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Introduction to Feedstock Recycling of Plastics

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ABBREVIATIONS
ABS  acrylonitrile–butadiene–styrene
APP  atactic polypropylene
ASR  automobile shredder residue
EVA  ethylene vinyl acetate
HDPE high-density polyethylene
HIPS high impact polystyrene
LDPE low-density polyethylene
Low (LD)PE low-molecular-weight polyethylene
MSW municipal solid waste
MW molecular weight
PA polyamides, Trade Name Nylons
PC polycarbonate
PE polyethylene
PET polyethylene terephthalate
PIB polyisobutylene
PP polypropylene
PS polystyrene
PTFE polytetrafluoroethylene, Trade Name Teflon
PU or PUR polyurethane
PVC polyvinyl chloride
WEEE waste electric and electronic equipment

1 INTRODUCTION

This review focuses on some technical and practical aspects of the pyrolysis or thermal cracking of waste plastics, to yield liquid fuels and monomers as a main product. It
briefly enumerates some alternative products, such as synthesis gas, carbon, hydrogen chloride, or bromine, or techniques, such as combustion, partial oxidation or gasification, or feedstock recycling by chemical rather than thermal methods.

Some of the practical aspects to be considered are:

- the adequate availability and ensured supply of waste plastics,
- their collection, transportation, handling, storage, pre-treatment, and conditioning for feedstock recycling;
- their general management, as well as the typical cost of such operations.

2 NOMENCLATURE

Plastics are a generic group of synthetic or natural materials, composed of high-molecular chains whose sole or major element is carbon. In common usage the terms plastics, polymers and resins are roughly equivalent. A plastic material is (Society of Plastics Industry, cited in Brady and Clauser, [1]) ‘any one of a large group of materials consisting wholly or in part of combinations of carbon with oxygen, hydrogen, nitrogen, and other organic or inorganic elements which, while solid in the finished state, at some stage in its manufacture is made liquid, and thus capable of being formed into various shapes, most usually through the application, either singly or together, of heat and pressure.’

Plastics are manufactured from monomers, i.e. a repeatable molecular unit and building block, by means of various chemical processes, such as:

- a catalytic or peroxide-initiated polymerization of monomer(s), e.g. ethylene, propylene, or butadiene + styrene (copolymers);
- a polycondensation of dissimilar monomers (e.g. bifunctional organic acids and alcohols or amines);
- polyaddition of reactive monomer molecules.

Especially the first group forms an attractive feedstock for pyrolysis processes.

Important monomers are polymerization grade (i.e. very high purity) ethylene, propylene, butadiene, three products obtained by thermal cracking or pyrolysis of e.g. naphtha, light gas-oil, or liquefied petroleum gases (LPG = propane or butane) and purified by low-temperature, high-pressure distillation, up to polymerization grade chemicals. Adding hetero-atoms to the monomer, such as chlorine in vinyl chloride monomer, creates additional difficulties in pyrolysis processes and methods for separating waste plastics at the source or by mechanical means, e.g. sink/float, froth flotation, separation after identification on the basis of absorption or reflection spectra, or electrostatic sorting after tribo-electric charging, is an important practical consideration.

Before its conversion into plastic products the resulting resin is almost always compounded with various additives of different nature and constitution, meant to improve processing, stability, or mechanical specifications as a function of a given application (outdoors, i.e. UV-light exposed, oxidation, high-temperature processing). Such additives are regularly used as:

- antioxidants (1%),
- heat and light stabilizers (5%),
- plasticizers (40%),
• impact resistance enhancers (10%),
• pigments, colorants and dyestuffs (5%),
• flame retardants (15%),
• mould-release agents,
• foaming agents (2%),
• fillers (40%)

(maximum amount encountered, in weight percent). Other additives are used as anti-blocker, anti-fogging and anti-static agents, bio-stabilizers, chemical blowing agents, cross-linking agents, high polymeric impact strength additives and processing aids, lubricants, metal deactivators, optical brighteners, property modifiers, reinforcements, smoke and afterglow suppressants, wetting agents, etc. Their presence, as well as chemicals used in initiating or terminating polymerization, is a complicating factor in feedstock recycling, also termed chemical recycling or, in a more restricted sense, pyrolysis or thermal cracking of waste plastics, since their nature, amount, and behaviour during pyrolysis (thermal volatilization or breakdown) and eventual influence upon reaction products and mechanism are somewhat unpredictable, especially for waste plastics of unknown origin and formulation. PVC absorbs more additive volume than any other resin.

Plastics can be classified on the basis of numerous criteria, e.g.:

• chemical composition, directly connected with the nature of the monomer(s) and the method of polymerization. Plastics are thus subdivided into classes, e.g. polyolefins, vinyl polymers, styrenics, polyamides, polyesters, epoxy resins, polycarbonates, polyurethanes, etc.;
• chemical structure, e.g. linear (high-density polyethylene), branched (low-density polyethylene), cross-linked and three-dimensionally networked (thermosets, rubbers);
• stiffness: elastic, flexible, or rigid;
• type of application: commodity vs engineering, general purpose vs specialty plastics;
• processing method used (injecting moulding, extrusion, film blowing, blow moulding, thermoforming, casting, calendaring, and many other techniques);

Thermoplastics still soften when heated and harden again when cooled, because there is little or no bonding between individual molecular chains. Thermosets show three-dimensional structures and rather than softening, thermally decompose while heating. All commodity plastics are thermoplastic.

Rubber has a structure intermediate between thermosets and thermoplastics, with molecular chains linked by sulphur bridges during vulcanization. In pyrolysis, the main material is tyre rubber, a compound of styrene- butadiene- and isoprene-based rubber (SBR), of carbon black, sulphur, vulcanization aids, and zinc oxide.

The history, statistics, classification, barrier properties, main resins of bulk plastics, etc. can be read from websites [2], with typical applications [3]. Plastics also show some other characteristic properties:

• an amorphous, i.e. noncrystalline structure, related to disorder among polymer chains;
• low thermal conductivity;
• high electrical resistance;
• low softening temperatures;
• viscous–elastic behaviour.
The world production of plastics keeps rising, and so does waste generation, albeit with a time lag, dictated by lifetime. This lifetime spans from weeks (packaging), over months (agricultural film) and years (cars, household appliances, furniture), even to the order of a century (in some building applications). In numerous building applications (water distribution ducts, flooring, roofing, window frames) such lifetimes are not known with certainty. Still, take-back schemes more and more affect important markets, such as packaging, automobile, or electrical and electronic equipment. Such schemes are still developing, confronted with the immense variety in applications, resins, additives, and with the difficulty in identification and light weight of plastics.

Plastics waste arises at the levels of production, conversion, and consumption. In the first two categories source separation, identification, and recycling, is straightforward. Such simple source separation concepts no longer hold for post-consumer recycling, where entropy is immense: plastic products both geographically and functionally are widely spread, more often than not compounded with unknown additives, or mixed, soiled, composite, and difficult to collect at a reasonable cost.

Mechanical recycling, i.e. reusing as a plastic material in similar applications (closed-loop recycling, e.g. film-to-film) provides the highest value to waste plastics. Loss in mechanical properties restricts recycling to simpler applications and geomembranes, sometimes simply replacing low-grade wood, as in urban furniture, such as park benches. Feedstock recycling converts plastics into monomer, mixes of chemicals, or into synthesis gas or reducing gas. Thermal recycling (combustion) merely recovers the heat of combustion.

3 PYROLYSIS OF PLASTICS AND RUBBER

Pyrolysis, also termed thermolysis (Greek: pur = fire; thermos = warm; luo = loosen), is a process of chemical and thermal decomposition, generally leading to smaller molecules. Semantically, the term thermolysis is more appropriate than pyrolysis, since fire implies the presence of oxygen and hence of reactive and oxygen-bearing intermediates. In most pyrolysis processes, however, air is excluded, for reasons of safety, product quality, and yield.

Pyrolysis can be conducted at various temperature levels, reaction times, pressures, and in the presence or absence of reactive gases or liquids, and of catalysts. Plastics pyrolysis proceeds at low (<400°C), medium (400–600°C) or high temperature (>600°C). The pressure is generally atmospheric. Subatmospheric operation, whether using vacuum or diluents, e.g. steam, may be selected if the most desirable products are thermally unstable, e.g. easily repolymerizing, as in the pyrolysis of rubber or styrenics.

The thermal decomposition of polymers yields gases, distillates and char, albeit in widely variable relative amounts. These can be applied as fuels, petrochemicals, and monomers. Depending on the polymers or polymer mixtures fed and the operating conditions used, yields can vary widely. As a rule both gaseous and liquid products are mixtures of numerous different compounds. The problem of fractionating these effluents and upgrading to commercial specifications, while separating undesirable impurities, must be investigated on a case-by-case basis. The char incorporates fillers, pigments, and ash.

Pyrolysis processes involve breaking bonds and are often endothermic, so that ensuring a supply of heat to the reacting material is essential and generally rate-determining. Partial
oxidation supplies such heat internally, but the pyrolysis products are diluted by oxidation or combustion products.

Polyolefin resins contain only carbon and hydrogen, and additives, such as some antioxidants and UV stabilizers. Moreover, the presence of hetero-elements, such as chlorine and bromine is undesirable, as these elements distribute over the three product phases-gas, liquid, and solids, reducing the market potential and value of each of these. Studying their elimination is a major consideration in developing processes for mixed plastics.

3.1 SURVEY OF PREVIOUS WORK

Most work on plastics pyrolysis has been academic and directed at the analysis of polymers, their molecular structures and thermal stability, at the study of pyrolysis products, e.g. fire research, or at feedstock recycling at a laboratory or pilot scale. An early survey was given by Madorsky [4]. Given the large number of possible purposes, or different resins, additives, and operating conditions, the field is as wide as the sky!

Since the introduction of modern instruments (ca 1962) the thermal analysis of polymers as a research field has expanded very rapidly, encompassing specific techniques such as:

- differential scanning calorimetry (DSC), for measurements of specific heat and enthalpies of phase transition;
- differential thermal analysis (DTA), measuring the temperature difference between the sample and a reference and indicating the occurrence of any heat effect and of abrupt changes in heat capacity;
- thermogravimetric analysis (TGA), for assessing thermal stability and decomposition temperatures;
- thermomechanical analysis (TMA), for establishing the mechanical response of polymer systems to temperature changes. It includes dilatometry, penetration, torsion modulus, and stress/strain behaviour, as well as establishing the softening temperature, as determined by the Vicat penetration test, the deflection temperature or heat distortion test, the zero strength temperature test, the polymer melt or stick temperature test;
- flammability testing. Plastics used in furniture, mattresses, cars, electronics, etc. must satisfy specifications regarding fire behaviour and flame retardancy.

These techniques are often coupled with evolved gas analysis. TGA is a basic technique in studies on thermal decomposition. An excellent introduction is given in [5]. A systematic study of both physical and chemical aspects in plastics pyrolysis was launched in the E.U. Cycleplast project [6], aiming at a systematic scientific evaluation of various steps. The (German) Society for Thermal Testing listed methods relating to thermal testing [7]. Since 1965, prestigious, at present biannual meetings on Analytical and Applied Pyrolysis have been chaired by authoritative scientists such as G. Guiochon (1965), C.E.R. Jones (1972), J. Kistemaker (1976), T. Szekely (1979), K.J. Voorhees (1982), I. Lüderwald & H.-R. Schulten (1984), C. Gutteridge (1986), I. Ericsson (1988), J.J. Boon (1990), W. Kaminsky (1992), S. Tsuge (1994), G. Audisio (1996), A. Kettrup (1998), F.J. Gonzalez-Vila (2000), J. Fink (2002), R. Font & A. Marcilla (2004), and M. Blaszo (2006). Themes such as instrumentation and analytical methods, elucidation of chemical structure, thermo-oxidation and photo-oxidation, mechanisms and kinetics are much more central in such work than is feedstock recycling.
On the industrial side, there has been a lively interest in plastics pyrolysis, since the breakthrough of mass production of plastics in the 1960s. A major tribute is to be paid to a first wave of Japanese enterprise, actively promoting plastics pyrolysis as a technical solution. New initiatives in Japan were launched in the 1980s and 1990s, such as the double fluid bed systems operated by Ebara Co. (Stardust Project, Yokohama), and, with less success, Tsukishima Kikai. At present these steady efforts are culminating in nationwide pyrolysis systems for converting waste plastics, separately collected from households, to yield liquid fuels and monomers, or used as a reducing agent in blast furnaces or as a coal substitute in coking plants. Plastics are converted in liquid phase, stirred tank reactors in plants at Niigata and Sapporo, PVC in rotary kiln units to coke and HCl by the former Nihon Kokan (at present JFE Holdings). Ube Industries jointly with Ebara Co. have developed an elevated pressure gasification process; the synthesis gas is cleaned and piped to a synthesis plant at the same site.

