

# Overview of Commercial Pyrolysis Processes for Waste Plastics

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## 1 INTRODUCTION

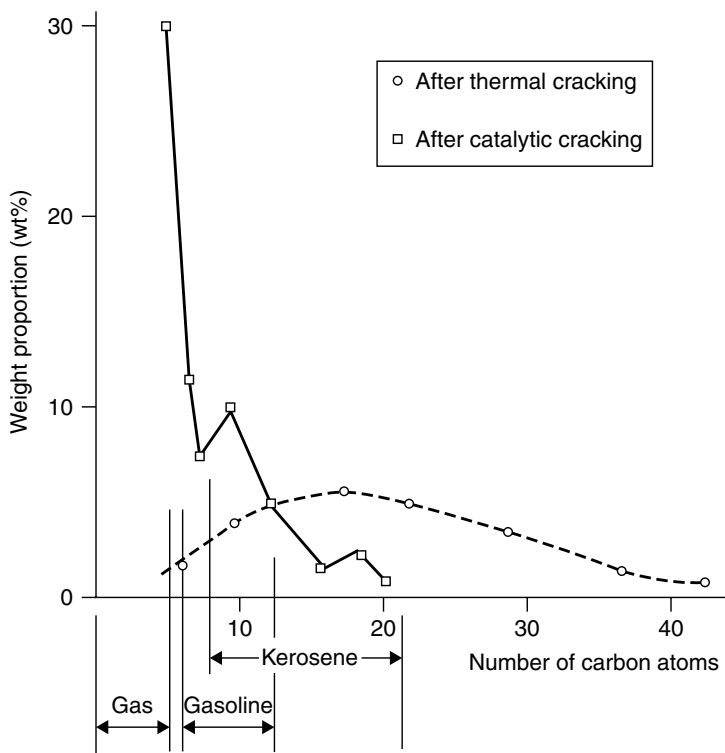
The production of gasoline, kerosene and diesel from waste plastics is an emerging technological solution to the vast amount of plastics that cannot be economically recovered by conventional mechanical recycling operations.

Plastic pyrolysis involves the thermal degradation of the wastes in the absence of oxygen/air. It provides for the disposal of plastic wastes with recovery of valuable gasoline and diesel-range hydrocarbons. During pyrolysis, the polymeric materials are heated to high temperatures, such that their macromolecular structures are broken down into smaller molecules, resulting in a wide range of hydrocarbons being formed. These pyrolytic products can be divided into a noncondensable gas fraction, a liquid fraction (consisting of paraffins, olefins, naphthenes and aromatics), and solid residues (i.e. char).

Pyrolysis of waste plastics appears simple in concept. However, thermal cracking often yields low-value mixtures (cocktails) of hydrocarbons having very broad compositional range, sometimes extending from light alkane gases to coke (Figure 15.1). It is therefore necessary to find the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel or gasoline) from plastic wastes. Catalytic degradation yields a much narrower product distribution of carbon atom number and reduces the reaction temperature. Such a mixture of hydrocarbons may be used as transportation fuels.

Pyrolysis recycling of mixed waste plastics into generator and transportation fuels is seen by many as the answer for deriving value from unwashed, commingled plastics as well as managing their desired diversion from landfill.

Pyrolytic recycling of plastic wastes has already been achieved on a commercial scale, albeit to a limited extent. Nevertheless, the development and improvement of pyrolysis plastics recycling technologies in recent years has shown great commercial



**Figure 15.1** Schematic showing difference in yields and carbon length distribution for thermal cracking and catalytic cracking. Note different distribution of carbon atoms in liquid fuels made by thermal cracking and catalytic cracking of polyethylene

potential. The development of bench-scale experiments carried out in laboratories, through to full-scale pyrolysis processes, have now resulted in a number of technically mature processes.

Through the use of low-temperature vacuum pyrolysis and cracking catalysts, liquid fuel yields of up to 80–85% are possible, with the resultant product resembling diesel fuel, kerosene, gasoline or other useful hydrocarbon liquids. There are now emerging a number of processes that will take post-consumer plastics and catalytically convert them into gasoline and low-sulfur diesel fuel. This diesel fuel meets or exceeds both European and Federal EPA standards for emissions and is designed specifically for the solid waste disposal industry that has significant investment in diesel-powered equipment. The types of plastic targeted as feedstock for this project have no commercial value and would otherwise be landfilled.

A distinct advantage of plastic pyrolysis into fuels as a means of recycling is its ability to handle mixed and unwashed plastics. Post-consumer plastics are often commingled and contaminated with extraneous materials such as soil, dirt, aluminium foils, paper labels and food remnants. While soil, dirt and glue can be removed from post-consumer plastics by washing, this is a fairly expensive operation and it leads to secondary waste streams

such as waste-water. Pyrolysis recycling of mixed plastics thus has great potential for heterogenous plastic waste that cannot be economically separated.

### 1.1 ADVANTAGES OF PYROLYSIS

The advantages of pyrolysis of waste plastics into liquid fuels include:

- it allows the recycling of waste mixed plastics that cannot be efficiently recycled by alternative means;
- it permits the recycling of unwashed and soiled plastics (e.g. agricultural plastics, mulch/silage/greenhouse films and dripper/irrigation tube);
- it enables recycling of plastic laminates, coextrusions and multilayer packaging films, particularly those with aluminium foil layers that are difficult to recycle using traditional reprocessing technologies.

Most commodity hydrocarbon plastics are suitable for pyrolysis. Generally the larger the substituent in the side chain, the easier the plastic can be degraded. The order of increasing side chain size is polyethylene < polypropylene < polyvinyl chloride < polystyrene.

Problems with many pre-existing plastic cracking technologies include:

- noncontinuous (batch) processes (not commercially viable);
- coking and carbon deposits on heat exchanging surfaces;
- stickiness of sand particles in fluidized-bed processes;
- unsatisfactory fuel quality;
- relatively high sulphur levels (100–700 ppm) in end product.

In the last five years however, a limited number of plastic pyrolysis processes have been developed to overcome these limitations.

### 1.2 THERMAL CRACKING

Thermal cracking often yields a low-value mixture of hydrocarbons with a very broad volatility range that can extend from hydrogen to coke. It is therefore important to determine the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel) from mixed plastic wastes.

The pyrolysis product yield and composition are controlled not only by the temperature, but also by the duration of the residence time. As a general rule of thumb the higher the pyrolysis temperature, the higher the yield of noncondensable gaseous products and the lower the yield of liquid fuels such as diesel. The optimum temperature range for the production of diesel products from waste plastics is 390–425°C. Studies in a tubular reactor have highlighted the importance of short residence time with high-temperature pyrolysis for obtaining a high yield of light olefins.

There is a dramatic increase in gas yield with increasing temperature of pyrolysis. While the hydrocarbon pyrolysis product yield increases with pyrolysis temperature, the yield of the oil fraction is higher at the lower pyrolysis temperatures. The composition of the pyrolysis oil also changes with pyrolysis temperature, generally containing larger

quantities of aliphatic compounds at the lower temperatures than at higher temperatures where aromatics are the dominant compounds.

### 1.3 CATALYTIC CRACKING

The poor selectivity of the thermal decomposition of polyolefins has promoted the development of catalytic cracking. Catalytic cracking lowers the pyrolysis process temperature and lowers the boiling temperature range of the resultant liquid products. The use of molecular sieves and amorphous silica–alumina catalysts for the cracking of waste polymers into a range of hydrocarbons has been widely studied (see Chapters 3–5, 7, 8).

Catalytic cracking has some distinct advantages over thermal cracking, such as, lowering the cracking temperature, increasing the reaction rate and increasing the production of iso-alkanes and aromatics which are desirable for diesel fuel. Suitable cracking catalysts have the ability to both substantially reduce the pyrolysis temperature and control the pyrolysis products.

Using catalysts does not only lower the activation energy, reduce the energy consumption and improve the process efficiency, but can also improve the selectivity and quality of the products produced.

Catalysts with acidic surface sites and hydrogen ion donating ability enhance the isomerization of products and thereby increase the yield of isomeric hydrocarbons that have a beneficial effect on the cetane rating and fuel quality. Catalysts having stronger acid sites of higher density are thus more effective in cracking polyolefins. However, strong acidity and large pore size both lead to faster deactivation of the catalyst. Pyrolyzing with catalysts having mild acidity and long life are preferred for the cracking of polyolefins. A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation deactivating the catalyst over time. The cost of these catalysts also influences their selection and commercial viability.

The amount of the catalyst to be added to the waste plastic for catalytic cracking is at least 5% by weight (typically 5–10% by weight).

The problems associated with the use of a catalyst in the pyrolysis vessel are:

- the catalyst is a consumable and therefore adds to the running cost;
- the catalyst can have a short life-cycle due to poisoning/deactivation;
- the catalyst leads to increased levels of solid residue that requires disposal.

Figure 15.1 highlights the differences between thermal and catalytic cracking in terms of the breath and distribution of carbon chain lengths of the products.

## 2 FEEDSTOCK OPTIONS

The composition of the plastic feedstock for pyrolysis processes has a direct bearing on the quality of the resultant fuel products, especially flash point, cetane index, low-temperature properties and heteroatom content (e.g. sulphur, chlorine and nitrogen).

