

4.1 INTRODUCTION

We have seen in Chapter 1 that any waste materials, including polymers, are best managed within an integrated waste management scheme. The most sustainable waste management option is always reduction at source, *i.e.* reduced consumption of materials and products, followed by direct re-use. At the other end of the spectrum is disposal by landfill, which wastes valuable resources, both material and energy, and increases the amount of solid waste in the environment. In the waste management hierarchy, recycling sits somewhere in between, depending on the resources used and wastes generated in the overall recycling operations, which must not exceed the environmental benefits of recycling. The latter are explored at length in Chapters 6 and 7, but in this chapter we concentrate on recycling methods and technologies available for plastic materials.

Three generic options are available for the recycling of polymers:

- mechanical recycling,
- chemical recycling,
- energy recovery.

Mechanical recycling uses physical means, such as grinding, heating and extruding to process waste plastics into new products. Chemical recycling on the other hand uses chemical processes to convert waste into useful products, such as monomers for new plastics, fuels or basic chemicals for general chemical production. These two options are often referred to as material recycling. The third recycling option, energy recovery generates heat or electricity (or both) either by direct incineration of polymer waste, *e.g.* in municipal solid waste (MSW) incinerators, or by replacing other fuels, *e.g.* in blast furnaces, cement kilns or power stations.

The recycling activity can be divided into two main steps:

- recovery of post-consumer polymer waste (*i.e.* its collection and delivery to the recycling facility);
- waste sorting and separation.

Recovery of post consumer waste is discussed in Chapters 3 and 5; here, we examine examples of sorting, separation and processing using currently available technologies for each of the three recycling options. A number of interesting technologies for the future, some of which are still at an experimental stage, are described in Chapter 8.

4.2 IDENTIFICATION AND SEPARATION OF POLYMERS

Despite intense efforts over recent years to increase the recycling and re-use of post-consumer waste plastics, the proportion that can actually be recycled is still extremely small, not least because of the many technological and technical factors that constrain recycling. One of these is the fact that some of the recycling options require prior sorting or separation of polymers by type. The reasons for this may be technical, or based on environmental or health issues. For example, mechanical recycling is only economically and technically feasible for single materials while incinerators must separate out PVC from the MSW to avoid the formation of toxic dioxins. Both these issues will be discussed further later in this chapter.

We now explore how some of these constraints can be overcome using existing and developing technologies to identify, separate and process waste polymers.

4.2.1 Identification of Polymers

Some polymers, such as PET in soft drink bottles or PE in milk and water jugs, may be relatively easy to identify. However, many polymers in use often resemble one another and

Key Facts

- The environmental costs of recycling must not exceed the benefits.
- Materials recycling (mechanical or chemical) is the preferred recycling option in most national and international directives.

are clearly difficult to differentiate, even for a polymer scientist or engineer who may be familiar with the polymer. In 1988, the Society of the Plastics Industry (SPI) proposed the Voluntary Plastic Container Coding System, a series of seven numbered classifications (Figure 4.1) to help consumers classify different plastics and to make it easier to identify the polymers in the waste stream. In practice, the code is impressed or printed on the plastic component.

Typical examples of these polymers in post-consumer waste are:

- PET: beverage containers, boil-in food pouches, processed meat packages.
- HDPE: milk bottles, detergent bottles, oil bottles, toys, plastic bags.
- PVC: food wrap, vegetable oil bottles, blister packaging.
- LDPE: shrink-wrap, plastic bags, garment bags.
- PP: margarine and yoghurt containers, caps for containers, wrapping to replace cellophane.
- PS: egg cartons, fast food trays.
- Other multi-resin containers or microelectronic components.

In 1991, the American Society for Testing and Materials (ASTM) issued a more general system, based on abbreviations recommended by the International Organisation for Standardisation (ISO), and encompassing over 100 polymers and polymer blends. The issue of waste stream identification is important in the automotive industry, which has been quite pro-active in exploring the recovery and recycling options. The Society of Automotive Engineers (SAE) employs a third system¹, which is very similar to the ISO model, to identify the polymers used in automotive components.

This diversity of identification systems is one of the obstacles for more effective separation of polymeric materials. The universal adoption of an industry agreed product marking system such as ISO 11469² for the identification of a variety of plastics would ease sorting problems during recycling. In some cases, recognition is already possible and some of the methods that are available are discussed below, but improved analytical and recognition methods are needed.

Separation is further complicated by the current design of products in which polymers are commingled with other materials. Disassembly and separation of materials can be simplified by appropriate product design and choice of materials. Various 'Design For the Environment' (DFE) approaches have been developed to assist designers and engineers in designing and manufacturing more sustainable products. DFE is discussed in more detail in Chapters 6 and 7.

4.2.2 Sorting and Separation of Polymers

Polymers are currently sorted and separated either manually or mechanically. Considerable work has been undertaken to develop automated technologies that can separate mixed waste streams according to polymer type or to remove foreign matter (contaminants) from the waste stream. While some of these techniques are becoming quite sophisticated, in some cases the process is still in its infancy and more development work is required before the technique may be used on anything greater than a laboratory scale.

The choice of the appropriate technique will depend on a number of factors, including:

- complexity of the polymer mixture, *i.e.* the number of polymers present and recoverable;
- physical form of the polymer(s), *i.e.* whether the material is in bulk or granulated;
- quality, *i.e.* acceptable level of contamination in the recyclate for future use;
- nonplastic contaminants, *i.e.* the nature and concentration of additives;
- market, *i.e.* the eventual use to which the recyclate will be put;
- economics, *i.e.* the scale and cost of the separating operation and whether the scale is sufficiently large to justify the more expensive automatic detection and sorting methods.

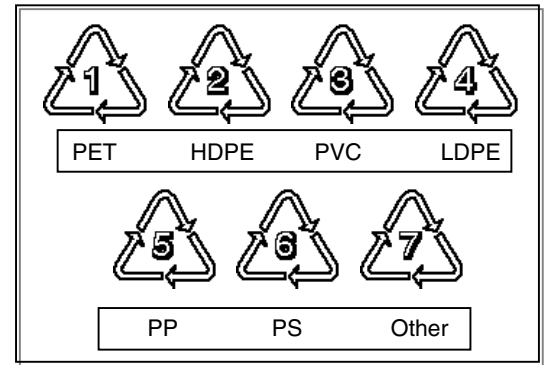


Figure 4.1 Codes used to identify important commercial polymers used in packaging

Key Facts

- Polymers are difficult to identify unless labelled at source, but there are currently three labelling systems in use.

Key Facts 

- Pre-separation by consumers is not always reliable.
- Chemical identification of polymers often needs several techniques in combination, which is expensive.

To date, most of the development work has been carried out to separate mixed plastic bottles and containers into clean fractions of their main polymeric components and these will be discussed in greater detail. You can see from Table 4.1 that many techniques are being used or examined for the detection and separation of whole bottles and containers from the waste stream. For instance, bottles may be collected by consumers (either having undergone some sorting by polymer type or simply collected as mixed plastic waste) or by contractors (as mixed recyclable material or within MSW). If some pre-sorting has already taken place (perhaps through a 'kerb-side' or 'bring' scheme), then the materials may be fed directly into a recycling operation (although some further sorting will be necessary as sorting at source, *i.e.* by consumers, is not always reliable). These materials can be shredded to potentially yield a clean flake with minimal treatment (*e.g.* to remove contaminants such as labels or lids, *etc.*) prior to granulation and cleaning. If this is the case, then a selection of techniques is already available for the detection and separation of granulated or polymer flake (Table 4.2). In some of these cases, recognition of different polymer types is already possible on a commercial scale but, as already mentioned, there is a need for improved analytical and recognition methods.

The following methods can be used for polymer recognition:

- infrared spectroscopy or mass spectroscopy (specific chemical groups);
- thermal analysis, *e.g.* differential scanning calorimetry (energy changes such as, decomposition, melting or thermal transitions);
- nuclear magnetic resonance (molecular structure);
- opto-mechanical pattern recognition (based on size and form);
- X-ray fluorescence (presence of metals or hetero-atoms).

The efficiencies of Fourier transform infrared (FTIR) and Fourier transform Raman (FTR) spectroscopies have also been tested. Although it was possible with both techniques to

Table 4.1 Detection and separation techniques for whole bottles and containers.

