The Chemical Recycling of Polyethylene Terephthalate – An Overview

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1. Introduction

When talking about the circular economy of plastics in general or of polyethylene terephthalate (hereinafter referred to as PET) in particular, the process of chemical recycling of PET is the basic prerequisite for speaking of a true, closed material cycle [1]. There are clear limits to the number of mechanical recycling cycles of PET due to thermal and hydrolytic degradation, a property of all organic polymer materials that inevitably comes into play due to repeated melting during processing and regranulation.

Some market participants who produce and use recycling PET (r-PET) are trying to give the impression that mechanical recycling is meeting the requirements of a true circular economy for plastics.

What is left out is that a recycling rate of 100% can only be achieved in open systems. This means: A partial stream of primary made r-PET from virgin material must always be added to a PET-recycling-process after a limited number of use cycles.

In the case of PET bottles, these are especially colorless PET bottles, from manufacturers outside of an internal material cycle. Many smaller market participants who do not carry out their own collection, regeneration and bottle production enable companies with their internal polyester bottle cycle to achieve a recycled content of 100%.

For PET bottles, the number of cycles without the addition of virgin PET is around 5, although even with 5 cycles without the addition of primary r-PET, a significant impairment in the quality of the bottles, trays or A-PET film produced from them can be expected.

When talking about chemical recycling, it is necessary to first draw sensible process and process boundaries. Chemistry offers various options for splitting a polymer molecule into its starting materials, with three process levels to consider:

a. Conversion of the molecular chain into the monomers and only one type of polymer is in the process → depolymerization [2]

b. Conversion of the molecular chain into the basic raw materials for the production of monomers to obtain hydrocarbons from a mixture of different polymers → pyrolysis oil [3] (e.g.)

c. Conversion of the molecular chains of a mixture of synthetic and organic polymer waste into synthesis gas to produce the basic raw materials → e.g. B. Fischer-Tropsch synthesis [4]

The present comments on the current status of the development of chemical recycling of polyethylene terephthalate (PET) refer to the first level mentioned above, the conversion of pure polyester waste into the monomers terephthalic acid or its esters and monoethylene glycol.

This chemical recycling of PET is not a new topic and has been part of the polyester industry since the beginning. The inventors of PET included the recovery of polyester raw materials through chemical recycling very early on in the development of PET manufacturing processes.

So, at that time, efforts were focused on “recovery” and “depolymerization” rather than “recycling,” as most PET manufacturing plants used dimethyl terephthalate (DMT) and monoethylene glycol (MEG) as raw materials. Methanolysis of production waste and recovery of DMT was therefore the

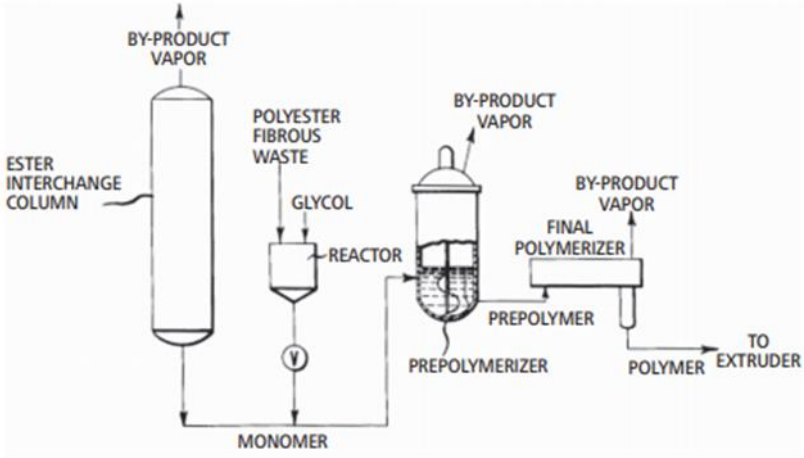
process of choice. As early as 1962, Glanzstoff Fabrik AG registered a process for recovering DMT from production waste from polyester production as US patent 3,037,050. The melted polyester waste was reacted with methanol at 220 to 250 ° C under supercritical pressures.

An important reason for using methanolysis as a depolymerization process was the presence of titanium dioxide (TiO_2) in concentrations of 0.3 to 2% in most filament and fiber waste. TiO_2 is very easy to remove by distillation of the DMT obtained during depolymerization, compared to the difficulties of filtration, which does not allow the separation of TiO_2 with particle sizes of ~ 0.5 µm.