Japanese ventures were confronted with their counterparts in Europe and the USA during the International Symposia on Feedstock Recycling from Plastics, or ISFR, held at Sendai (1999), Ostend (2002) [8, 9] or at Karlsruhe (2005).

3.2 PRODUCTS FROM POLYMERS

3.2.1 Major Operating Conditions

The major factors of influence determining the product distribution resulting from plastics pyrolysis are summarized in Table 1.1.

Chemical composition plays a dual role:

1. Mass conservation dictates that the pyrolysis products, distributed over the three phases, gas, liquid, and solid, consist of the same elements as the raw materials and that their relative amounts are conserved. There is a redistribution of relevant elements during pyrolysis, with hydrogen and chlorine enriching the gas phase, carbon in the coke.

2. There is a direct link between polymer structure and its primary pyrolysis products, the latter primarily resulting from the breakage of bonds followed by some molecular or free radical rearrangement. Of course, secondary reactions do occur and gradually convert the primary products into more stable, less reactive alternatives. The product distribution hence depends on time, and relative rates of bond breakage and subsequent processes, but can be found only by experiment. As a rule, bond breakage becomes easier at high temperature.

Temperature is the most important operating variable, since it determines both the rate of thermal decomposition and the stability of feedstock and reaction products. High temperature (>600°C) and both vacuum and product dilution favour the production of simple small gaseous molecules, low temperature (<400°C) and increased pressure lead to more viscous liquid products, higher rates of pyrolysis, a higher coking tendency, more secondary products and dehydrogenation.

Pyrolysis, for most plastics, begins at ∼300°C and for some thermosensitive resins even earlier, e.g. for vinyl-based polymers. The onset of the pyrolysis reaction is strongly influenced by the presence of additives, such as stabilizers, plasticizers and pigments. In most processes a medium temperature (400–500°C) is selected and the plastics are in
### Table 1.1 Factors affecting product distribution

<table>
<thead>
<tr>
<th>Factor of influence</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition of the resins</td>
<td>The primary pyrolysis products relate directly to the chemical structure and composition of the resin, and also to the mechanism of its decomposition (purely thermal or catalytic)</td>
</tr>
<tr>
<td>Pyrolysis temperature and heating rate</td>
<td>Higher operating temperatures and high heating rates both enhance bond breaking and favour the production of small molecules</td>
</tr>
<tr>
<td>Pyrolysis time</td>
<td>Longer residence times favour a secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>Low pressure reduces the condensation of reactive fragments forming coke and heavies</td>
</tr>
<tr>
<td>Presence of reactive gases, such as (air) oxygen or hydrogen</td>
<td>Such presence internally generates heat, dilutes the products and influences upon equilibriums, kinetics, and mechanisms</td>
</tr>
<tr>
<td>Use of catalysts</td>
<td>Their use influences upon kinetics and mechanisms, and hence, the product distribution</td>
</tr>
<tr>
<td>Additives incorporated</td>
<td>The additives generally either evaporate or decompose. Some may influence kinetics and mechanism</td>
</tr>
<tr>
<td>Liquid or ‘gas’ phase</td>
<td>Liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions</td>
</tr>
</tbody>
</table>

A molten state. ‘Gas phase’ processes feature liquid polymer films, distributed over the grains of fluidized bed pyrolysis reactors.

The required reaction time is determined principally by reaction temperature. The formation of primary products, e.g. monomers, is favoured by short residence times, the formation of more thermodynamically stable products (H₂, CH₄, aromatics, carbon) by long ones. Low pressure (under vacuum, or in the presence of inert diluent) favours the production of primary products, including monomer, high pressure that of complex, liquid fractions.

The reactor type is selected mainly on the basis of technical considerations, mainly its heat transfer and feed and residue handling characteristics. In many processes proposed the polymer is first dissolved in a bath of molten polymer or wax, or dispersed in a salt bath, to reduce the viscosity of the melt. Other processes suggest the use of the excellent heat transfer and mixing properties of fluidized bed thermal or catalytic reactors. Increasing temperatures has an influence upon thermodynamics, i.e. the relative stability of various products, as well as upon kinetics and physical conditions of the reacting mixture. High temperatures and heating rates, low pressures and residence times favour the formation of primary products. Conversely, long residence times lead to a preponderance of stable products. In the Hamburg pyrolysis process developed by Professor Kaminsky and Professor Sinn, conditions were so selected that the main output was aromatics, whatever the feedstock.
In the presence of oxygen, part of the feedstock is oxidized (partial oxidation) and carbon monoxide and dioxide are inevitable products, while oxygenated organics are also arising as by-products. The process is termed *gasification* when the production of combustible gas or synthesis gas is emphasized. Gasification is a high temperature process that completely destroys the original chemical structures. However, the resulting gas is tailor-made to requirements using well-known and large-scale techniques.

Pyrolysis or gasification, as processes, are both much easier to control than direct firing of plastics. The latter is impossible on mechanical grates, equipping conventional incinerators for municipal solid waste (MSW). On the other hand, thermal conversion is feasible by means of fluidized bed technology. The few percent of plastics, as in traditional MSW is unproblematic and the calorific content is converted into heat and often into power, albeit at a disappointing level of conversion efficiency, of the order of 15–25%.

Theoretically, waste plastics have excellent fuel value, quite comparable to that of gas oil, when only polyolefins are considered. Introducing hetero-atoms, such as oxygen, nitrogen, or chlorine, reduces the heating value. Moreover, chlorine acts as an inhibitor and generates strongly acid gas. In practice, however, plastics are difficult to burn, because of an almost uncontrollable combustion rate, locally leading to oxygen deficiency and products of incomplete combustion.

Hydrogenating conditions lead to the elimination of hetero-atoms and yield more saturated products as well, an important consideration regarding the marketing of pyrolysis products.

*Catalysts* are a class of compounds specially selected, designed and optimized for influencing the reaction mechanism. The main purpose of catalysts is to convert vapour-phase products into a higher-octane petrol (gasoline). Another purpose may be in accelerating decomposition, using acids and bases for promoting the decomposition of polyamides and polyesters. Throw-away catalysts may be used for scavenging impurities. Catalyst activity, selectivity, and stability are major considerations. Some research directions can be derived from the themes of 2nd ISFR papers [9]:

- catalytic cracking of polyolefins, possibly containing EVA, by J. Aguado et al.;
- the presence of polycyclic aromatic hydrocarbons in the product fractions, by P.T. Williams and R. Bagri;
- co-catcracking with residues from light Arabian crude, by M. F. Ali;
- comparison of fresh, steam deactivated, and used FCC catalyst, by S. Ali and A. Garforth;
- PP and PET cracking over TiO$_2$/SiO$_2$ catalysts, by K. Nakano et al.;
- using red mud as a low-grade hydrocracking catalyst by J. Yanik et al.;
- hydro-cracking of MSW-plastics with vacuum gas oil by T. Karayildirim et al.;

*Catalytic cracking* is potentially an important route to produce high-value products from plastic feedstock. The catalyst converts naphtha to higher-value petrol (gasoline). Little is known on the effect of fillers or coke precursors (styrene, butadiene) on catalytic activity and catalyst fouling, coking, or clogging. Another area of interest is the effect of catalyst addition on the thermal decomposition in the liquid phase. It seems unlikely that the macromolecules can contact the internal catalyst surface in a productive fashion. Some additives may also influence the product distribution by modifying the cracking mechanism and hence, product distribution. Generally, their effect is unknown but also often much smaller than that expected from catalysts.
3.2.2 Decomposition Modes

As a rule, the pyrolysis of plastics follows complex routes that cannot be described by one or more chemical reactions, but only and still rather imperfectly by either empirical formulas featuring fractional stoichiometric coefficients or comprehensive systems of elementary reactions, i.e. reactions that really proceed as written. Moreover, the composition and structure of these reaction systems may vary with details of molecular structure, such as chain irregularities, incorporation of initiators or catalysts, etc. As a consequence, precise mechanisms are of only scientific interest, an industrial approach being limited to overall considerations, such as the heat effect and the product distribution resulting under particular reaction conditions.

Decomposition modes are often subdivided according to the prevailing reaction patterns, which are mainly dictated by molecular structure and the presence of catalysts:

1. Decomposition into monomer units (PMMA, PA 6) mainly, often termed *unzipping*. This decomposition mode is of very large practical interest, since monomer is a high-value product, typically commanding a price several times the equivalent of fuel value. The pyrolysis of PMMA is in general use and economically warranted, with typical scrap prices of the order of 300–400 €/tonne, monomer yields well in excess of 90%, and monomer values of the order of up to 1500 €/tonne. Hence, PMMA waste is highly valued! The MMA generated is not necessarily fit as polymerization grade, and often used as a viscosity index improver of lubricating oil, in acrylic varnishes, rather than as a monomer.

2. *Random fragmentation* of the principle polymer chain (PE, PP) into fragments of variable, intermediate length. The size distribution over the resulting fragments is largely Gaussian, with the average M.W. continuously descending with rising pyrolysis temperature and time. Thus, polyolefins are converted into PE waxes and oils, often high in α-olefins and a sulphur-free, premium diesel oil. Conversely, PP products yield a much more branched product mix.

3. Decomposition according to both previous schemes combined (PS, PIB). In a polystyrene production plant, PS could conveniently be converted into monomer, since facilities for separating the various pyrolysis products (styrene and its oligomers, ethylbenzene, toluene, benzene, etc.) are available already on site. However, huge PS production plants generally generate insufficient off-spec. scrap to feed a pyrolysis unit of even a small industrial size!

4. *Elimination of simple, stable molecules* from adjacent atoms (PVC yields HCl, PVAc yields acetic acid, PVOH yields water). Such thermal cleavage leaves unsaturated, charring, residual chain residues.

5. *Elimination of side-chains*, followed by cross-linking and creating a porous charred residue, including the non-volatile additives. This scheme is followed by most thermosets and other cross-linked polymers.

Polymer resins and their major possible products are collected in Table 1.2. A high purity of the feedstock is the best guarantee of clean and possibly marketable products. Generally, the value of the products obtained is insufficient to warrant the process. However, recently the concept of feedstock recycling created a political current that is more favourable to pyrolysis than the corresponding economic context.
Table 1.2  Polymer resins and major possible products of thermal decomposition

<table>
<thead>
<tr>
<th>Resin</th>
<th>Mode of thermal decomposition</th>
<th>Low-temperature products</th>
<th>High-temperature products</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Random chain rupture</td>
<td>Waxes, paraffin oils, α-olefins</td>
<td>Gases and light oils</td>
</tr>
<tr>
<td>PP</td>
<td>Random chain rupture</td>
<td>Vaseline, olefins</td>
<td>Gases and light oils</td>
</tr>
<tr>
<td>PVC</td>
<td>Elimination of HCl from the chain, chain dehydrogenation and cyclization</td>
<td>HCl (&lt;300°C), benzene</td>
<td>Toluene (&gt;300°C)</td>
</tr>
<tr>
<td>PS</td>
<td>Combination of unzipping, and chain rupture, forming oligomers</td>
<td>Styrene and its oligomers</td>
<td>Styrene and its oligomers</td>
</tr>
<tr>
<td>PMMA</td>
<td>Unzipping</td>
<td>MMA</td>
<td>Less MMA, more decomposition</td>
</tr>
<tr>
<td>PTFE</td>
<td>Unzipping</td>
<td>Monomer</td>
<td>TFE</td>
</tr>
<tr>
<td>PET</td>
<td>β-Hydrogen transfer, rearrangement and de-carboxylation</td>
<td>Benzoic acid and vinyl terephthalate</td>
<td></td>
</tr>
<tr>
<td>PA-6</td>
<td>Unzipping</td>
<td>Caprolactam</td>
<td></td>
</tr>
</tbody>
</table>

3.2.3 Resins and Products

A systematic study of both physical and chemical aspects in plastics pyrolysis was launched in the Cycleplast project [6]. Thermal degradation of commodity polymers, including kinetic factors and mechanism, were systematically investigated by Professor Bockhorn and collaborators, using thermogravimetry, linked with mass spectrometry, as well as closed loop laboratory-scale pyrolysis reactors. The resulting kinetic parameters are discussed further.

Polyolefins, mainly PE and PP, the main commodity plastics, decompose into a range of paraffins and olefins, according to route 2. The molecular weight distribution and the paraffin-to-olefin ratio decrease with rising reaction temperature and time.

