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Chemical Recovery of Useful Chemicals from Polyester (PET) Waste for Resource Conservation: A Survey of State of the Art

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In this paper we present the main technologies developed over the last decades on chemical recycle of PET from a practical and economical point of view. We show details of plants used to carry out solvolitic reactions emphasising steps of purification, which are sometimes not considered when discussing chemical, recycle but which, in fact, are the key feasibility factors. The recycling or modification of PET to obtain monomers and other useful chemicals as intermediates and additives is carefully considered.

KEY WORDS: PET; polyesters; chemical recycle; depolymerisation; DMT; Therephthalic acid.

INTRODUCTION

Over the last decades, PET consumption has tremendously increased due to its ever-increasing use in fibre manufacturing and packaging. At present the global yearly PET production is approx. 13 million of metric tons [1]. These amounts further contribute to increasing the consumption of non-renewable resources (hydrocarbons); in fact, PET, like other plastics, almost certainly ends up in a landfill or an incinerator, at least, this way, allowing a certain energy recovery. If we consider the numerous reactions and processes needed to prepare monomers from hydrocarbon feedstocks, it is clear that their recovery from polycondensates, like polyester or nylons, may be interesting for economical reasons, in addition to the environmental ones.

In this paper we outline, from a practical point of view, the state of the art of the main technologies which allow us to recycle PET.

Great attention is paid to chemical recycling, which basically means the recovery of monomers, but which can actually be used for processes, which produce interesting chemicals or intermediates from PET waste. In Table I we can see the prices for various grades of PET-R [2] and for virgin monomers in Italy throughout the last years; it is quite evident that chemical recycling may be a good solution to obtain profits by using depolymerisation processes discussed in the following paragraphs.

The processes, which will be discussed throughout this paper, are solvolitic reactions, which, through ester bond cleavage, give various depolymerisation products. A complete treatment of ester bond

Abbreviation: 1,2-PG, 1,2-propylene glycol; BD, Butanediol; DEG, diethylene glycol; DMT, Dimethyl therephthalate; EG, Ethylene glycol; MA, Maleic anhydride; PET, Poly(ethylene therephthalate); PET-R, Post consumer Recycled Poly(ethylene therephthalate) (colour separated and washed); TA, Therephthalic acid; DPG, Dipropylene glycol; BHET, Bis hydroxy ethyl terephthalate; BHBT, Bis hydroxy butyl terephthalate; HDPE, High density polyethylene.

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Table I. Prices of PET-R (Post Consumer Bottles) and Monomers

PET-R grade	Minimum price 2002 (euro/ton)	Maximum price 2002 (euro/ton)
PET colourless	94.41	142.44
PET coloured	42.48	64.10
PET azure coloured	56.65	85.47
Monomers	Price in 2003	Price in 2004
TA	800	730
DMT	750	900
EG	670	750

cleavage chemistry is beyond the purposes of this work, and more detailed descriptions can be found in other works [1, 3]. However, in Fig. 1 schematic pathways of solvolitic reactions are given, while in Table II main products and their uses are shown.

Before carrying out any chemical process to recover monomers from PET, a preliminary purification to remove contaminants is usually needed.

The technologies of commercial PET scraps recovery processes were initially developed in the US where one of the first recycling facilities for PET bottles [4] was set-up for entire containers. The processes currently available can be summarised as follows (Fig. 2):

- Shredding of bottles to facilitate a fast proceeding of the feed into a granulator
- Conveyance via a loader tube to an air classification system to remove paper and light residues
- Washing with water and rinsing
- Floatation to separate polyolefins deriving from its cap and liner, and, if necessary, aluminium and other metallic contaminants.
- Separate spin drying of light and heavy fractions
- Hot air drying of each stream

At present, new packaging applications are incoming on the market, in particular multi-layer films or coated bottles are being produced to improve gas-barrier properties of pure PET, which are

