CHAPTER II

THEORETICAL CONSIDERATION

2.1 Overview of municipal plastic wastes [4-13]

2.1.1 Municipal Solid Wastes (MSW)

Many parts of the industrial world face serious problems of managing the generation and disposal of MSW. It is estimated that 73% of the MSW went to landfill or was otherwise disposed of, 13% recycled, and 14% incinerated. The disproportionate amount of waste going to landfills, the closing of many of these sites, and the lack of equal numbers of replacement sites is the disposal aspect of the solid waste problem. This has received much attention in the media and is generally know as the "landfill crisis". In the past two decades, the member of active operating landfills in USA has decreased by 75%. Within the next five years, one-third of the landfills currently in operation will be forced to close because of stricter governmental regulation on ground and water contamination and on landfill capacity.

Plastics in the MSW stream are a minor component (about 8% by weight or 16% by volume), but it is plastic materials which have attracted the greatest attention of the environmental pressure groups. The reason for this attention appears to be related to two factors : most plastic materials are readily identifiable in the waste stream and plastics are not

biodegradable and retain their integrity is landfills (only 1% of plastics waste is recycled. That is a recycling rate about 1/10 that of glass and a mere 1/25 that of aluminium cans). As a number of observers have pointed out neither of these factors is strictly peculiar to plastics, many so-called biodegradable materials remain identifiable even after long periods of burial in landfill sites. What is undeniable is the public awareness of plastic packaging as a source of litter and also the potential for post consumer waste plastic, especially bottles, to be separated by the consumer from the rest of the waste stream.

The plastic component of the MSW stream consists predominantly of commodity thermoplastic materials, a feature which reflects the high contribution from packaging waste. The types of plastic in municipal wastes are shown in Figure 2.1. A breakdown of the sources of post-consumer wastes is presented in Figure 2.2.
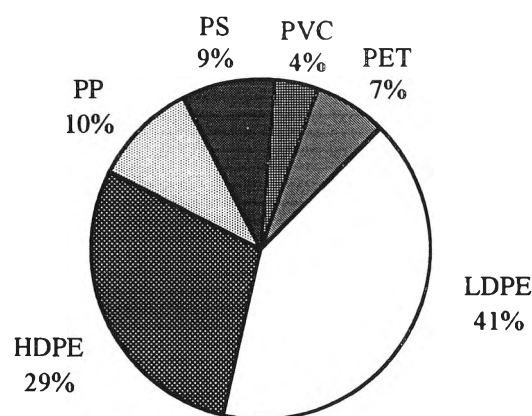

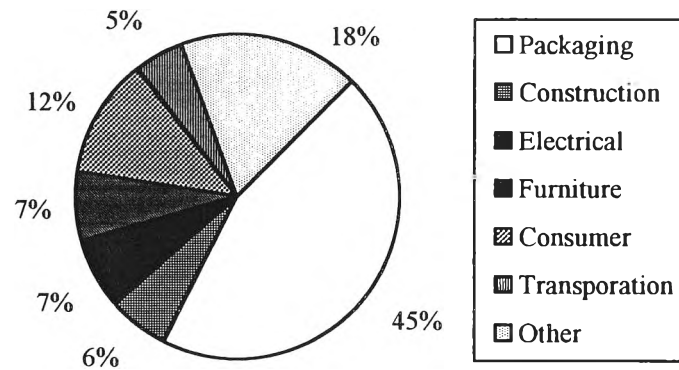**Figure 2.1** Plastic Materials in post-consumer waste [7].

Figure 2.2 Product categories of post-consumer waste [7].

2.1.2 *Plastic Code*

The solution is a study in simplicity : an easy-to-read, universal code that identifies each plastic container by resin. The voluntary coding system proposed by The Society of the Plastics Industry (SPI) consists of an acronym of the resin used and a corresponding code number as shown in Figure 2.3. This information, molded into the bottom of a container, will aid in recyclers' sorting efforts.
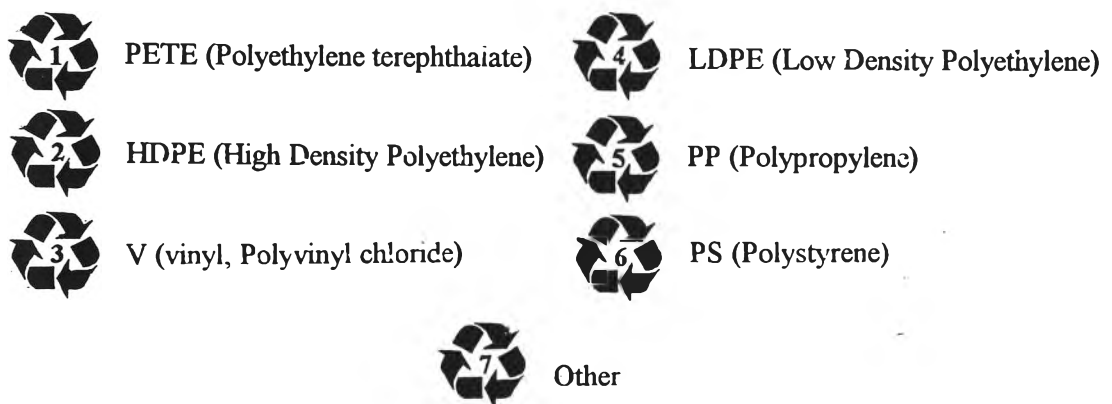

Figure 2.3 Plastics recycling by number.