Polystyrene PS mainly yields styrene, as well as its oligomers, mainly dimers and trimers. Mixtures of PS + PE decompose as usual in the case of PS, with the pyrolysis products somewhat more saturated, the PE providing the required hydrogen. The decomposition of PE is somewhat accelerated by the presence of PS.

Polyvinylchloride (PVC) decomposes into two distinct steps, the first yielding hydrogen chloride and benzene, the second a mix of aromatics. The kinetic results vary with the amount of sample and the experimental modes (programmed heating or isothermal) are different for hydrogen chloride evolution, with activation energy 136 vs 120 kJ/mol, and reaction order 1.54 and 1.98.

PET decomposes via β-hydrogen transfer, rearrangement and decarboxylation, with major products benzoic acid and vinyl terephthalate.

Polyamide 6 depolymerizes into caprolactam with high yields. The decomposition is catalysed by both strong acids and bases.

Kinetic study may describe decomposition, generally using first-order models and a reaction rate parameter linked to temperature by the Arrhenius law. Closer scrutiny reveals a more complex behaviour, with kinetic parameters that continuously evolve with experimental conditions. These studies yield values for activation energy ranging...
from \( \sim 140 \text{ kJ/mol} \) (PVC-dechlorination) to 290 kJ/mol (second step in PVC-pyrolysis, and dynamic cracking of PS). Also the reaction orders observed vary widely, from 0.3 (dynamic cracking of PP) to 2 (dynamic cracking of PVC, second step). However, such kinetic parameters vary with the experimental conditions, in line with the complexity of the reaction system, composed of innumerable elementary chemical reactions.

In actual industrial practice, these figures are relatively meaningless, since actual pyrolysis kinetics are normally determined by the rate of heat transfer [10]. A number of interesting simulations of the effect of heat transfer upon apparent rates were performed by both Hornung et al. and by Vergneaud in the framework of the E.U. Cycleplast project [6].

Other studies focused on a mix of MSW plastics, whether resulting from selective collection or mechanical separation. Six thermoplastics, which represent more than two-thirds of all polymer production in western Europe, were pyrolysed in a static batch reactor in a nitrogen atmosphere. These were high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and polyvinylchloride (PVC). The heating rate used was 25°C min\(^{-1}\) to a final temperature of 700°C. These six plastics were then mixed together to simulate the plastic fraction of municipal solid waste found in Europe. The effect of mixing on the product yield and composition was examined. The results showed that the polymers studied did not react independently, but some interaction between samples was observed. The product yield for the mixture of plastics at 700°C was 9.63% gas, 75.11% oil, 2.87% char and 2.31% HCl. The gases identified were H\(_2\), CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_6\), C\(_3\)H\(_8\), C\(_4\)H\(_8\), C\(_4\)H\(_{10}\), CO\(_2\) and CO. The composition of oils were determined using Fourier transform infrared spectrometry and size exclusion chromatography. Analysis showed the presence mainly of aliphatic compounds with small amounts of aromatic compounds [11].

The results of an interesting study on copyrolysis of naphtha and added polyolefins or their kinetics and degradation products were presented at the Analytical and Applied Pyrolysis meeting at Alicante [12] (Table 1.3). The product yields from cracking (450°C) of LDPE and PP are quite different, with more liquid fraction from PP:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>n-Pentadecane, wt</th>
<th>1-Pentadecene, wt</th>
<th>1,14-Pentadecadiene, wt</th>
<th>Ratio C(<em>{&lt;15})/C(</em>{&gt;15})</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td>2.80</td>
<td>3.58</td>
<td>0.64</td>
<td>1.27</td>
</tr>
<tr>
<td>550°C</td>
<td>0.97</td>
<td>2.16</td>
<td>0.59</td>
<td>2.22</td>
</tr>
<tr>
<td>650°C</td>
<td>0.46</td>
<td>1.23</td>
<td>0.42</td>
<td>2.67</td>
</tr>
</tbody>
</table>

The relative and absolute amount of paraffin thus decreases with temperature, that of olefins and di-olefins tends to increase; simultaneously, the ratio of light products (C\(_{<15}\))
to heavies ($C_{>15}$) rises continuously with temperature. The authors also determined the overall kinetic parameters and product distribution for naphtha cracking proper, or after adding LDPE or PP. The kinetics and product distribution were little affected but the rate of coking somewhat increased in the sequence:

$$\text{Naphtha} < \text{naphtha} + \text{LDPE} \ll \text{naphtha} + \text{PP}$$

These authors studied the possibility of blending LDPE and PP into the feedstock of a naphtha cracker. Such units have huge yearly capacity, of the order of 400 000 tonne ethylene or about 1 Mton of feedstock (naphtha). Most plastics pyrolysis units have only a modest scale, ranging from an annual 2000 to 20 000 tonne. This difference in scale obviously reflects in differences in cost, since labour is almost identical for small, medium, or large plant, whereas investment cost $I$ of petrochemical plant typically varies with capacity $C$ as ($R$ = reference basis):

$$\frac{I}{I_R} = \left(\frac{C}{C_R}\right)^{2/3}$$

This means that plant cost varies as shown in Table 1.4.

### 3.2.4 By-products

The major product of pyrolysis is either a monomer (PMMA, PS), or a series of fuel fractions. By-products of plastics pyrolysis are related to the presence of:

**Heteroatoms:**
- oxygen in the resin or the pyrolysis atmosphere leads to the formation of water and oxygenated products;
- chlorine leaves pyrolysis units mainly as (an irritating and corrosive) hydrogen chloride gas. Normally, no chlorine gas is formed, due to the strongly reducing conditions. Bromine, under similar conditions, is somewhat easier to form;
- nitrogen yields various substances of concern, such as ammonia, hydrogen cyanide, and possibly organic compounds, such as nitriles and amines.

**Additives:**
- mineral additives generally report to the coke fraction;
- organic additives either volatilize, or decompose. A major additive, in relative amounts, are PVC plasticizers. Some PVC products (flooring) may contain more additives than PVC resin.

<table>
<thead>
<tr>
<th>Capacity (tonne/year)</th>
<th>Plant investment cost (relative values)</th>
<th>Relative values per unit capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.215</td>
<td>2.15</td>
</tr>
<tr>
<td>3</td>
<td>0.448</td>
<td>1.49</td>
</tr>
<tr>
<td>10</td>
<td>1.000</td>
<td>1.00</td>
</tr>
<tr>
<td>30</td>
<td>2.080</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Secondary reactions: Under pyrolysis conditions, most pyrolysis products have only a precarious stability, as well as a marked residual reactivity towards more stable products and ultimately its elements carbon, hydrogen, as well as simple, stable molecules, such as water, ammonia, hydrogen chloride, etc. In some cases conversion along the pyrolytic route will be halted at some point, in order to preserve high-value primary products and reduce the difficulty of separating more complex mixtures.

Coke formation:

- generally, coke formed by pyrolysis is a by-product only. It is a main result of pyrolysing thermosets and PVC. Moreover, resins can be ordered on the basis of coking tendency, but the reaction conditions as well as external surfaces, such as reactor walls or fillers, play a major role;
- coke could be upgraded, by activating it to activated carbon, or leaching out fillers. There is no evidence, however, that this has ever been contemplated seriously;
- depending on pyrolysis conditions, polyolefins can be converted almost quantitatively into volatiles. Polystyrene has stronger their coking tendency, and polyvinylchloride always leaves some coke. Thermosets and rubbers leave coke as a major product;
- coking tendency, however, depends on operating conditions and polymer structure, as analysed by Van Krevelen [13]. Moreover, some coke may derive from secondary reactions, involving readily polymerizable products, such as dienes and olefins, or coke precursors, such as aromatics. Metal surfaces and coke may actively catalyse coking.

3.3 HETERO-ATOMS AND SIDE PRODUCTS

A major problem in pyrolysis is in the rather unpredictable specifications of both feedstock, if it is a mix of plastics, and products. Especially the presence of halogens has been considered problematic, both because of product quality and operating problems, such as:

- corrosion by HCl, especially in the presence of water vapour;
- clogging by CaCl₂, a problem that once plagued the plant at Ebenhausen, based on the Hamburg University pyrolysis process.

3.3.1 Reactor Types and Processes (Table 1.5)

Professor Fontana and Dr Jung classified all major gasification routes and pyrolysis processes, studying their mass and energy balances as well as operating conditions (refer 2nd ISFR Ostend) [9], predicting the behaviour of mixed plastics during pyrolysis and gasification, in order to assess the production of valuable substitution fuels. Their model was validated by laboratory-scale experiments and the quality of the resulting substitution fuels evaluated, to choose the best thermal process for industrial plants according to the properties of available waste streams.

**Extruders** are available with capacity of more than 1 tonne/h, to mix and melt plastics and provide profiles, tubes, sheet, etc. They are mostly heated electrically, or else using circulating thermal oil, and can be used in pyrolytic systems for feeding plastics, straining the molten feed, eliminating HCl from PVC at temperatures up to some 400°C. Professor
Table 1.5 Reactor types and their characteristics

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Particular characteristics</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder</td>
<td>Operating temperature is limited. Degassing of premature decomposition products is essential</td>
<td>Production of waxes from PE</td>
</tr>
<tr>
<td>Tubular reactor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stirred tank reactor, possibly with external heating loop and/or reflux cooler</td>
<td>Simplicity</td>
<td>Molten polyolefins</td>
</tr>
<tr>
<td></td>
<td>Conventional liquid phase reactor. Stirring improves heat transfer. Clogging of downstream ducting has to be avoided</td>
<td>Mixed plastics: BASF, Ludwigshafen Chiyoda Engineering, Niigata</td>
</tr>
<tr>
<td>Vertical or shaft reactor</td>
<td>Gravity flow</td>
<td>Rubber pyrolysis Foster Wheeler</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Mainly for catalytic reactions, converting vapours from a first reactor</td>
<td>PMMA pyrolysis</td>
</tr>
<tr>
<td>Salt or lead bath reactor</td>
<td>The bath acts as a heat transfer agent. Residues accumulate on top of the layer, requiring a periodic shutdown for cleaning</td>
<td></td>
</tr>
<tr>
<td>Fluidized bed reactor</td>
<td>The fluidized bed acts as a heat transfer agent, dispersing the melting plastic in thin layers. Residues are carried out with the products, requiring a delicate filtration of fines (pigments, fillers)</td>
<td>NKK PVC-pyrolysis</td>
</tr>
<tr>
<td>Rotary kiln</td>
<td>Simple units, featuring tumbling action and gravity flow. Sealing is delicate.</td>
<td>NKK PVC-pyrolysis</td>
</tr>
<tr>
<td>Autoclave</td>
<td>Reactor for operating under pressure, generally in a batch mode</td>
<td>Hydrogenation</td>
</tr>
</tbody>
</table>

Menges and his successor Professor Michaelis conducted pyrolysis at RWTH-Aachen in an externally heated extruder, up to 430°C, a temperature maximum dictated by materials selection considerations. Early extruder pyrolysis systems were developed by Union Carbide and Japan Steel Works [14].

*Tubular,* or fixed-bed thermal or catalytic reactors, are a conventional technology in chemical engineering, and provide plug flow, but lack the positive displacement, mixing and plasticizing effect of single or double screw extruders. They were used to a limited extent, e.g. by Japanese Gasoline and Sanyo Electric Co., the latter featuring dielectric heating. *Shaft reactors* have been proposed for rubber pyrolysis, e.g. the cross-flow units in the Warren Spring Laboratories developed process, proposed by Foster Wheeler. *Rotary kiln* reactors have provided an alternative in rubber pyrolysis and were used by Sumitomo Cement and Kobe Steel, at present by Nippon Kokan for PVC [14].

*The stirred tank reactor,* possibly with external heating loop and/or reflux cooler, is widely proposed as a plastics liquid phase pyrolysis reactor. Both BASF [15] and Professor Bockhorn [6] have used a cascade of well-mixed reactors to produce a step-by-step pyrolysis of resin mixtures.

The required *heat of reaction* is supplied by external heating of the reaction vessel, or, for laboratory-scale or pilot units, by electrical heating. Full-scale plant is either directly fired, or heated by circulating reacting liquids through an external pipe still. Some
processes propose a circulating heat carrier, e.g., superheated steam, molten salts, sands or pebbles, to heat the charge. One process (Sanyo Co.) used dielectric losses, arising from the high-frequency oscillation of electrically polarized molecules. The problem of heat transfer can be eliminated altogether by partial oxidation of the reactor contents. In this case, the product stream is diluted, by combustion products that dilute and oxidize the pyrolysis products. This makes the recovery of useful products more difficult and reduces the calorific value of the pyrolysis gas produced.