While condensation polymers such as PET and polyamides can be broken down into their monomer units by thermal depolymerization processes, vinyl (addition) polymers such as polyethylene and polypropylene are very difficult to decompose to monomers. This is because of random scission of the carbon-carbon bonds of the polymer chains during thermal degradation, which produces a broad product range.

### 2.1 POLYETHYLENE (PE)

There have been many reports on the thermal and catalytic degradation of high-density polyethylene (HDPE), as it is one of the main polymers in municipal solid wastes [1].

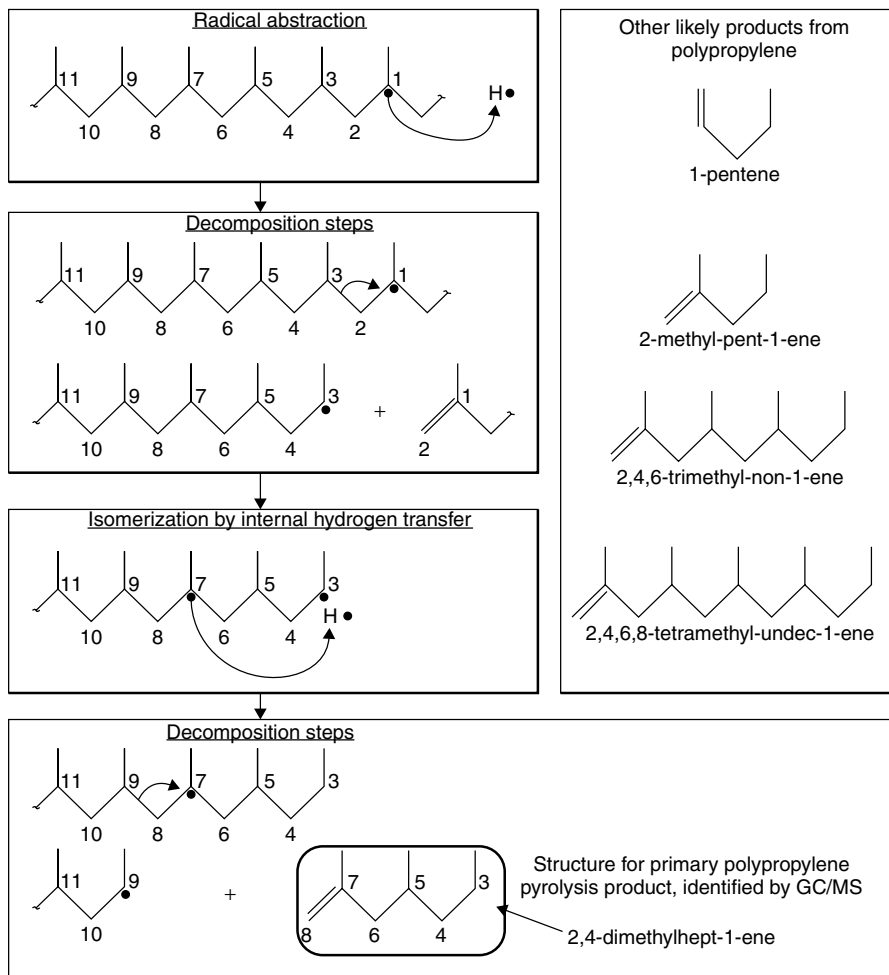
PE-derived fuel has a very low cetane rating and is very high in linear paraffins and 1-olefins. Paraffins are straight-chain hydrocarbons that are normally present in diesel. They are the first components to come out of solution as diesel cools. The tendency of paraffin crystals to aggregate up at low temperatures to form sheets can result in fuel-filter blockages, ultimately leading to interruption of the fuel flow. Paraffin crystals form in the fuel, making the gelled suspension appear cloudy. As these suspended flakes pass through the filter, they gum up its microporous surface.

Due to the high concentration of linear *n*-paraffin hydrocarbons in fuel derived from PE, it is desirable to isomerize them in order to lower the cloud point and the freezing point of the fuel. The branched isomers do not exhibit the same tendency to crystallize as linear paraffins, so that wax crystals do not form until lower temperatures are reached.

### 2.2 POLYPROPYLENE (PP)

The liquid products of the pyrolysis of PP contain primarily olefins that resemble the molecular skeleton of PP (i.e. branched hydrocarbons). A distinguishing feature of PP pyrolysis is the predominant formation of a particular C<sub>9</sub> olefin in the pyrolysis product. The level of this C<sub>9</sub> compound identified as 2,4-dimethylhept-1-ene can be as high as 25%. Also present are C<sub>5</sub> olefin, C<sub>6</sub> olefin, several C<sub>15</sub> olefins and some C<sub>21</sub> olefins [2]. The tertiary carbon sites in PP allows for the facile chain cleavage and rearrangements according to the Rice-Kossiakoff cracking mechanism shown in Figure 15.2. The non-condensable gas from PP pyrolysis contains elevated levels of propylene, isobutylene and *n*-pentane.

Compared with PE, PP produces less coke residue and more liquid products, but with a higher content of 'lights'. In the pyrolysis process of PP the intramolecular radical transfer is preferred to the intermolecular one, thus the low oligomer formation predominates, skewing the carbon number distribution towards the light end of the distillate spectrum. Consequently the pyrolysis oil of PP is much more volatile than that of PE, decomposing mainly through intermolecular radical transfer. The difference in the backbone structure of the products of these polymers is more important from the point of view of fuel properties. The isoalkanoic structure of PP is maintained in the thermal decomposition products, thus the octane number of the pyrolysis oil is typically high.



**Figure 15.2** Rice–Kossiakoff cracking mechanism for polypropylene showing that the pyrolysis products of PP retain a branched structure

### 2.3 POLYSTYRENE (PS) PYROLYSIS

Neat polystyrene feedstocks will depolymerize in a pyrolysis process to give predominantly styrene monomer—a liquid fuel with good energy content.

The optimum pyrolysis temperature is 395°C to give a recovery ratio of 0.97 (i.e. 1000 kg polystyrene will yield 970 L liquid monomer) and 5 to 10% char residue. Fuel made from polystyrene feedstock will be high in aromatic character and have an energy content of 50 MJ/kg and a pour point of −67°C. However the flash point is only 26°C and the cetane rating only 12.6. The fuel needs to be blended with polyolefin-derived diesel or regular diesel in order to upgrade the flash point and cetane rating to within specification.

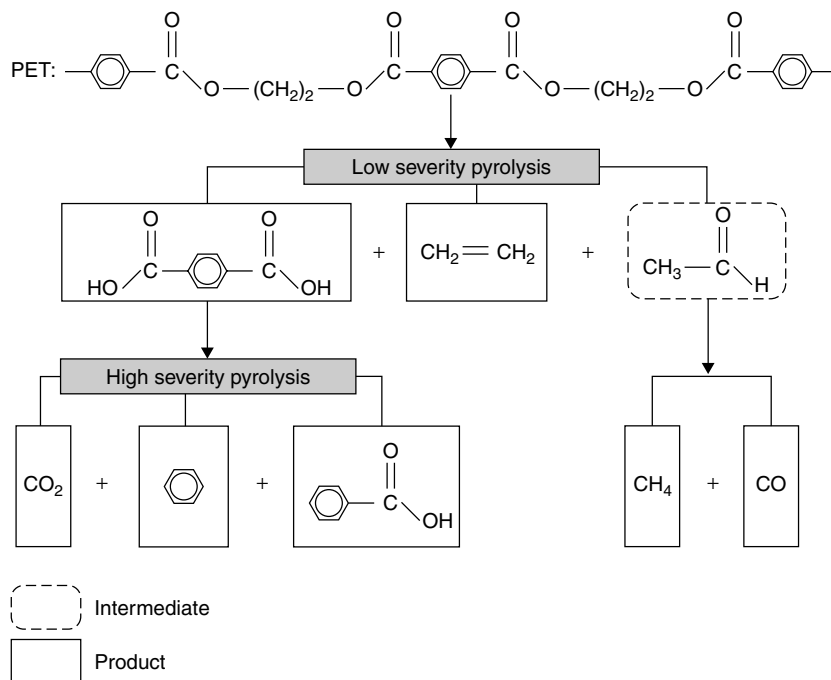
Polystyrene has somewhat lower thermal stability than the polyolefins and its pyrolysis can be undertaken between 380 and 420°C without producing gases or leaving significant

amount of residue after total conversion. PS cracks to styrene, ethyl benzene, toluene, trimethylbenzene and some benzene. In spite of the fact that the majority of the carbon atoms are assembled into phenyl side groups in this polymer, a negligible amount of benzene is formed (1–3%) at these temperatures. This is because the aryl–alkyl bond connecting the phenyl group to the polymer chain is stronger than the bond of alkyl carbons along the chain.

The pyrolysis of PS yields dominating components, styrene (bp 145°C) in the gasoline boiling range, styrene dimer in the diesel oil range, and styrene trimer boiling at 400°C. This pyrolysis product distribution suggests that the intermolecular radical transfer is negligible in PS. The pyrolysis of PS produces fuel with a high aromatic content and low storage stability. The high aromatic content of PS-derived oil helps to compensate for the low cetane number of PE oil.

## 2.4 PET

Pyrolysis of PET under mild conditions predominantly forms terephthalic acid (TPA). Since TPA easily sublimes it is often found in the condensing units of pyrolysis plants. Under high-severity conditions however, little TPA is observed. This is because at higher temperatures TPA is decomposed into benzene, carbon dioxide and benzoic acid (Figure 15.3) [2].