Method	Mode of operation	Advantages	Disadvantages
Manual separation	Feedstock passed along a conveyor belt for operator to identify visually, sort by polymer category and separate articles.	Cheap in terms of capital investment (no sorting technology employed).	Labour intensive and slow (<i>ca.</i> 50–200 kg h ⁻¹ depending on number of operations). Potentially inaccurate (<i>ca.</i> 80–95% accuracy) at economic speeds (6–10 bottles <i>per</i> second).
Manual separation assisted with some degree of automation	Feedstock passed along a conveyor belt for operator to identify visually and sort by polymer category by activating automatic ejection mechanism.	Relatively simple to blow/push bottles/containers into side chutes using basic electronics.	Less labour intensive but still slow and prone to errors.
Automatic bottle sorting according to polymer type	X-ray detection is used to detect chlorine in PVC with mechanical removal from waste stream. PE is separated from PET using optical sensor (differentiates opaque, translucent, transparent bottles) or near infrared spectroscopy.	Detection accuracy can be very high (lower than 1 error in 10 000). High throughput achievable (1 tonne h ⁻¹).	High capital costs. Requires good quality feedstock and accurate presentation of PVC bottles if high accuracy/throughput to be achieved. Errors usually due to overlapping bottles or smaller units (<5 cm).
Polymer markers	Addition of markers or tracers added during manufacture: infrared dyes in PET or fluorescent dyes.	High detection accuracy for different polymers or even different grades of polymer (up to 90% for coloured particulate contamination from clear PET flake ³).	Much development work required. Universal acceptance of markers is essential for success. Some risk of cross-contamination and mixing.

recognize most usual polymers, severe limitations of FTIR were experienced, including a high sensitivity to the surface state. FT Raman proved to be a rapid and highly selective method, giving information even on the mineral fillers present in plastic. In most cases, a combination of different analytical methods is necessary and this has serious implications for the cost of the operation.

Increasing the complexity of the polymer mixture leads to a significant increase of the costs of separation. Engstrom³ estimates that if pre-sorting has taken place then an operation involving collection skips, baling equipment and transportation will cost of the order of DM 50 000 to 200 000 (approximately £17 000–£65 000) for a throughput of 1–2 tonnes h⁻¹. Manual separation will raise the labour costs, but involves little in the way of capital investment. However, if substantial automatic separation becomes necessary, then the costs for the equipment can be as high as DM 200 000 to 2 000 000 (depending on

Table 4.2 Detection and separation techniques for granulated or flaked polymer material (selected data collated from ref. 3).

Method	Mode of operation	Advantages	Disadvantages
Flotation tanks (Reprise Technologies)	Separation in liquid by means of differences in polymer densities.	Can effect coarse separation. Improvements are being examined with supercritical fluids and other non-organic solvents to replace water.	Needs at least two stages for good separation. Problems encountered if polymers have very similar densities.
Hydrocyclone (Byker reclamation plant, Newcastle, UK)	Pressurised separating fluid (usually water) containing polymer particles forms vortex (250 times the force of gravity). Separation effected by centrifugal force.	Allows better separation than static flotation tanks. May separate PE from heavier PVC, PET or PS. Higher throughput than static float and sink tanks.	Problems encountered if polymers have very similar densities or if grain size and shape differ greatly.
Compressed air separation	Rotating drum with an air flow to fluidise light component (plastic film/paper labels/cloth) and allow separation by density.	Allows better separation than flotation tanks. May separate PE from heavier PVC, PET or PS.	Problems encountered if polymers have very similar densities.
Micronising (Reprise Technologies, UK and Ecoplas, Belgium)	Pulverising and sieving polymer fractions to 600 μm , utilising the possibility that different polymers have different grinding characteristics.	PET contamination in PVC can be reduced from 2 % to 0.2 %. Cryogenic grinding improves efficiency. By freezing the samples (below T_g), the integrity of the solid samples is maintained and separation facilitated.	Economic and environmental costs of cryogenic grinding are high due to high energy requirements.
Electrostatic separation Devtech Labs. (USA) Kali und Salz Co. (Germany)	Charged polymer flakes fall between charged plates and separated based on their capacity to retain charge, which is related to bulk and surface resistivity.	Good removal of residual contamination from PVC or PET.	Critically dependent on pretreatment of flake surface to achieve a reproducible charge.
Melt filtration Herbold Co. (Germany) Gneuss (Germany)	Polymer components heated on band conveyor and a rotating drum picks up softened material. Contaminants can be removed from molten polymer by allowing the molten polymer to flow through screen apertures.	Problems may be encountered with ensuring that the filter area is continuously renewed without interrupting the process.	May be difficult to move beyond coarse scale separation.
Separation of coloured particles (Reprise Technologies, Radex Systems, Ltd., Sortex, Envirotechnics, UK)	Low technology optical detection and air jet removal; or laser detection and air jet removal.	Optical discrimination (Reprise) effective to remove greater than 90 % of coloured contaminants.	Very low levels required difficult to achieve for PET using optical methods.

Key Facts

- Mechanical recycling is best suited to clean waste streams such as packaging, mixed wastes must be pre-sorted.
- Thermosets are ground up for use as fillers; thermoplastics are pelletised or extruded into new products.

the sophistication of the technique and the number of sorting operations required). He also cites the cost of a modern, materials' recycling facility (MRF) (to handle the separation of plastic bottles from other recyclable materials, such as paper and glass) as DM 2–20 million for a medium sized town. Finally, automating the separation of polymers from MSW would require additional effort to implement feedstock recovery or incineration and Engstrom³ estimates the cost of such a facility as at least DM 100 million (~£35 million). Sorting and recycling costs are further discussed in Chapter 5.

4.3 TECHNOLOGIES FOR POLYMER RECYCLING

4.3.1 Mechanical Recycling

Separation of different polymers is particularly important for mechanical recycling because processing mixed materials would otherwise produce recyclate of low quality, which could only be used in a limited number of applications. Hence, mechanical recycling is really best suited to clean plastic waste, such as packaging material.

Mechanical recycling of mixed waste necessarily starts with a manual sorting process, which means high labour costs and the separation is not always as efficient as it needs to be to produce high quality products. Thereafter, depending on the polymer type, the processing involves:

- Thermosets: some form of grinding and particulation for re-use as filler for new materials to improve properties such as the modulus, elongation-at-break or impact strength.
- Thermoplastics: re-melting and extrusion into new products or pelletising to be sold on as a raw material for further processing.

The following sections describe some of the processes developed for mixed wastes and for specific polymer types.

Mechanical Recycling of Mixed Plastics

A number of manufacturers are developing designs for a fully automated mechanical recycling plant, which eliminates the need for manual sorting. One such process has been developed and tested in pilot plant trials at the RWTH University of Aachen in Germany⁴ and the layout of this process is shown schematically in Figure 4.2. The system accepts bags of waste and empties them on to a conveyor. A magnetic separator suspended above the conveyor removes magnetic materials first, then fibrous material is pulped and cleaned in a specially designed unit. The time material spends in the pulping unit varies between

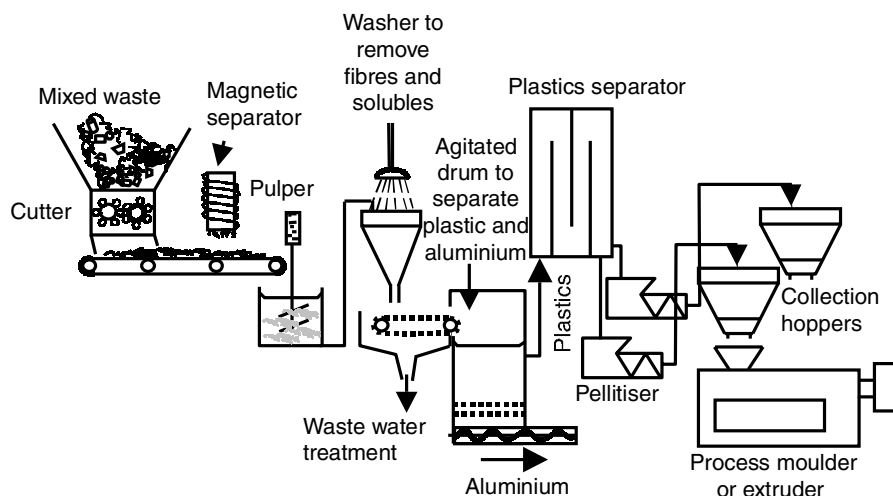


Figure 4.2 Process diagram for a plastic preparation and compounding unit DLR (German dual system) and BNIBF (German Ministry of Education, Science, Research and Technology) Process⁴. Reproduced with permission from J. Kabovoc (ed.). *Recycling of Polymers, Macromolecular Symposia*, 135, 1998. Copyright (1998) Wiley-VCH, Weinheim

5 and 20 min, depending on the quantity of composite material in the feed and the time taken to dissolve the parts that are less soluble in water.

After the pulping process is completed, the whole contents are fed into the washing drum. Here, the dissolved or suspended paper fibre content flows through a screen to the process water cleaning unit. The remaining material in the drum contains dirt, metal and heavy, noncellulosic fibres and is washed with process water before being discharged from the drum. An agitator vessel then separates aluminium from plastics by their relative density. The aluminium, being the heaviest, settles in the sediments and is discharged by a screw conveyor and de-watered, after which it can be recycled.

The mixture of plastics is then transferred into a series of separators to be segregated into its different components. The chlorine-bearing PVC is separated using an electrostatic plate-type separator. The separation of PS is achieved in another density separator using a higher density-separating medium.