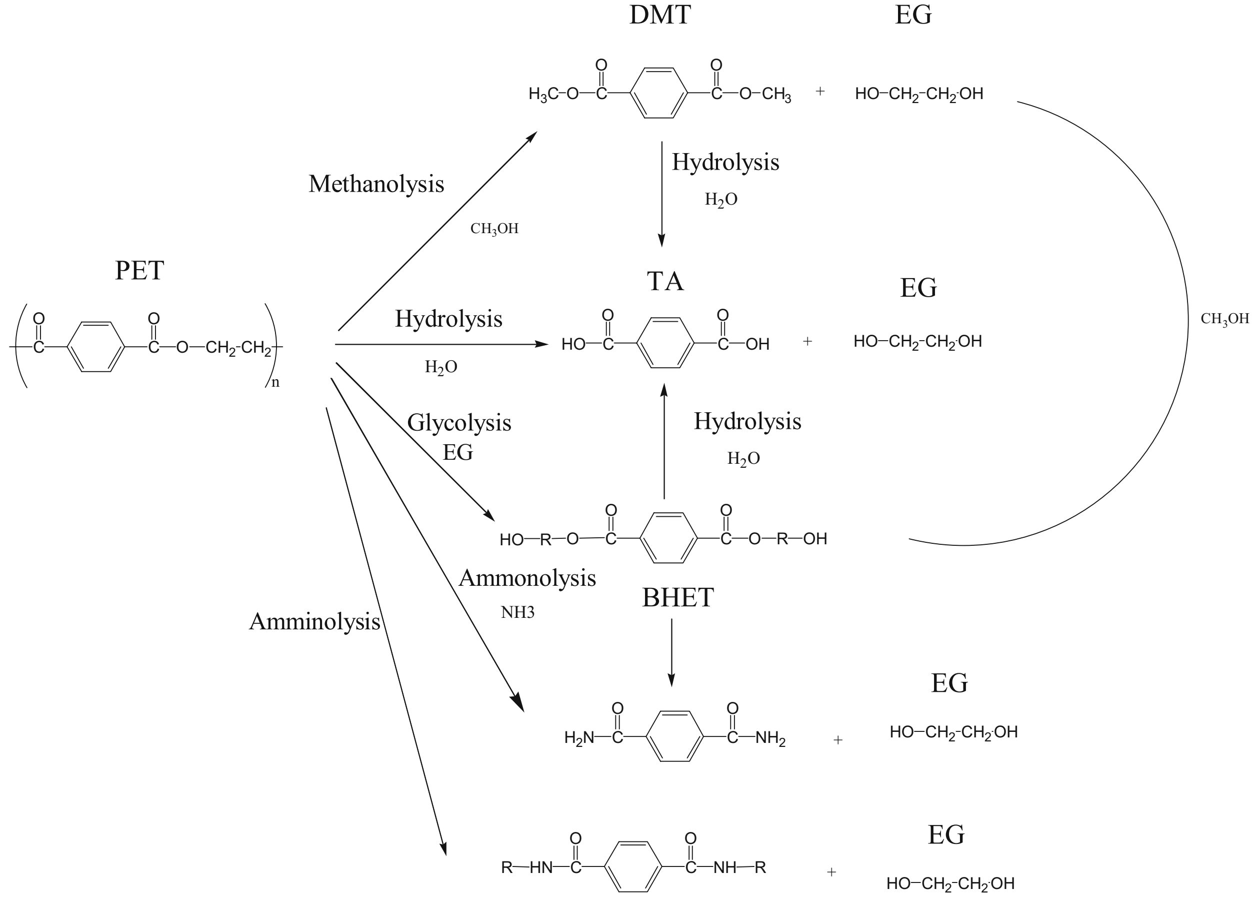

Fig. 1. Chemistry of solvolitic processes.

Table II. Products of Solvolitic Processes and Their Uses [3]

	Methanolis	Glycolysis	Other transesterfication processes	Hydrolysis	Ammonolysis	Aminolysis
Depolymerisation agent	Methanol	EG, DEG, PG, DPG, BD, generic glycol	Monohydroxylic alcohols, carboxylic acids, esters	Water	Ammonia (anhydrous)	Amines or polyamines
Use of depolymerisation products	DMT, EG. Re-use in PET production	BHET, BHBT and oligomeric diols (polyols), for various uses (polyurethanes, unsaturated resins). BHET can be used as starting monomer for PET synthesis or converted into DMT by methanolysis	TA esters for plasticisers or coating materials, EG	TA, EG. Re-use in PET production	TA amide (useful to prepare corresponding dinitriles and diamines), EG	TA amine derivatives, additives

unsatisfactory for many uses. The corresponding multi-layer scraps may be very difficult to recycle with suited technologies, as shown above. In this case, where PET is welded with foreign plastic materials or present even in multi-layer films, many solutions have been developed since the seventies [5, 6].

A very interesting example may be found in US 3,652,466 [5] were a method to recover polyester from photographic scraps is described. The technology is quite complicated and has probably become economically attractive due to the fact that silver salts are also recovered during this process. A description taken from this patent is given in the following drawing (Fig. 3).

Small pieces or chips, deriving from scraps, are continuously fed through conduit 1 to a vessel 2

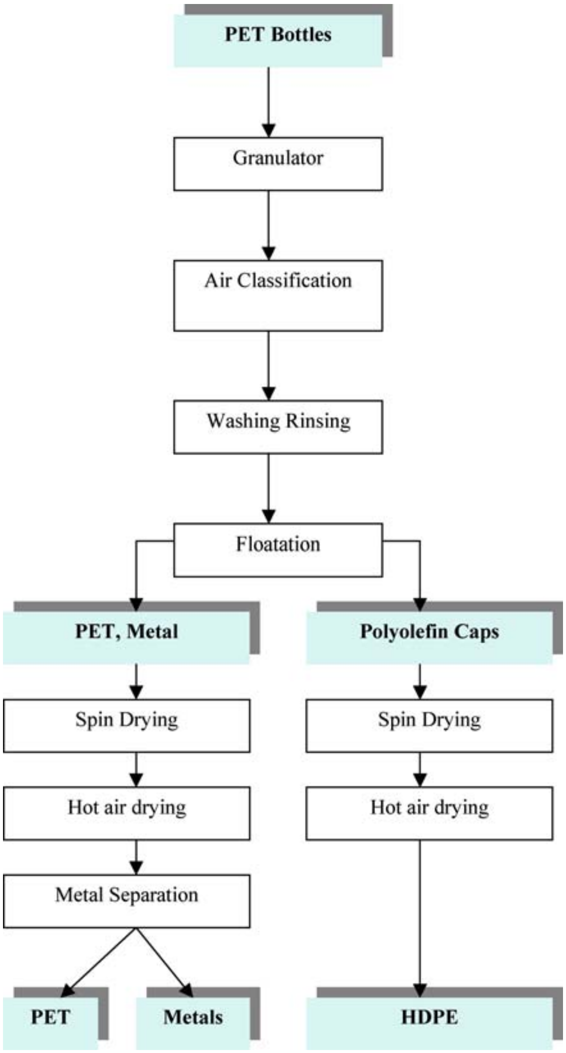

Fig. 2. Steps of pet scrap purification.