Numerous liquid phase processes make use of a tank reactor, containing a bath of molten plastics, or a dedicated heat transfer agent, such as molten lead, tin, or salts. The bath is indirectly heated, generally by being mounted into a furnace. The bath contents are stirred, to obtain homogeneous operating conditions, improve heat transfer and avoid charred residues forming upon overheated heat transfer surfaces. A possible alternative to stirring is to circulate the molten plastics using pumps, by transferring the reactor contents through an external furnace or heat exchanger.

Early developments were made by Mitsui Shipbuilding and Engineering, Ruhrchemie (molten salts), Kawasaki Heavy Industries and Mitsubishi Heavy Industries [14]. Mitsui processed low-M.W. PE and atactic PP to form:

- 4–5% gas, mainly \( C_1 - C_4 \) hydrocarbons;
- 90% oil, consisting mainly of \( n \)-paraffins, 1-olefins and their isomers;
- 5–6% of residue – fillers, stabilizer residues, pigments, etc.

Mitsubishi Heavy Industries pioneered a two-step pyrolysis of mixed plastics. A primary vessel is used for decomposing PVC at 300°C. Then, HCl is scrubbed out from the effluent. Molten material is fed into a second vessel operating at 400–500°C. The same concept was much later applied by BASF at Ludwigshafen, and extended to achieve a selective pyrolysis, making use of differences in thermal stability of the different resins.

Potential operating problems may occur, due to:

- clogging of effluent lines by entrained droplets or waxy materials. At the Niigata plant such an obstruction led to an uncontrolled pressure rise in the reactor, pushing out part of the reactor contents through the feeder system, and eventually causing a fire;
- charring and fouling of heat transfer surfaces;
- deficient level control.

A fluidized bed is a second frequently used type of reactor. Early developments include Japan Gasoline Co. (PS-waste), Sumitomo Shipbuilding and Machinery Co. and the University of Hamburg. The latter developments led to the construction of a demonstration plant at Ebenhausen that was halted after being confronted to a number of technical operating problems.

### 3.3.2 Product Specifications

Distinction should be made between monomers, specific petrochemicals, and more or less typical oil fractions, produced by mixed plastics pyrolysis. Potential pyrolysis products from polyolefins are naphtha, kerosene, or gas-oil. These are blends of numerous different
Table 1.6  Typical naphtha specifications and testing methods [18]

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Test method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (15.6°C)</td>
<td>g/cm³</td>
<td>ASTM D-4052</td>
<td>0.735 max.</td>
</tr>
<tr>
<td>Reid vapour pressure</td>
<td>psig</td>
<td>ASTM D-323</td>
<td>12 max.</td>
</tr>
<tr>
<td>Color Saybolt</td>
<td></td>
<td>ASTM D-156</td>
<td>18 min.</td>
</tr>
<tr>
<td>Lead content</td>
<td>wt ppb</td>
<td>ASTM D-3559</td>
<td>50 max.</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>wt ppm</td>
<td>ASTM D-3120</td>
<td>100 max.</td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>°C</td>
<td>ASTM D-86</td>
<td>50 min.</td>
</tr>
<tr>
<td>Final boiling point</td>
<td>°C</td>
<td>ASTM D-86</td>
<td>165 max.</td>
</tr>
<tr>
<td>Paraffins</td>
<td>wt%</td>
<td>G.C</td>
<td>80 min.</td>
</tr>
<tr>
<td>Olefins</td>
<td>wt%</td>
<td>G.C</td>
<td>1 max</td>
</tr>
<tr>
<td>Naphthenes + aromatics</td>
<td>wt%</td>
<td>G.C</td>
<td>Balance</td>
</tr>
<tr>
<td>Total chlorides</td>
<td>wt ppm</td>
<td>IP-AK/81</td>
<td>10 max.</td>
</tr>
</tbody>
</table>

hydrocarbons, but they still need to satisfy some common commercial specifications. Off-specification products have no market, even if they can be blended in small amounts into other streams that are less critical with respect to the specification compliances. The latter are measured according to established standards, e.g. those of the American Society for Testing Materials (ASTM), the American Petroleum Institute. Most monomers (polymerization grade) are high-purity products: 99.99% or more. The latter is difficult to attain in plastics pyrolysis!

The terminology used in oil refining is found at numerous websites, [16, 17]. As an example, naphtha specifications (Table 1.6) typically involve:

Specifications of other oil fractions obtained may involve (diesel oil) a cetane index, measures of unsaturation, or handling or safety data, such as cloud point or flash point.

3.4 FUNDAMENTALS

3.4.1 Aspect of Fluids Mechanics

As their name implies, plastics are easily deformable and once molten they may be heated not only externally, but also internally, by dissipating friction or dielectric heat. Once the pyrolysis temperature is attained, the melt viscosity starts decreasing rapidly and rising pyrolysis vapour bubbles agitate the mix. Many properties of plastics can be derived using methods used and developed by Van Krevelen [13]. The pyrolyzing plastic’s rheology is poorly-documented, however, since the evolution of molecular size and structure with time and the effects of extraneous matter are difficult to predict.

In a number of processes the plastics prior to pyrolysis are dissolved into product oil for example, so that the viscosity is quite controllable. Other options, though today somewhat obsolete, are the use of a molten lead, tin or salt bath. Unfortunately, residues accumulate on top of this bath, and periodic shut-down for cleaning is inevitable. The process has been used commercially for PMMA.

In fluidized bed units the plastics are dispersed over the surface of innumerable sand or catalyst particles, greatly facilitating heat and mass transfer.
3.4.2 Liquid vs Gas Phase Operation

It is somewhat difficult to visualize plastics as a liquid. The viscosity of a plastic melt markedly decreases as the temperature is raised to levels at which pyrolysis becomes rapid for all resins, i.e. 450°C. Several means may be used to bridge the gap between feed temperature, generally room temperature, and reactor temperatures, namely:

- melting, plasticizing and possibly pyrolysing the feed in an extruder–feeder;
- dissolving the cold feed into hot liquid, serving as thermal flywheel and dissolver. Part of the bath must periodically be discharged, to prevent the accumulation of residues and coke. Coking is often a self-catalytic process!

Some processes feature a stepwise heating and decomposition. The idea has been applied for analytical purposes (polymer blends), but seems also attractive for industrial purposes, since it allows initially eliminating hydrogen chloride from mixtures containing polyvinylchloride at low temperature (250–400°C), then passing to a second step of pyrolysis conducted at a more conventional, higher temperature (~450°C), thus ensuring a low residual chlorine content of the products eventually produced. It is essential, however, to ensure a high-quality disengagement of HCl from the melt; otherwise, some HCl reacts, leaving organochlorine compounds in the melt.

Liquid phase pyrolysis often yields liquid fractions of an intermediate boiling point. When applied to polyolefins it leads to synthetic oil fractions, the boiling range of which decreases with rising pyrolysis temperature. Since lighter fractions have higher value than high-boiling ones, there is interest in combining pyrolysis with a simple type of distillation, i.e. refluxing the heavier fractions into the pyrolysis vessel. Another reason for separating heavies at an early stage is the hazard created by having downstream lines clogged by high-molecular-weight paraffin products.

Obviously, it is unfeasible to process polymers directly in the vapour phase. Most gas phase operations feature a fluidized bed, either constituted of inert sand particles, or of a cracking or reforming catalyst. The plastics fed into the bed are almost immediately melted, coating the individual bed particles and pyrolyzing as a multitude of thin layers.

3.4.3 Mass Balances – Processing Margins

It is essential to determine the yield of each major product rather precisely and at different values of the various operating parameters, mainly temperature, residence time, and pressure. Many studies are incompletely documented, considering only gas or liquid phase products, without mention of residues or mass balances. Moreover, in practice the product yield of pyrolysis is reduced by losses inherent to consecutive purification. Inevitable losses occur further during storage, transfer, and separation. Moreover, each raw material as a rule contains nonproductive constituents, such as some moisture, metal inserts, coatings, reinforcement agents, or fillers. These loss factors explain why laboratory data may lead to overly optimistic views regarding possible industrial yields!

Establishing mass balances after pyrolysis tests is also important for economic reasons. Economic figures are related directly with the operating margins, being the difference between the value of the products and the cost of raw materials.

\[
[\text{Operating margin}] = [(\text{Unit value of product})_{i} \times (\text{Yield of product})_{i}] - (\text{Unit cost of raw material})
\]
This operating margin must cover all charges, such as equipment depreciation, and the cost of manpower, and utilities (power, steam, cooling water, compressed air, etc.). Raw materials of good purity and quality command a reasonable price in the marketplace.

3.5 VALUE OF THE RESULTING PRODUCTS

Some pyrolysis products have high value. These are mainly monomers, such as methylmethacrylate, caprolactam (the monomer of PA 6), tetrafluoroethylene, or styrene. Others are comparable to standard products with specifications of naphtha, kerosene, or gas-oil. Such fractions have a well-known market, as follows from Table 1.7.

However, it is still questionable as to how far plastics pyrolysis can yield product fractions, according to current specifications without extensive post-pyrolysis purification. At Sapporo University, good olefin yields were obtained in the thermal cracking of oil, derived from the local plastics-to-oil plant. The Niigata oil is locally used in a diesel engine and not for sale!

Today important flows of plastics originate in mandatory recycling schemes, such as those imposed by take-back obligations on packaging, End-of life vehicles, or waste electric and electronic equipment (WEEE). For such materials, the drive for collection and recycling is not normally economic, but mandatory. In such cases, there is often a dump fee, to be paid for further processing a stream of waste plastics into recycled products. The value of such fees varies from some 50 €/tonne for injection into blast furnaces in the European Community to as much as 50–100 kYen (~370–750 €/tonne)

3.5.1 Heat Balances

The major terms in the heat balance of a pyrolysis reactor are:

- evaporating any moisture contained;
- supplying sensible heat and latent melting heat to the plastics;
- supplying heat of reaction to the plastics.

Process heat requirements tend to be lower if the feed is stepwise heated, as in certain multistep or selective decomposition schemes of plastics mixtures, or in case the

| Table 1.7 | Some commodity prices (Financial Times, 3 August 2004) |
|-----------------|-----------------|-----------------|
| Oil-Brent Blend (Sep) | 39.95 | $/bbl |
| Unleaded gas (95R) | 441–443 | $/metric tonne |
| Gas Oil (German Htg) | 376–378 | $/metric tonne |
| Heavy Fuel Oil | 163–165 | $/metric tonne |
| Naphtha | 403–405 | $/metric tonne |
| Jet Fuel | 422–424 | $/metric tonne |
| Diesel (French) | 399–401 | $/metric tonne |
| NBP Gas (Aug) | 20.65–20.70 | £/MWh |
| Euro Gas (Zeebrugge) | 22.43–22.63 | £/MWh |
| UKPX Spot Index | 22.84 | £/MWh |
| Conti Power Index | 28.9373 | £/MWh |
| Global COAL RB Index™ | 62.45 | $/metric tonne |

bbl = barrel
heat of condensation of product vapours can be used to preheat the feed. On the other hand, such provisions also complicate plant construction and operation, and add to the investment cost.

Another important factor is the rather poor thermal conductivity of plastics. Bockhorn et al. [6] cite values for the heat conductivity of PS and PP as low as 0.17 W m$^{-1}$ K$^{-1}$, for PET as 0.21 W m$^{-1}$ K$^{-1}$, and for HDPE 0.41 W m$^{-1}$ K$^{-1}$. The viscosity at 250°C attains 2–3 Pa s (20 s$^{-1}$).

Heat transfer at a wall is related to the Reynolds number, generally to the power $\sim$0.7. Thus, there is great interest in securing a low viscosity when the heat of pyrolysis is to be supplied. Dissolving the feed in oil is a possible procedure.

### 3.5.2 Thermodynamics

The relative stability of molecules can be read directly from some literature data tables. The composition corresponding to thermodynamic equilibrium and the corresponding heat of reaction can be derived relatively easily, as long as the required thermodynamic data is available, e.g. in the Janaf Tables [19].

### 3.5.3 Kinetics and Mechanism of Pyrolysis

The study of kinetics and mechanism of pyrolysis is of considerable scientific interest, with regard to the thermal behaviour of organic molecules, the precise constitution of molecules or copolymers, including irregularities, such as structural defects and incorporation of initiator molecules and radical scavengers, used to control the MW.

Some important results from the team of Professor Bockhorn (Cycleplast project) [6] are shown in Table 1.8.