Each of the separated plastic materials is then ground, washed and dried. A new product is generated directly by extrusion (see Chapter 3 for an explanation of extrusion). Extruded products may be upgraded by the addition of fibres, mineral fillers, stabilisers, pigments, flowing aids, etc.

The process water produced in the pulping and cleaning is purified and re-circulated by a water-cleaning unit. Contaminated water is pumped into a thickener where a flocculant is added to improve settling out of solids, which are then discharged at the bottom and de-watered to be disposed of as a fairly dry cake.

The process recovers materials such as solid aluminium, aluminium-plastic composites and polyolefins very effectively, with a high yield and purity of material that can be used as secondary feed in industrial production elsewhere.

Clearly, the whole process is complex, which means that the initial capital cost of the equipment is high, but, being fully automated, the continuing running costs are then low relative to a process that requires manual intervention. It should be borne in mind, however, that automated separation requires a large scale operation to justify the investment costs and that may pose problems in providing an adequate volume of waste.

A second example which accepts pre-sorted plastic waste, free of iron, glass, stone and organic matter is the REVIVE system, invented by Renato Fornasero Development SAS Cadauta and promoted by the Commission of the European Communities⁵. Other impurities can be tolerated at a level of 5% or less. Polymer waste is crushed, mixed, dried and injected into a vessel to be homogenised in the molten state. The molten mixture is then either compacted and shaped into a final product, extruded as consumer products or granulated and collected as pellets for further processing (see Figure 4.3).

Key Facts 

- Running costs of an automated plant are low compared to a manually operated plant, but the initial capital costs are high.
- Running an automated plant economically requires a high throughput of material and an adequate supply of waste.

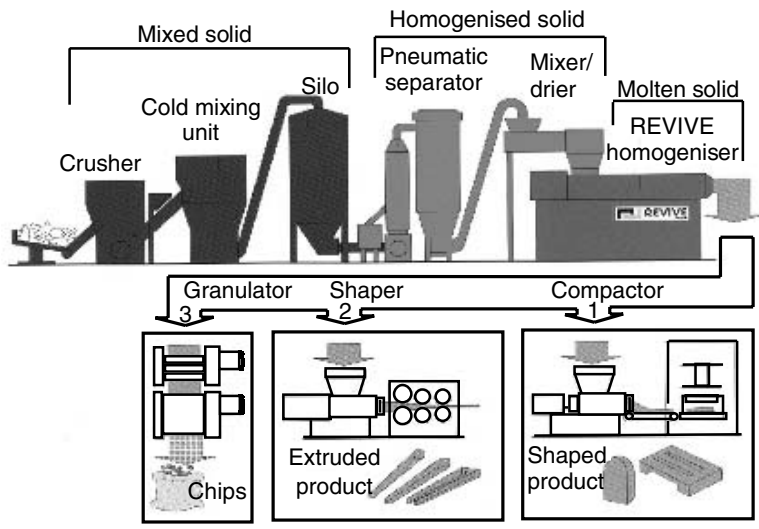


Figure 4.3 The REVIVE process for re-use of mixed plastic wastes

Recycling of Specific Polymer Types

A few specialised processes are being developed commercially for mechanical recycling of specific polymer waste sources. Two processes are illustrated here in more detail:

- selective froth flotation for recycling of PVC and PET;
- recycling of PET bottles from a homogeneous PET waste stream.

Selective Froth Flotation for PVC/PET Mixtures

As we have seen in Chapter 3, PVC and PET are two of the most used polymers. They can be reprocessed and re-melted a number of times without any significant change in their properties, due to the lack of cross-linking between the polymer chains. They have almost the same density, which makes them difficult to separate using their specific gravity. However, a selective froth flotation process has been developed by Recovery Process International, Inc.^{6,7}, which uses differences in hydrophobicity of the two polymers to separate and recycle them.

A simplified flow diagram of the process is shown in Figure 4.4. It is a two-step process of alkaline treatment and froth flotation and requires the size of the polymer material to be reduced to less than 10 mm to improve the efficiency of separation. The mixture is first treated with about 1–3 % sodium hydroxide for between 75 and 85 min at a temperature of about 70–85 °C, during which time the PET hydrophobicity is reduced significantly, while the hydrophobicity of PVC is only slightly affected.

After the alkaline treatment, the particles are screened and rinsed with water at a pH of 6–9. An anionic surfactant is then used at a concentration of 15–30 mg l⁻¹ for 1–2 min to generate froth. Other types of surfactant can be used, provided they have strong frothing capabilities and low affinity for the PVC and PET. PVC then floats to the top preferentially and is collected from the overflow froth over the following 5–10 min, leaving the PET behind to undergo further screening, rinsing and drying.

Laboratory scale trials on small test samples indicate that the PET recovery rate is almost 100 %, with PVC about 70 %. Most importantly, the physical properties of polymers do not deteriorate significantly during processing.

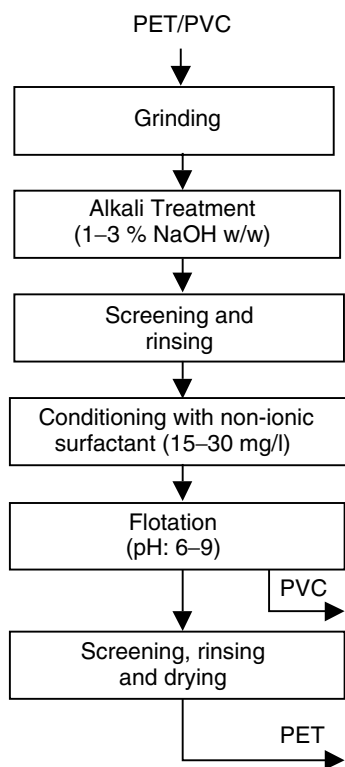


Figure 4.4 A simplified froth flotation process flowsheet for the selective recovery of PET from PVC/PET mixtures^{6,7}. Reproduced with permission from ‘*In Polymer Engineering and Science*’ v. 38/9, p. 1379–1387. Copyright (1998) SPE

PET Bottle Recycling

The Centre for Plastic Recycling Research (CPRR)⁸ in the USA has developed a process to recycle PET from a pure stream of PET bottles, which involves the following steps (see Figure 4.5):

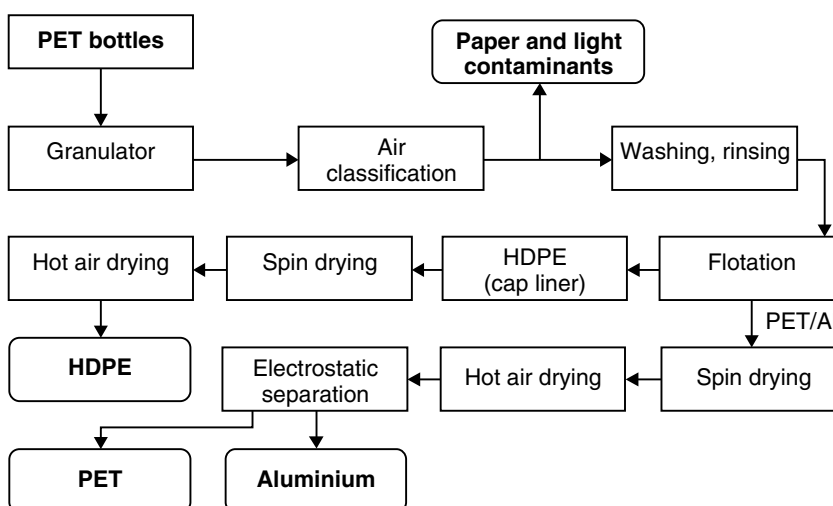


Figure 4.5 CPRR process for recycling of PET bottles⁸. Reproduced with permission from J. Kabovoc (ed.). ‘*Recycling of Polymers*’, *Macromolecular Symposia*, **135**, 1998. Copyright (1998) Wiley-VCH, Weinheim

- (1) shredding the bottles to facilitate a fast granulation, followed by grinding to 1/4 inch particles;
- (2) separation of paper and light contaminants in an air stream;
- (3) washing and rinsing the remaining material;
- (4) flotation to separate the lighter HDPE, cap liner and plastic label from the heavier PET and aluminium (from the bottle seal);
- (5) separation and spin drying of lights and heavies;
- (6) hot drying of each stream;
- (7) electrostatic separation of PET and aluminium, where the nonconducting PET collects a charge and is attracted to oppositely charge plates;
- (8) packaging and sale of aluminium and clean, uniform, granulated resins.

In summary, mechanical recycling involves the use of relatively simple processes and generates polymer materials of high quality. However, this process is mainly suitable for homogeneous waste streams which often requires clean waste of the same type or a high degree of sorting, which can increase the costs of operation. On the other hand, most of the chemical recycling processes can accept mixed or soiled waste, which are converted into feedstock for chemicals production or for use as fuel. Furthermore, the products can be separated relatively easily. The following sections outline some of the more important chemical recycling processes.