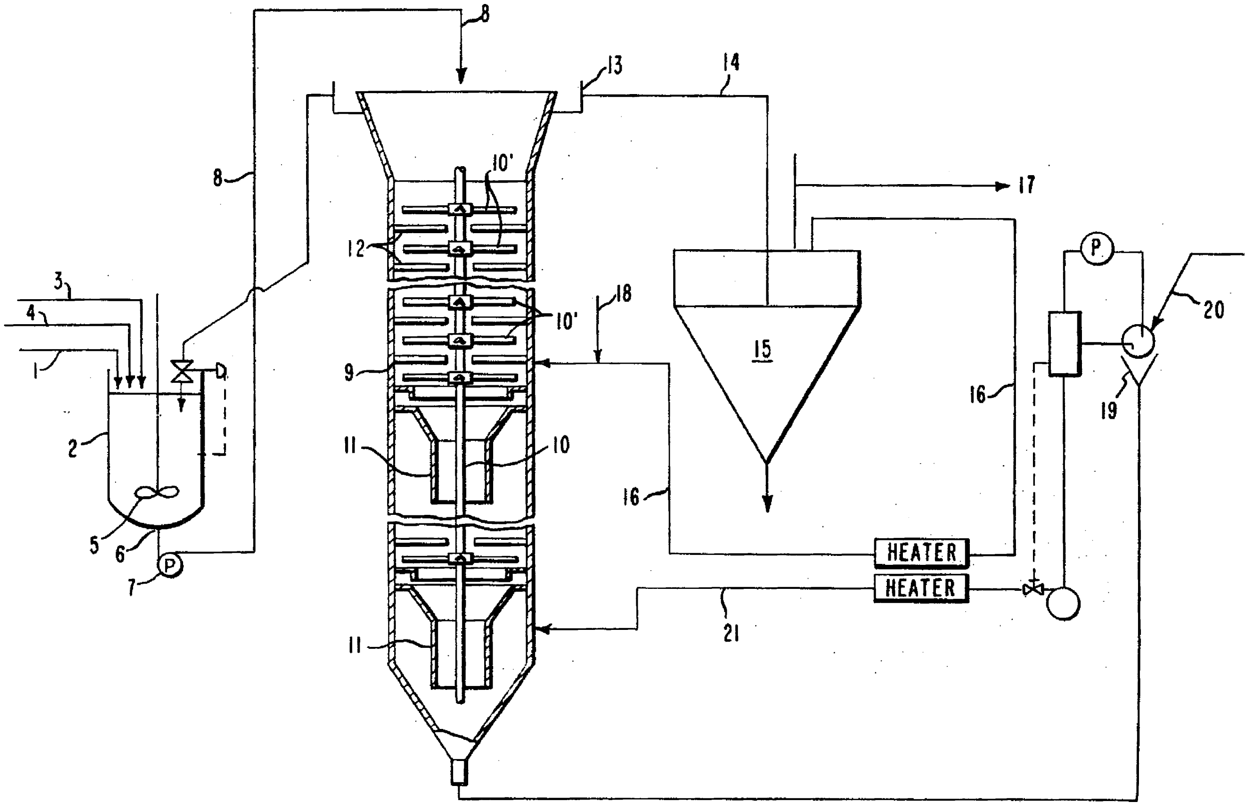

Fig. 3. Multi-layer scraps separation plant.

which is provided with conduit 3 for feeding an aqueous solution containing a surfactant into the vessel and conduit means 4, for feeding a hot caustic liquid such as sodium or potassium hydroxide, into the vessel. This vessel is provided with an agitator 5 and has an outlet 6 at the bottom for withdrawing slurry of caustic materials and any removed coating materials. This slurry is forced to the top of a classification column 9.

In this column, the flakes come into contact with a counter current flow of liquid which elutriates the polymer skins and other coatings; as the flakes pass from one section to another, they are washed by the upward flow of water in the column. The flakes in the column and the coating components, have a slower settling rate and overflow from the column, passing to the settling tank where the main portion of silver compound is removed by sedimentation. Flakes settling at the bottom of the column pass to a filter 19, after which washing water is added to the main flow trough 20. The filtered flakes can be dried and stored after washing. The classification phenomenon of the washing column does not depend on the weight of the materials but on the settling rate of the components. The settling rate of polyester is greater than that of other organic components.

A more recent conceptually similar technology has been studied for bottles with gas-barrier layers [7] like silicon oxide from vacuum deposition (CVD).

Another interesting solution to remove foreign materials (specially PE or PVC contaminants) from PET waste for monomer recovery is proposed in US 5,223,544 [8]. This process consists of the depolymerisation of the polyethylene terephthalate stream into low viscose liquid melt, and then by feeding it into a separation device (Fig. 4). In this separation device, low-density foreign materials migrate to the surface of the liquid melt, while high density foreign materials migrate to the bottom of the liquid melt. The partially depolymerised and relatively pure polyethylene terephthalate can be recovered from an area, which is located intermediately between the surface of the liquid melt and the bottom of the liquid melt. This stream can be fed to another process for further treatments.

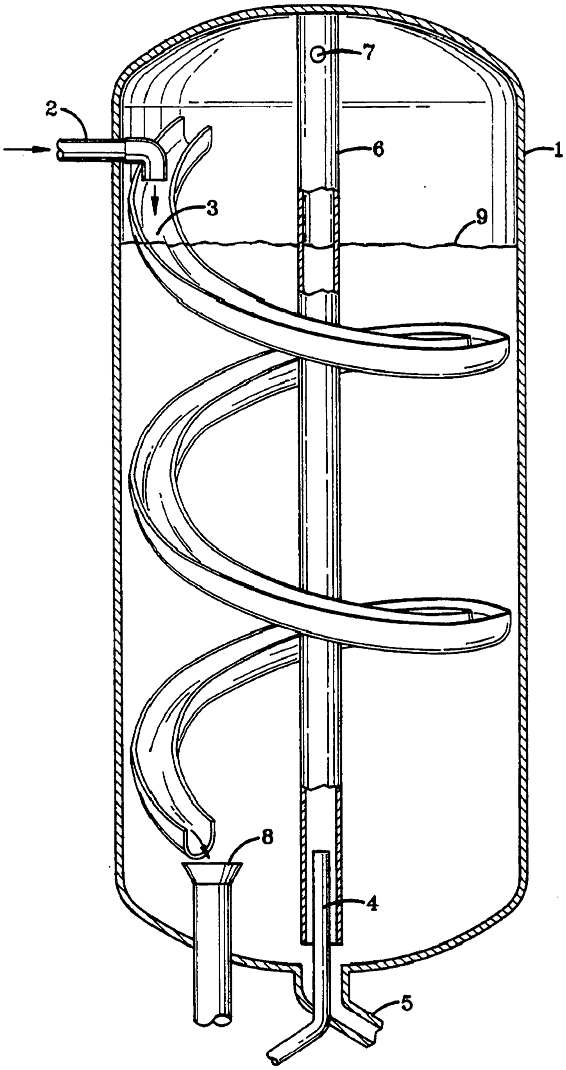

Fig. 4. Melt separation device.

This separation device is essentially vessel 1. The depolymerised PET produced in the depolymerisation step is fed through inlet pipe 2. The melt discharged through pipe 2 flows down trough 3 to the surface of the melt 9 in the separation device. The trough 3 allows the melt, obtained during the depolymerisation step, to be gently discharged onto the surface of the melt 9 regardless of the melt level in the separation device. This prevents low-density foreign materials from sinking deep into the melt. At the same time, the low-density foreign materials simply remain on the surface of the melt without the need to float to the surface of the melt 9 from areas far below. In the separation device shown in Fig. 4, the trough 3 simply turns around the inside wall of the closed vessel 1; this spiral design causes a certain spinning action and some centrifugal force which facilitates the separating action.

CHEMICAL RECYCLING

Hydrolysis

As can be seen in Fig. 1, hydrolysis enables TA and EG to be recovered. This solvolitic reaction can be conducted in acidic medium [9–11] or basic medium [12–16] or neutral conditions [17]. In US 4,355,175 [10] a PET hydrolysis at room temperature using concentrated sulphuric acid, which completely depolymerises the polymer in about 30 minute, is described (Fig. 5).