The kinetic parameters given are derived from the thermogravimetric experiments. The mechanisms of pyrolysis, as discussed by this team, are too complex and varied to be treated here in more detail.

E. Hakejova et al. [12], studied the pyrolysis of individual hydrocarbons, and of naphtha, kerosene, gas oil, and hydro-cracking fractions, as well as their copyrolysis with hexadecane, heptane, iso-octane, cyclohexane, and also with heavier feedstocks, i.e. dewaxing

<table>
<thead>
<tr>
<th>Type of resin</th>
<th>Melting point, (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>Temperature range (°C)</th>
<th>Maximum rate of decomposition at (°C)</th>
<th>$E$ (kJ/mol)</th>
<th>Apparent reaction order, $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6</td>
<td>218–224</td>
<td>1.12</td>
<td>310–450</td>
<td>415</td>
<td>211</td>
<td>$\sim$1</td>
</tr>
<tr>
<td>PS</td>
<td>110</td>
<td>1.05</td>
<td>320–415</td>
<td>355</td>
<td>172</td>
<td>1.04</td>
</tr>
<tr>
<td>PVC</td>
<td>&gt;140</td>
<td>1.4</td>
<td>210–350 (I)</td>
<td>250–280 (I)</td>
<td>140</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>350–500 (II)</td>
<td>425 (II)</td>
<td>290</td>
<td>1.8</td>
</tr>
<tr>
<td>HDPE</td>
<td>134</td>
<td>0.954</td>
<td>340–500</td>
<td>475</td>
<td>262</td>
<td>0.83</td>
</tr>
<tr>
<td>PP</td>
<td>163</td>
<td>0.91</td>
<td>340–460</td>
<td>425</td>
<td>190</td>
<td>0.3</td>
</tr>
<tr>
<td>PET</td>
<td>260</td>
<td>1.41</td>
<td>360–410</td>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
cakes, high-boiling hydro-cracking fractions, and waste polymers. Heavier feedstock could not be separately treated, because of coke formation in steam cracking.

The purpose was to evaluate the effects on processing and the product distribution obtained by thermal cracking at 450°C when adding oil and wax products as an additional feedstock, blended with naphtha, the regular feedstock. The thermal cracking mechanism proposed is a Rice–Herzfeld type of free radical mechanism. Using the notations β and μ, respectively for a reactive radical, mainly engaged in H-abstraction and for a larger, mainly decomposing radical, a simple scheme can be written as:

\[
\begin{align*}
\text{Initiation:} & \quad \mu - H \rightarrow \beta + \beta' \\
\text{H-transfer:} & \quad \mu - H + \beta \rightarrow \mu + \beta - H \\
\text{Decomposition:} & \quad \mu \rightarrow \beta + \text{Olefin} \\
\text{Isomerization:} & \quad \mu \leftrightarrow \mu' \\
& \quad \mu + \mu - H \leftrightarrow \mu' + \mu - H \\
\text{Addition:} & \quad \beta + \text{Olefin} \rightarrow \mu' \\
& \quad \mu + \text{Olefin} \rightarrow \mu'' \\
\text{H-transfer:} & \quad \mu - H + \mu' \rightarrow \mu + \mu' - H \\
\text{Termination:} & \quad 2\mu \rightarrow \text{Products} \\
& \quad \beta + \mu \rightarrow \text{Products} \\
& \quad 2\beta \rightarrow \text{Products}
\end{align*}
\]

for describing the kinetics and mechanism of high temperature pyrolysis. Some studies use standard software for this purpose, e.g. Thergas, Kingas [20, 21].

Obviously, depending on the type of catalyst and the operating conditions used, different mechanisms and modes prevail in catalytic cracking.

4 FEEDSTOCK RECYCLING

4.1 SURVEY

Feedstock recycling encompasses processes that convert polyolefins and mixed plastics into oil products, or PVC into HCl and coke. Such plastics pyrolysis, as yet, either in Western Europe or the USA, is not an industrially relevant process, since only the reverse process, the polymerization of monomers to high-molecular entities, creates value. Plastics pyrolysis is technically and economically feasible only for selected polymers that yield high-value, readily marketable monomer products, e.g. PMMA or PA 6. For bulk polymers, such as polyolefins, polystyrene, polyesters, and PVC the scale of production is too small and the margins too low to make plastics pyrolysis an economically viable process. The presence of additives, soil, or other resins, incorporating hetero-atoms, leads to both operating and product specification problems, rendering pyrolysis generally economically unviable. Another important factor is securing an adequate dump fee, to sustain the operation financially, as well as the availability of raw materials, a problem of finding sources, optimizing logistic factors (plastics are light and bulky), sorting, cleaning and handling, and ensuring steady specifications.

The raison d’être of feedstock recycling, i.e. thermal or chemical conversion of plastics that cannot be recycled by mechanical routes, is thus not to create economic value, but
rather a purely political decision, with limited economic value at current cost and capacity factors.

Polyesters, polyamides and other poly-condensation polymers can be chemically recycled simply by reversing their synthesis process by raising the process temperature, using traditional processes such as hydrolysis, ammonolysis, acidolysis, transesterification, etc. Bayer and other interested suppliers pioneered such processes that are beyond the scope of this book. Such processes can also be used for adjusting the MW required in one application (e.g. PET-bottles) to that needed in a different market (e.g. polyester fibres).

Gasification is another route potentially important in feedstock recycling. Basically, plastics are fired with a sub-stoichiometric amount of oxygen + steam or of air, generating a synthesis gas that can eventually be converted into ammonia, methanol, OXO-alcohols, or hydrogen. The processes required for treating and purifying such gases are well known, as well as their fundamentals. On a pilot scale, Texaco Inc. and Shell developed proprietary processes, in which the more usual liquid or pulverized coal fuels are replaced by molten plastics. A few years ago, Texaco intended testing its technology in Rotterdam, The Netherlands at a plant capacity of 50 000 tons of waste plastics a year. The only operating plant at present is that of Ube Industries in Japan, in which plastics arising from households are collected and baled, then gasified in a pressurized fluid bed reactor, developed jointly by Ube and Ebara Co. An alternative is converting mixed, but chlorine-lean plastics into the reducing gas, required in a blast furnace to reduce iron ore and produce pig iron. The process is used in Japan by Nihon Kokan NKK (at present merged into JFE-Holdings). In Europe, the process was also pioneered by Bremen Stahl (Arcelor Group).

Hydrogenation has been pursued at the industrial level at the test plant by Veba Oel in Bottrop, Germany [15].

Some of the techniques used may also apply to other organic compounds with medium-high or high molecular weight, such as rubber, adhesives and glues, varnishes, paints or coatings. Pyrolysis has also been used for cleaning purposes, e.g. separating paints, plastics or rubber from metals. Since such operations are conducted on a small scale and in view of metal recovery, it is uneconomic to recover organics. Rather, these are destroyed by thermal or catalytic post-combustion.

4.2 PROBLEMS WITH HETERO-ATOMS

The major hetero-atoms appearing in polymers are: oxygen, nitrogen, chlorine, bromine, fluorine. After plastics pyrolysis, these elements either appear as intermediate organic compounds still incorporating the hetero-element, or as stable inorganic compounds, i.e. water, ammonia and hydrogen cyanide, hydrogen chloride, hydrogen bromide and bromine, hydrogen fluoride. Most of these are hazardous and corrosive and require a careful selection of construction materials, as well as methods to neutralize or inhibit their effect.

The presence of halogenated polymers and fire retardants, of heavy metals, and the potential formation of dioxins are some of the problems addressed in various studies presented at the successive Symposia on Feedstock Recycling (ISFR). Dehalogenation is a major topic. Some important commercial polymers (PVC, PVDC, chlorinated PE) introduce the element chlorine in almost any mixed feedstock, including those that are
derived from MSW plastics, WEEE, or ASR materials. Moreover, the latter two streams also contain brominated fire retardants that may pose problems during recycling. The following important topics were addressed at the 2nd ISFR Symposium:

- elimination of chlorine from mixed plastic fractions, to produce oil, coke and gas fractions, free from chlorine;
- scavenging of halogens from a reaction mixture;
- scrubbing of HCl and HBr from an off-gas flow;
- closing the Br loop, to create a sustainable solution to the problem of fire retardants;
- interactions between the flame retardants based on Br and on Sb in feedstock recycling.

Dehalogenation has been studied at several levels, namely that of (Contributions presented at the 2nd ISFR Symposium [9]):

1. **Dehalogenation** prior to or during the **pyrolysis** process. Okuwaki and Yoshioka monitored debromination of Printed Circuit Boards (PCBs), at rising temperatures while heating these under helium. These researchers treated various products arising from plastics liquefaction plant in an autoclave using a mixture of NaOH and water, and obtaining deep dechlorination after 3 h at 250°C. H. Ishihara and M. Kayaba (Hitachi Chemical Co. Ltd., Japan, Sony Co., Japan) focused on epoxy resins, used in most PCBs, and developed a technology to depolymerize brominated epoxy resins in a solvent, in the presence of alkali metal compound. Thus PCBs separated into resin solvent, glass cloth, and metals, including mounted devices and solder. M. P. Luda et al. studied the thermal degradation of brominated bisphenol A derivatives. Sakata et al. used iron oxide and calcium carbonate compounds to produce a halogen-free oil, or treat gaseous effluents. Kamo et al. studied liquid phase cracking in H-donor solvents, such as tetralin and decalin.

2. **Dehalogenation** of liquid products, using a catalyst prepared from goethite and phenol resins for the dechlorination of chlorocyclohexane as a test substance (Matsui et al.).

3. HCl and HBr removal from **gaseous effluents**. Bhaskar et al. examined Ca-, Fe-, Zn- and Mg-based sorbents for this purpose, obtaining good results with Ca-Z. Hakata et al. tested an iron oxide-carbon composite catalyst for the selective vapour phase dechlorination of chloroalkanes.

4. **Dehalogenation** in the presence of antimony, studied by Uddin et al.

5. Closing the bromine cycle, with initiatives of the European Brominated Flame Retardant Industry Panel (EBFRIP) in cooperation with the Bromine Science and Environmental Forum (BSEF), including a study prepared by ECN (Petten) on a two-stage pyrolysis/high-temperature gasification process.

### 4.3 COLLECTION SYSTEMS

Under pressure from legislation, in particular the Packaging and Packaging Waste Directive, 94/62/EC, recycling of packaging products has increased dramatically from 1995. In numerous E.U. countries, collection of waste plastics is part of the mandatory recycling, imposed by the Packaging Directive and National Laws deriving from it (Table 1.9).

Eight countries recovered over half the waste plastics from packaging in 2000: the Netherlands, Switzerland, Denmark, Norway, Germany, Sweden, Austria and Belgium.
### Table 1.9  Plastics packaging waste management systems in the E.U.

<table>
<thead>
<tr>
<th>Country</th>
<th>System responsible for collecting packaging waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>Pro Europe sprl</td>
</tr>
<tr>
<td>Austria</td>
<td>ARA Altstoff Recycling Austria AG</td>
</tr>
<tr>
<td>Belgium</td>
<td>asbl Fost Plus vzw</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>EcoPack Bulgaria</td>
</tr>
<tr>
<td>Cyprus</td>
<td>Green Dot Cyprus Public Company Ltd.</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>EKO-KOM, a.s.</td>
</tr>
<tr>
<td>Finland</td>
<td>PYR Ltd</td>
</tr>
<tr>
<td>France</td>
<td>Eco-Emballages SA; Adelphe</td>
</tr>
<tr>
<td>Germany</td>
<td>Duales System Deutschland</td>
</tr>
<tr>
<td>Great Britain</td>
<td>Valpack Ltd; BIFFPACK; WASTE-PACK</td>
</tr>
<tr>
<td>Hungary</td>
<td>ÖKO-Pannon p.b.c.</td>
</tr>
<tr>
<td>Ireland</td>
<td>Repak Ltd.</td>
</tr>
<tr>
<td>Italy</td>
<td>CONAI (Consorzio Nazionale Imballagi)</td>
</tr>
<tr>
<td>Latvia</td>
<td>Latvijas Zalais Punkt, NPO, Ltd</td>
</tr>
<tr>
<td>Lithuania</td>
<td>Zaliis Taskas, UAB</td>
</tr>
<tr>
<td>Luxemburg</td>
<td>Valorlux asbl</td>
</tr>
<tr>
<td>Malta</td>
<td>GreenPak Malta</td>
</tr>
<tr>
<td>Norway</td>
<td>Materialretur A/S; RESIRK</td>
</tr>
<tr>
<td>Poland</td>
<td>RekoPol-Organizacja Odzysku S.A.</td>
</tr>
<tr>
<td>Portugal</td>
<td>Sociedade Ponto Verde, S.A.</td>
</tr>
<tr>
<td>Slovak Republic</td>
<td>Envi-pak, a.s.</td>
</tr>
<tr>
<td>Slovenia</td>
<td>Slopak d.d.o.</td>
</tr>
<tr>
<td>Spain</td>
<td>Eco-embalajes Espana, S.A.</td>
</tr>
<tr>
<td>Sweden</td>
<td>REPA-Reparegistret AB; RETURPACK PET</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>SVM-PACT</td>
</tr>
<tr>
<td>Turkey</td>
<td>CEVKO</td>
</tr>
</tbody>
</table>

Waste electrical electronic equipment (WEEE) is being selectively collected in an increasing number of E.U. countries, so that this stream can be considered available and harnessed. ASR is available at car shredding plants.