Former Hoechst AG's U.S. Patent 5,481,024 is a useful literature source on the methanolysis depolymerization process and its long history dating back to the early years of the polyester industry.

The development of depolymerization by glycolysis began in parallel with methanolysis. In 1961, DuPont published in U.S. Patent 3,222,299 a process in which the glycolysis product of waste fibers and filaments is an integral part of a continuous polyester line (Fig. 1).

Fig.1: Continuous polyester process with integrated glycolysis reactor (USP 3,222,229)



The recovery of terephthalic acid from the waste generated during the production of fibers and filaments was registered as US patent 3,120,561 by Societe Rhodiaceta in 1964. The spinning waste is reacted with water at 230 - 250°C and the resulting pressure of 28 - 40 bar. After about three hours of reaction time, a yield of about 80% is achieved

In 1973, Eastman published in U.S. Patent 3,728,287 a detailed teaching of how to depolymerize PET by hydrolysis under normal pressure, the proposed laboratory-scale process being primarily used for polymer composition analysis.

From the 1980s onwards, the polyester industry began to develop rapidly, first in the USA and the Far Eastern countries of India, Japan, Taiwan, Indonesia, Malaysia and Thailand and, after the turn of the millennium, especially in China. In addition, with the production of high-purity terephthalic acid (PTA) in the 1980s, polyester production began to switch from the raw material DMT to PTA. The background to this development was the fact that production costs could be reduced by around 15% through the use of PTA instead of DMT. This development was accompanied by an enormous increase in the production capacities of the individual polyester production plants. From 100 t/day per line in the 80s to 600 t/day in the years around the turn of the millennium to plants with capacities between 1000 and 2000 t/day in the present. At the same time, the yield of salable A-grade quality product rose to well over 95% and is now > 98% in many systems.

The switch from DMT to PTA and the simultaneous increase in yield meant that the widespread and usual recovery of DMT from production waste in the “DMT era” could not be transferred to PTA-based polyester production. There was no easy-to-use process analogous to methanolysis for the recovery of PTA. In addition, it was and is currently more cost-effective for the plant operators to sell the resulting production waste to external processing companies, which use it to produce marketable products through mechanical recycling. In summary, the development described is the reason why a large proportion of polyester producers have withdrawn from internal chemical recycling to reuse their own production waste.

With the introduction of the PET bottle for all types of beverages in the 1980s, the development of mechanical recycling processes began. Above all, the closed shape of the PET bottles made it easy to collect and sort the bottles according to their use, and systems were soon developed for the effective separation of the collected plastic waste. An important requirement for the mechanical PET recycling processes was the removal of all toxic impurities to ensure that no contamination of the food occurs when the polyester is used again in contact with food.

In addition to mechanical PET recycling, which is primarily based in the plastics processing industry, some PET manufacturers began developing partial chemical recycling at the turn of the millennium. A partial stream of 10 – 20% of purified PET bottle flakes was and is still fed into the polyester process, whereby the flakes are depolymerized in the esterification reaction mixture and polymerized homogeneously with the virgin material. This procedure was mainly used by the large one’s beverage manufacturers. The disadvantage is that the maximum r-PET addition depends very much on the pre-cleaning of the flakes and only colorless and transparent flakes can be processed. This means that this process is in direct competition with mechanical recycling.

2. Fundamental problems of chemical PET recycling on an industrial scale

There is little or no information on the question of which process steps and methods are used to purify the monomer mixtures produced by chemical cleavage. For all chemical processes, it can be assumed that, in addition to terephthalic acid (TA), approximately 3% isophthalic acid (IPA) is produced and, in addition to MEG, approximately 2% diethylene glycol (DEG) and smaller amounts of cyclohexanedimethanol (CHDM) are contained in the monomer mixture, whereby type and the concentration of these co-monomers depends heavily on the composition of the PET waste.

Distillation processes and recrystallization and extraction processes are used to separate these components.

The issue of purifying the monomer mixtures obtained becomes much more complex due to the various impurities in the PET waste used, which inevitably leads to the PET waste being pretreated by sorting, separation and, if necessary, washing before the chemical splitting step.

This pretreatment applies to all chemical recycling processes and ultimately defines the costs of the entire process. At this point, an economic conflict between chemical and mechanical recycling can also become visible if the pre-cleaned PET waste achieves a higher profit through mechanical recycling.