If the aqueous solution is basic enough to salify TA, the reaction is based on saponification. It is evident that basic or acid solutions greatly speed up the depolymerisation process but, on the other hand, purification procedures may be more difficult due to catalyst residues. Furthermore, reactors and other devices must be built up using corrosion proof materials. In neutral conditions at a temperature of 275°C, complete depolymerisation requires about an hour and its TA yield is usually above 95% [18]. Unfortunately, further operations are essential, even in this case, in order to obtain polymer grade TA. From patent literature this step seems to be very important, particularly in a case of high temperature hydrolysis.

As mentioned above, purification is probably one of the most important steps in monomer preparation during hydrolytic treatments.

Indeed, the depolymerisation of polyethylene terephthalate by neutral hydrolysis can result in the production of oligomeric byproducts; derivatives of terephthalic acid; cyclic trimers. Unfortunately, the depolymerisation product of waste polyethylene terephthalate in the shape of bottles, film, fibre and other manufactured articles largely contains dyes and other contaminants, as mentioned in the first paragraph. For example deep blue polyester fabric before hydrolysis may contain up to 6.5% dyes and other contaminants. Correspondingly, although various processes are available for hydrolysing PET waste, the purification of terephthalic acid typically requires several steps to remove dyes, pigments, and other impurities including inorganic compounds such as catalyst residues and organic compounds which can result from the depolymerisation reaction.

In the already cited U.S. 4,355,175, the difficulties encountered in preparing a purified terephthalic

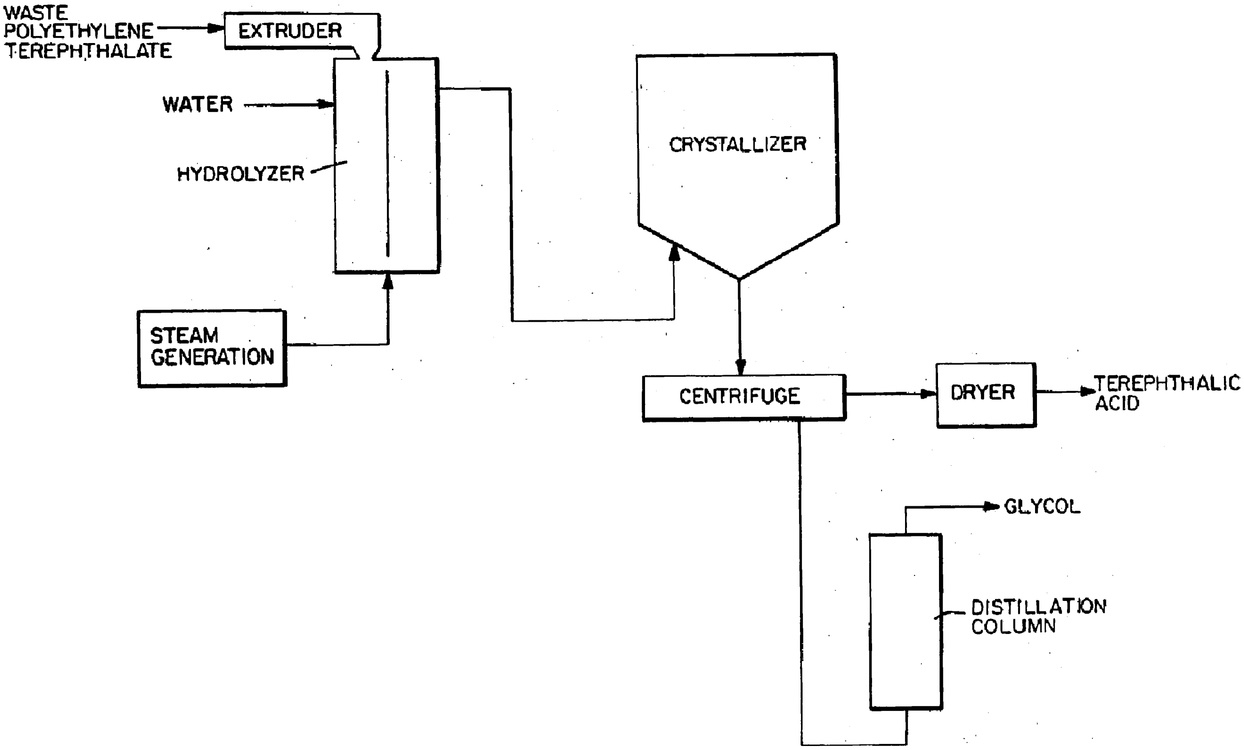

Fig. 5. A PET hydrolysis plant in neutral conditions [18].

acid from PET are highly exemplified. Polyester scrap, such as pieces of film, fabric, yarn, or bottles, was depolymerised at room temperature with a mixture of concentrated sulphuric acid and water to form crude terephthalic acid. In this patent, a solution which can be dark brown, or black in colour, containing the crude terephthalic acid resulting from depolymerisation, is filtered to obtain a clear liquid which may be light brown in colour. The obtained solution is then acidified with sulphuric acid to precipitate the terephthalic acid. TA is then filtered and washed. The TA obtained by means of this simple procedure is not very pure and may often be dark or yellow in colour. Because of this lack of quality and relative cost of multistep purifications needed, respect to that of virgin purified terephthalic acid; TA from waste polyethylene terephthalate has so far not been considered a viable economic replacement for fibre grade virgin purified terephthalic acid obtained from paraxylene.

In US 5,095,145 [19] an interesting technology for TA purification following hydrolysis is provided. The solution of crude terephthalic acid deriving directly from a neutral hydrolysis step is cooled to precipitate the crude acid; the precipitate is then separated and washed with water. This precipitate is then reslurried in water and catalytically hydrogenated at a temperature in the range of 220–310°C. The hydrogenation reaction mixture is cooled to precipitate the terephthalic acid which is then separated from the mother liquid, washed with water and dried. After this hydrogenation, TA is reported to have a sufficient purity comparable to fiber grade TA.

Methanolysis

Methanolysis allows us to convert PET scraps directly into DMT and EG; methanolysis has to be carried out at various temperatures which usually forces us to use high pressure due to extremely high vapour pressure of methanol.

The depolymerisation rate is a function of temperature and of transesterification catalyst concentration when used; solubility of PET and its oligomer in reaction medium is another important factor affecting the kinetics of this process. So, it is reported that the reaction rate can be highly improved by adding a solvent like toluene [20] to the reacting medium.