4.3.2 Chemical Recycling

Several processes can be included under the heading of chemical recycling, including gasification, hydrogenation, pyrolysis (sometimes referred to as thermolysis), and the use of waste polymer as a reducing agent in a blast furnace. The main characteristics of these processes are summarised in Table 4.3⁹.

Table 4.3 Chemical recycling processes⁹. Reproduced with permission from Sasse and Emig, 'Review: Chemical Recycling of Polymer Materials.' In *Chemical Engineering Technology*, Vol. 2:1 (1998). Part 10, pp. 777–789. Copyright (1998) Wiley-VCH, Weinheim.

Process	Reactor	Reaction conditions	Products	Note
Gasification	Fluidised-bed, fixed-bed, pneumatic transport reactor	15–30 MPa 800–1600 °C	Synthesis gas (CO and H ₂), energy	Co-gasification with municipal waste, coal, heavy oil
Hydrogenation	Bubble column	20 MPa, 500 °C	Syncrude Bitumen	25% mixture with vacuum residuals, capacity approximately 40 000 tonnes year ⁻¹
Pyrolysis (thermolysis)	Fluidised bed, rotary kiln, tubular crackers	400–900 °C	Wax, oil, gas, energy	Mainly pilot plants, with capacity of e.g. 15 000 tonnes year ⁻¹
Reduction in a blast furnace	Blast furnace	2000 °C	Pig iron, furnace gas	

We will now look at a few examples of each process and discuss their important features.

Gasification

Gasification can be defined as the partial oxidation of hydrocarbons in the presence of lower oxygen levels than are required for complete stoichiometric combustion. The main products of gasification are synthesis gases such as CO and H₂. This is already a well-developed industrial process for the gasification of coal and heavy oil fractions, which can be modified for use with plastics waste. The process is carried out at temperatures from 800 °C up to 1600 °C and pressures of 15–30 MPa. Air, oxygen, steam, flue gas, carbon dioxide

Key Facts

- Chemical recycling can (generally) accept mixed or soiled waste and convert them to gaseous fuel or to feedstock for chemical plant.
- Gasification is the partial oxidation of hydrocarbons at reduced levels of oxygen and the main products are synthesis gases such as CO and H₂.

Key Facts

- Fluidised beds are generated by passing a high velocity gas through a bed of solid particles (e.g. sand) which become separated and fluidised in the gas.
- Polymers are gasified in fluidised beds by first melting and coating on to sand particles and then by cracking at high temperatures.
- HCl from the decomposition of PVC can be removed by the addition of calcium oxide.

and sometimes hydrogen can all be used as the gasifying agents, either separately or in combination with each other.

Plastics waste is converted into brickettes prior to recycling in fixed bed gasifiers and used as secondary input to supplement coal. There are two general types of gasification technology: fixed-bed and fluidised-bed processes. In both processes, the plastics waste is mixed with coal (lignite) and fed to the gasifier. Plastics and lignite are partially oxidised to synthesis gas ($\text{CO} + \text{H}_2$), which can be used as raw material for methanol synthesis or to generate electricity in a power plant. In the process developed, for example, by SVZ Schwarze Pumpe GmbH, gasification is carried out between 800 and 1300 °C at a pressure of 25 bar^{9,10}. The process can accept up to 50 % plastic waste.

In the case of fluidised-bed gasification, the mixed feedstock enters the fluidised-bed, dry, at a pressure of about 30 MPa. The products of the process are synthesis gas, which is filtered to remove dust and cooled, to extract the process heat. An example of a coal gasification process in current use is the high temperature Winkler process, where gasification is conducted using an autothermal (i.e. self-heating from the heat of reaction) fluidised-bed reactor at 1000 °C, in an air and steam mixture. Once again, up to 50 % plastics can be admixed with the coal but the quality of the synthesis gas produced can vary depending on the feed ratios of the reactants, temperature and reactant purity.

Fluidised-bed technology can be used not only in gasification but also in other chemical recycling processes, as discussed later, so a more detailed, general description of fluidised beds is given in Textbox 4.1.

Textbox 4.1 Fluidised-bed technology

If a gas is passed upward through a bed of solids with a velocity high enough for the particles to separate and become freely supported in the fluid, the bed is said to be 'fluidised'. Fluidised beds are used in the chemical industry because of their advantages over fixed-beds, including a more intimate contact between solids and gas, the high rates of heat transfer and the uniform temperatures within the bed.

In the applications for polymer recycling, particles of plastic are rapidly melted and coated on to sand particles and thus dispersed throughout the bed. The polymer cracks to lower molecular weight material at the high temperatures of the bed. The higher volatility components vaporise and are collected at the top of the reactor (as syngas, for example), leaving heavier fractions (such as wax) and metallic and mineral fractions to be collected at the bottom. Typically 80–90 % of the waste plastic feed is recovered in one form or the other.

Like other processes, plastics recycling in a fluidised-bed can generate unwanted byproducts. For example, if PVC is not separated out prior to treatment, the principle impurity in the hot gas stream is HCl from the thermal degradation of PVC. There is also a potential for generation of dioxins during this process and other impurities, including volatile metal chlorides. The HCl can be removed efficiently and cheaply by introducing calcium oxide (lime) into the bed. This also makes the fluidised-bed more attractive than a fixed-bed, where the gas clean-up has to be carried out separately. Generation of dioxins can be prevented by operating with a minimum gas residence time of 2 s and maintaining a uniform temperature in the bed, which is relatively easy to achieve in a fluidised-bed.

There are also a number of processes that have been developed specifically for gasification¹¹ of plastic waste and we will look at just two, namely the Purox system and the Andco-Torrex system, both of which use fixed-bed reactors.

The Purox System¹¹

The reactor for this system, shown in Figure 4.6, was developed by Union Carbide and uses pure oxygen as the gasifying agent. Metals are removed from the plastic waste by a

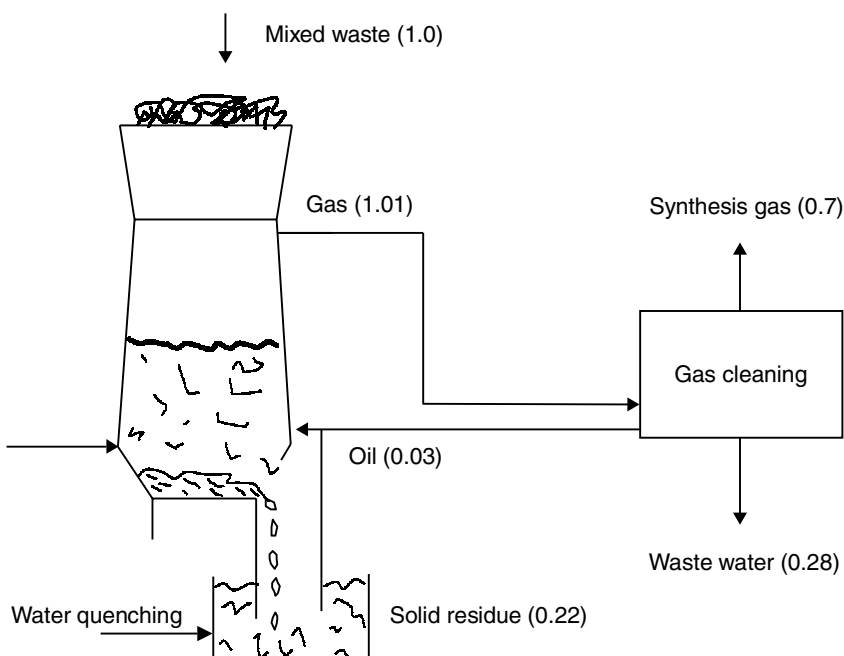


Figure 4.6 The Purox fluidised-bed gasification system¹¹ (the numbers in brackets in the figure show materials flows based on 1 tonne of solid waste). Reproduced with permission from Xanthos and Leidner, *J. Thermolytic Process, Makromolekulare Chemie (Die)*. Macromolecular Symposia, 1998, **135**, pp. 407–423. Copyright (1998) Wiley-VCH, Weinheim

magnetic shredder before it is fed into the reactor from the top. This allows the waste to dry and then burn more efficiently as it falls into the reactor at temperatures up to 1700 °C. The process generates fuel gas, a mixture of CO, CO₂, H₂ and water vapour. It contains 80% of the energy of the plastic waste and can be used directly as a fuel, or to produce methanol. However, prior to use it is first cleaned of suspended oils in an electrostatic precipitator and water vapour is removed by condensation. The oil is returned to the pyrolyser and the water is further treated to remove organics. The solid residue remaining in the pyrolyser (about 3% of the initial waste) is sterilised by the high temperatures, which reduces the disposal costs, but the cleaning unit and the need for pure oxygen make the whole process expensive.