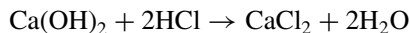
**Figure 15.3** Thermal cracking mechanism for polyethylene terephthalate. Note under mild conditions terephthalic acid predominates, but under more severe pyrolysis conditions the terephthalic acid decomposes to benzoic acid and benzene

The pyrolysis of PET by Sakata [3] has been found surprisingly to yield no liquid products. It is widely known that compounds that undergo sublimation, such as terephthalic acid and benzoic acid, are produced by the thermal decomposition of PET and this causes problems in plastic pyrolysis plants. Interestingly Yoshioka *et al.* [4] found that the addition of calcium hydroxide (slaked lime) gives high selectivity for benzene formation without producing sublimation compounds such as terephthalic acid. The yield of benzene is around 35 wt% at 700°C and a 10.0 calcium hydroxide/PET molar ratio.

## 2.5 PVC

PVC is not recommended as a feedstock material for pyrolysis. The reasons for this being that it contains about 57% chlorine by weight which will affect diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid that is very corrosive and toxic.

The presence of 1–3% PVC in the feedstock stream results in the product fuel oil having a total chlorides level of 5000–10 000 ppm. However at the same PVC levels the total chloride concentration in the diesel can be reduced to less than 10 ppm by the addition of lime hydrate according to the following reaction:



PVC in the feedstock stream in limited amounts can thus be tolerated if a HCl removal process based on calcium hydroxide (slaked lime) injection is used. This is essentially a form of *in situ* scrubbing in the pyrolysis reactor itself. This method is used by a number of pyrolysis processes since the fuel oil end products need to be low in chlorine to minimize engine corrosion problems. In the pyrolysis of commingled plastics, lime can be added to the input material and the PVC content reduced down to 2–3% in order to avoid deposits of CaCl<sub>2</sub> in pipework. The chlorine content of the final diesel should not exceed 10 ppm.

It has been demonstrated that oil recovered from PVC-containing plastic feedstock can be used as a fuel. Cost is the main obstacle since it requires a large amount of slaked lime to neutralize the HCl gas that is produced by the thermal cracking. Table 15.1 shows the effect that slaked lime has on reducing the chlorine content of fuel oil derived from the pyrolysis of PE (55 wt%), PP (28 wt%) and PS (17 wt%) at a decomposition temperature of 420°C.

**Table 15.1** Effect of slaked lime addition on the pyrolysis of plastic containing 1% PVC. (Reproduced by permission of Masataka Tsukada)

| Slaked lime added (%) | Total chlorine in fuel (mg/L) | HCl in fuel (mg/L) |
|-----------------------|-------------------------------|--------------------|
| 0.0                   | 1139.3                        | 490                |
| 1.2                   | 72.5                          | 26                 |
| 2.0                   | 54.2                          | 20                 |



As shown in Table 15.1, adding 1–2% of slaked lime enables the desired level of chlorine in recovered fuel to be achieved, thereby allowing the fuel to be suitable as a diesel fuel. However some chlorine still remains. There is always a small percentage of moisture existing in the waste plastic. It is later separated out and condensed as water. This water reacts with chlorine species in the fuel and produces hydrochloric acid.

## 2.6 HALOGENATED POLYMERS

Since the pyrolytic recycling of waste plastics containing halogen atoms (e.g. Cl, Br, F) poses special problems, the pyrolysis process can incorporate a special halogen elimination step such as dehydrochlorination. Hydrogen chloride, evolved from PVC during heating, can be fixed by metal oxides (e.g. calcium oxide) to form the corresponding metal chlorides. Electronic scrap contains high levels of halogenated flame retardants as well as various metals and fillers in addition to plastic materials. The pyrolytic recycling of the mixed plastics from electrical and electronic waste solves a number of problems such as dehalogenation of the product (see Chapter 20).

## 2.7 PLASTIC FEEDSTOCK SPECIFICATION

Plastic feedstock specifications are extremely important in order to obtain satisfactory and consistent fuel quality (see Table 15.2). A rigid ‘incoming feedstock specification’ (IFS) ensures that limits are placed on ‘critical’ contaminants. The critical contamination is based around the so-called ‘hetero-atoms’. These are listed below in order of priority:

- S (e.g. vulcanized rubber and S-containing sources such as food preservatives);
- Cl and Br (e.g. PVC, PVDC and brominated flame retardants);
- N (e.g. nylon, ABS, PU foam)

Periodic feedstock audits also need to be conducted to ensure the IFS are being adhered to.

**Table 15.2** Properties of fuel produced by pyrolysis of various plastic feedstocks. (Reproduced by permission of Masataka Tsukada)

| Fuel property                | PE     | PP     | PS     | Nylon  | PP 50%, PE 43%,<br>NYLON 7% |
|------------------------------|--------|--------|--------|--------|-----------------------------|
| Flash point (°C)             | 33.6   | 27.8   | 26.1   | 34.8   | 26.0                        |
| Pour point (°C)              | 2.7    | –39    | –67    | –28    | –5.0                        |
| Water content (ppm)          | 0.18   | 0.13   | 0.67   | 2500   | 310                         |
| Ash (wt%)                    | 0.013  | 0.010  | 0.006  | 0.018  | 0.001                       |
| Viscosity (cSt at 50°C)      | 2.190  | 1.9    | 1.4    | 1.8    | 1.485                       |
| Density (g/cm <sup>3</sup> ) | 0.858  | 0.792  | 0.960  | 0.926  | 0.799                       |
| Cetane rating                |        | 56.8   | 12.6   |        | 54.3                        |
| Sulphur (wt%)                | 0.01   | 0.01   | 0.01   | 0.01   | 0.013                       |
| Nitrogen (ppm)               | 0.2    | 0.2    | 0.2    | 6400   | 1750                        |
| Energy content (kJ/kg)       | 52 263 | 53 371 | 50 365 | 44 403 | 46 270                      |

**Table 15.3** Typical Input Specifications (from BP's Grangemouth Pyrolysis Plant)

| Property                            | Specification   |
|-------------------------------------|---|
| Polyolefins (LDPE, LLDPE, HDPE, PP) | 80 wt.% (min 70%)   |
| Polystyrene (GP-PS, EPS, HIPS)      | 15 wt.% (max. 30%)  |
| PET                                 | 3 wt.% (max. 5%)  |
| PVC                                 | 2 wt.% (max. 4%)  |
| Total plastic content               | 95 wt% (min. 90%)   |
| Ash                                 | 2 wt.% (max. 5%)  |
| Moisture                            | 0.5 wt.% (max. 1%)  |
| Metal pieces                        | Max. 1 wt.%   |
| Size                                | 1–20 mm   |
| Fines (sub 250 $\mu\text{m}$ )      | Max. 1 wt%  |
| Bulk density                        | 400 $\text{kg}/\text{m}^3$ (min. 300 $\text{kg}/\text{m}^3$ ) |

Typical input specifications for BP's Grangemouth pyrolysis plant are shown in Table 15.3.

### 3 OPERATIONAL CONSIDERATIONS

The development of commercially viable plastic pyrolysis processes has up to now been hindered by the need to engineer around various process problems such as reactor fouling by carbon deposits, poor heat transfer of molten plastics, the requirement for integrated fractionation of products, separation of water and suspended carbon from the liquid fuels and integrated desulphurization.

#### 3.1 PREVENTING COKING

One of the main technical barriers to the pyrolysis of plastic wastes is the formation of carbon (coke) deposits in the reactor. The coking deposits over the heat exchanging surfaces of the reactor and deactivates catalysts (if used). In this regard, PE and PP are preferred feedstocks over PS due to the high coking potential of PS. Batch reactors with mixers can generally be run only semi-continuously, since after a few days of operation they must be stopped for cleaning and coke/char removal. Carbonaceous coke that accumulates on the inside walls of the pyrolysis vessel can lead to poor heat transfer to the plastic. The char is generally removed by scrapers attached to the agitator shaft. The char is a solid carbonaceous residue that is black, brittle and porous and resembles coke with its honeycomb structure and metallic lustre.

Scraped surface heat exchangers (SSHE) have been used as tubular reactors for plastics pyrolysis. SSHE overcome coking and carbon deposits forming on heat exchanging surfaces when the plastic pyrolyzes to hot gases. A tubular reactor with a special internal screw mixer has been developed in Poland [5]. The purpose of the specially shaped internal mixer is to mix the molten plastic and to scrape coke from the internal surface

of the tube reactor. The advantage of these systems is the continuous coke removal from the reactor tubes.

The Thermofuel process uses a simple pot (kettle) design with an internal mixer/scrapper that extends up the walls of the chamber to continuously remove the coke deposits. Some pyrolysis processes (e.g. Smuda) have a means for withdrawing the thermal cracking residue from the lower portion of the thermal pyrolysis vessel. The powdered coke or solid residue that forms on the bottom of the vessel can be removed on an intermittent basis either by an auger positioned in the floor of the pyrolysis chamber or through a hollow agitator shaft by a vacuum extraction system. It is critical that the char removal process incorporates an 'airlock' that prevents oxygen ingress into the pyrolysis vessel.

### 3.2 PREVENTING CORROSION

In general, halogen-containing polymers (e.g. those containing Br and Cl) are not acceptable feedstock for pyrolysis because they would necessitate the use of special alloys to prevent corrosion and pinholing of the plant components (e.g. condensor coils).