2.1.3 *Type of Plastic Waste*

Waste plastics consist of plastics resin or product that must be reprocessed or disposed of.

Industrial Plastic Waste is plastic waste generated by various industrial sectors, non-consumer plastic, which includes waste from molders, converters, packers, resin manufacturers, and so on. Normally this plastic waste is easy to identify, comes from a single source, can be processed on traditional molding equipment and may be commingled. Some cleaning may be required.

Post-Consumer Plastic Waste is any plastic that has been used by the consumer and discarded. It applies to an individual plastic or to mixture of plastic. It could be one type of plastic, such as HDPE milk jugs ; two types of plastics, such as PET beverage bottles with HDPE base cups ; or a mixture of a large variety of plastics.

Commingled Plastic Waste may be a mixture of two plastics or a variety of plastics. PET and PE, the focus of most post-consumer plastic waste collection programs, are said to be commingled. "Commingled" also is used to describe post-consumer plastic waste that includes a mixture of all types of resins that are in multilayered, printed, laminated, plated, pigmented, painted, or modified forms.

Contaminated Plastic Waste may have non-plastic material enclosed, such as paper foil, wood chips, floor sweepings, lunch bags, product residue, aluminium closures, wire reclaim, fibre waste, magnetic strips, and plating.

Nuisance Plastics are waste plastics that cannot be reprocessed into viable commercial products under the existing technical-economic conditions.

Scrap Plastics are waste plastics that are capable of being reprocessed into commercially acceptable plastic products.

2.1.4 *Separation of Plastic Waste*

Both industrial and post-consumer plastic wastes often occur as mixtures of generic groups of plastics. There are many attempt to separate them. The following separation techniques have been examined : (1) float/sink separation, (2) electrostatic separation, and (3) automated sortation.

2.1.4.1 *Float/Sink Separation*

The three main plastic components of municipal plastic waste - Polyolefins, PVC, and PS - have slightly different densities. The density of the 5 most frequent bulk plastics are shown in Figure 2.4. The flowchart of such a process, proposed by the U.S. Bureau of Mines, is given in Figure 2.5. The separation is achieved using four liquid media : water ($\rho = 1$ g/cm^3), two water-alcohol mixtures ($\rho = 0.93$ and 0.91 g/cm^3), and an aqueous salt solution ($\rho = 1.20$ g/cm^3).
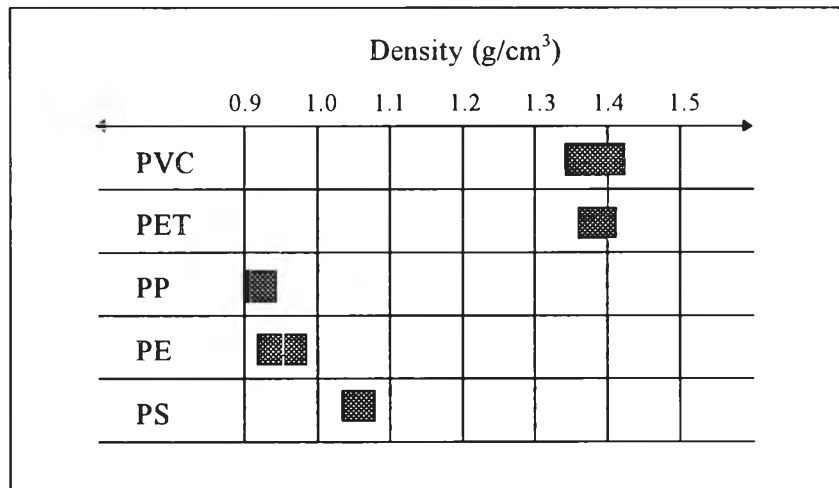
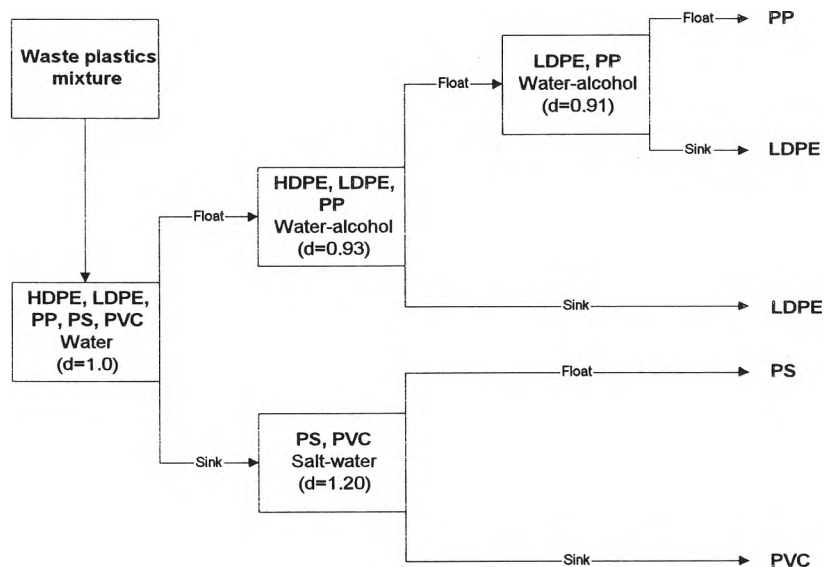**Figure 2.4** The densities of 5 most frequent bulk plastics.