Andco-Torrax System¹¹

In this process, the waste polymer is fed straight into the top of the vertical reactor (see Figure 4.7). It dries and burns as it falls in a stream of pre-heated air. Synthesis gas generated during thermal degradation mixes with nitrogen from the air and continues up the bed, where it is then dried before exiting the reactor. Compacted waste in the top zone acts as a seal that prevents the gases from escaping. Oil and wax, also products of degradation, fall into the combustion at the bottom of the reactor and burn, thus maintaining the reactor temperature at between 400 and 550 °C. Some of the oil droplets escape into the gas stream but are scrubbed by the descending waste and returned to the combustion zone.

Dilution of the gas stream with nitrogen means that its calorific value is half that of gas generated by the Purox reactor. However, the lack of a separate gas cleaning unit means that the exit temperature is high (400–550 °C), which makes it ideal for producing hot water and steam for heating.

In summary, the choice of the most suitable gasification process will depend on the composition of the waste stream and the desired

Key Facts

- The synthesis gas from the Purox process has higher energy (and economic) value than the nitrogen-diluted gas from the Andco-Torrax process, but the latter exits with a higher temperature, suitable for generating hot water or steam.
- The production of pure oxygen gas is an economically and environmentally costly process.

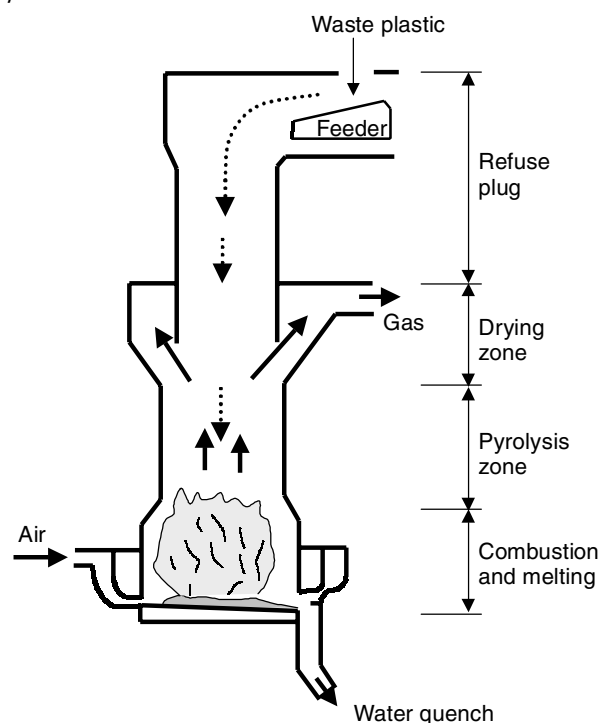


Figure 4.7 The Andco-Torrax fluidised-bed gasification system¹¹. Reproduced with permission from Xanthos and Leidner, *J. Thermolytic Process, Makromolekulare Chemie (Die)*. Macromolecular Symposia, 1998, **135**, pp. 407–423. Copyright (1998) Wiley-VCH, Weinheim

Key Facts 

- Pyrolysis involves the high temperature decomposition of polymers in the absence of oxygen.
- Typical products of pyrolysis are monomers, oligomers or others organic compounds.
- Pyrolysis is best suited to waste with a high hydrocarbon and low PVC content.

output. The highest value product is an H₂- and CO-rich synthesis gas, which can be used in the synthesis of methanol. The lowest value product is nitrogen-diluted fuel gas, which can be used for heat generation. Economically, the production of synthesis gas is obviously preferable, but relies on the availability of a suitably pure waste polymer feedstock and expensive oxygen feed. Gasification has a number of advantages compared to other chemical recycling processes, because of low capital cost and high product value, but it does rely on additional pretreatment processes to separate out waste plastics, which increases the running costs¹¹.

Pyrolysis

Pyrolysis is thermal decomposition at temperatures from 350–700 °C in the absence of oxygen and other gasifying gases. The polymers decompose to their monomers, oligomers and other organic substances that can be collected separately and used as a feedstock or for energy generation. Pyrolysis is most suitable for waste with high hydrocarbon contents, such as Municipal Solid Waste or mixed textiles waste. However, as in other chemical recycling processes, high PVC contents limit the application of some processes and additional pretreatment is necessary to reduce the PVC content. Pyrolysis of PVC itself yields hydrochloric acid or chloride salts, depending on the presence or absence of hydrogen and metal impurities and, potentially, toxic dioxins.

As there is no oxygen in the system, pyrolysis is not a combustion process but a set of complex reactions, which depend on the type of plastic and the nature of the process used. Several reaction pathways can be defined¹¹:

- decomposition into monomers;
- fragmentation of the principal chains into organic components of variable size;
- simultaneous decomposition and fragmentation to monomers/oligomers;
- elimination of simple inorganic components leaving charred residues;
- elimination of side chains, producing complex, cross-linked polymer structures.

The pyrolysis process can be carried out in a variety of reactor systems and we will again look at a few specific model systems.

BP Chemicals Pyrolysis Process

This process is still being developed and is currently operating as a pilot plant in Grangemouth, UK. It was developed and operated jointly by BP, Fina, DSM, Enichen and Ilochern together with the University of Hamburg¹².

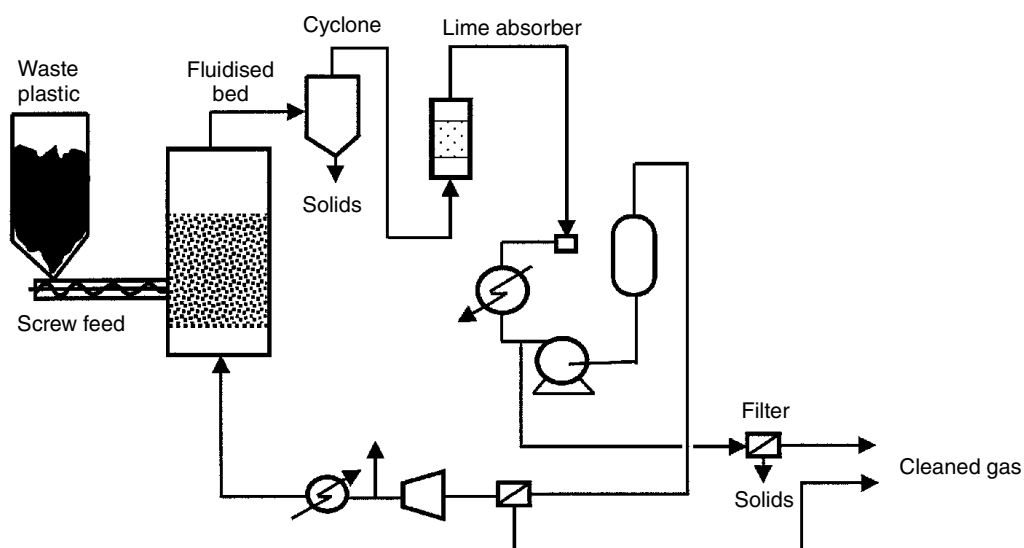


Figure 4.8 The BP pyrolysis process¹². Reproduced with permission from Xanthos and Leidner, *J. Thermolytic Process, Makromolekulare Chemie (Die)*. Macromolecular Symposia, 1998, **135**, pp. 407–423. Copyright (1998) Wiley-VCH, Weinheim

The BP process¹², shown in Figure 4.8, can be used at a relatively small scale to prepare feedstocks for existing refinery and petrochemical plants. After some preliminary preparation, such as size reduction and removal of most of the nonpolymeric materials, the waste is fed into a heated, fluidised-bed reactor. The reactor operates at 500 °C in the absence of oxygen and produces hydrocarbons, which vaporise and leave the bed with the fluidising gas. This then passes through a hot cyclone to remove solids, such as metals and coke, followed by hot lime to absorb acids and a filter to take out fine solids. The purified gas is cooled to condense out the heavier hydrocarbons, which can then be used in downstream processes, such as production of liquified petroleum gas (LPG) and gasoline products. The remaining, lighter hydrocarbons can be re-used in the reactor as fluidising gas, or as fuel for the reactor.

BASF Thermolysis Process

The BASF process⁹, which has a capacity for about 15 000 tonnes annually of plastic polymer waste, integrates both product recycling and energy recovery. The first step in the process, as shown in Figure 4.9 is liquefaction of waste at a temperature between 300 and 350 °C in a cascade of stirred-tank reactors. Pyrolysis takes place in a tubular cracking reactor at temperatures between 400 and 450 °C, followed by a two-step, cooling fractionation, first at temperatures of 330–380 °C and then at 110 °C, to produce mainly naphtha, olefins, aromatics and a heavy fraction. The naphtha can be used as a feedstock to a steam cracker to produce ethylene and propylene (and later polymers); the olefins can be processed to produce alcohol, amines and surfactants, and the heavy fraction can be gasified to produce synthesis gas for the manufacture of methanol.