### 3.3 TANK/KETTLE REACTORS

Discontinuous (batch process) and continuous (alternating batch or cascade) stirred tanks reactors are generally used in commercial-scale melt-phase pyrolysis plants. These units are relatively simple, basically consisting of a large stainless steel vessel with indirect heating (either flame or hot air), a large stirrer and possibly internals such as baffles to enhance mixing and heat exchanger surfaces. Internals however may gradually become coated with coke and other impurities and are therefore generally avoided [6].

### 3.4 REFLUX

Reflux describes the process by which the heavy end of the hot pyrolytic gases are selectively condensed and flow back into the pyrolysis chamber for further cracking. Seth and Sarkar [7] compared the effects of degradation with and without a reflux on the MWD of the product. They found that when polypropylene is heated in an inert atmosphere and the volatile products are condensed, the molecular weight distribution (MWD) of the product obtained is very wide. In addition, this product is very waxy, has poor flow properties, and is unusable as a liquid fuel. To improve the product quality, ZSM-5 and other catalysts are usually used in the recycling process. However, these catalysts are costly. On the other hand, if the higher boiling fractions of the volatiles evolved due to degradation are *not* allowed to escape, then the MWD and chain length distribution of the final liquid product can be improved.

### 3.5 PROBLEMS WITH BATCH PYROLYSIS

Problems with batch pyrolysis plants are often mechanical in nature and are related to residue extraction problems, coking/fouling of heat exchanging surfaces, corrosion by

aggressive products, clogging of condensers and ducts by waxes and other solidified or sublimed products (e.g. terephthalic acid) [6].

### 3.6 CONTINUOUS SYSTEMS

Extruders are often used in continuous pyrolysis plants for supplying a molten stream of plastic to the main pyrolysis vessel. The extruder may also be vented to eliminate HCl (from PVC) and water vapour from the waste plastics. In contrast to conventional extrusion, there is no need to build up high melt pressure or to shear the polymer. These pyrolysis extruders are more like heated augers than polymer processing equipment.

### 3.7 FLUIDIZED-BED PROCESSES

For large-scale continuously operating pyrolysis plants, a fluidized-bed reactor has numerous advantages such as improved heat transfer to the plastic, continuous dosing of catalyst and continuous coke removal. Fluidized-bed processes are however not efficient when applied on a relatively small scale.

Fluidized-bed processes are either bubbling or internally circulating. The fluidized-bed reactor is very versatile for the pyrolysis of polyolefins. Nevertheless one of the problems with fluidized-bed pyrolysis of post-consumer plastics relates to the stickiness of the sand particles (the fluidization medium) that becomes coated with fused plastic. In order to solve these problems, new reactors have been proposed, such as the conical spouted bed, the conical rotary reactor, a sphere circulation reactor and a reactor with mechanical particle stirring.

### 3.8 FLUID-BED COKING

Fluid-bed coking is a continuous version that delays coking. Here the cokes are formed on fluidized coke particles that are circulated between the coking unit where the endothermic pyrolysis reaction takes place and the regenerator in which the coke particles are reheated by partly burning off.

### 3.9 FLUID CATALYTIC CRACKING (FCC)

Fluid catalytic cracking (FCC) has been used since the 1950s to turn heavy distillates (vacuum gas oil) into a series of light and dense fractions. The FCC catalysts can also be used as pyrolysis catalysts.

### 3.10 CATALYTIC CRACKING

It has been found for the catalytic cracking of a plastic mixture consisting of LDPE and ethylene–vinyl acetate (EVA) copolymer (86/14 w/w), that nanometer sized HZSM-5 was more active at cracking this plastic mixture at 420°C than the mesoporous catalyst

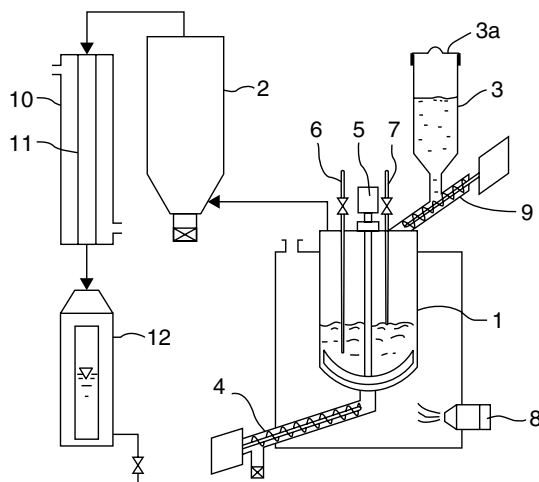
Al-MCM-41. This was ascribed to the occurrence of cross-linking reactions, leading to a fast deactivation of the mesoporous Al-MCM-41 catalysts by coke fouling [8].

## 4 ENGINEERING DESIGN ASPECTS

### 4.1 PYROLYSIS CHAMBER DESIGN

The pyrolysis and/or catalytic cracking process is generally carried out in a continuous stirred tank reactor (CSTR) also called a chamber or vessel. Pyrolysis vessels generally have a dished or cone bottom for strength. Flat-bottom vessels tend to distort readily, especially at process temperatures of 390–425°C. The floor of the vessel is either conical or torispherical. The torispherical shape of the bottom of industrial vessels allows the agitator/scrapper to be placed very close to the bottom, making this impeller/tank configuration very efficient for suspending heavy dispersions and minimizing coking and fouling of the base. A typical stirred tank pyrolysis vessel is shown in Figure 15.4. A torispherical or conical base allows the solid residue or coke to accumulate at a central point for removal.

Pyrolysis vessels can range from 3 to 20 m<sup>3</sup> in volume. Towards the upper end of the size range, heat transfer limitations occur and it is necessary to use heat exchanging pipes internally to assist with heat transfer. The problem with an array of heat exchanging pipes internally however is that they are susceptible to fouling and coking by a carbonaceous residue.



**Figure 15.4** A schematic of a typical continuous stirred tank pyrolysis process. Legend: 1 pyrolysis vessel with internal agitator; 2 catalyst chamber; 3 plastic feedstock hopper; 4 char auger to remove solid residue; 5 agitator drive motor; 6 lower temperature sensor; 7 upper temperature sensor; 8 burner for furnace; 9 feed auger for plastic feedstock; 10 condenser cooling jacket; 11 condenser; 12 oil recovery tank (adapted from Saito, K. and Nanba, M., United States Patent 4,584,421 (1986) 'Method for thermal decomposition of plastic scraps and apparatus for disposal of plastic scraps')

## 4.2 PYROLYSIS VESSEL CONSTRUCTION

Pyrolysis vessels are generally made from SS316 or 9Cr 1Mo steel. Maximum corrosion allowance should be made for the pyrolysis chamber as the metal will potentially be exposed to hydrochloric acid and hydrobromic acid that can cause pinholing of SS304. The pyrolysis chamber needs to have a relief valve or PSV (pressure safety valve) to vent to a safe location in case of a sudden pressure build-up.

## 4.3 AGITATOR SPEED

In kettle-type pyrolysis systems the melt is agitated to ensure good heat transfer, heat distribution and to keep char particles from caking out. Stirring of the melt in a pyrolysis vessel greatly accelerates the heat transfer process. In the Thermofuel process the agitator currently runs at 6–7 rpm. In the Smuda process in Korea the agitator speed is 30 rpm. Higher agitator speeds are clearly beneficial in ensuring better heat transfer, heat distribution and anti-coking. In the Fuji Process the melt in the pyrolysis chamber is not stirred, but instead recirculated *via* a centrifugal blender to a melting pot and back again.

Curved-blade impellers are generally used in CSTR pyrolysis vessels. Generally the gap between the scraper and the vessel wall is between 6–9 mm to allow for thermal expansion effects.

## 4.4 BURNER CHARACTERISTICS

The pyrolysis chamber is generally heated with a high velocity gas burner. In order to avoid hot-spots, an impingement plate is used such that there is no flame impingement on the vessel itself. In newer designs however the chamber is heated indirectly with a hot air burner so that hot spots and flame impingement problems are eliminated.

## 4.5 INERT PURGE GAS

After filling the chamber it is necessary to purge with inert gas (i.e. nitrogen) in order to exclude oxygen or alternatively to apply a vacuum. It is customary to purge the pyrolysis chamber with nitrogen to evacuate any residual air in the vessel before pyrolysis. After pyrolysis N<sub>2</sub> purging is also required to evacuate hydrocarbon gases until the hydrocarbon levels are low enough (in the order of parts per million) to open the vessel and to commence air purging.

Instead of using an inert purge gas to blanket the polymer in the chamber the chamber atmosphere can also be evacuated to remove air/oxygen. Pyrolysis under vacuum reduces the incidence of secondary reactions in the gas phase in contrast to pyrolysis at atmospheric pressure. Under vacuum, the residence time of the pyrolysis products is short and so the secondary reactions are limited.

#### 4.6 DISTILLATION COLUMNS

The pyrolysis gases typically contain a broad boiling point range of materials. Most state-of-the-art pyrolysis processes that convert waste plastics into liquid fuels send the pyrolysis gases into some form of separator such as a distillation column; where the stream is separated into typically at least three fractions – a light, middle, and heavy fraction. The light fraction contains (e.g. 177°C) gasoline range material and gases. The middle fraction is typically a middle distillate range material, such as the diesel fuels range, (e.g. 177–343°C). The heavy fraction is lube oil range material (e.g. 343°C).