In very recent patents [21] and scientific works [22–24] depolymerisation was conducted in super critical methanol usually at a temperature near to

300°C and at a pressure above 10–15 Mpa. According to the results of Yang [23], the optimal reaction conditions have a reaction time of 40–60 minutes, temperature of 533–543 K pressure of 9.0–11.0 MPa and weight ratio (methanol to PET) of 6–8. Under the optimal reaction conditions, PET wastes can be readily depolymerised to monomers. Methanolysis has been carried out by partially depolymerizing PET-R in DMT or low molecular weight oligomers, after this treatment to decrease melt viscosity, a stream methanol is added to the oligomer mixture [25]. An analogous solution [26–31] is described below.

Figure 6 illustrates a system for carrying out a process of methanolysis. Scrap polyethylene terephthalate is loaded into scrap bins 10, pumped by pump 12 to air conveyor 14, and conveyed through rotary air locks 16 to dissolver 18. At start-up, oligomers of a glycol such as ethylene glycol (EG) and dimethylterephthalate oligomers are introduced into dissolver 18, and jacket 24 is heated to bring the temperature of the oligomers to a temperature in the range of 230–290°C. The scrap polyethylene terephthalate and the oligomers are mixed in dissolver 18 for a period sufficient to allow the scrap polyethylene terephthalate to mix with the oligomers and form a start-up melt. The start-up melt is drawn through the filtration device 26 and transferred by pump 28 via line 30 to reactor 32. The start-up melt can be returned via the return line 34 to dissolver 18, which is useful during start-up and which after start-up, supplies molten polyester to the top of dissolver 18 to initiate melting of fresh polyester scrap feed. Super-heated methanol vapour is provided to reactor 32 as shown. The super-heated methanol vapour passes through the contents of reactor 32, heating the reactor contents to form a melt comprising low molecular weight polyesters and monomers, monohydric alcohol-ended oligomers, glycols, and dimethylterephthalate.

Reactor melt is transferred from reactor 32 and provided to dissolver 18 via line 36. The reactor melt

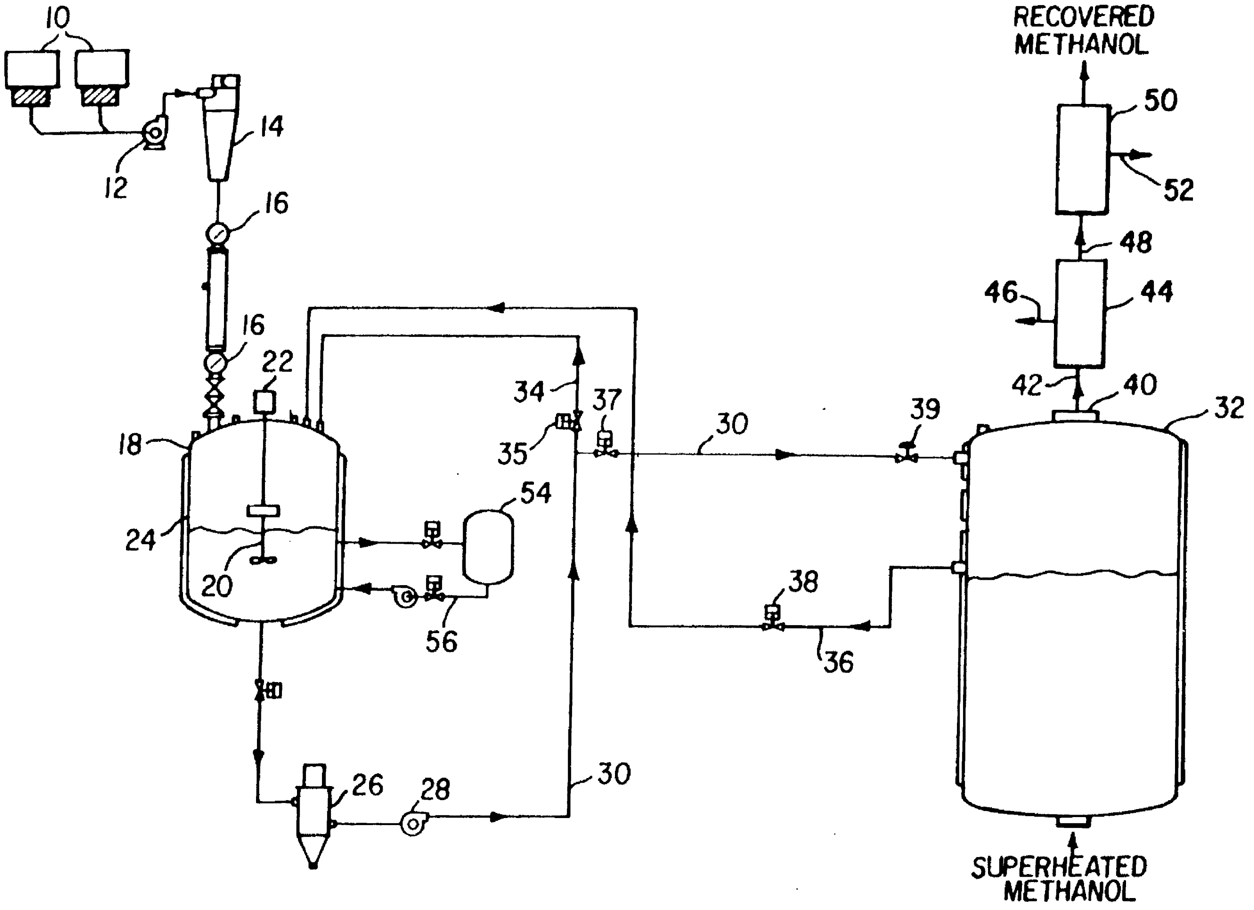

Fig. 6. Methanolysis process plant.

reacts and equilibrates with the molten scrap polyester chains to shorten the average chain length, and thereby greatly decreases the viscosity, of the dissolver contents. Dissolver 18 runs at atmospheric pressure with little methanol present, greatly increasing process safety. Reactor 32 runs at a higher pressure than dissolver 18, eliminating the need for pumping means to transfer the reactor melt from reactor 32 to dissolver 18. A vapour stream, comprising dimethylterephthalate, glycols (including EG, diethylene glycol, and triethylene glycol), methylhydroxyethyl terephthalate, and methanol leavesreactor 32 via outlet 40 and line 42. The methanol is the depolymerisation agent and the vapour helps to remove other vapours from the reactor by acting as a carrier gas stream and by stripping the other gases from the solution. The effectiveness of the super-heated methanol for heating the contents of the reactor and for stripping gases, depends on its flow rate; it is clear that the depolymerisation rate in reactor 32 depends on the methanol flow rate to reactor 32. The distillation device 44 is provided to separate methylhydroxyethyl terephthalate from the vapour stream by passing from the recycling reactor 32 to the dissolver via line 46. Methylhydroxyethyl terephthalate is useful as a low molecular weight oligomer for shortening the average polyester chain length and decreasing the viscosity of the melt in the dissolver.

