb_2O_5 allows the conversion of mixed aromatic plastic waste to arenes can happen simultaneously. This catalyst also shows high selectivity in the conversion of single-component plastic waste, which minimizes the production of the undesired product [12].

2.2. PET into terephthalic acid

Arias and Thielemans reported an efficient and straightforward procedure that can convert PET into terephthalic acid (TPA) and ethylene glycol (EG) in one minute at 120°C by using microwave-assisted heating. This allows the process to achieve 100% PET conversion and to be known as the fastest procedure. The researchers showed a combined use of microwave irradiation and a solution of potassium hydroxide in anhydrous alcohol to develop an energy-efficient non-aqueous hydrolysis process [1]. In this process, reaction efficiency is improved using microwaves, instead of heterogeneous hydrolysis in aqueous. This increases heating efficiency which further reduces the impact on environmental energy, thereby shortening the reaction time. As only alkali and alcohol are used in the depolymerization step, the process is more straightforward and sustainable than the other approach (pre-soaking PET in organic solvents). The by-product potassium sulfate, an essential fertilizer used to improve the quality and yield of production by providing potassium to the soil, and the improvement in reaction efficiency makes the process more competitive than the others [13].

A mixture of KOH-in-Methonal and PET flakes was added into a high-pressure vial and sealed hermetically before being put into a microwave reactor. The potassium methoxide that precipitated with terephthalate salts in white solid form, was diluted by adding distilled water after the reaction time was achieved. After filtration and purification, the production was collected.

Metallic sodium was added with methanol in a dry high-pressure vial with the support of an argon flux. PET was added after all sodium was reacted, and the sealed system was then placed into the microwave reactor. The same process as the above was repeated after the reaction time was achieved.

Based on the results from a comparison of the depolymerization of PET by basic solutions of potassium hydroxide in methanol, ethanol, isopropanol, and tertbutanol in the absence of water. Arias and Thielemans found that alcohol is acts as a medium for the alkaline catalyst, and the ability of the alcoholic medium to dissolve the base is directly related to its efficiency in the hydrolysis of PET using the alkaline catalyst. As the reaction speed and conversion rate increased with increasing concentration of base, methanol was used in further reactions.

The result of the base cation test shows that the high stability of KOH in methanol speed up the reaction more significantly than NaOH in methanol. Therefore the efficiency of KMH was further studied and shows that the reaction speed is increased and requires less energy than the traditional aqueous approaches. The reaction was completed in 5h with 100% conversion of PET. The time taken for conversion to complete was further improved with the use of Microwave. It is observed that PET conversion is proportional to the reaction time for all investigated temperatures. The results showed that the essential (minimum) condition for PET to achieve 100% conversion is 4min at 100°C. Whereas under 120°C only 1 min was taken.

3. Hypothetical industrial feasibility and green chemistry metrics

Based on Arias and Thielemans's report, there are two useful products that can be produced from PET waste through this process as shown in Figure 1. The yield of terephthalic acid was 93.8%, and several characterization techniques were used to confirm its purity. The green chemistry metrics shown in Figure 2 shows the comparison between the other literature reports on depolymerization using microwaves.

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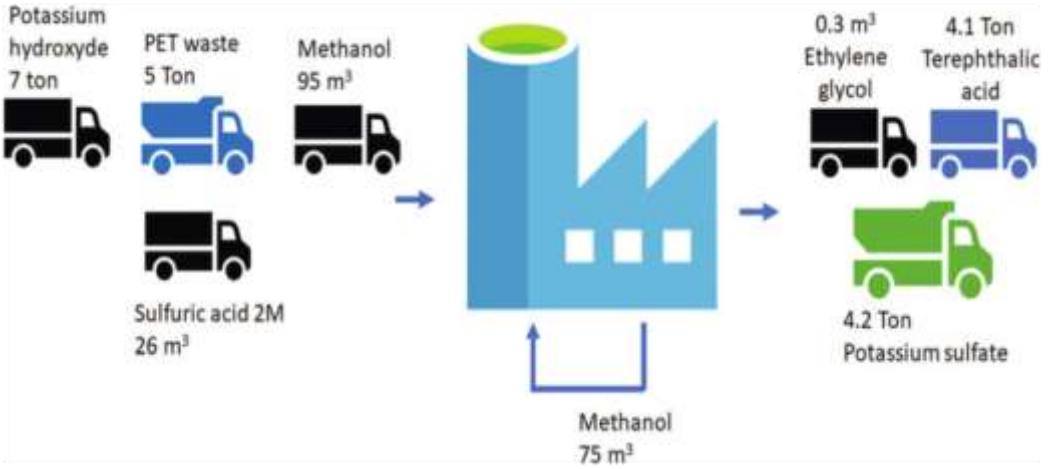