Figure 2.5 Theoretical four-stage sink-float scheme for separating

waste plastics mixture

At present the separation of plastics according to density in practice is only used for the combined separation of polyethylene (PE) and polypropylene (PP) in water using a hydrocyclone or a flotation unit. It is not possible to separate polyvinylchloride (PVC) from PET or PE from PP because the difference in density is too small or they have the same density.

2.1.4.2 Electrostatic Separation

The mixed plastic are first subjected to pre-treatment and then given opposite charges by friction (Figure 2.6 shows the principle of the electrostatic separation process).   When the particles come into contact, some electrons pass over with each contact, so that the contact partners become positively or negatively charged.
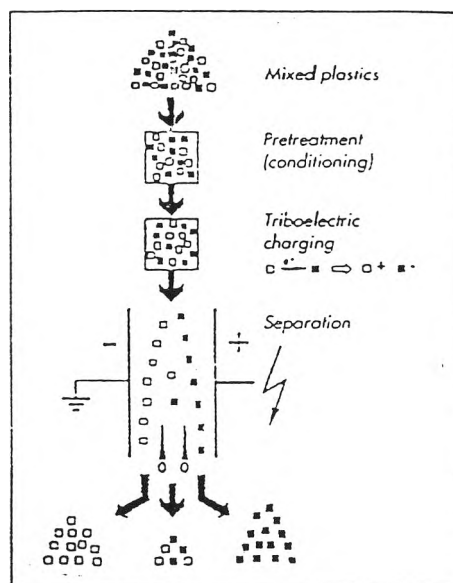

Figure 2.6 Electrostatic Separation Process

The intensity of the charging and the +/- sign depend greatly upon the pretreatment.   Examples of the parameters are relative atmospheric humidity and the type of conditioning medium.   These are surface-active substances which are added in parts-per-million.

Particles treated in this way are charged so that when free-falling in a high-voltage field, they may be deflected to the electrodes and so can be separated from each other.   The two separating flaps at the bottom may be used to control the quality of the concentrates.   The unseparated middle product is fed back into the process again.

Accordingly, this process should ideally be used to separate binary mixtures. If a mixture has more than two plastics, it is very difficult to control the charging behaviour. However, PVC is an exception to this. As PVC is almost always negatively charged in relation to other plastics, it can usually be separated out of mixtures of any number of plastics. The triboelectric charging sequence is shown in Figure 2.7. According to this, in principle all the plastics listed may be separated from each other, regardless of their density.
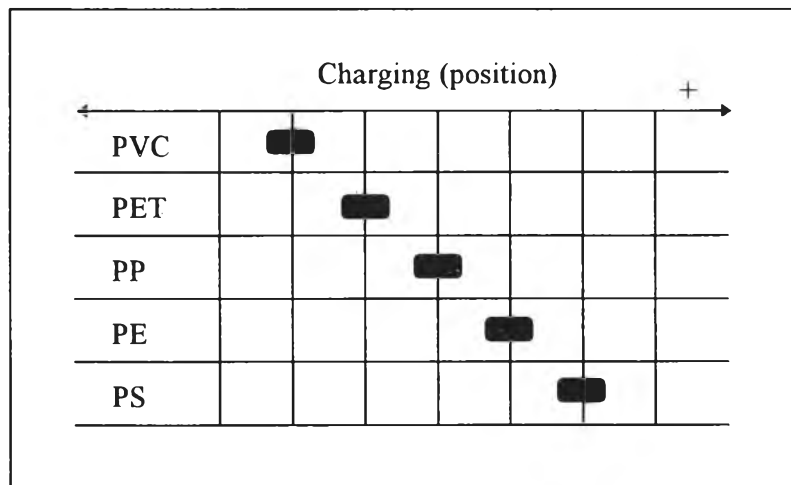

Figure 2.7 Triboelectric charging sequence

2.1.4.3 Automated Sortation

Automating the container-sorting process has been a major cost-containment goal of the recycling industry. Basic sorting technology was developed in 1989 when the plastics recycling industry began to move beyond PET soda bottles. In 1991 the first automated commercial lines were sold to separate PET and PVC, and by the middle of 1994, over 64 automatic sorting lines were operating nationally. In addition

to sorting PET/PVC, automated systems were also used to separated HDPE, colour separated PET, and PVC. By the end of 1994, the American Plastics Council (APC) plans to install a plastics recovery facility (PRF) in Oregon capable of sorting all of the common packaging plastics by resin type.

Automated systems improve the quality of the separated product by eliminating subjective judgement on difficult-to-distinguish materials. PET/PVC separation is not effective when only manual sorting techniques are used, but automatic systems help get final concentrations of PVC in PET to parts-per-million levels.