Distillation columns can have trays or packing. The advantage of packing is that the column can be smaller in diameter and marginally shorter.

#### 4.7 CENTRIFUGE

In order to remove water and particulate impurities from the liquid fuel products, a liquid centrifuge is normally employed, running at 12 000 rpm (for example Alfa Lavel 2000 which has a capacity of 1200 L/hr). Such a system gives three-phase separation of diesel, water and sludge. It is important that the diesel is cooled (using a pipe-in-pipe heat exchanger for instance) since the centrifuge should not process diesel over its flash point range (i.e. 60–70°C) due to explosion risks.

#### 4.8 SCRUBBER

A wet alkali scrubber is generally employed to scrub acidic impurities from the non-condensable gas stream. The gaseous, water-soluble inorganic compounds are removed by scrubbing the noncondensable pyrolysis gas with an alkaline aqueous stream. In the scrubber, desulphurization and/or denitrogenation and/or dechlorination occurs. Most of the acidic gases such as HCl, SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>S, etc. resulting from pyrolysis are absorbed in the scrubber.

#### 4.9 DECHLORINATION

The plastic feed may contain chlorine in the form of PVC or PVDC. Preferably, a substantial portion of any chlorine in the feed is removed by the addition of a chlorine scavenger compound to the feed, for example, sodium carbonate or slaked lime (calcium hydroxide) to the feed. It reacts in the pyrolysis zone with the hydrogen chloride to form sodium chloride or calcium chloride which becomes part of the residue at the bottom of the pyrolysis vessel. Preferably, the chlorine content should be removed to less than about 5 ppm.

#### 4.10 HYDROTREATING

Hydrotreating of pyrolysis-derived fuels is particularly desirable as a means of saturating olefinic end groups (i.e. unsaturation) and for the reduction of sulphur levels to meet

fuel standards. A hydrotreating step is advantageous to improve thermal and oxidative stability and colour of the liquid fuels. In the Smuda process prior to catalytic isomerization dewaxing, the pyrolysis effluent is hydrotreated to remove compounds such as N-, S- or O-containing compounds, that could deactivate the isomerization dewaxing catalyst or produce an unstable fuel oil composition (e.g., colour instability). Hydrotreating is typically conducted by contacting the pyrolysis effluent heavy fraction with a hydrotreating catalyst at hydrotreating conditions. A conventional catalytic hydrotreating process may be used. The hydrotreating is done under conditions to substantially remove all heteroatoms, while minimizing cracking. Typically, hydrotreating conditions include temperatures ranging around 190–340°C, pressures of from about 400 psig to about 3000 psig.

#### 4.11 CATALYTIC DEWAXING AND ISOMERIZATION DEWAXING

Dewaxing is required to reduce the concentration of highly paraffinic oils which are produced from PE-rich feedstocks. The higher-molecular-weight straight chain normal and slightly branched paraffins present in such fuel cause the fuel to exhibit high cloud points and high pour points. If adequately low pour points are to be obtained, the waxes must be wholly or partially removed. In the past, various solvent removal techniques were employed to remove such waxes, such as propane dewaxing and MEK dewaxing, however, these techniques are both costly and time consuming. Catalytic dewaxing processes are more economical and remove the waxes by selectively cracking the longer-chain *n*-paraffins. Both catalytic dewaxing and selective paraffin isomerization dewaxing technology has been applied to plastic-derived fuels.

Because of the requirement for selectivity, dewaxing catalysts generally comprise an aluminosilicate zeolite, having a pore size which admits the straight chain *n*-paraffins but which excludes more highly branched materials, cycloaliphatics and aromatics. Zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38 have been used for catalytic dewaxing.

Catalytic isomerization dewaxing on the other hand preferentially isomerizes the paraffins, reducing the diesel pour point and cloud point while keeping the high-cetane components in the diesel product. It also favourably decreases the boiling range of the fuel (T95) and produces a higher mid distillate yield.

Isomerization dewaxing is carried out using a large-pore, high-silica zeolite dewaxing catalyst such as high-silica Y or zeolite-beta which isomerizes the waxy components of the base stock to less waxy branched chain isoparaffins. Catalytic isomerization dewaxing uses such large pore zeolites as ZSM-22 or ZSM-23. In this process the *n*-paraffins become isomerized to iso-paraffins to form liquid range materials which contribute to a low-viscosity and low-pour-point product. Isomerization dewaxing is generally a higher-cost process, but delivers higher yields and better properties at the same level of cloud point reduction.

Dewaxing catalysts are manufactured by both Akzo Nobel and Mobil. Mobil's Isomerization Dewaxing (MIDW) first commercialized in 1990 uses a Pt-based zeolite catalyst to crack and isomerize *n*-paraffins to iso-paraffins, thereby converting fuel oil to low-pour-point distillates.



## 5 QUALITY OF THE OUTPUT FUELS

Many pyrolysis processes produce a petrol fraction with a favourable octane number, but strong gum-forming tendency due to the presence of mainly branched olefins.

A common method of classification for petroleum is the PONA system (PONA is an acronym for paraffins, olefins, naphthenes, and aromatics). Paraffins are straight-chain or branched hydrocarbons in which there are no double or triple bonds between carbon atoms. Olefins are similar to paraffins, but they contain at least one multiple bond in their chemical structure. Naphthenes are saturated hydrocarbons, just like paraffins, but they incorporate a ring of carbon atoms into their chemical structure. Aromatics contain a benzene ring in their structure.

### 5.1 UNSATURATION

Similar to petroleum-derived cracking the fractions from plastics pyrolysis can contain a significant concentration of unsaturated hydrocarbons (especially  $\alpha$ -olefins) [9]. The mono- and diolefin content makes the diesel fuel prone to instability due to polymerization and the formation of deposits (i.e. gums). Since the plastic-derived diesel fuel has an appreciable olefins content it is important to subject it to a hydrogenation step (e.g. hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> at 300–320°C and 3 MPa H<sub>2</sub>) which lowers the bromine number from typical values of 22–28 g Br<sub>2</sub>/100 g to less than 0.5 g Br<sub>2</sub>/100 g [9].

### 5.2 CARBON RESIDUE IN THE FUEL

Carbon residue may be present in the diesel fuel in suspended form. The carbon residue can be removed by ultracentrifuging. In the Smuda process some of the light layered clays can be carried out of the pyrolysis vessel with the hot pyrolytic gases and can be entrained in the condensed fuel.

### 5.3 LOW-TEMPERATURE PROPERTIES

Polyethylene-derived diesel is susceptible to waxing problems. It is not just the molecular weight (i.e. chain length) that will cause waxing, it is the presence of linear (unbranched) *n*-alkane chains (i.e. paraffins) and these are more likely to be formed from PE feedstocks. Such straight chains can readily fold and pack tightly to form crystals.

The solubility of linear alkanes present in diesel quickly decreases with temperature. The temperature at which the first crystals appear is called the cloud point and is one of the most important specifications for fuels concerning their low temperature behaviour. The utilization of a fuel is restricted to temperatures above their cloud point. Cloud point measures the temperature at which the wax crystals form a haze. Below the cloud point, the presence of crystals in suspension impairs the flow, plugging fuel filters. Immediately below the cloud point the fluid stops flowing, reaching what is known as pour point. The CFPP test measures the highest temperature at which wax separating out of a sample

can stop or seriously reduce the flow of fuel through a standard filter under standard test conditions.

The exact temperature at which the cloud point is reached depends on the total *n*-alkane content of the fuel, the average size of the *n*-alkane molecules, their size distribution and chain structure (e.g. degree of branching). Conventional diesels contain as much as 20% of long-chain *n*-alkanes of limited solubility in the fuel. Pyrolysis-diesels from PE feedstocks can contain more than 40% long-chain *n*-alkanes. Paraffins crystallize at low temperature into very thin rhombic plates which can clog filters, transfer lines, and pumps, and can lead to engine failure at low temperatures.

Two processes are commonly used to produce fuels within a given specification. The use of additives, such as cloud point depressants, and, fuel blending where a fuel with an excessively high cloud point is mixed with a low-cloud-point fluid to produce a fuel that meets the specifications. Most often both approaches are used simultaneously, since cloud point depressants have a limited action.

#### 5.4 FUEL INSTABILITY

Newly manufactured diesel fuel from waste plastics can sometimes begin to deteriorate as soon as it is produced. Within days of the diesel fuel being produced it goes through a repolymerization and oxidation process. This process forms sediment and 'insoluble gums' in the fuel caused by the unsaturated fuel molecules (i.e. reactive olefins) lengthening and linking together. These components then drop to the bottom of the fuel storage tanks and form a sludge. The fuel also begins to turn dark in colour and develop a strong smell.

This will result in an increase in asphaltene agglomerations, polymerization and a dramatic loss of combustion efficiency. The chemistry of diesel fuel instability involves the chemical conversion of precursors to species of higher molecular weight with limited solubility. The conversion process often involves oxidation of the precursors. Fuel solvency plays a role, since the development of insolubles is always a function of both the presence of higher molecular weight species and the fuel's capacity to dissolve them.