### 4.4 LOGISTICS OF SUPPLY

Plastic resins are bulk commodities. A naphtha cracker producing ethylene has a typical yearly capacity of 500 000 tonnes of ethylene, necessitating about 1.2 Mtonnes of naphtha feedstock! Polymerization to resins is conducted with a somewhat lower capacity, but still at the same order of magnitude, say 150 000 tonnes. Engineering plastics are produced at lower capacity, but this lower rank is still far superior to the capacity of the largest feedstock recycling units conceived to date!

The problem with post-consumer plastics is their immense variety and widespread application. One tonne of plastics can be converted into either 20 000 two-litre drinks bottles or 120 000 carrier bags! Collecting, sorting, baling, and transporting such numbers of lightweight materials is a tremendous task, with typical cost levels as shown in Table 1.10.

From a dispersed source, such as households, curbside collection, followed by sorting, cleaning, baling, is very expensive. The only way to reduce such cost is to introduce take back systems.
Table 1.10  Cost factors in selective collection from household refuse

<table>
<thead>
<tr>
<th>Activity</th>
<th>Cost, €/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curbside collection</td>
<td>750–1000</td>
</tr>
<tr>
<td>Sorting</td>
<td>200–250</td>
</tr>
<tr>
<td>Recycling</td>
<td>50–750</td>
</tr>
<tr>
<td>Residue elimination, ∼15% of feed</td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td>1000–3000</td>
</tr>
</tbody>
</table>

In some cases plastics or rubber are easier to collect. Automobile shredder residue is such a potential source of waste plastics, arising at car shredding plant, as can be seen at the following web site [22]. Solving the collection problem is trivial, since the waste accumulate only at a limited number of plants. However, it is a mix of numerous different resins, with embedded dirt, metal, and glass, and the best way to derive value is to dismantle very large items (bumpers, dashboard, tyres, battery boxes) and mechanically or thermally treat the balance. Automotive shredding residues are at present generally sent to landfill. Ebara developed a fluid bed gasifier with subsequent combustion of the producer gas and melting of entrained dust in a cyclonic combustion chamber. The molten ash is tapped and granulated in a water quench. The demonstration plant at Aomori, Japan, has operated on two lines since March 2000.

Waste from electrical and electronic equipment arises at the sorting plant, where the frame, the printed circuit board PCB, the cathode ray tube, etc. are separated for recycling. The remaining plastics fraction is in part flame-retarded, hence contains brominated and antimony compounds. The number of WEEE recycling plants is growing, so that the logistics are no longer a major problem.

Sources of raw materials, methods of identification and sorting have been reviewed by Buekens [14, 23, 24]. It is remarkable that the general trends have remained largely unchanged over the years, albeit that today there is another attitude regarding waste management priorities and conceivably a much larger choice in automated sorting systems. Still, sorting on the workfloor has remained mainly a manual operation until very recently: the introduction of automated scanning and take-back machines created a market for sorters, based on spectral fingerprints of bulk plastic streams. Advances are periodically presented at Identiplast [25].

4.4.1 Voluntary Commitment of the PVC Industry

In the frame of Vinyl 2010 [26] the PVC Industry in the European Union made a number of voluntary commitments, regarding the control of emissions from VCM-producing plant, the phasing out of cadmium (both already realized) and lead-based stabilizers (to be completed by 2015) and the voluntary recycling of 200,000 tonnes per year by 2010. Some projects allow for mechanical recycling (Solvay’s Vinyloop, at Ferrara), but feedstock recycling is also being considered [26].

In Japan, Nihon Kokan (now merged with Kawasaki Steel into JFE Holdings) developed a rotary kiln technology for converting PVC into HCl and coke and operates a pilot plant at Yokohama. The organic vapours are combusted prior to the recovery of HCl by wet scrubbing.
5 SOME FEASIBLE PROCESSES

A brief survey is given of a number of processes that have been used in Europe for plastics pyrolysis. At present, all of these projects have been mothballed. The most relevant initiatives are according to [15]:

1. Hamburg University Pyrolysis Process, high-temperature pyrolysis of mixed plastics, using a fluid bed reactor. Demonstration plant at Ebenhausen has not survived shake-down, due to various operating problems.
2. BASF low-temperature pyrolysis of mixed plastics, using a battery of stirred tank reactors for liquefaction.
3. BP low-temperature pyrolysis of mixed plastics, using a fluid bed reactor.
4. Veba Oil hydrogenation technologies.

5.1 PILOT AND INDUSTRIAL PLANT OPERATION

5.1.1 Hamburg University, Ebenhausen

A plant operating according to the Hamburg University pyrolysis process was built at Ebenhausen, with a capacity of 5000 tonnes per year. The feasibility of converting polyolefins by pyrolysis was successfully demonstrated, with yields from PE/PP mixtures of typically 51% (m/m) gas, 42% (m/m) liquids and the balance unaccounted for. However, the gas to liquids ratio is very sensitive to pyrolysis temperature. Since gas and oil are the major pyrolysis products, economic viability crucially depends on the price of crude oil. Under present conditions, profitability and economic viability are unsatisfactory at this small scale of operation.

5.1.2 BASF, Ludwigshafen

The BASF feedstock recycling process was designed to handle mixed plastic waste, as supplied by the DSD (Duales System Deutschland) green dot packaging collection system. A large pilot plant, with a substantial capacity of 15 000 tonne/yr, was started up in Ludwigshafen in 1994. At that time DSD estimated the total volume of mixed packaging plastics available for feedstock recycling at around 750 000 ton/yr. BASF offered to erect a full-scale industrial plant with a capacity of 300 000 ton/yr, but decided in 1996 to shut down the pilot plant, since no agreement could be reached on a guaranteed long-term waste supply and a gate fee sufficient to cover the costs.

In the BASF process, plastic waste is converted into petrochemical products in a three-stage process. Before feeding, the plastics are shredded, freed from other materials and agglomerated, to improve handling and enhance the density. In the first stage, the plastics are melted and liquefied in an agitated tank. The gaseous hydrochloric acid, evolving from PVC at temperatures up to 300°C, is absorbed in a water washer, and further processed to aqueous hydrochloric acid, to be reused in other BASF production plants.

In a second stage, the plastic oil was fed into a tubular cracker reactor, heated at over 400°C and thus cracked into compounds of different chain lengths, forming petrochemical raw materials. The oils and gases thus obtained are separated in a third stage, resulting in the production of naphtha, aromatic fractions, and high-boiling oils. About 20–30% of gases and 60–70% of oils are produced and subsequently separated in a distillation column.
The naphtha produced by the feedstock process is treated in a steam cracker, and the monomers (e.g. ethylene, propylene, butadiene) are recovered. These raw materials are then used for the production of virgin plastic materials. High-boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. All these products have outlets in the local BASF production plants.

During two years of trial operation, the pilot plant demonstrated its suitability. Although the process can be considered proven, it is at present neither used by BASF, nor elsewhere in Germany, because the quantities of plastic waste and dump fee needed for the plant to be economically viable are not available in Germany (Figure 1.1).

The process products are:

- HCl, which is either neutralized, or processed in a hydrochloric acid production plant;
- naphtha to be converted into monomers in a steam cracker;
- various monomers, which can be used for the production of virgin plastic materials;
- high-boiling oils, to be processed into synthesis gas or conversion coke;
- process residues, consisting typically of 5% minerals and metals, e.g. pigments or aluminium can lids.

Processing plastic waste by the BASF process would have required a gate fee of 160€/tonne for a plant with a capacity of 300,000 tonne/yr and a fee of 250€/tonne for a plant capacity of 150,000 tonne/yr [15].

### 5.1.3 BP, Grangemouth

In the early 1990s BP Chemicals first tested technology for feedstock recycling, using a fluid bed cracking process. Research on a laboratory scale was followed (1994) by demonstration at a continuous pilot plant scale (nominal 50 kg/hr) at BP’s Grangemouth site, using mixed waste packaging plastics. The technology was further developed with some support from a Consortium of European companies (Elf Atochem, EniChem, DSM, CREED) and from APME. In 1998, BP Chemicals, VALPAK and Shanks & McEwan, set up a joint project (POLSCO), to study the feasibility of a 25,000 tonne/yr plant, including logistics infrastructure for supplying mixed plastics from Scotland. The project was seen as a remedy to the expected UK shortage in recycling capability, required to comply with EU and UK Packaging and Packaging Waste Directive.
Some preparation of the waste plastics feed is required before pyrolysis, including size reduction and removal of most nonplastics. This feed is charged into the heated fluidized bed reactor, operating at 500°C, in the absence of air. The plastics thermally crack to hydrocarbons, which leave the bed together with the fluidizing gas. Solid impurities and some coke either accumulate in the bed or are carried out as fine particles and captured by cyclones.

The decomposition of PVC leads to HCl formation, which is eventually neutralized by contacting the hot gas with solid lime, resulting in a CaCl$_2$ fraction to be landfilled. The process shows very good results concerning the removal of chlorine. With an input of 1% Cl, the products contain ~10 ppm Cl, somewhat higher than the 5 ppm typical of refinery use. Also, metals like Pb, Cd and Sb can be removed to very low levels in the products. Tests have shown that all hydrocarbon products can be used for further treatment in refineries. The purified gas is cooled, condensing to a distillate feedstock, tested against agreed specifications before transfer to the downstream user plant. The light hydrocarbon pyrolysis gases are compressed, reheated and returned to the reactor as fluidizing gas. Part of this stream could be used as fuel gas for heating the cracking reactor, but as it is olefin-rich, recovery options were also considered. The flow scheme is illustrated in Figure 1.2.

The process flow diagram shows hydrocarbon recovery in two stages, since the heavy fraction becomes a wax at about 60°C. Once recovered, the light and heavy fractions (about 85% by weight) could be combined together for shipment to downstream refinery processing if the plastic feed is passed on as hydrocarbon liquid to the downstream plants. The balance is gaseous at ambient temperature and could be used to heat the process. In this way nearly all of the plastic is used with just solids separated as a waste product. The gas has a high content of monomers (ethylene and propylene) with only some 15% being methane.

Conceptually, the process can run in self-sufficient heating mode. In this case, overall gas calorific requirement may need a small net export or import as the product gas quality.

Figure 1.2  Schematic representation of the BP process. (Reproduced by permission of TNO)
varies with plastic feed specification and operating conditions. The other main utilities needed are:

- electrical power $\sim$60 kWh/tonne feed plastic;
- cooling water 40 m$^3$/tonne feed plastic;
- steam 1.2 tonne/tonne feed.

All emissions are very low and should comply with local regulations.

The cost of treatment depends on many factors such as scale, location, scope, required preparation stages, and economic parameters used. Hence, comparison of the processes is difficult. The investment costs of a plant of 25 000 tpa, located in Western Europe in 1998, were estimated as 15–20 M€. Under these conditions, a gate fee of some 250 €/tonne is necessary. For a 50 000-tonne plant this gate fee could be some 150 €/tonne. These figures exclude the cost of collection and of preparation.

5.1.4 Veba Oil, Bottrop, Germany

From 1981 Veba Oil AG operated a coal-to-oil hydrogenation plant at Kohleöl Anlage Bottrop (KAB) in Germany, using the Bergius Pier coal liquefaction technology to convert coal into naphtha and gas oil. In 1987 the plant was modified, applying Veba Combi Cracking (VCC) technology to convert crude oil vacuum distillation residues into synthetic crude. Since 1988 a share of the petroleum residue feedstock was substituted by chlorine-containing waste (containing, e.g. PCBs). In 1992/1993 a depolymerization unit was added in front, to process exclusively mixed plastics waste from packaging, as collected by DSD. In 1998 some 87 000 tonnes were treated. DSD and Veba both agreed to terminate their contract in 1999, instead of in 2003: hydrogenation was unable to compete economically with treatment in blast furnaces and with the SVZ process at Schwarze Pumpe.