Figure 1. A hypothetical industrial process in industrial scale [8].

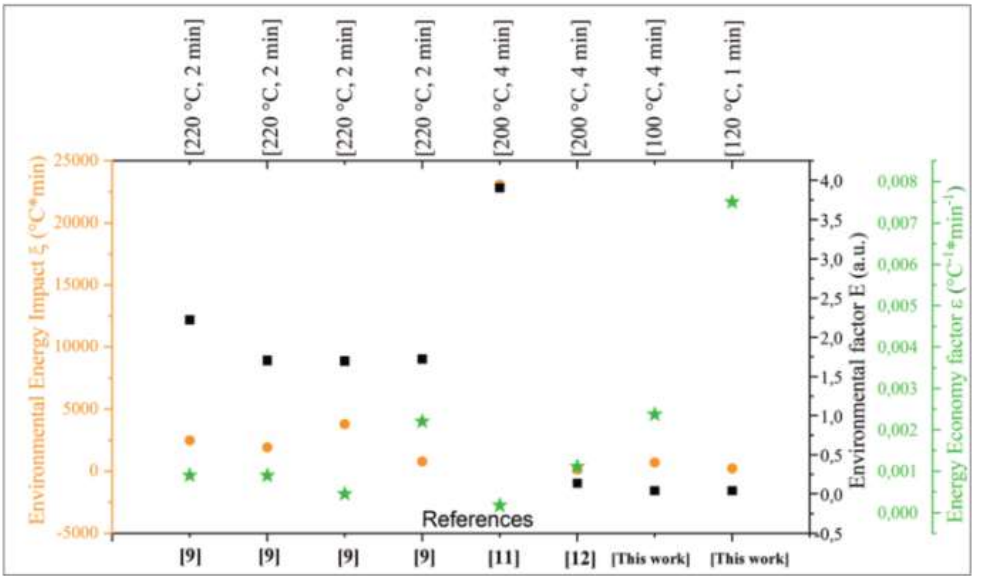

Figure 2. Comparison between the other literature reports on depolymerization using microwaves [8].

In Arias and Thielemans's process, the catalyst is converted into a valuable byproduct, potassium sulfate. This could compensate for the lack of catalyst recovery. The ease of the current method makes it possible to be used straightaway in small factories adjacent to areas where garbage is produced. The use and production of KMH solution make the process more environmentally friendly and decrease the consumption of energy, compared to the process that uses organic solvents, e.g. tetrahydrofuran, and chloroform. Due to the solubility of most plasticizers, the containments can be separated straightforward from the desired monomer. This make the process more competitive than the mechanical recycling process [8].

4. Conclusion

In conclusion, the procedure developed by Arias and Thielemans shows a feasible and promising method to recycle PET. The reagents used has a minimum effect to the environment compared to organic solvents, and the byproduct produced can be put into other industries. The work done by

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Wang can supplement the recycling problems of other aromatic plastic. The combination of the two methods can initially form a part of the plastic cycle, and PET recycling can be prioritized. This paper only covers the two most promising technologies in the experimental stage considered by the authors, but whether they can be applied to industrial needs to be further analyzed in a more comprehensive way.

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