This leads to the requirement from the outset that chemical recycling must be able to process more contaminated feedstock than mechanical recycling.

All chemical PET recycling processes therefore have the following questions in common:

→ Type/origin/source of PET waste

A clear distinction must be made between industrial waste, packaging waste (yellow bag) and textile waste. Industrial waste is largely homogeneous in composition. The effort required for pre-cleaning is low. Packaging waste is very inhomogeneous. Separation of foreign polymers and enrichment are required. Textile waste is problematic due to its complex composition. Pre-sorting is required.

→ PET content of the waste

The details of chemical recycling processes on an industrial scale depend primarily on the type and composition of the polyester waste used. Processes that can produce recycled PET of high purity even in the presence of 10 - 20% of foreign substances are desirable.

It is known from a technical process of methanolysis based on the Teijin process that foreign polymers (e.g. polyamides from zippers or polyurethane) are largely removed from the textile waste by means of manual sorting, but up to 10% of cotton impurities are tolerated by the process, with the cotton content being reduced be separated mechanically during methanolysis [25].

→ Sensible system size/capacity

In contrast to mechanical recycling, which can be operated economically with low production capacities of around 10,000 t/a, chemical recycling plants have to be set up in the range of 100,000 t/a, which corresponds to a daily capacity of around 270 t. This capacity, which is comparatively high compared to mechanical recycling, is derived from the cost-capacity ratio of chemical plants, in which production costs reduce non-linearly as capacity increases.

3. Chemical recycling process of polyethylene terephthalate

Linear polyesters such as polyethylene terephthalate (PET) synthesized through equilibrium reactions are depolymerized by forcing the reverse reaction from the polymer to the monomers by adjusting the appropriate equilibrium parameters. Depending on the choice of process parameters, terephthalic acid (TA) and monoethylene glycol (MEG) are formed during hydrolysis in the presence of water, the polyester precursor dimethyl terephthalate (DMT) and MEG during methanolysis in the presence of methanol, or the polyester precursor Bis during glycolysis in the presence of MEG (β-hydroxyethyl) terephthalate (BHET).

In general, the processes of depolymerization can be represented schematically as follows:

Hydrolysis:

$H[O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_2H_4\text{-}]_n OH + H_2O$ (p,t,T,c-cat) ⇆ $HO\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}OH + HO\text{-}C_2H_4\text{-}OH$

Glycolysis:

$H[O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_2H_4\text{-}]_n OH + HO\text{-}C_2H_4\text{-}OH$ (p,t,T,c-cat) ⇆ $HO\text{-}C_2H_4\text{-}O\text{-}OC\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_2H_4\text{-}OH$

Methanolysis:

$H[O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_2H_4\text{-}]_n OH$ + CH3-OH (p,t,T,c-cat) ⇆ $CH_3\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}CH_3$+ $HO\text{-}C_2H_4\text{-}OH$

3.1. Hydrolysis

When it comes to the hydrolysis of polyester, the simplicity of the chemical reaction and the complexity of purifying crude terephthalic acid on an industrial scale are diametrically opposed. In recent years, a number of processes have been proposed for the hydrolysis of polyester waste, in which it is broken down into TA and MEG by treatment with alkali and special catalysts. Table 1 provides an overview of these process developments.

Table 1: Process for the hydrolytic degradation of polyester waste

Company	Process	Product	Status	Literature
Gr3n	alkaline hydrolysis, microwave reactor	TA obtained is directly polymerized back into PET	pilot line	[5]
Carbios/Technip	enzymatic hydrolysis	r-PTA	pilot line	[6] [7]
Teijin	methanolysis to DMT and subsequent hydrolysis to PTA	r-PTA	commercial production plant	[8] [9] [10] [11]
FENC	alkaline hydrolysis	r-PTA	development project with Coca-Cola	[12] [13]

3.2. Glycolysis

The majority of process developments for chemical PET recycling are based on the degradation of the polymer chain through glycolysis with MEG to produce bis(2-hydroxyethyl)terephthalate (BHET). Thanks to MEG's boiling temperature of 197°C, the degradation reaction can be carried out predominantly at normal pressure. Metal acetates such as zinc or manganese acetate are primarily used as catalysts. To improve the separation of the catalysts after the degradation reaction has ended, organic substances that can be removed by distillation or ionic liquids that are separated from the reaction mass using strong magnets due to ferromagnetic properties are proposed. An important advantage of glycolysis is the fact that BHET is the only product of depolymerization, whereas hydrolysis and methanolysis produce two monomers each, TA + MEG in hydrolysis and DMT + MEG in methanolysis, which are laboriously separated from each other following depolymerization need to become. The glycolysis processes currently under development are summarized in Table 2.