The plant includes first a depolymerization section and then the VCC section (Figure 1.3). In the first section, the agglomerated plastic waste is depolymerized and dechlorinated at 350–400°C. The overhead product is partly condensed. The main part (80%) of the chlorine introduced evolves as gaseous HCl in the light gases and is washed out, yielding technical HCl. The condensate, still containing some 18% of the chlorine input, is fed to a hydrotreater where the chlorine is eliminated together with the water formed. The resulting chlorine-free condensate and gas are again mixed with the depolymerizate for further treatment in the VCC section.

There, the depolymerizate is hydrogenated under high pressure (about 10 MPa) at some 400–450°C, using a liquid phase reactor without internals. Separation yields a synthetic crude oil, which may be processed in any oil refinery. Light cracking products end up in the off-gas and are sent to a treatment section, for removal of ammonia and hydrogen sulphide. A hydrogenated bituminous residue comprises heavy hydrocarbons, still contaminated with ashes, metals and salts. It is blended with coal for coke production (2 wt%).

The input specifications for the plastic waste are:

- particle size <1.0 cm;
- bulk density 300 kg/m$^3$
- water content <1.0 weight %;
- PVC <4% (2 weight % chlorine);
INTRODUCTION

Figure 1.3 Schematic representation of the Veba Oil process. LPH = Liquid phase hydrogenation and GPH = Gas phase hydrogenation. (Reproduced by permission of TNO)

• inerts <4.5 weight % at 650°C;
• metal content <1.0 weight %;
• content of plastic resins >90.0 weight %.

The process outputs are:

• Syncrude, derived from the VCC section. It is free from chlorine and low in oxygen and nitrogen;
• a hydrogenated solid residue, which can be blended with coal for coke production;
• HCl;
• off-gas.

In 1997, successful treatment tests were completed on electric and electronic waste with bromine-containing flame retardants. For this test, 50 tons of WEEE plastics were mixed with some 250 tons of DSD waste.

The liquid products of the coal oil plant in Bottrop were pumped to the Ruhrol refinery, which also processes the plant’s let-down gas. The solid residues are coked. A comparison of the yields obtained in pyrolysis and hydrogenation shows that, roughly speaking, 50% of the pyrolysis product is gas and 40% is oil, whereas 10% of the hydrogenation product is gas and 85% is oil. Hetero-atoms contained in the plastics (Cl, O, N, S) are split off and largely absent from product oil. The presence of PVC makes the process more resource-intensive (increased consumption of hydrogen, required neutralization of HCl, disposal of salts) and, hence, the input of Cl should not exceed a certain limit value. Mixed waste plastics also contain physical impurities, such as fillers, pigments and adhering dirt.

Hence, Veba Oil developed a commercial process, operating in a temperature range of 350–450°C and requiring a high hydrogen partial pressure (50–100 bar). The hetero-atoms are hydrogenated to products such as hydrochloric acid or ammonia. A synthetic oil distillate is obtained as the main product. Solid particles are concentrated in the sump of the distillation column. The gate fee for the VCC process was 250 €/tonne. The technology was realized in the coal-to-oil plant at Bottrop, with a capacity of 40 000 tonne annually, doubled at the end of 1995. One tonne of waste plastics yielded:

• 800 kg high-quality liquid products;
• 100 kg methane–butane gas and a further
• 100 kg hydrogenation residues, containing inert and inorganic components.
Schematic representation of the Texaco process, the Shell process, the AKZO steam gasification process, the Linde KCA process, the NCR process and the BSL incineration process are given by TNO [15].

5.2 CONCLUSIONS

Only few polymers can be recycled by pyrolysis under economically favourable conditions. Nevertheless, important amounts are collected with the aim of realizing recycling quota that were introduced under environmental pressure. The logistical problems of plastics waste collection are huge: even collecting astronomical numbers of films or bottles generates only rather modest amounts of materials, sufficient only to feed a pilot plant.

6 WASTE MANAGEMENT

6.1 PRINCIPLES

Waste management was once a down-to-earth technical problem, to be solved under thrifty, yet environmentally ‘acceptable’ and hygienic conditions and preferably performed by unskilled labour. Most waste was disposed of in landfills, except in densely populated regions, where volume reduction by incineration was a practical necessity. The recovery of heat, distributed in district heating systems or converted into electrical power was a means of cooling flue gases prior to their cleaning, but barely contributes to cost reduction, especially since a deep cleaning of flue gases became mandatory.

Today, however, waste management has turned into a fashionable legislation-driven business, a responsibility of top management, as part of the environmental profile of each corporation, and requiring expert knowledge in Law, Ethics, Politics and Sustainable Development. Operators belong to the world’s largest service companies.

The E.U. waste management policy focuses on waste hierarchy, giving great priority to waste prevention or reduction (elimination of technical or economic impediments and distortions that encourage the over-production of wastes) followed by re-use, recycling, recovery and residual management. Such a strategy includes an integrated approach to waste management with emphasis on material recycling that is preferred over energy recovery.

Waste prevention (or reduction) involves both (upstream) alterations in product design as well as in consumer habits (downstream). Such strategies assure that the two objectives of (quantity) less waste produced and (quality) less hazardous constituents utilized in production (so that less hazardous wastes is generated) are both met. Waste prevention is a strategy that prevents waste and its associated risks from being produced in the first place.

In this process also the costs have soared, starting from a logic that the more expensive it is to engender waste, the less there will be procreated and the more one will seek to segregate it at the source or after a selective collection, and upgrade it to a secondary raw material.
6.2 **PLASTICS WASTE**

Pre-consumer plastic wastes are generated during the manufacture of virgin plastics from raw materials (oil, natural gas, salt, etc.) and from the conversion of plastics into plastic products. The nature of waste arising in various processing methods is discussed in [14]. Such waste streams are soiled (floor sweepings, skimmings from wastewater treatment, crusts from polymerization reactors), mixed (laboratory testing), or off-specifications. Both production and conversion waste are easily identified and collected and handled by professional scrap dealers that discover and develop applications and market outlets that allow the use of secondary resins with less stringent and less defined specifications.

The amount of plastic waste generated is still considerably less than that of plastics produced: in numerous applications (building, furniture, appliances) plastics meet long-term requirements before their disposal and therefore do not yet occur in the waste stream in big quantities. The majority of plastic wastes are found in municipal solid waste (MSW), as well as in waste streams arising in distribution, agriculture, construction and demolition, furniture and household ware, automotive, electronic and electrical, or medical applications. For a number of years the APME has ordered studies to be made that compile inventories of on the one hand production figures, on the other waste arising, by resin, country, and application and activity.

In their efforts to educate the public and curtail the expansion of waste arising the authorities have devised a number of legal instruments to make inappropriate disposal more expensive (various levies, such as landfill taxes) and recycling more attractive, if not mandatory. More and more waste streams are forced into this route, by means of take-back obligations and minimum recycling quota. Under pressure from legislation, recycling of packaging products has increased dramatically from 1995. These directives are:

- Packaging and Packaging Waste Directive 94/62/EC;
- ROHS Directive 2000/95/EC.

However, the effect is not identical for all materials. Table 1.11 shows the results of such take-back obligation for different packaging materials in Belgium, the collection and recycling of which is entrusted to Fost Plus.

It follows that in Belgium (10 M inhabitants) Fost Plus pays more than 280 €/ton for ensuring the collection and recycling of used packaging, including:

- 5.77 kg PET/inhabitant per year;
- 1.65 kg HDPE/inhabitant per year.

In Denmark the amount of plastic packaging waste collected for recycling amounted in 2001 to 3.9 kg per inhabitant or 8.6 kg per household, compared with the potential amount, equivalent to 28.1 kg per inhabitant or 62.0 kg per household.

Waste from the automotive industry, particularly from *end-of-life-vehicles (ELV)*, has been identified by the E.U. as another priority waste stream. After dismantling larger parts suitable for mechanical recycling, the vehicle is shredded, the metal fraction (about 75%) is removed, and the remaining residue is known as automotive shredder residue (ASR),
Table 1.11 Packaging materials recycled by Fost Plus, Belgium (2003)

<table>
<thead>
<tr>
<th>Material recycled</th>
<th>Tonnage (kton)</th>
<th>Contribution (M€)</th>
<th>Contribution (€/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>309.6</td>
<td>7.2</td>
<td>23.3</td>
</tr>
<tr>
<td>Paper and board</td>
<td>133.3</td>
<td>2.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Steel</td>
<td>80.8</td>
<td>5.1</td>
<td>63.1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>9.9</td>
<td>2.2</td>
<td>222</td>
</tr>
<tr>
<td>PET</td>
<td>57.7</td>
<td>16.3</td>
<td>282</td>
</tr>
<tr>
<td>HDPE</td>
<td>16.5</td>
<td>4.7</td>
<td>285</td>
</tr>
<tr>
<td>Beverage cartons</td>
<td>20.5</td>
<td>5</td>
<td>244</td>
</tr>
<tr>
<td>Other recyclables</td>
<td>98.2</td>
<td>36.8</td>
<td>375</td>
</tr>
<tr>
<td>Other nonrecyclables</td>
<td>0.8</td>
<td>0.3</td>
<td>375</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>727.3</strong></td>
<td><strong>79.7</strong></td>
<td><strong>110</strong></td>
</tr>
</tbody>
</table>

A mixture of many different materials (Wittstock, BASF, at 2nd ISFR). ASR is a major problem, since car manufacturers in Europe and Japan are forced to respect high recycling quotas, suggesting the following conclusions (Schaeper, Audi AG, at 2nd ISFR):

- weight-related quota for mechanical recycling impede a lightweight design;
- feedstock processes are favourable to recover lightweight cars;
- feedstock processes should count as recycling processes;
- there is a need to increase acceptance of feedstock processes.

Feedstock recovery of ASR is conceivable via conversion into reducing gases after injecting into the blast furnace in integrated iron and steel mills. Other gasification routes were developed by Dow, Shell, Texaco, and Lurgi (Schwarze Pumpe). Ebara Co. developed fluid bed gasifiers for MSW, ASR and plastics from selective collection. The latter are converted into synthesis gas at an operating pressure of 2–3 MPa, a development in collaboration with Ube Industries. Full-scale plants are operating at present on each of these feedstocks, e.g. Sakata (MSW), Aomori (ASR) and Ube (mixed plastics).

At 2nd ISFR, T. Yamamoto presented the gasification/melting system developed by Sumitomo Metal Industries for converting MSW into high-calorific gas using metallurgical techniques and oxygen.

Yasuda et al. studied the hydro-gasification of HDPE. Advanced rapid coal hydro-gasification (ARCH) in Japan is developed as a route in the conversion of coal into synthetic natural gas.

Worldwide use of plastics in consumer electronics and electrical equipment is growing very rapidly, as is the waste volume related to such products, albeit with a time lag. Similar rules affect the resulting electronic and electrical scrap (E & E), consisting of a broad mix of thermoplastics (e.g. HIPS, ABS, ABS-PC) for the casings and thermosets (epoxy resins) as major printed circuit board (PCB) material. The material is shredded, metal parts separated and sent to metal processing companies. Van Schijndel and Van Kasteren consider reprocessing using reactive agents such as siloxanes. The heavy metal content of casings, e.g. from computer monitors or TV sets, is very low and these streams can be separately shredded. An innovative depolymerization process using supercritical CO₂ can process heavy-metal-containing thermosets. In this way monomer recovery takes place and heavy metals are separated from the materials for reprocessing.
INTRODUCTION

Several case studies in electronic and electrical scrap were presented at 2nd ISFR:

- components of a telephone were pyrolysed by Day et al. (National Research Council of America),
- Satoh et al. (Sony Co.) reclaimed the magnetic material from tapes using supercritical water to dissolve the resin;
- Noboru Kawai et al. (Victor Company of Japan, Ltd; National Institute of Advanced Industrial Science and Technology) tackled the Chemical Recovery of bisphenol-A from waste CDs or other polycarbonate resins.

An interesting alternative solution was developed in Denmark by Watech. However, industrial preference was given to another process, combining hydrolysis as a method for converting chlorine into hydroxyl substituents.