The automate detectors fall into four categories : X-ray, single wavelength infrared (IR), full-spectrum IR, and colour. The earliest automatic separation systems used X-rays, which are still the most effective means of determining the presence of PVC. The chlorine atom in the PVC molecule emits a unique signal in the presence of X-rays presented by either X-ray transmission (XRT) or X-ray fluorescence (XRF). The XRT signal passes through the container, ignoring labels and other surface contaminants, and is capable of detecting a second container that may be stuck to the first. XRF bounces off the surface of the container and is useful for finding any PVC, including labels and caps.

Systems for separating multiple types of plastics utilize a single wavelength of the near infrared (NIR) spectrum. These systems focus on simple determination of opacity; they separate the stream of mixed containers into clear (PET and PVC), translucent (HDPE and polypropylene), and opaque (all pigmented materials and normally mixed, coloured HDPE) streams.

The newest and most sophisticated detectors employ full spectrum near infrared. Since all materials absorb IR to different degrees, each resin has a unique "fingerprint" which allows these detectors to accurately separate each of the resins. Currently, filters for individual

wavelengths are used for rapid identifications. There is promise for even faster, lower-cost systems.

The colour detectors are very small cameras capable of identifying a number of colours. When combined with a resin-specific detector, they permit a variety of sorts.

Detectors are usually arranged in one of three configurations as shown in Figure 2.8 :

- *Single detector/single container* : This is the simplest set-up for singulated containers. As each container passes the detector, several in-line readings are taken and a decision is made by the computer. While usually accurate, this process is subject to errors if the container has a large label blocking the signal and limiting the amount of data to the computer.
- *Multiple detector/single container* : As each container passes, it is to identify by a series of detectors taking multiple readings resulting in a more accurate reading.
- *Multiple detector/multiple container* : The standard configuration for a mass-flow system. Detectors are spaced to cover the width of the conveyor. When the target material is spotted, its position on the belt is noted and an ejector removes it prior to falling off the end of the belt.

Chamberlain/MRC, Hunt Valey, Md. and Automation Industrial Control, Baltimore, have introduced their PolySort automatic plastic bottle sorting system as illustrated in Figure 2.9.
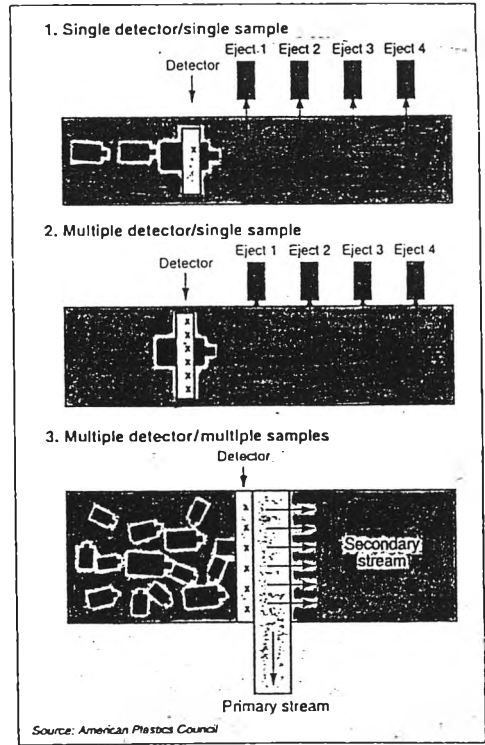
Figure 2.8 Three main detector systems are used in typical separation and sorting setups.
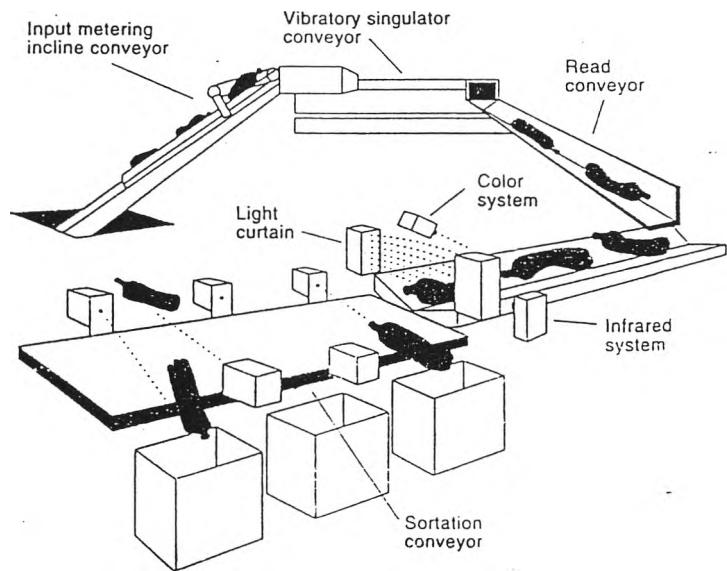

Figure 2.9 Typical automated sorting system for plastic bottles and optical scanning device.