'Dark fuel' is in general indicative of oxidation and is a sign that the process of fuel degradation is in a far advanced stage. Hazy fuel is indicative of polymerization of the fuel. These components sink to the bottom of the fuel tank and form asphaltene also known as diesel sludge. The fuel begins to turn dark, odorous and in most cases causes engines to smoke. The engines smoke because some of these clusters in the early stages are small enough in size to pass through the engine filtration and into the combustion chamber. As these clusters increase in size, only part of the molecule gets burned. The rest exits the exhaust as unburned fuel and smoke. With increases in cluster size they begin to reduce the flow of fuel by clogging filters.

The diesel needs to be 'stabilized' with diesel fuel additives that will inhibit 'diesel polymerization' and inhibit oxidation, darkening and agglomeration of certain components of the diesel. One such effective stabilizing additive is Octel FOA-6. Octel FOA-6 and FOA-3 are amine-based antioxidants that are recommended for antioxidant protection of distillate fuels such as diesel. FOA-3 and FOA-6 together with AO-22, generally give their best performance when added 'hot and early' to the fuel, usually to a cracked component in the run-down from the cracker.

### 5.5 DIESEL ADDITIVES

Additives are often required to bring the low-temperature properties of the diesel into specification. The most important parameter for measuring the low-temperature characteristics of diesel fuel is the cloud point (or more simply, CP) which indicates the temperature corresponding to the commencement of segregation of wax crystals representing linear high-boiling paraffins. These crystals, particularly just after starting a diesel engine, block the filters which protect the injection system. This causes the engine to stop, which then requires a very elaborate procedure for its restarting.

Other significant parameters related to the low-temperature characteristics are pour point (PP) and cold filter plugging point (CFPP). These parameters are coded and measured by the ASTM and DIN methods and generally vary in a mutually coherent manner. The pour point can be reduced by using additives, but these have no appreciable effect on the cloud point.

As diesel is cooled, there comes a point at which the waxes begin to separate and appear as a cloud or haze. The temperature at that point is known as the cloud point. As discussed in Section 5.3, the cloud point is basically the temperature at which small wax crystals start to form in the diesel. This is simply performed by placing the diesel into a fridge and cooling to  $-5^{\circ}\text{C}$  and then allowing it to come to room temperature. The temperature at which a thermometer can be inserted into the gelled diesel is the 'pour point' and then the temperature at which the crystals disappear is the 'cloud point'. Mixing heating oil with diesel fuel has the effect of reducing the cloud point of the diesel. For example, mixing 23 parts of heating oil to 100 parts diesel (1:4 mixture), reduces the cloud point by  $2^{\circ}\text{C}$ . Kerosene may also be blended with diesel fuel to improve its low temperature flow performance. The addition of 25 parts kerosene to 100 parts diesel will lower the cloud point of the diesel fuel by  $8^{\circ}\text{C}$ . However kerosene may then bring the flash point out of the lower specification range.

Diesel made predominantly from polyethylene has a higher proportion of paraffins and therefore a higher cloud point. The paraffins crystallize as the temperature is lowered, leading to small visible crystals forming in the diesel. It is these wax crystals that can plug filters at low temperatures.

The addition of small amounts of cold flow improvers (also known as pour point depressants) brings the pour point of the diesel into the normal range. This can be achieved for example by addition of 1000 ppm of Callington Haven Roxdiesel Pour Point Depressant.

It has been found that additives such as pour point depressants can lower the pour point, but not the cloud point. It has been found empirically that styrene monomer can lower the cloud point since the paraffinic wax crystals are more soluble in the styrene than in the diesel. Styrene monomer is proposed as a suitable additive to depress the cloud point.

### 5.6 STORAGE STABILITY OF PLASTIC-DERIVED DIESEL FUEL

As diesel ages a fine sediment and gum forms in the fuel brought about by the reaction of diesel components with oxygen from the air. The fine sediment and gum will block fuel filters, leading to fuel starvation and engine failure. Frequent filter changes are then

required to keep the engine operating. The gums and sediments do not burn very efficiently in the engine and can lead to carbon and soot deposits in injectors and other combustion surfaces.

Diesel fuel made from the thermal cracking of plastics is more susceptible to oxidation and polymerization than refinery-made diesel fuels. This is because plastic-derived diesel fuels generally have terminal unsaturation (i.e. double bonds) at the ends of the diesel chains as a result of the  $\beta$ -scission chain cleavage. Over time free radicals that form in the plastic-derived diesel fuels during storage cause the diesel chains with double bonds ( $\alpha$ -olefins) to polymerize resulting in a sludgy sediment also known as 'gum'.

Factors which decrease storage life of diesel:

- fuel composition, especially the presence of olefins and styrene monomer in the plastic-derived fuel;
- exposure to high temperatures;

The ageing process can be accelerated by the following conditions:

- contact with zinc, copper or metal alloys containing them. These metals will quickly react with diesel fuel to form unstable compounds;
- exposure to dust and dirt containing trace elements, that can destabilize the fuel (such as copper and zinc).

The expected life of a diesel fuel is indicated by the oxidation stability test (ASTM D-2276). The test measures how much gum and sediment will be deposited after conditioning the fuel at 120°C in the presence of oxygen for 16 h. It roughly corresponds to a years storage at 25°C. A result of less than 20 mg/L of sediment and gum after the test is considered acceptable for normal diesel.

In order to improve the stability of synthetic diesels and biodiesels it is necessary to add free-radical trapping additives known as antioxidants (such as DTBHQ, IONOX 220, Vulkanox ZKF, Vulkanox BKF, and Baynox). Butylated hydroxy toluene (BHT) in particular prevents oxidation and radical polymerization reactions that can lead to diesel fuel ageing.

The nominal antioxidant concentration required to give diesel fuel an extended storage stability and suppress polymerization, is 1000 ppm (i.e. 1000 mg/kg).

HSD Stabilizer (Diesel Stabilizer) additive is a multicomponent, oil soluble formulation, specially designed to maintain the total sediments level in diesel fuel within the specified limits, as per ISO 1460:1995. The additive will ensure that the diesel does not deteriorate on storage and the fuel system is protected from deposit formation and corrosion. The additive consists of three major components, namely:

*Antioxidant.* Fuel oils are subject to deterioration due to oxidation and this occurs both during storage and in service. Oxidation gives rise to formation of gums and sludge. Olefinic compounds produced by cracking are more susceptible to oxidation. Gum is the product of a series of oxidation and polymerization reactions. Antioxidants function by combining with peroxide free radicals and by decomposing hydroperoxides into stable substances. The antioxidants used in the additive are a combination of sterically hindered phenol-type antioxidants.

*Detergent.* The detergent and dispersant, keeps oil insoluble combustion products in suspension and also prevents resinous-like oxidation products from agglomerating into

solid particles. Thus they prevent formation of deposits on metal surfaces, oil thickening and sludge deposition. The component used is ethoxylated products of alkyl phenols.

*Metal deactivator.* Metal deactivator prevents precipitation of metal ion oxidation reactions and precipitation of insoluble metal compounds. Metal deactivator in combination with other antioxidants, shows strong synergistic effects. Oxygen and moisture present, diffuse through oil film and cause corrosion. Amine derivative, used in the additive has good water-displacing properties. They impede sludge formulation, disperse sediments and reduce corrosion in various fuel systems.

### 5.7 CHARACTERISTICS OF THE SOLID RESIDUE

The carbonaceous coke formed during plastics pyrolysis is automatically scraped off and accumulates in the bottom of the pyrolysis chamber where it is reduced by attrition to a free-flowing black powder. The internal agitator/scrapper constantly removes the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic. The char residue produced is about 2–3% of the output for relatively clean polyolefin feedstocks and up to 8–10% for PET-rich feedstocks.

It is difficult to generalize about the chemical composition of the coke stream, since it is directly dependent on the composition of the feedstock stream, which of course varies from one location to another. It is to be expected however that the char stream from a mixed plastic packaging feedstock will be rich in the following elements: Cr, Cd, Mn, Co, Fe, etc., since compounds containing these metals are used in additives (such as pigments and catalysts) used in commodity plastics. The carbon matrix has a metal ‘fixing’ effect and binds up the metal ions so that limited leaching occurs after disposal. The leachability potential of the coke (known as TCLP) needs to be determined before the coke can be landfilled. TCLP stand for toxicity characteristic leaching procedure. The TCLP provides a means to determine the potential for waste leaching in a landfill environment.

### 5.8 GASEOUS EMISSIONS

Ammonia ( $\text{NH}_3$ ) and other nitrogen-containing compounds in the fuel gas can lead to the emission of the oxides of nitrogen ( $\text{NO}_x$ ) in the combustion product gases. Ammonia is a potential product in all pyrolysis processes whenever protein materials are being processed. Proteins are collections of amino acids that contain small quantities of the amine group ( $\text{NH}_2$ ) attached to a carbon atom. The nitrogen in amino acids would be the ‘fuel nitrogen’ for protein material if it were used directly as pyrolysis feedstock. A portion of these amine groups will convert to ammonia during the pyrolysis process and thus can be released into the fuel gas. The most common way to treat the fuel gas in order to remove ammonia is to scrub it with water at modest temperature conditions. There can also be sulphur in the feedstock used for pyrolysis. In the normal range of temperatures for pyrolysis processes, only a portion of the sulphur is released into the fuel gas. Most of this sulphur is in the form of hydrogen sulphide ( $\text{H}_2\text{S}$ ) that can be removed by an alkaline scrubbing of the fuel gases.