6.3 RUBBER WASTE

Rubber tyres are by far the most visible of rubber products. Identification is trivial and collection is well organized. Recycling and disposal, however, are less evident. A major route for tyres is their use as a supplemental fuel in cement kilns. Major compounds in tyres are: styrene–butadiene rubber (SBR), synthetic and natural polyisoprene rubber, steel cord, carbon black, zinc oxide, sulphur and vulcanization-controlling chemicals. Tyres can be retreaded, which is economic for large sizes (truck tyres), or ground to crumb or powder (cryogenic grinding). Such materials have some limited market potential as an additive in asphalt, and in surfaces for tennis courts or athletics.

The macromolecular structure of (vulcanized) rubber can be degraded using thermal, mechanical, and chemical means [14]. The resulting reclaim was once incorporated in limited amounts in new tyres. Safety and quality considerations dried up this outlet.

Pyrolysis of tyres is a feasible, yet technically difficult operation. The handling of the remnants of the steel carcass, the carbon black, the zinc oxide, as well as the tendency to repolymerize of the major products are serious stumbling blocks. Various rubber pyrolysis technologies have been developed, using, e.g. fluid bed, rotary kiln (Sumitomo Cement), molten salts, or cross-flow shaft systems (WSL/Foster Wheeler).

Microwave pyrolysis results in relatively high-molecular-weight olefins and a high proportion of valuable products such as ethylene, propylene, butene, aromatics, etc. The short process time contributes to a reduction in the processing cost. Whole tyres or larger chips can be processed, which greatly reduces pre-processing cost. The rubber is transformed from a solid to a highly viscous fluid within milliseconds. With additional curative agents the viscous material can be moulded into new products.

Supercritical water can be used to controllably depolymerize the rubber compounds. Tires decompose into high-molecular-weight olefins (MW 1000–10 000), or oils (max. 90%). Roy [9] discussed vacuum pyrolysis at 2nd ISFR.

6.4 PLASTICS PYROLYSIS AS A WASTE MANAGEMENT OPTION

6.4.1 Status in the E.U

Almost since its foundation (1975) the Association of Plastics Manufacturers in Europe (APME, Brussels) has monitored plastics production, consumption and waste generation.
Major sectors are packaging, building and construction, automotive, electrical and electronics (E & E), agriculture, and others (e.g. furniture, houseware, toys, engineering). After a short (e.g. packaging), medium (e.g. toys) or long lifetime (e.g. building) the plastic product reports to one of various waste streams, such as municipal solid waste (MSW), separately collected packaging, other recyclables, shredding waste (cars, white goods, etc.), construction and demolition waste, agricultural waste, E & E-waste etc.

Such waste streams differ internally with respect to their composition, the feasible methods or modes of collection, and their legal status: producer responsibility has been introduced for a steadily rising number of streams, requiring separate collection, adequate treatment, and often mandatory recycling.

Already in the early 1970s the pyrolysis of plastic wastes to liquid fuels raised considerable interest, first in Japan, later also in Western Europe, with pioneering work of Professor Hansjorg Sinn and Walter Kaminsky, who developed the fluid bed Hamburg pyrolysis process, and of Professor Menges at the RWTH Aachen. However, despite extensive work at laboratory, pilot, or even an industrial scale, such work was jeopardized by both technical problems and disastrous economic figures. Hence, in Western Europe and the USA it is still at best a tentative process, balancing between political pressures and economic reality. Major corporations, such as BASF, BP, Shell, Texaco considered various options in pyrolysis and gasification, yet concluded that their large-scale implementation remains illusory as long as suitable dump fees fail to be guaranteed on the basis of contracts of sufficiently long duration and consequent volumes.

In Japan, however, plastics pyrolysis can now be considered to be state-of-the-art, and making part of the integrated waste plastics recycling system. Still, the process is operating at huge losses at both the levels of (1) collection cost and (2) treatment cost, and very few signs are apparent that one day this situation may reverse. Treatment cost is of the order of 100,000 Yen/tonne of household plastics supplied at the plant. At 2nd ISFR [9] Kusakawa reviewed and explained current Japanese environmental regulations, including the status of polymer recycling and activities in industrial segments, such as packaging, automotive, electrical/electronic industries. He mentions the relevant technological development in Japan and importance of polymer recycling efforts to comply with the regulations. Among these are the Recycling Promotion Law, the Containers and Packaging Recycling Law, the Electrical Appliances Recycling Law, the Building Recycling Law, the Foods Recycling Law, the Automotive Recycling Law.

Thus, the average consumer and industry are paying for realizing political long-term views based on sustainable systems and oil and gas scarcity.

6.4.2 Japanese Initiatives and Processes

Both the Ministry of International Trade and Industry (MITI) and the Plastics Waste Management Institute (PWMI) have been very active in promoting plastics recycling from early in the seventies. In Tokyo, plastics and metals were considered as waste, unfit for incineration and separately collected (1973) and treated in a Nippon Steel shaft furnace. Early Japanese systems, e.g. from Japan Steel Works, Japan Gasoline Co., Kawasaki H. I. Co., Mitsui Shipbuilding & Engineering Co., Mitsubishi H. I. Co., Nichimen, Sanyo Electric Co., Sumitomo Shipbuilding, Toyo Engineering Co have been reviewed [14, 26]. A large variety of pyrolysis systems, featuring extruders, tubular reactor units, as well as
larger fluidized bed or stirred tank reactor units was tested, as soon as plastics became a visible component of municipal solid waste. More recently various commercial plants for feedstock recycling of waste plastics are operating at a full scale:

1. ‘Liquefaction’ units (not to be confused with the hydrogenation processes) using continuous stirred tank reactors, at Niigata and Sapporo.
2. Blast furnace at the NKK (now JFE Holdings) Mikasa works.
3. Coke oven pyrolysis by Nippon Steel Corp.
4. High-pressure gasification by EBARA-UBE.
5. ASR gasification at Aomori (Ebara Co.).
6. Glycolysis of PET bottles by Teijin. Separated PET bottles are now used as raw material for polyester fibres.

These Japanese successes are related to the practical implementation of the Containers and Packaging Recycling Law, carried out in 1997 for PET bottles and in 2000 for the other plastics. This law affords allocating the cost for feedstock recycling of waste plastics separated in homes. It has created attractive markets and thus the separated waste plastics are even in short supply in Japan. Recovery of plastics increased dramatically since 2000, when the law was carried out. On the other hand, the cost for recycling decreased gradually. This trend suggests that active competition improves both techniques and logistic systems.

The Home Appliances Recycling Law came into full force in 2001 and is to be revised within a few years. In such processes, not only the plastic cases, but also printed circuit boards are recycled. the Law for Recycling End-of-Life Vehicles passed through the Parliament, 2002. Clearly this law should promote the recycling of automotive shredder residue.

The environmental policy of the Japanese Government traditionally has promoted the recycling of waste plastics in Japan [27].

6.4.3 Ethical and Political considerations

In principle, it makes no sense to collect waste streams separately, unless suitable outlets are secured for such flows. This seems the case for soiled and mixed plastic packaging wastes, since these cannot be reprocessed to any better materials than those that substitute low-grade wood and since the option of feedstock recycling is operating at a huge economic loss. Moreover, no serious health, toxicity, or safety problems become apparent in case of less strict collection requirements.

However, Green parties contend that the only way to reduce waste generation is to make it prohibitively expensive. As a counter-argument, it may be stated that the funds lost in plastics recycling are better invested in health, education, and social needs. At present, most recycling options have mainly been introduced on an ideological basis, with limited attention to their economic cost and social consequences. These can be tackled using life-cycle analysis methods, i.e. the study of all environmental elements in a product’s life-cycle [28]. According to RDC-Environment, Belgium, and Pira International, UK, the selective collection and recycling of plastics has a positive cost–benefit balance for some important applications, but is negative for others. Local parameters (quality of collected
material, availability of output market, efficiency of the selective collection) play an important role.

### 6.4.4 Safety Aspects

Plastics are often considered quite harmless and were specifically excluded from early lists of hazardous waste, e.g. in Belgium (1976) and the Netherlands (1977). An exception was the plastic packaging that served for packing hazardous compounds, such as pesticides.

Still, some harmful compounds can appear in waste plastics, e.g. additives containing antimony, cadmium, lead, zinc, or hexavalent chromium, and plasticizers. Brominated flame retardants spreading into the environment is another reason for concern and a rational argument for dealing with WEEE and ASR-plastics [37].

### 6.4.5 Environmental Aspects

Little has appeared on the environmental effects of waste plastics pyrolysis. Conceptually, the topic can be subdivided in those environmental aspects related to:

- collection, transportation of feed materials;
- pre-processing;
- heating and pyrolysis;
- pyrolysis products.

Sorting of plastics is often manual and can cause allergic and health problems. Remarkably, plastic waste is not without a smell, and air extracted from storage and handling is thermally deodorized, e.g. at the Ube Industries gasification plant. Part of the pyrolysis products can be regarded as toxic.

### 6.4.6 Useful Publications

APME (Association of Plastics Manufacturers Europe, today Plastics Europe), with member companies given in [29] has classified plastic waste in a series of categories and monitors their origin and recycling, according to their field of application. Several early publications are still of interest, to compare past and present. A recent book on plastics recycling is Scheirs [38]. A few sites of interest are also:

- **Community Recycling**, a comprehensive guide to setting up, maintaining or expanding a local recycling scheme [30];
- **Waste at Work**, a practical guide to dealing with office waste, reducing and reusing everything from toner cartridges through to toilet rolls, as well as a step-by-step guide to setting up an office recycling scheme [31];
- **The National Recycling Directory**, listing United Kingdom national and regional contacts for recycling of various materials including local authority, industry and community organisations [32];
- **The Recycled Products Guide**, the searchable UK listing of products made from recycled material [33];
7 CONCLUSIONS

Plastics pyrolysis has long been topical in academic circles and also continues to inspire industrial R&D and demonstration projects. Still, the pyrolysis of mixed plastics is economically to be proven, because of the small scale of the potential pyrolysis plant and the huge cost expenditure for collecting, cleaning and grading considerable tonnages of plastics. It is hoped that these costs will be covered by the value of the products obtained and, economically speaking, incineration is today a more reasonable option for the larger part of household plastics waste. Indeed, in only very few cases plastics pyrolysis is an economically viable process, e.g. PMMA and PA-6 pyrolysis, because of the high value of the monomers produced. The size of pyrolysis plant there is limited by the availability of scrap.

Still, today industry is obliged by political pressure to consider plastics pyrolysis, or more in general, feedstock recycling attentively: under green pressure there is a legal obligation to collect and recycle certain streams, such as those of packaging, automobile shredder residue ASR, and waste electronic and electrical equipment. Industry has an obligation to take back and recycle such materials, and is forced to consider all options, optimizing or at least testing recycling processes as a function of technical possibilities, feedstock characteristics, and, most of all, legal constraints. The boundary conditions of directives and their translation into national laws is still open for discussion, as follows from the different modes and levels of recycling, applied in the various member states and from the exportation of such flows to low-labour-cost countries.

The concept of feedstock recycling is based on a thermal and sometimes catalytic breakdown of polymer structure, yielding monomers (PMMA, PA-6, PS, PTFE), oil fractions, aromatic fractions, synthetic crude, or synthesis gas. To some extent plastics can be converted in the framework of oil refinery processes, such as viscosity breaking, fluid catalytic cracking, hydro-cracking and delayed coking, or in coal liquefaction [36], but these applications may require a preliminary thermal breakdown or dissolution into or extensive dilution by more conventional feedstock. The desired product and its specification requirements are essential in selecting operating modes and conditions and should be considered on a case by case basis.

The ‘thermal cracking’ of this plastic waste stream is realized via pyrolysis, hydrogenation, or gasification. Since the recovered hydrocarbon products are mostly used in petrochemical processes, their specifications limit the amounts of halogens into the ppm range. Subsequently, the collected mixed waste streams are pre-treated and graded according to their chlorine content. Another possibility is thermal dehalogenation, either in a liquid or in a fluidized bed pyrolysis, before the pre-treated product is further processed. The hydrochloric acid produced is either neutralized or separated for industrial use, e.g. in the pickling of steel, or in chemical industry.

Feedstock recycling is complementary to mechanical recycling since it is less sensitive to unsorted or contaminated plastics waste and enlarges the overall recycling capacities for large waste quantities to be supplied in the future. Examples of such mixed streams are
specific composites (laminated films, artificial leather, footwear), but mainly packaging, ASR, WEEE. These materials are connected to each other for performance reasons, but economic separation is impossible.

Technical processes for feedstock recycling have inspired large corporations, universities, and inventors alike and are the origin of numerous patents. As many of the feedstock recycling processes described in this chapter are still in development, their economic viability also remains yet to be established. This will become clearer over the next several years, in tandem with technical progress and the increased volumes of available plastics wastes [38].

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