The PolySort is designed to receive commingled plastic bottles in either baled or crushed form. The bottles are prepared in a manner consistent with other sorting systems. The heart of the system is a sophisticated video camera and colour monitor incorporating a strobe to detect and distinguish colours in the inspected plastic bottles.

This optical scanning device interfaces with a 486-based computer to match the colour of the bottle against a master. The detector is reputed to detect matches for up to 16 million shades of colours.

In addition, the system can be programmed to disregard labels on the bottles. Following colour detection, a near-infrared detection system designed to scan the single-bottle stream at a rate of approximately 3000 times per minute, to determine in less than 19 ms the primary resin found in each one. This is accomplished by matching the interferogram produced by the bottle to a known "master" for each base resin as down-loaded in the system.

Another supplier of automated sorting systems for all plastic bottles is Magnetic Separation Systems (MSS), Inc. Its system, BottleSort, incorporates a sensory apparatus designed to detect and mechanically separate commingled plastic bottles in a process that includes six functions : debaling, screening, sensing, separation, and electronic control. Sensing is performed both optically and with X-ray fluorescence.

An optical sensing device having a transmission output range of 200 to 1500 nm detects both the resin composition and the shape of the inspected container. Additionally, a video camera is employed to identify coloured containers via computerized spectrographic matching. This information is also processed through a high-speed microprocessor that has the ability to perform algorithmic analyses and alarm the programmable logic controller to actuate an ejection apparatus to sort the

desired bottle. Finally, an X-ray fluorescence sensor is designed to sort PVC bottles from the PET bottle fraction.

2.1.5 *Plastic Recycling*

ASTM D-5033-90 classified plastics recycling into four types of technologies as follows:

1. *Primary Recycling* : The conversion of scrap plastics by standard processing methods into products having performance characteristics equivalent to the original products made of virgin plastics.

2. *Secondary Recycling* : The conversion of scrap or waste plastics by one or a combination of process operations into products having less demanding performance requirements than the original material.

3. *Tertiary Recycling* : The process technologies of producing chemicals and fuels from scrap or waste plastics.

4. *Quaternary Recycling* : The process technologies of recovering energy from scrap or waste plastics by incineration.

2.2 Chemical Recycling [14-15]

Reversing polymerization through pyrolysis regenerates monomers, or in some instances, precursors to monomers, all of which have been derived from natural gas or crude oil. Converting a plastic back into its monomers creates a feedstock for reconstructing the same generic polymer. Conversion of a plastic into its monomeric precursors leads to either new plastics, or other products like gasoline, heating oil, and asphalt.

The appropriate technique depends upon the type of plastic in the waste stream. Plastics such as polyesters, polyamides, and polyurethanes are created via reversible reactions. It is feasible to convert these plastics back to their immediate starting materials, which are valuable and can be used to remake the plastic. Other plastics such as HDPE, PP, and PVC are created via irreversible reactions. These plastics can be converted into basic petrochemical components through pyrolysis. Further refining and purification steps isolate monomers and high-performing fuel ingredients.
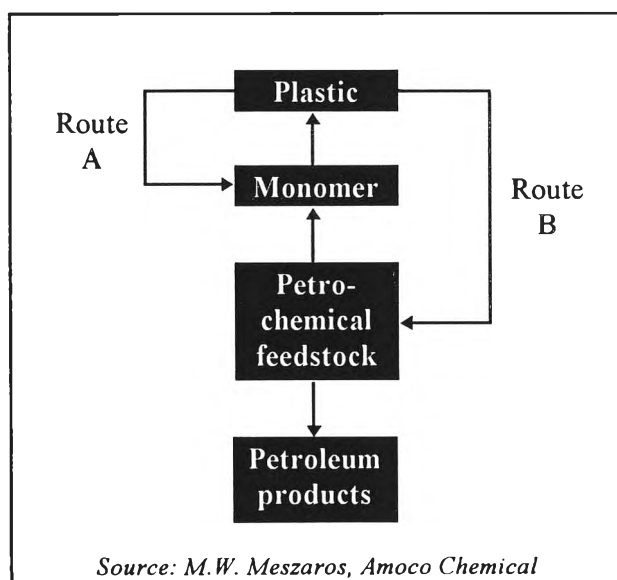

Source: M.W. Meszaros, Amoco Chemical

Figure 2.10 The alternative depolymerization routes

Figure 2.10 illustrates the basic concepts of depolymerization. Plastics produced through reversible reactions can be recycled through Route A or B in the figure, with Route A usually providing more valuable materials.

Plastics produced via irreversible reactions must travel through Route B. The new products produced via either route are indistinguishable from those produced from virgin raw materials. The following techniques are identified by the recycling route outlined in the figure: chemical and thermal depolymerization (Route A); pyrolytic liquefaction and gasification (Route B)

2.2.1 *Chemical and Thermal Depolymerization*

Alcoholysis-hydrolysis is a form of chemical depolymerization (Route A). Step growth (condensation) polymers, which include polyesters, polyamides, polyurethanes, and polyethers, can be recycled in this manner. Forms of alcoholysis called methanolysis and glycolysis effectively reduce condensation polymers to monomer or polymerizable oligomers by reversing the preparative chemistry. For years, polyester makers have converted industrial PET plant scrap to monomer via methanolysis and glycolysis.