The vapour stream is transferred via line 48 to the distillation device 50 which separates methanol from other vapour stream components; the methanol is then recovered for further use.

A common problem found in methanolysis is the separation of EG from DMT and catalyst residues while methanol is easily removed due its low boiling point. In US 5,414,106 [32] DMT is recovered from a stream containing EG and catalyst residues by a liquid–liquid extraction. This stream is mixed with a solvent (methyl benzoate) and water is added. EG and catalyst residues (mainly Sb_2O_3) are extracted from water from the organic phase containing DMT. The resulting organic phase contains highly pure DMT.

In some processes, a further hydrolysis stage is conducted to convert DMT into TA [32], which is currently more required for PET production.

Glycolysis or Polyfunctional Alcohol Solvolysis

Glycolysis, when carried out using EG, allows us to prepare BHET, which can be directly used in PET synthesis. Unfortunately, this solvolitic reaction creates some problems concerning BHET purification [34]. It may be quite often difficult to remove metallic ion [35] deriving from catalyst residues; other problems may be superior oligomer separation or minimisation, organic contaminants which impart undesirable yellow colouration.

In US 4,609,680 [36] a typical process [37, 38] of PET depolymerisation using EG is described, in this patent a process where PET scraps are mixed with BHET and oligomers at high temperature is described (220°C). Subsequently, EG is added to the melt to complete depolymerisation.

In a recent patent of Teijin [39] PET is depolymerised using EG and Sodium Carbonate to give BHET, which is fed to a reactor where by using methanol it is converted to DMT which is more economically attractive. This conversion of BHET inot DMT has been recognised as an interesting process since the seventies in US 4,163,860 [40] where an atmospheric process using magnesium catalyst to convert BHET into DMT is described.

Glycolysis can be carried out in solvent like xylene using EG or other glycols; in this process, lower temperatures can be used, and higher purity products can be obtained [41].

An extremely rapid glycolysis using microwave radiations has also been proposed [42]; the main advantage is the very short reaction time reported, between 4 and 10 minutes, in which complete PET degradation is achieved; methanol, propylene glycol, and polyethylene glycol 400 were used as solvolitic agents.

When glycolysis is conducted with various glycols other than EG, many products of low molecular weight or new polyesters [43] can be obtained. Glycolizates of relatively low molecular weight can be used for many uses like unsaturated polyester resin production, alchid resins, or polyurethane polyols (see next paragraphs). In US 5,266,601 [44] PET scraps are converted to high molecular weight PBT after a glycolysis using 1,4 butanediol and a subsequent polycondensation. This process could be interesting since a good quality and relatively high priced PBT is initially prepared from very low cost PET scraps (see Table I).

Amminolysis

Amminolysis is a bond cleavage reaction carried out by using an amine. This reaction on PET [45] initially attracted attention for modification of fibres to improve some specific properties [46, 47].

Currently, amminolysis has been receiving renewed attention due to its possibility to prepare some interesting chemicals or intermediates.

In a recent paper [48], an interesting process to obtain terephthalohydrazide in two steps is described: PET-R powder is firstly reacted with EG by using lead acetate as a catalyst at 195°C and under atmospheric pressure; a low molecular weight product of PET-R was obtained using this reaction. Hydrazine monohydrate, chlorobenzene, and cyclohexylamine were then introduced to convert the low molecular weight product of PET glycolysis into terephthalohydrazide. Another similar process used to prepare terephthalohydroxamic acid and Terephthalohydrazide was recently proposed [49], these products with an overall yield superior to 90% were prepared through PET depolymerisation in boiling EG, followed by its treatment with hydroxylamine or hydrazine at room temperature over 1 hour.

When PET-R is depolymerised using polyfunctional amines, degradation products can be used for many thermosetting systems. PET-R for example [50] can be depolymerised with triethylenetetramine and triethanolamine to give products useful as epoxy resin hardeners. Similar results and studies were performed by others [51, 52], who describes the chemical degradation of PET waste with polyamines or triethanolamine. These compounds were tested as a polyol component for the manufacture of rigid polyurethane foam formulations as replacement for common polyols. The obtained polyurethane foams have a density of about 30 kg/m^3, a compression strength of 80–160 kPa, and a thermal conduction coefficient suitable for thermal insulation materials.

The solvolysis of the polymer ester bonds was caused by diethylenetriamine, triethylenetetramine, and their mixtures, as well as mixtures of triethylenetetramine and *p*-phenylenediamine or triethanolamine. Products of aminolysis or aminoglycolysis of PET obtained in reactions were carried out at about 200°C. Other interesting examples of aminolised PET uses can be found in patent literature, but probably the most interesting ones are in the epoxy or urethane resins sector [53].

Ammonolysis

Ammonolysis is a solvolitic reaction which gives therephthalamide (TAD) and EG usually by using concentrated Ammonia. TAD is not an economically interesting chemical but it can be converted into a more added value product (Fig. 7). In US 4,973,746 [54] a process of ammonolysis of the PET scrap is described by General Electric. The procedure involves contacting PET dispersed in EG with ammonia and applying pressure and heat whereupon the PET reacts with the ammonia to produce terephthalamide and ethylene glycol. The initial moiety of EG provides a reaction and heat exchange media as well as a partial solvent for the PET. Poly(ethyleneterephthalate), ammonia, and EG are heated to a reaction temperature between approx. 120 and 180°C, and are pressurised, due to the low boiling point of ammonia; this reaction produces terephthalamide in a yield superior to 90% and at a purity higher than 99%. Terephthalamide, which is insoluble in the EG, is then separated, there from, by simple filtration in order to yield terephthalamide in powdered form. Substantially, pure terephthalamide can be obtained by washing and filtering terephthalamide with deionised water and then by drying it. Terephthalamide is then further processed by pyrolytic dehydration to