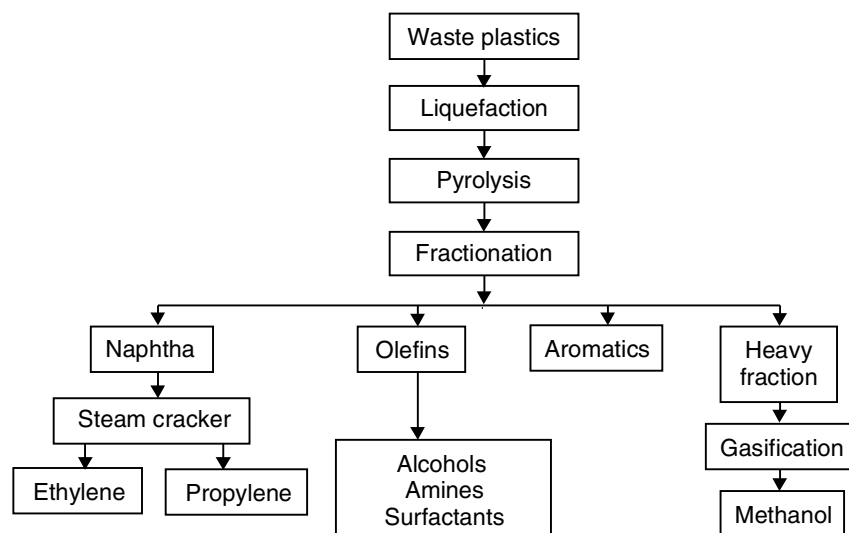


Figure 4.9 BASF integrated thermolysis plant⁹. Reproduced with permission from Sasse and Emig, 'Review: Chemical Recycling of Polymer Materials.' In *Chemical Engineering Technology* (1998), Vol. 21(10), pp. 777–789. Copyright (1998) Wiley-VCH, Weinheim

Fuji Process

The Fuji process is similar to the two above and is currently operated by Fuji Recycle Industries KK, Japan who have two plants with capacities of 400 and 5000 tonnes annually⁹. The special feature of the process is that ZSM5 zeolites are used to convert up to 80% of the hydrocarbon gas produced into mixed liquid petrochemical products.

Circulating Fluidised-Bed Pyrolysis System

This system produces the same gases as the Purox System described above, but without the use of oxygen¹¹. It uses two circulating fluidised beds with sand as the fluidising and heat transfer medium; one bed is used for pyrolysis at temperatures between 800 and 850 °C

Key Facts

- Pyrolysis products such as naphtha are steam cracked to form ethylene and propylene.
- Olefins are converted to alcohols and amines and heavy fractions are further gasified to produce synthesis gas, all of which products can be used as feedstocks for chemical synthesis of new materials.

Key Facts

- The capital cost of a hydrogenation plant is high, but this is offset by the high value of the synthetic crude oil product.

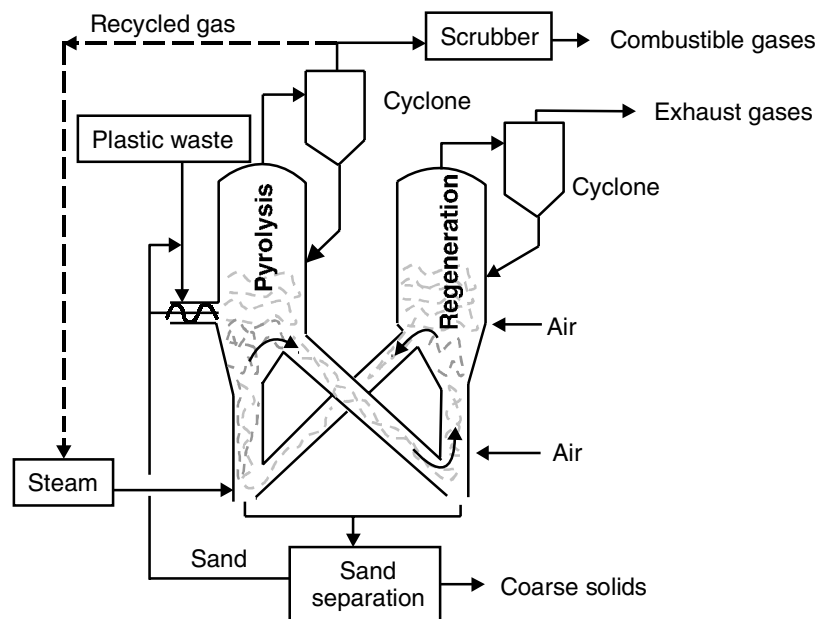


Figure 4.10 Circulating fluidised-bed pyrolysis system⁹. Reproduced with permission from Sasse and Emig, 'Review: Chemical Recycling of Polymer Materials.' In *Chemical Engineering Technology* (1998), Vol. 21(10), pp. 777–789. Copyright (1998) Wiley-VCH, Weinheim

and one for regeneration at 950 °C (see Figure 4.10). Solid waste, fed into the pyrolysis bed, is fluidised by superheated steam. Some of the products of the pyrolysis process are removed from the reactor to generate steam and some carbonaceous products are burned in the regeneration bed to generate heat for the pyrolysis process.

Hydrogenation

Catalytic hydrogenation was originally developed to gasify coal as methane and for the treatment of vacuum residues that are produced in large amounts by the petroleum refining industries. Plastic waste can also be introduced into a hydrogenation unit to produce bitumen and a synthetic crude oil, known as syncrude. In order to allow the waste to be mixed to higher proportions with vacuum residues, it is first depolymerised in a separate reactor. The melt from the polymerisation reactor is mixed with the residues and converted into syncrude by reaction with hydrogen. The syncrude is further refined for use in the petrochemical industry. Although hydrogenation processes have high capital costs, they are quickly recovered through the high value of the products.

The Bottrop and Bergius-Pier processes are two typical examples of hydrogenation technology.

The Bottrop Process¹³, shown in Figure 4.11, was developed by Veba-Oel AG. The plastic feed is depolymerised at a temperature of about 420 °C; the hydrocracking process then occurs in a bubble-column reactor in hydrogen at a temperature of 480 °C and pressure of 20 MPa. The main gaseous products are hydrocarbons and ammonia and the solid products are bitumen and syncrude. The main problem is that the process is sensitive to the presence of heteroatoms (e.g. sulphur, chlorine, nitrogen, etc.) in the polymer, which limits its usability.

The Bergius-Pier process¹³ is similar to the Bottrop process, but has the advantage of being able to handle heteroatoms efficiently by binding them to hydrogen to form acids, which are then neutralised to an easily deposited salt.

In summary, chemical recycling is a form of material recycling, which is particularly well suited to mixed plastics waste. These technologies, many still under development, break the plastics down into their chemical constituents that can be used to manufacture a wide range of new industrial intermediate and consumer products. In effect, the plastics are reprocessed at the place of origin, the petrochemical complex. This can be compared to

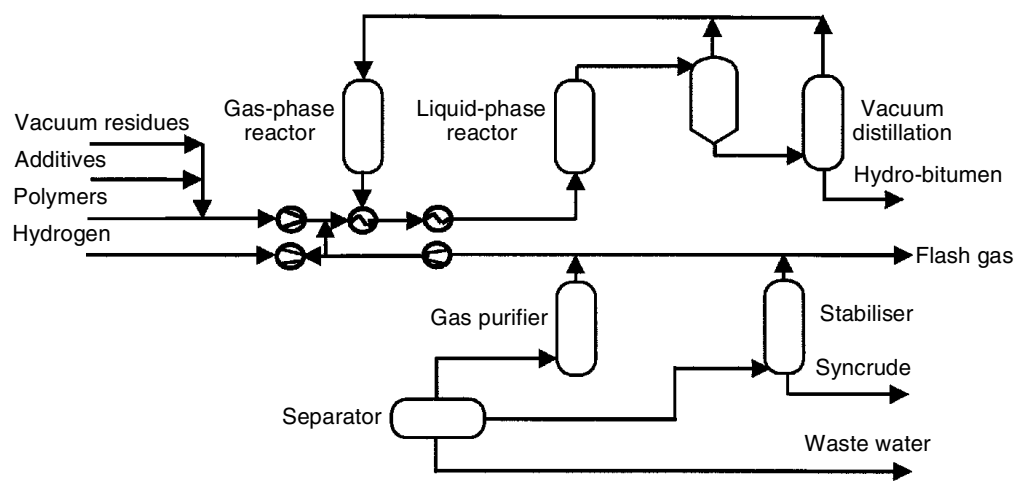


Figure 4.11 Flowchart of the Bottrop hydrogenation process¹³. Reproduced with permission from Mackey (1995), Review of Advanced Recycling Technology. Chapter 14 in 'Plastics, Rubber and Paper Recycling.' ACS Symposium Series. Vol. 609, pp. 161–169. Edited by Rader *et al.* Copyright (1995) ACS

paper recycling, whereby the waste paper is converted back to pulp for reprocessing into new paper-based products.

Many of these processes require high capital investment, which means that an additional 'gate fee' will be required in order to compensate for the investment costs of the unit. However, the payback period is reduced by the usually high value of the recovered products. In many cases, existing oil refinery and petrochemical plants can be adapted for plastics recycling, which reduces the capital costs.