Thermal depolymerization also falls under Route A. When certain plastics such as polymethylmethacrylate, polystyrene, and various acetal homopolymers are heated in the absence of oxygen, high yields of component monomers result. The monomers are isolated, purified, and subsequently used to synthesize new polymers. Such a process is in commercial use in India, where scrap polymethylmethacrylate is thermally depolymerized to methylmethacrylate (its monomer). The recaptured monomers are used to produce virgin polymethylmethacrylate.

2.2.2 *Pyrolytic Liquefaction and Gasification*

Pyrolytic liquefaction falls under Route B. The process is similar to thermal depolymerization, but produces liquid precursor products instead of monomers. This liquefaction must be conducted in the absence of oxygen to prevent production of oxygenated products.

The liquid products are similar to naphtha, a valuable refinery stream. Many petrochemical and plastics feedstocks are derived from naptha. The liquids produced by pyrolysis of plastics are particularly valuable because they are principally aliphatic compounds, rich in hydrogen.

Although pyrolytic liquefaction yields a wider variety of petrochemical products under Route A, it has certain advantages: First, pyrolytic liquefaction treats all plastics and not just those that cannot be recycled under Route A. Second, liquefaction process conditions can be selected to meet the overall thermal degradative requirements of most plastics. The makes prior separation of waste plastics unnecessary, including the removal of food and paper impurities, which also are pyrolyzed to other chemical products. Finally, this process converts waste plastics into a liquid that is ready for transport and introduction to a plant as a petrochemical feedstock.

Catalytic cracking, which produces much of the refinery's gasoline and petrochemical feedstocks, uses high temperatures and catalysts to reduce the molecular weight of various refinery streams. Amoco recently showed that polyethylene, polypropylene, and polystyrene can be converted to useful hydrocarbon products in a catalytic cracker. High-octane naphtha, which has value as gasoline or petrochemical feedstocks, is produced from catalytic cracking of plastics. One drawback is that impurities found in plastics, such as chlorine or metals, can deactivate the catalyst.

Pyrolytic Gasification falls under Route B. Gasification processes usually require harsh conditions, such as high temperatures or catalysts, and produce an olefin-rich hydrocarbon gas or a synthesis gas product [15].

One pyrolytic gasification process is steam cracking, which produces olefins form the lighter hydrocarbons (naptha) via crude-oil distillation. The olefins can yield polypropylene and the various polyethylenes. Steam cracking often employs a fluid-bed reactor, in which a relatively inert material (like sand or gravel) is used as a heat-transfer or catalytic medium to produce a fast pyrolytic reaction.

Naphtha is continuously fed into the cracker, and the product goes to existing separation and purification units to produce monomers for making new plastics. British Petroleum has already demonstrated that plastics, after liquefaction, mix well with naphtha to give excellent yields of ethylene and propylene in a steam cracker.

Battelle has a patent-pending pyrolytic gasification unit that reduces a commingled waste stream of low- and high-density polyethylene (LDPE and HDPE), polystyrene (PS), and polyvinylchloride (PVC) into a gas of 40% ethylene, 27% methane, 17% hydrogen, and other fractions [15].

Synthesis gas, a mixture of carbon monoxide and hydrogen, is produced by the partial oxidation of plastics using high temperatures and a specific amount of oxygen. These gases are valuable feedstocks for the manufacture of ammonia, methanol, methyl-t-butyl ether (MTBE), and acetic acid.

2.3 Material Profiles [16-18]

2.3.1 Polyethylene terephthalate (PET)

After the partial ban on the use of acrylonitrile-based barrier plastics by the US authorities (Food and Drug Administration, FDA), thermoplastic polyesters have been used in their place.

Manufacture [16]

PET is manufactured by the usual method from dimethyl terephthalate or terephthalic acid and ethylene glycol with antimony, germanium or titanium oxide as catalyst (Figure 2.11). Continuous polymerization in the melt results in products with high resistance to heat and thermo-oxidation. In all cases, solid phase polycondensation at temperatures between 180 and 240°C is carried out. Volatile compounds are removed by passing nitrogen or by vacumm.
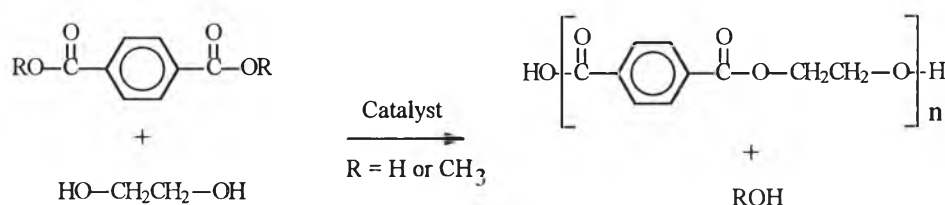
Figure 2.11 Manufacturing of Polyethylene terephthalate

The bottle grades must have a low crystallization rate (in contrast to injection molding grades) to remain crystal clear. This is achieved by high molecular weight (>23,000), high diethylene glycol content and slight nucleation (low catalyst concentration).