## 6 CATALYTIC CRACKING

### 6.1 CATALYST ACTIVITY AND SELECTIVITY

Zeolite catalysts produce liquid products with a boiling point distribution in the range of motor engine fuels. The acidic zeolite catalysts (HZSM-5, H-ultrastable Y-zeolite (H-US-Y)) are more effective in converting polyolefins than the less acidic, amorphous silica–alumina and mesoporous MCM-41. There are considerable differences in product selectivities among the various catalysts. For instance, nanosized HZSM-5 zeolite (with high external surface area and strong acid sites) promotes end-chain scission reactions of the polyolefins, producing mainly light hydrocarbons (C<sub>3</sub>–C<sub>6</sub>); while heavier products are obtained over mesoporous HMC-41. Thus indicating that random scission reactions are predominant as a result of the large pores and mild acidity of this material. From a commercial perspective, the cheaper silica–alumina catalyst give very good selectivity, and their lower activity can be compensated for by increasing the catalyst to polymer ratio.

The larger pore zeolites (H-Y) show rapid deactivation in contrast to the more restrictive HZSM-5 and the non-zeolitic catalysts (silica-alumina, MCM-41), since coke deposits can accumulate inside the channel system of large pores. In contrast, coke deposits only on the outer surface of the zeolites having narrow pores. Furthermore the catalysts having weaker acid sites of lower density are better at tolerating coke deposition. For instance, the mild acidity of clays (and their pillared versions, e.g. pillared montmorillonite) show good resistance to deactivation by coking.

Walendziewski [10] has reported that the optimum thermal cracking temperature of waste polyolefins is 410–430°C, whereas in the case of catalytic pyrolysis, lower temperature (e.g. 390°C) can be used. Higher than 90% yield of gas and liquid fractions with bp <360°C was attained.

Manos [11] studied the catalytic degradation of high-density polyethylene to hydrocarbons over different zeolites. The product range was typically between C<sub>3</sub> and C<sub>15</sub> hydrocarbons. Distinctive patterns of product distribution were found with different zeolitic structures. Extra large-pore ultrastable Y-, and β-zeolites, alkanes were the main products with less alkenes and aromatics and only very small amounts of cycloalkanes and cycloalkenes. Medium-pore mordenite and ZSM-5 gave significantly more olefins. In the medium-pore zeolites, secondary bimolecular reactions were sterically hindered, resulting in higher amounts of alkenes as primary products. The hydrocarbons formed with medium-pore zeolites were lighter than those formed with large-pore zeolites. The following order was found regarding the carbon number distribution: (lighter products) ZSM-5 < mordenite < β < Y < US-Y (heavier products). A similar order was found regarding the bond saturation: (more alkenes) ZSM-5 mordenite < β < Y < US-Y (more alkanes).

The catalytic cracking of polypropylene waste in a fluidized-bed reactor was reported by Ji [12]. It gave a yield of liquid product of 50%, the research octane number of the gasoline produced from plastic waste was 86, and the cetane index of the diesel fuel produced from the plastic waste was 43.

Modification of ZSM-5 zeolite can result in improved liquid yields and a doubling of the isoparaffin index of the liquid fuels which indicates higher liquid quality compared with the parent ZSM-5 zeolite. The high catalytic activity of modified ZSM-5 was explained by its unique acidic properties with a sharp increase of the number and strength of weak acid sites and a decrease of strong acid sites [13].

A major shortcoming of zeolite-type catalysts is their sensitivity to hydrogen chloride and HCl acid, which causes destruction of a catalyst in concentrations above 200 ppm HCl. Considering the fact, plastic wastes often contains PVC the application of expensive zeolite-type catalysts is disadvantageous.

## 6.2 LAYERED CLAY CATALYSTS

A layered silicate clay framework with ordered nickel (or iron) atoms inside can be used as an effective cracking catalyst. Manos [14] showed that two natural clays and their pillared analogues were able to completely decompose polyethylene although these clays were found to be less active than US-Y zeolite their yields to liquid products were around 70%, compared with less than 50% over US-Y zeolite. Moreover, the liquid products obtained over the clay catalysts were heavier. Both of these facts are attributed to the milder acidity of clays, as the very strong acidity characterizing zeolites leads to 'overcracking'. Furthermore, this milder acidity leads to significantly lower occurrence of hydrogen transfer secondary reactions compared with US-Y zeolite, and as a consequence, alkenes were the predominant products over the clay catalysts. An additional advantage of these catalysts is the considerably lower amount of coke formed.

Another important group of catalytic compounds contain the layered double hydroxides (sometimes called 'anionic clays' or 'hydrotalcites'). Presently, many researchers study these materials because of their adsorptive and catalytic properties.

Unlike thermal cracking, the use of catalysts requires less energy and forms valuable hydrocarbons in the gasoline and diesel ranges, thus eliminating the requirement for further processing.

Tu *et al.* [15] report on the catalytic cracking of low-density polyethylene (LDPE) over three types of base catalysts based on layered double hydroxides (LDH) [15]. LDH constitutes a class of layered compounds, resembling the naturally occurring hydrotalcite, and are generally considered complementary to the clays in that they contain positively charged layers and anions in the interlamellar space. Due to the relative ease of their synthesis, LDHs represent an inexpensive and versatile source of a variety of solid catalysts [16]. The catalytic cracking of low-density polyethylene (LDPE) over the three LDHs (MgAl, NiAl, and ZnAl) was examined at 350 and 400°C. The catalytic activities and product distributions obtained with these materials were compared with those corresponding to thermal cracking and cracking over acid solid HY-Zeolite catalyst. All cracking reactions were performed by a semi-batch operation with polymer to catalyst ratio of 100:1. Volatile hydrocarbons were collected from a stream of inert helium gas. Both liquid and gaseous products were analysed by gas chromatogram [15].

At 350°C, the thermal cracking of low-density polyethylene was almost negligible (<1% conversion). The final product after the reaction was that of the melted LDPE, showing that the thermal degradation of LDPE at 350°C was very slow. In all experiments at 400°C, the initial LDPE was totally converted to liquid product, gaseous product, wax and coke. At 400°C, catalytic cracking of LDPE over LDH catalysts showed higher cracking activity than thermal cracking. The liquid yields are: 40 wt% wt. for NiAl, 38 wt% for ZnAl-, 27 wt% for MgAl and 20 wt% for purely thermal cracking. NiAl and ZnAl-LDHs proved to have better potential catalytic properties for LDPE cracking rather

than MgAl-LDH. Solid HY acid catalyst was also tested to compare the performance of the LDHs. HY showed similar activity with NiAl and ZnAl-LDH. However, being more basic in nature, LDHs produced heavier hydrocarbon liquid than the HY. The order was as follows: (lightest products) HY-Zeolite < NiAl < ZnAl < MgAl < thermal only (i.e. no catalyst) (heaviest products). In addition, LDHs showed less coking than their HY counterpart, this is due to the negligible or nonoccurrence of hydrogen transfer secondary reactions. HY showed a high level of isobutane production, which is indicative of high level of secondary reactions. The production of isobutane however decreased considerably as the cracking process progressed, hence HY showed rapid deactivation [15]. Furthermore, all reactions produced considerably lower gaseous products (less than 5 wt%). This is of great benefit as gaseous products are considered less superior to the more valuable liquid product. It was concluded that NiAl and ZnAl LDHs proved to be promising candidates for the catalytic cracking of polyethylene. Catalytic cracking of LDPE over these two catalysts produced a high level of valuable hydrocarbons liquid, with very little gaseous product and coke [15].

### 6.3 EXTERNAL CATALYSTS

A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation, which gradually deactivates the catalyst. For this reason the catalyst is often positioned outside the main pyrolysis reactor such as in a second reactor where the pyrolysis oil is upgraded over a suitable catalyst (e.g. zeolite HZSM-5 or Ni-supporting rare earth metal exchanged Y-type zeolite (REY)) in order to obtain a high quality gasoline. For instance a two-stage catalytic degradation of polyethylene using amorphous silica–alumina and HZSM-5 zeolite catalysts in series has been developed for converting the polymer into high-quality gasoline-range fuels. Firstly the silica–alumina catalyzes the degradation of polyethylene into a low quality pyrolysis oil, which is then transformed into high-quality gasoline on the strongly acidic sites of the zeolite.

### 6.4 PS CATALYTIC CRACKING

Thermal cracking and catalytic degradation of polystyrene (PS) at 375°C over HZSM-5 catalyst yields mainly styrene (over 50 wt% yield). On the contrary, the main products resulting from the catalytic cracking over HMCM-41 and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> are benzene, ethylbenzene and cumene, but in proportions lower than 20 wt% [17]. The results obtained over HZSM-5 zeolite are attributed to both its microporous structure and acid features. The external acid sites of the HZSM-5 zeolite are practically the only ones active for PS degradation, since this polymer is too bulky to enter the zeolite micropores. In addition, competitive cross-linking reactions also take place, which are highly promoted by the strength and Brönsted nature of the zeolite acid sites. Finally, the superior activity obtained over HMCM-41 is explained in terms of its uniform mesoporous structure and its medium acid strength [17].

Similarly the fluidized-bed pyrolysis of polystyrene in the presence of fluid catalytic cracking (FCC) catalysts was investigated at temperatures between 370 and 515°C [18]. In



the catalytic pyrolysis of polystyrene, the product distribution is changed from the usual main product styrene (61 wt%) (in noncatalytic experiments with simple quartz sand) to feedstock chemicals (18–26% ethylbenzene, 9–22 wt% benzene: 1–7 wt% styrene, 3–5% toluene) and coke (15–23 wt%).