The use of plastics as a chemical reactant in the production of the steel is another means of chemical recycling, but because it uses existing facilities it does not require capital investment. This option is described below.

Blast Furnace Reduction

Iron ore is reduced in a blast furnace using reducing agents such as carbon, carbon monoxide or hydrogen, and polymer waste agglomerate can be used as a substitute for heavy oil. Polymeric material is blown into the bottom of the blast furnace at a temperature of 2000 °C where it pyrolyses to form reducing gases and, at the same time, provides a source of heat. Hence, this process spans both chemical recycling and energy recovery. Because the chemical properties of polymeric materials and heavy oil are similar, heavy oil can be substituted by the same quantity of polymer. Almost 80% of the gases generated are utilised through a long blast furnace moving bed. As with most pyrolytic processes, the chlorine content must be kept low (<2%) to avoid chlorination and acid formation.

As is the case with other recycling technologies, some treatment of the plastics waste is required to ensure the specification of the recycling process is met. Although such treatment is generally less demanding than for example for mechanical recycling, an additional gate fee will be charged by the reprocessors.

Energy Recovery

If material recycling is for some reasons not viable, then energy can be recovered from the polymer waste as it has a high calorific value. Similarly certain polymeric products that have been removed from the waste stream destined for mechanical recycling may be recycled to recover energy, by either:

- burning in a municipal waste incinerator where plastics, together with other waste material, contribute to the generation of energy for heat and electricity;
- co-combustion, or mono-combustion, where plastics replace another fuel in varying proportions, thus displacing the need to use primary fossil fuels (e.g. in cement kilns).

Key Facts

- Plastics waste can be substituted for coal as a source of carbon in blast furnaces used for steel production, provided the PVC content is low.
- Plastics have a high calorific value and their stored energy can be recovered by burning them, either in an incinerator, or by substituting them for other fuels.

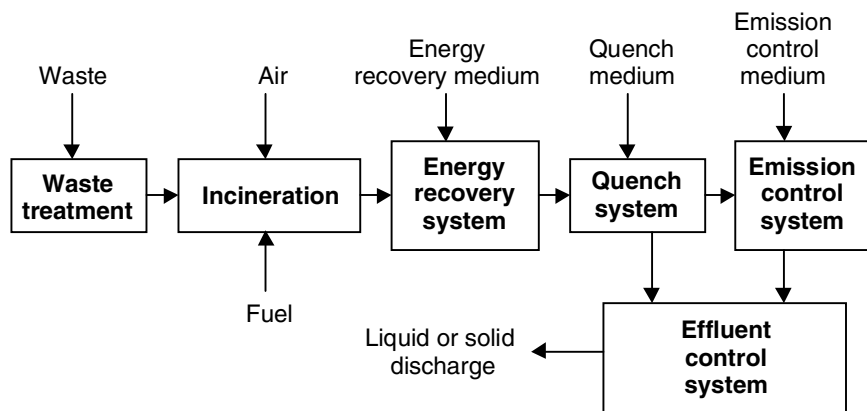


Figure 4.12 Flow diagram of an incineration system generating energy

Key Facts

- Incineration without energy recovery reduces the volume of waste but is not a sustainable recycling option, because it wastes valuable non-renewable resources and generates air emissions; combustor design and composition of the waste are important factors in reducing toxic emissions.

A schematic layout of an incineration system is shown in Figure 4.12. The type of incinerator used will influence the efficiency of energy recovery and emissions from combustion. The latter is a particularly sensitive issue because of public concerns over the possible health and environmental problems. Modern incinerators can keep the emissions to a minimum, provided the right operating conditions are chosen, depending on the waste properties and quantities to be treated. In the following sections we therefore examine the main incinerator types and discuss their advantages and disadvantages with respect to some of these issues. We will then look specifically at some of the issues surrounding emissions, from a scientific and technological viewpoint.

It should be noted that incineration without energy recovery is also possible but is not acceptable from the sustainability point of view because it only reduces the amount of waste, while wasting valuable nonrenewable resources. We do not therefore include it as one of the recycling options in this book.

The main types of incinerator currently in use can be categorised as:

- mechanical stoker,
- rotary kiln,
- fluidised-bed.

The stoker and rotary kiln designs have been in use since the 1970s and have the advantages of being relatively cheap to install and run, whereas the fluidised-bed technology is still under development and more expensive. It does have advantages of efficiency over conventional designs and also of better temperature control and distribution, which is important in controlling emissions.

Mechanical-Stoker Incinerator

This is the main type of incinerator for municipal solid waste. The waste is fed into the combustion zone by the operation of stoker gates or by a simple screw feed (see Figure 4.13) and heat is recovered using an exhaust heat boiler or as electrical power by utilising steam turbines. The schematic in Figure 4.13 shows a typical layout, with an integral boiler, which uses the hot combustion gases to generate steam or hot water.

Rotary Kiln Incinerator

The rotary kiln design¹⁴ is similar to the conventional mechanical stoker design above except that combustion occurs in an inclined, rotating cylinder (Figure 4.14). The pre-sorted plastic waste is fed by the rotating action of the kiln into the combustion zone at temperatures of about 1000 °C. The main advantage of the system is that the percentage of unburned material can be as low as 3%, but the technology is such that it is expensive and really only suitable for small applications, such as cement manufacture.

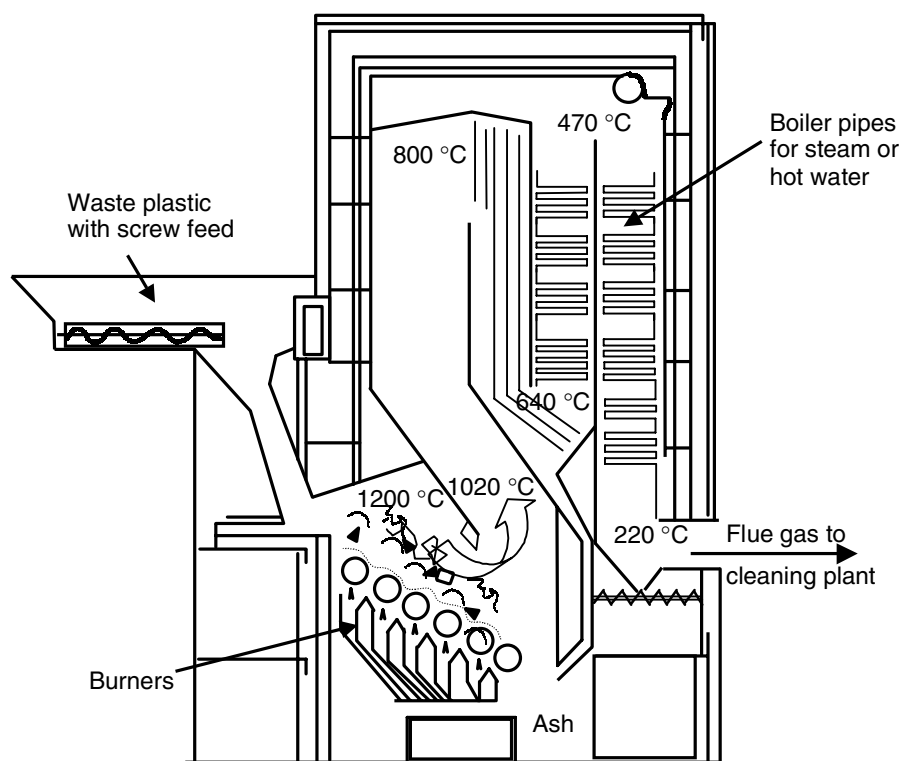


Figure 4.13 Schematic of a conventional mechanical-stoker incinerator

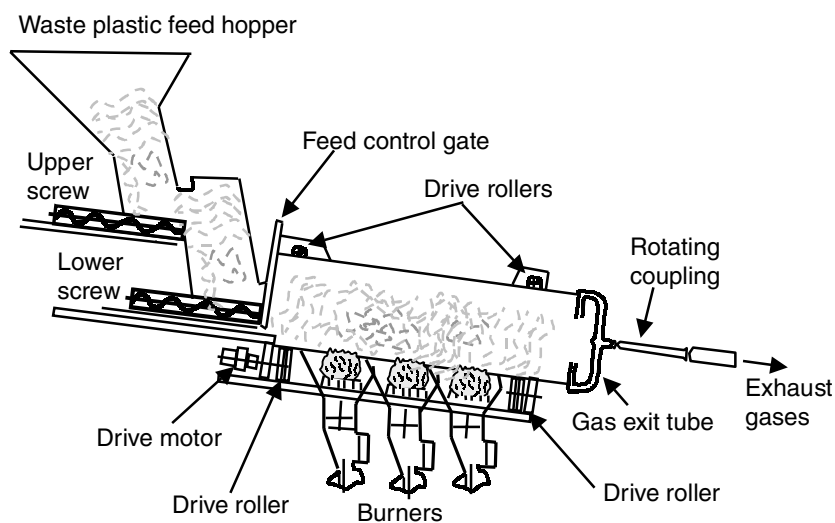


Figure 4.14 Body of a rotary kiln incinerator¹⁴. Reproduced with permission from J. Kabovoc (ed.). 'Recycling of Polymers'. In *Macromolecular Symposia*, **135**, 1998. Copyright (1998) Wiley-VCH, Weinheim

Fluidised-Bed Incinerators

Modern incinerator types are based on fluidised-bed technology, because of their simplicity of operation and freedom from problems associated with residual unburned fractions of waste. They are also suitable for MSW and direct combustion of waste plastic, rubber and tyres¹⁵.