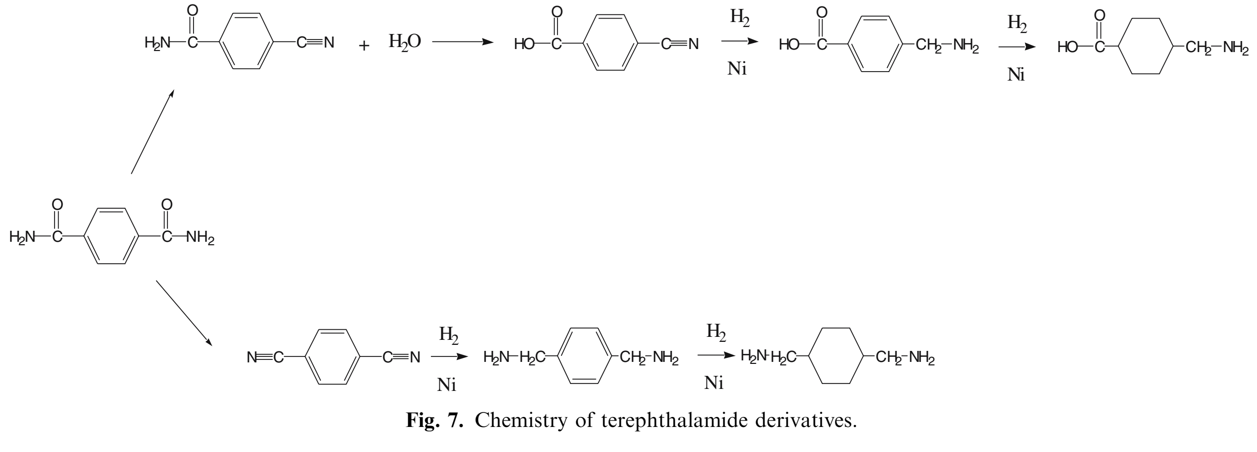

Fig. 7. Chemistry of terephthalamide derivatives.

produce terephthalonitrile. Pyrolytic dehydration of the terephthalamide to produce terephthalonitrile involves the transformation of the terephthalamide into terephthalonitrile at high temperatures. The diamide (terephthalamide) is heated at a temperature usually ranging from 340 to 370°C, to obtain the conversion of the terephthalamide to terephthalonitrile. At temperatures below 300°C the reaction is generally too slow and at temperatures above 450°C side reactions become predominant. This process, under the appropriate conditions, produces good yields of terephthalonitrile from terephthalamide. Terephthalonitrile is then separated from the unreacted terephthalamide by adding a selective solvent. For example, hot ethanol can be employed to dissolve the terephthalonitrile thus allowing the insoluble terephthalamide to be removed by filtration. The Terephthalonitrile can then be separated from the solvent by evaporating of the solvent used for its extraction. Terephthalonitrile obtained can be sold as a raw material or further processed to yield useful products; for example, terephthalonitrile can be processed by hydrogenation to yield very useful diamines.

Partial reactions and side reactions are possible during the pyrolytic dehydration of terephthalamide to terephthalonitrile. The dehydration of terephthalamide to terephthalonitrile proceeds in two steps: the loss of one molecule of water produces 4-cyanobenzamide; this dehydration product can then be converted to terephthalonitrile by the application of additional heat As mentioned above, side reactions are also possible, for example the water generated in the main reaction can react with the partial dehydration product to form 4-cyanobenzoic acid. This side product may be recycled via re-amidation to maximise the terephthalonitrile yield. Its production can be minimised by adding ammonia to reaction media. However, conditions of dehydration can be modified to promote the formation of 4-cyanobenzoic acid which may represent an interesting raw material.When 4-cyanobenzoic acid is hydrogenated the product is 4-aminomethylbenzoic acid, an attractive bi-functional monomer for the production of polyamide resins. The hydrogenation of terephthalonitrile to produce para-xylylenediamine or 1,4-bis(aminomethyl)cyclohexane involves contacting terephthalonitrile with hydrogen in the presence of an appropriate solvent and catalyst and applying high pressure. Solvent as a blend of 90% ethanol and 10% ammonia by weight can be used. Hydrogenation catalysts that may be employed are nickel catalysts which give efficient hydrogenation of terephthalonitrile to para-xylylene diamine or subsequently to 1,4-bis(aminomethyl)cyclohexanes. Hydrogen pressures of 30–70 MPa, a temperature range from 100 to 200°C and a time range from 2 to 8 hours are needed. The diamines obtained from this process find particular usage as monomers for the production of various polyamide polymers and copolymers.

Other Transesterification Processes

Many other transesterification processes have been developed to prepare added value products from PET-R. By these processes, PET has been used to prepare alkyd resins and thermosetting polyester resins, polyols for polyurethane manufacture, plasticisers for PVC etc (Fig. 8).

To date, many patents and academic publications consider the use of PET-R in the coating industry [55–57]; many examples have been reported on the preparation of powder coating or alkyd resins based on partially depolimerised PET using diols or other polyfunctional alchohols, neopentil glycol (NPG), trimetylolpropane (TMP), glycerol, diethylene glycol and propanediol are the most commonly used. In case of alkyd resins [58–62] generally unsaturated compounds like unsaturated fatty acids are added to the mass.

In an interesting example [63], terephthalic acid-based waste polyesters are depolymerised in the presence of ester-forming sulfonate or phosphate compounds, polyhydric alcohols, and a transesterification catalyst, esterified with fatty acids, and then dispersed in water to give title dispersions. In a reported example, PET was depolymerised using pentaerythritol, ethylene glycol, 5-sodiosulfoisophthalic acid, and dibutyltin oxide as a catalyst at 230°C, mixed with soya fatty acid and phthalic anhydride at 180°C, polycondensed at 240°C, and mixed with polyoxyethylene derivatives to give a formulation which was easily water dispersible.