General Description

The characteristic properties of partially crystalline PET are high strength and stiffness, favorable creep characteristics, hard surface capable of being polished, high dimensional stability, good slip and wear properties, good electrical, mediocre dielectric properties, and high chemical resistance.

The incorporation of bulky comonomer units such as isophthalic acid and/or CHDM (cyclohexane dimethylol) enables the crystallinity of PET to be reduced so that even thick-walled moldings are transparent. These amorphous modifications are used when the required properties are High transparency, high toughness, favorable creep characteristics, favorable slip and wear characteristics, resistance to stress cracking, low shrinkage and high dimensional stability.

Processing

PET bottles are manufactured in two stages. First a parison is injection molded. This is swung into a blow mold and biaxially oriented by stretch blow molding. The melt temperature must therefore not exceed 260 to 290°C. Residence time in the plasticizing cylinder must be short and shear stress during plasticization low.

Trade names

Polyethylene terephthalate has many different trade names up to the manufacturers, such as, Arnite from Akzo Engng. Plastics, Cleartuf from Goodyear Tire and Rubber Co., Kodar or Kodapak from Eastman Chem. Int., Polyclear from Hoechst., etc.

2.3.2 Terephthalic acid and Dimethyl terephthalate

Terephthalic acid , $C_8H_6O_4$, has the IUPAC name 1,4-benzenedicarboxylic acid. Dimethyl terephthalate , $C_{10}H_{10}O_4$, is also known as 1,4-benzenedicarboxylic acid dimethyl ester. (The chemical structures of terephthalic acid and dimethyl terephthalate are shown in Figure 2.12) The acids are produced by oxidation of the methyl groups on the corresponding p-xylene. After oxidation to a carboxylic acid, reaction with methanol gives the methyl ester, dimethyl terephthalate.
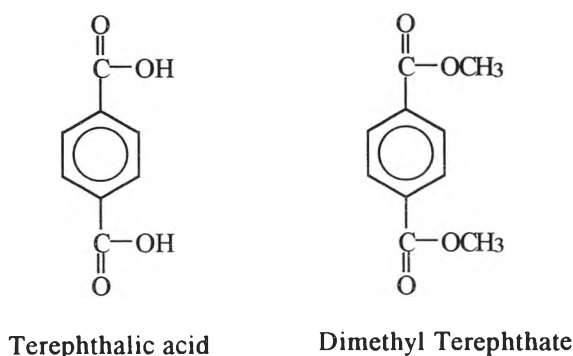

Terephthalic acid   Dimethyl Terephthate

Figure 2.12 Chemical structures of terephthalic acid and its dimethyl ester

Physical properties

Terephthalic acid , MW 166.13, is available a commercially as a free-flowing powder composed of rounded crystals. It forms needles if recrystallized slowly. Vapor pressure is low : 0.097 kPa at 250°C, with sublimation at 402°C (atmospheric pressure). Melting has been reported at 427°C.

Dimethyl terephthalate , MW 194.19, melts at 140.6°C and has sufficient vapor pressure for vacuum distillation. The molten form is

preferred commercially, but flakes and briquettes are available when long transport distances are required.

Terephthalic acid is a stable compound with low solubilities in most solvents. The acid is soluble at >10 g per 100 g solvent at room temperature with ammonium, potassium, or sodium hydroxide, dimethylformamide, and dimethylsulfoxide. Tetramethylurea and pyridine each dissolve ca. 7g/100 g.

Dimethyl terephthalate is also stable, and more soluble in common organic solvents than the acid. Its main physical properties are a melting point below the point of degradation, and a vapor pressure which allows for purification by distillation.

Production

p-Xylene is the feedstock for all terephthalic acid and dimethyl terephthalate production. Oxidation catalysts and conditions have been developed which give nearly quantitative oxidation of the methyl groups, leaving the benzene ring virtually untouched. These catalysts are combinations of cobalt, manganese, and bromine, or cobalt with a co-oxidant, e.g., acetaldehyde.