Table 2: Process for the glycolysis of polyester waste

Company	Process	Product	Status	Literature
Ioniqa und Acenture	glycolysis in presence of ionic liquids	r-BHET → r-PET	pilot line	[14]
Garbo	glycolysis	r-BHET	industry plant	[15]
IBM/Technip	glycolysis in presence of organic catalysts	r-BHET	process development	[16]

			finished engineering	
Ifpen/Jeplan	glycolysis, vacuum distillation for purification of BHET-	r-BHET	commercial pilot-line operates in Japan, process development for marketing	[17] [18]
Poseidon	glycolysis in presence acetates of transition metals, preferred zinc acetate	r-BHET	pilot line	[19]
PerPETual/ Polygenta	glycolysis	BHET-oligomers→ r-PET	industry plant	[20]
Soprema	glycolysis with polyols	r-polyols	industry plant	[21]

Another important advantage of glycolysis is the possibility of using the glycol ester of terephthalic acid (r-BHET) produced in this way in all polyester plants without costly investments or modifications. Also positive is the possibility of being able to transport BHET either in solid form as flakes or granules or in liquid form. A market investigation into the availability of sample quantities of r-PTA, r-DMT and r-BEHT revealed that only r-BHET samples could be obtained, which allows the conclusion that glycolysis is currently the preferred method for chemical PET Recycling. [22]

3.3 Methanolysis

As already explained in the introduction, the process of methanolysis of polyester waste has been tested on a large-scale chemical basis in various variants and is preferably used when the DMT produced is reprocessed into polyester directly at the same location. Well-known plants based on methanolysis operate in Japan at Teijin, in China at Jiaren and in Canada at Loop Recycling. If methanolysis and renewed polyester production are carried out at the same location, the recycling of the methanol required for methanolysis is advantageous. Polyester recycling based on methanolysis with the aim of marketing the r-DMT produced is not very promising given the current market situation in the polyester industry, as only a few polyester plants are still operated with the raw material DMT (<< 10% of world production). Eastman has chosen an interesting process for chemical PET recycling, in which the PET waste is converted into r-DMT through methanolysis, which is then processed into CHDM through hydrogenation. The CHDM obtained in this way is used as a co-monomer, especially for the co-polyester PETG produced by Eastman. A company list see table 3.

Table 3: Processes in development and those already in production based on methanolysis

Company	Process	Product	Status	Literature
LOOP Industries	methanolysis	r-DMT → r-PET	industry plant	[23]
Eastman	methanolysis	r-DMT → CHDM → PETG	pilot line	[24]
Jiaren/Teijin	methanolysis of waste-textiles	r-DMT → r-PET	industry plant	[25]

3.4 Outlook

Assuming that the amount of available renewable energy becomes so large that it can cover all energy consumption, including building heating, the entire transport sector and the supply of heavy industry, the coexistence and cooperation of mechanical and chemical recycling is absolutely necessary in order to achieve this to gradually achieve the desired goal of a zero CO_2 emissions economy. In this way it becomes necessary to establish a national carbon strategy.

The following principles should apply:

Anyone who produces plastics or imports plastics is obliged to carry out chemical recycling or to finance it.

Anyone who processes plastics is obliged to mechanically recycle them.

Anyone who brings plastics onto the market is obliged to take them back, collect and sort them.

Finally, a word about the chemical recycling of plastics, which includes all chemical processes for converting macromolecules into monomers or basic raw materials for producing the monomers. How was it even possible for Germany to wage a war without its own oil sources for fuel? The processes of Fischer and Tropsch or Bergius-Pier made it possible to produce liquid hydrocarbons from the coal that was abundant in Germany using basic chemical processes and to convert them into fuels. All of these processes exist and do not need to be reinvented in order to return carbon-containing multi-substance mixtures to the basic raw materials of the chemical industry, although hydrogen from renewable energy is also increasingly available today. In the end, for us it is just a question of costs and therefore the price that the general public is willing to pay to establish a circular economy.

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