In an interesting work [64], the hydroxyl functional groups of depolymerised products obtained by glycolysis of PET are converted to methacrylate groups to prepare UV-curing useful products. The obtained methacrylated oligoesters were tested for UV curability by UV irradiation, in the presence of a photo initiator. This gave cured films of high mechanical properties when these methacrylated oligoesters were either cured alone or as mixtures

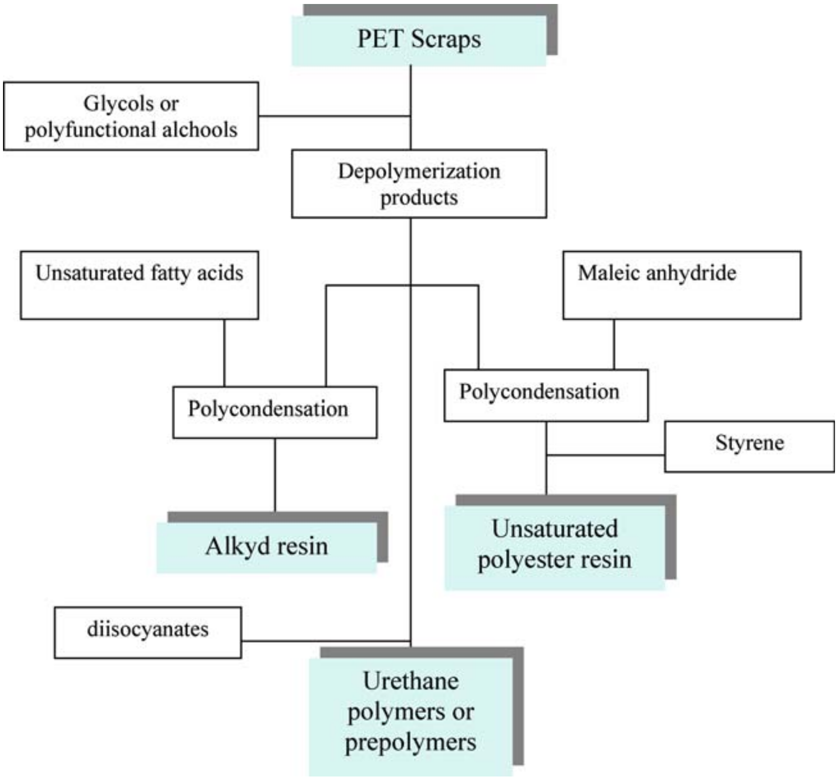

Fig. 8. Ways to alkyd, polyester and urethane resins starting from PET-R.

with other available diacrylate or dimethacrylate monomers.

Glycolysates can also be used for polyurethanic systems [65–68]; In the reference [69], for example, mixtures of aromatic polyols containing ester functionalities suitable for use as polyol extenders in rigid foams are prepared by reacting dibasic acids with an alkylene glycol, the reaction product of which is then reacted with recycled polyethylene terephthalate. These polyols may be blended with conventional polyols to yield excellent rigid foams; he also describes flexible polyurethane foam from recycled PET macrodiols. In reference [70], more recently, a similar process is proposed.

Polyurethanic adhesives have also been studied [71]; these adhesives are usually manufactured by using already mentioned hydroxy terminated glycolysis products of PET waste and common polyisocyanates and sometimes chain extenders.

Reported properties of unsaturated resins obtained by a partial depolymerisation of PET are similar and in some cases superior to those of conventional polyester resins [72–75].

The process used, usually proceeds through a first partial depolymerisation using glycols or other polyfunctional alcohols and a subsequent polycondensation with an unsaturated compound like maleic anhydride and by then adding styrene [76]. The resulting resins can be cured as a conventional polyester resin using peroxides.

A recent solution for the lengthy times needed to achieve a sufficient depolymerisation degree of PET scraps and the subsequent polycondensation is the use of devices which submit reaction mass to a microwave irradiation, in WO2003064510 [77], for example, PET is depolymerised and reacted with unsaturated compounds under irradiation to obtain a polyester resin.

Another interesting use of PET depolymerisation products are plasticisers which can be considered fundamental constituents in the preparation of some plastic products. For example, di octyl terephthalate (DOTP) is particularly useful to the PVC industry. Esters of this type are synthesised by mainly reacting mono-functional alcohols with DMT, analogous products can be prepared by PET depolymerisation. Typical examples of plasticisers which can be obtained using transesterification [78, 79] include dioctyl isodecyl terephthalate, diisodecyl terephthalate, dioctyl terephthalate, dinormal octyl

Table III. Some Economic Consideration

Chemical recycling technology	Qualitative plant cost	Economical aspects	Safety conditions	Note
Hydrolysis	High (high temperatures and pressures)	Can be competitive for large plants	High	Applied industrially, monomer purification may be difficult
Methanolysis	High (high temperatures and pressures)	Can be competitive for large plants	High	Applied industrially, easy purification of monomers
Glycolysis	Medium–Low	Small plants or bath reactor may be competitive	Medium	Applied industrially
Amminolysis	Low	Small plants or bath reactor may be competitive	Medium	Not applied
Ammonolysis	Low	May be economically attractive depending on product demand	Medium	Not applied

decyl terephthalate, dinormal octyl isodecyl terephthalate and diisononyl terephthalate. Typically, 500 g of polyethylene terephthalate scrap are mixed with between 800 and 1500 g of a given alcohol along with small amounts of a catalyst such as stannous oxalate. The resulting solution is heated to a temperature in the range of 185–235°C. Once the optimal temperature has been reached, it should be maintained for a period ranging from 3 to 6 hours depending on the type of alcohol used. If the boiling point of the alcohol or mixture of alcohols is too low compared to the optimal reaction temperature, it is necessary to pressurise the reaction vessel.

CONCLUSIONS

Each technology considered in this paper shows advantages and disadvantages that unfortunately cannot be clearly identified. Until now only few processes and plants for PET chemical recycling are actually operative, with some being sustained by government funds in Japan, country that shows high interest in recycling and in the rational use of non-renewable resources.

All plants have had trouble, which can be summarised essentially as discontinuity and not sufficient homogeneity of PET supplies, leading to long breaks and continuous process changes to adapt to new feed specifics. Reactor and batch processes are clearly more flexible and capital costs are lower but they could be economically attractive only for higher margin productions such as intermediates for varnishes or polyols for polyurethanes. These applications do not require expensive and time consuming purification steps for TA or DMT which mandate bigger plant sizes.

These processes will become economically competitive only at higher monomers prices on international markets. If we consider also the growing problems of access to petroleum feedstock, and the growing demand of chemical intermediates on the long term, an ‘‘explosion’’ of technologies for a more rational use of resources is predictable and among them chemical recycling will play an important role.

Although plants to depolymerise PET to TA and DMT already exist, unfortunately only few of them are able to treat post-consumer waste, the others being limited to using industrial scraps. For example, Japan, as mentioned above, is highly advanced in the field of chemical recycling technology; unfortunately, it is not easy to have a clear perspective of the economical competitiveness of processes that are currently working in a governmental subsidy regime. A recent report by Mitsubishi Heavy Industries, one of the most active companies in PET chemical recycling, shows that depolymerisation using supercritical methanolysis would be profitable at a scale of 20,000–40,000 ton/year of PET wastes.

Finally, Table III shows a short description and some qualitative economic characteristics of the above-mentioned processes.

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