Amoco Chemical and Mitsui Sekka participate in joint-venture companies, and both have licensed the famous process which is distributed around the world. Figure 2.13 illustrates the processing diagram of the Amoco Process. A soluble cobalt-manganese-bromine catalyst system is the heart of the process. A feed mixture of p-xylene, acetic acid as solvent, catalyst, and oxygen in compressed air as the oxidant is continuously fed to the oxidation reactor. The process is operated at 175-225°C and 1500-3000 kPa. Over 98% of the p-xylene is reacted, and the yield of terephthalic acid is >95 mol%.
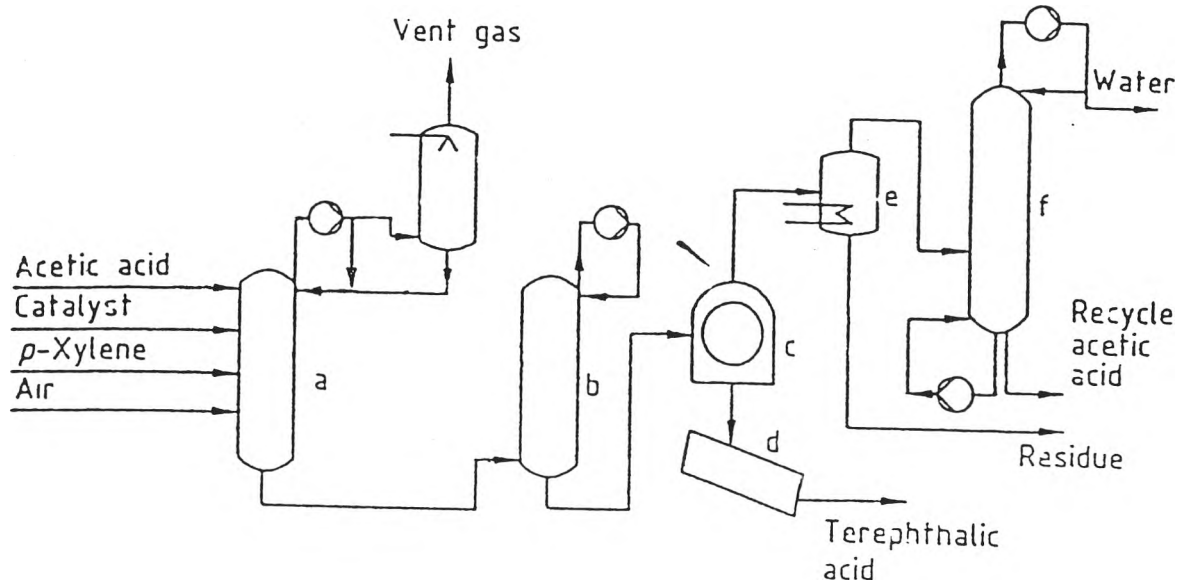
Figure 2.13 Catalytic, liquid-phase oxidation of p-xylene to
terephthalic acid by the Amoco Process [18]

a) Oxidation reactor;   b) Surge vessel;

c) Filters;   d) Dryer;

e) Residue still;   f) Dehydration column.

2.4 <u>Previous works</u> [19-25]

Early studies for the recycling of polyethylene terephthalate have been demonstrated in the following patent literatures.

Brownsombe [19] has reported that PET could be separated from mixed polymer by contacting the mixed polymer recycle stream with a solvent which selectively dissolves the PET. The PET recovered was preferably combined with "virgin" PET and further processed to increase its molecular weight. A large solvent recycle stream would be generated by the process. Discharge of the solvent to the environment must be avoided.

Dupont and Gupth [20] have decribed a process whereby terephthalic polyester was treated with an excess of an alcohol having 6-20 carbon atoms in the presence of a catalyst. Ethylene glycol could be distilled from the mixture and terephthalate diester was produced. Because transesterification is an equilibrium process, a large excess of the alcohol was generally required to obtain an acceptable yield of diesters of TPA (even though distillation of ethylene glycol favored the formation of the ester of the reactant alcohol because of the equilibrium), and, in order to obtain purified terephthalic acid (PTA), subsequent purification and hydrolysis steps would be required.

Cudmore [21] has pointed out that PET scrap could be used for recovering ethylene glycol and either terephthalic acid and dimethyl terephthalate (DMT). The process included depolymerization of a slurry of scrap PET by hydrolysis or methanolysis, and subsequently crystallization of the desired product. Because DMT was used less than PTA, the

methanolysis was not important. Moreover, The use of methanol in process would harm the environment.

Tindall and Perry [22] have shown a saponification process for the degradation of PET into salts of terephthalic acid. The polymer was first dissolved in concentrated sulfuric acid - a step which generally has a detrimental effect on the ethylene glycol portion of the resin.

Schwartz [23] has described a process for recycling polyester. The process steps generally included first combining polyester film with an alkaline solution to form a slurry. The slurry was heated to temperature between 205°C and 315°C , causing ethylene glycol to evaporate which could then be collected. The remaining product stream was then mixed with water and filtered to remove any undissolved impurities. The aqueous filtrate could be acidified causing terephthalic acid to precipitate.

Mandoki [24] has suggested a process for the neutral hydrolytic depolymerization of condensation polymers. The process was conducted in a continuous manner and comprised introducing condensation polymer into an aqueous hydrolysis zone at a temperature of between 200°C and 300°C, and superatmospheric pressure of at least 15 atmospheres. High pressure steam was introduced into the lower portion of the hydrolysis zone underneath the level of the polymer. The steam agitated the polymer to provide heat transfer to accelerate the hydrolysis reaction. Further, a portion of the steam condensed to provide water which was a reactant in the hydrolysis reaction. An aqueous solution of the product(s) of the hydrolysis reaction was withdrawn from an upper portion of the hydrolysis zone.

Tustin [25] has indicated a process for recovery of terephthalic acid and ethylene glycol from PET. The process was a six-step process including : (1) contacting a resin with water and pressurized with nitrogen at elevated temperature, (2) cooling the resulting mixture, (3) recovery of the ethylene glycol from the liquid portion in the presence of water vapor at elevated temperature to produce a vapor containing terephthalic acid and water, (5) cooling terephthalic acid water vapor mixture to a temperature below the dew point of terephthalic acid and (6) collecting the polymer grade terephthalic acid.