The fluidised-bed incinerator, shown in Figure 4.15, uses sand as the combustion zone, because it can stand the high temperatures generated by the high calorific values of the waste stream. Incombustible materials such as metal and stones are taken from the bottom of the sand bed after the waste is incinerated. The temperature is more or less uniform throughout the bed. For more detail on fluidised-bed technology, including the emission prevention methods, see Textbox 4.1.

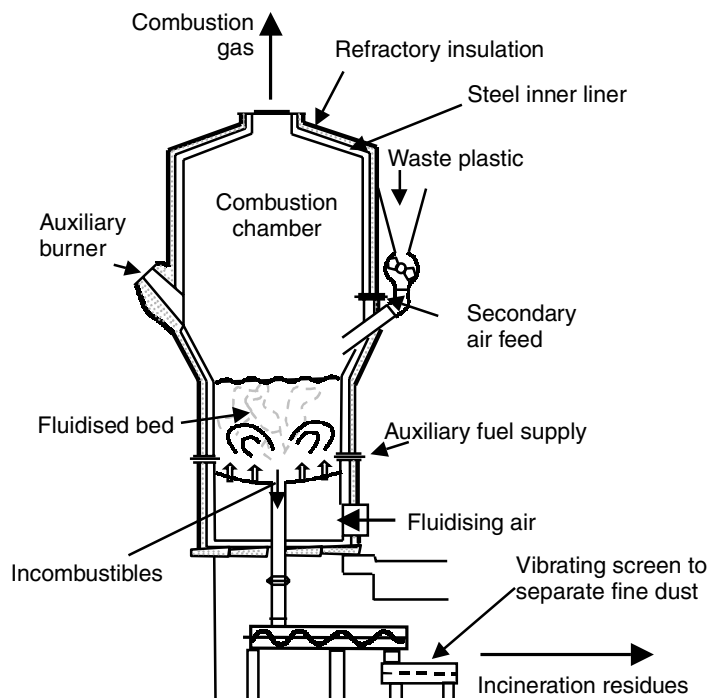


Figure 4.15 Structure of a fluidised-bed incinerator¹⁴. Reproduced with permission from J. Kabovoc (ed.). 'Recycling of Polymers'. In *Macromolecular Symposia*, **135**, 1998. Copyright (1998) Wiley-VCH, Weinheim

Advantages of this type of incinerator are that:

- the combustion is easy to control;
- the system operation is simple;
- the exhaust gas treatment is not complicated;
- waste volume reduction is very good.

Energy can be recovered in the form of hot water, steam or electricity. Electricity generation is more economic in a larger plant, so small and medium plants tend to go for production of hot water or steam. Plant operating conditions vary widely around the world. The power generating incineration plants in Europe and the United States have steam conditions in a pressure range of 4–10 MPa and temperatures of 370–500 °C. Germany uses pressures in the range up to 20 MPa and temperatures up to 540 °C, but Japan uses temperature and pressure conditions of around 2.5 MPa and 280 °C. Lower temperatures mean lower thermal efficiency, but prevent high temperature corrosion by chlorine, which can reduce generation efficiency by up to 14%¹⁴. Designs that superheat the steam from the exhaust heat boiler using the exhaust gas from the power generating gas turbine increase the overall efficiency by as much as 30%.

New technologies are continually being developed to process waste in all shapes and forms and the reader is referred to Chapter 8 for a summary of some of the newer ideas and processes currently being developed.

Incinerator Emissions

As we have already highlighted, energy recovery from end-of-life plastics can only be considered a sustainable option if the environmental costs of incineration do not exceed the benefit of energy recovery. Hence, it is important to minimise the emissions from incineration. The gaseous pollutants often present in the flue gas include CO, HCl, SO₂, NO_x, particles, heavy metals and dioxins and furans. The latter two often collectively referred to as simply dioxins, are in particular a subject of a continuing debate between the proponents and opponents of incineration over the levels of emissions and the related human toxicity. The literature body on the formation and control of dioxins is vast and a further discussion

Table 4.4 Comparison of the existing and proposed EC Directives on incineration¹⁷. Reproduced with permission from NSCA (2000). *Pollution Handbook 2000*. Copyright (2000) National Society for Clean Air and Environmental Protection, Brighton.

Pollutant	EC Directive 89/369 (for MSW > 3 tonnes h ⁻¹) (mg Nm ⁻³) ^{a, b}	Proposed Directive (covering both MSW and hazardous waste) (mg Nm ⁻³ , as daily average)
Total dust	30	10
Heavy metals (total):	6.2	0.6 ^c
Pb + Cr + Cu + Mn	5	
Ni + As	1	
Cd + Hg	0.2	
Hydrochloric acid (HCl)	50	10
Hydrofluoric acid (HF)	2	1
Sulphur dioxide (SO ₂)	300	50
Carbon monoxide (CO)	100	50
Organics (as total C)	20	10
NO _x (NO and NO ₂)	–	200
Dioxins and furans	–	0.1 ng m ^{-3d}

^aEmission limits are expressed as a function of the capacity of the incineration plant; the example shown corresponds to the plant with the capacity of greater than 3 tonnes h⁻¹ of waste. Combustion gases must be kept at least 850 °C for 2 s in the presence of at least 6% oxygen. The emissions are expressed based on a standard gas condition of 101.325 kPa, 0 °C, 11% oxygen or 9% carbon dioxide, dry gas.

^bNm³ Gas volume at standard conditions (N stands for 'normal' or standard conditions)

^cExpressed as average value over sample period, min. 30 min, max. 8 h.

^dExpressed as average value over sample period, min. 6 h, max. 8 h.

of this subject is outside the scope of this book. However, for a technically minded reader, a good overview of dioxin formation and control mechanisms can, for example, be found in a paper by Acharya *et al.*¹⁶

Most countries now regulate gaseous and solid discharges from incineration and, as an example, Table 4.4 lists the existing and proposed EC gaseous emission limits. It is apparent that the proposed emission limits are in some cases much more stringent than the existing values, particularly for heavy metals, HCl and SO₂. The proposed directive also includes limits on dioxins, which the existing directive does not regulate.

These new emission limits can be achieved by the use of best available techniques, which should include the following:

- a control system for the supply of primary and secondary air (to control emissions of CO, NO_x and dioxins);
- control of temperature and residence times in the combustion chamber, boiler and flue treatment units (to prevent formation of dioxins);
- a flue gas treatment system, including cyclones, electrostatic precipitators and filters (for fly ash removal), scrubbers (to remove HCl, HF, SO₂), activated carbon beds (for heavy metals and dioxins) and selective catalytic reduction (for NO_x and dioxins).

A recent study sponsored by the plastics industry investigated co-combustion of plastics with MSW¹⁸ and emissions from incineration. The study concluded that the addition of plastics waste to MSW can be beneficial to the combustion process. Depending on the quantity added, there can be an improvement in combustion efficiency, together with an overall improvement in combustion stability. According to this study, there was no increase in dioxins concentrations in the effluent gases, even with the inclusion of 8–10% w/w of PVC (precursor for the formation of dioxins), which is the European market average. With the addition of lime and activated carbon to the scrubbing system, the concentrations of dioxins could be kept to less than 10% of the permitted daily limit (*i.e.* 0.01 ng m⁻³). The study also examined the potential for energy recovery of polyurethane- and polystyrene-based building and insulation foams which can present special challenges for waste management

Key Facts

- Incinerators emit potentially toxic products, the levels of which are regulated by national and international standards.
- CO, NO_x and dioxins in effluent gas can be minimised by controlling the operating conditions of the incinerator.
- Dioxin emissions are further limited by controlling combustion temperature and residence times.
- Flue gas scrubbers are used to control ash, acids, heavy metals, NO_x and dioxins.

because of the presence of chlorofluorocarbons (CFCs) used at one time as blowing agents, and of flame retardants based on bromine, chlorine and phosphorus. Trials in this study demonstrated that co-combustion with MSW is an environmentally recommended option for these foams.

4.4 SUMMARY AND LEARNING OUTCOMES

In this chapter we have examined and discussed some of the current technologies available to identify, sort, separate and process polymer waste. After studying the material in this chapter, you should be able to understand the following technological aspects of polymer waste management:

- the main recycling options and when it is appropriate to use them;
- how polymers can be identified in the waste stream and sorted from it;
- the main technologies for mechanical and chemical recycling and energy recovery;
- advantages and disadvantages of different options and their implications for sustainability.

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