### 6.5 CATALYTIC DECHLORINATION

Waste-plastic-derived oil that was prepared by thermal degradation of municipal waste plastics at 410°C was dehydrochlorinated to remove chloroorganic compounds using various catalysts such as iron oxide, iron oxide–carbon composite, ZnO, MgO and red mud. The iron oxide catalysts were effective in removing the chloroorganic compounds. MgO and ZnO catalysts were deactivated during the reaction by HCl, which is produced by the dehydrochlorination of chloroorganic compounds. Iron oxide and its carbon composite were found to be stable in the dehydrochlorination of municipal waste plastic derived oil [19].

A red mud catalyst (waste from alumina production) was evaluated as both a cracking and dechlorination catalyst for the catalytic degradation of PVC-containing mixtures (such as PVC/PE, PVC/PP and PVC/PS) by [20]. Using stepwise pyrolysis, over 90% chlorine in the feed plastic was recovered as HCl gas. A silica–alumina catalyst accelerated the rate of polymer degradation and lowered the boiling point of liquid products, but the chlorine content of oil over silica–alumina was also the highest. Red mud and iron oxides sorbents showed good effect on the fixation of evolved HCl however, they had no effect on the cracking of polymers.

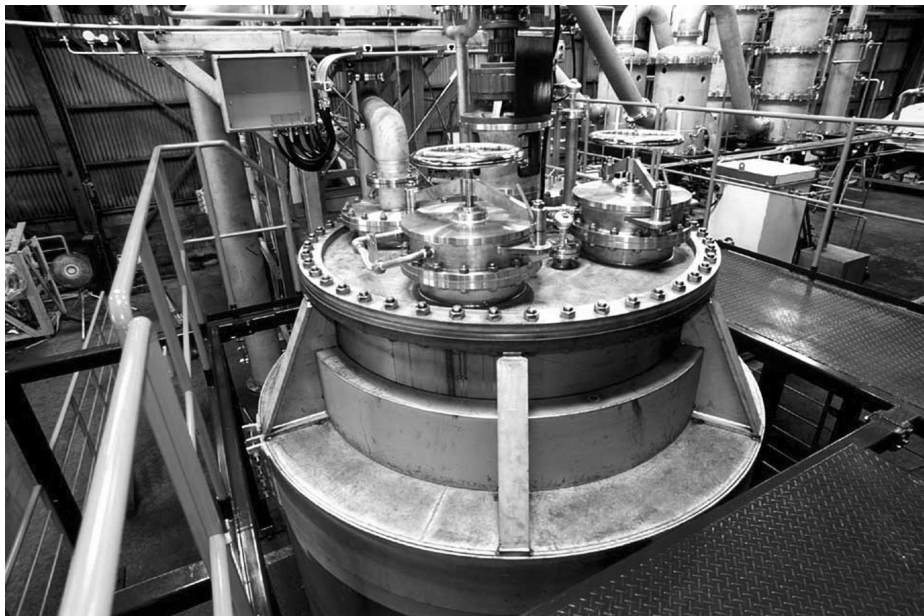
## 7 COMMERCIAL PLASTIC PYROLYSIS PROCESSES

### 7.1 THERMOFUEL™ PROCESS

In the Thermofuel process, plastic waste is first converted to the molten state and then ‘cracked’ in a stainless steel chamber (Figure 15.5) at temperatures in the range 350–425°C under inert gas (i.e. nitrogen). The hot pyrolytic gases are condensed in a specially designed two-stage condenser system to yield a hydrocarbon distillate comprising straight- and branched-chain aliphatics, cyclic aliphatics and aromatic hydrocarbons. The resulting mixture is essentially equivalent to regular diesel. A process flow diagram of the Thermofuel process is shown in Figure 15.6.

The essential steps in the Thermofuel™ pyrolysis of plastics involve:

- uniformly heating the plastic within a narrow temperature range without excessive temperature variations;
- ensuring the plastic is homogeneous and stirred to prevent hot-spots;
- excluding oxygen from pyrolysis chamber, yet at the same time allowing rapid egress of the hot pyrolytic vapours;
- constantly removing the carbonaceous char by-product before it builds up on the pyrolysis chamber walls and acts as a thermal insulator, thereby lowering the heat transfer to the plastic;



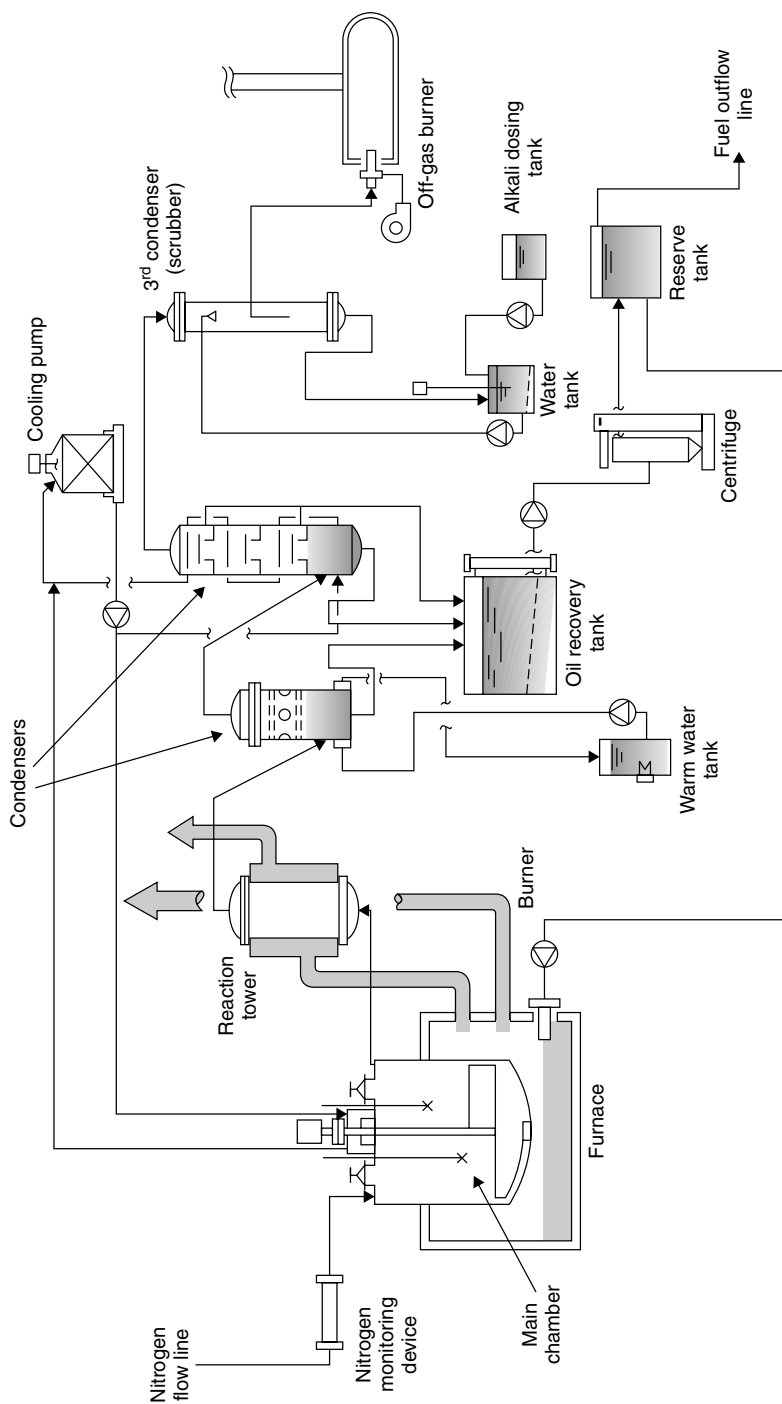
**Figure 15.5** Close-up of pyrolysis chamber of commercial plastics pyrolysis plant which can convert 10 tonne of unwashed, mixed plastics into 10 000 L of diesel fuel per day. (Reproduced by permission of Ozmotech Pty Ltd)

- reactive distillation, which means the hot pyrolytic vapours can condense and be returned to the main pyrolysis chamber until the correct carbon chain length is achieved;
- careful condensation and fractionation of the pyrolysis vapours to produce diesel of good quality and consistency.

The core technology of the Thermofuel process is the catalytic reaction tower (or catalytic converter, Figure 15.7). The catalytic reaction tower contains a system of plates made from a special catalytic metal alloy. The metal plates are positioned so that the hot pyrolytic gases must travel a tortuous path, in order to maximize contact area and time. The catalyst chamber is heated to 220°C using the exhaust gases (not pyrolysis gases) from the furnace of the pyrolysis chamber.

The metal catalyst ‘cracks’ paraffinic chains longer than C<sub>25</sub> and ‘reforms’ chains shorter than C<sub>6</sub>. This is especially important to convert the  $\alpha$ -olefin chains (1-alkenes) to saturated alkanes. The catalyst ensures that the final fuel has a carbon chain distribution in the range C<sub>8</sub>–C<sub>25</sub> peaking at C<sub>16</sub> (cetane) (Figure 15.8). The catalytic tower uses technology borrowed from the petrochemical industry for the hydrogenated of C=C double bonds, e.g. Raney Nickel or so-called Adams catalyst.

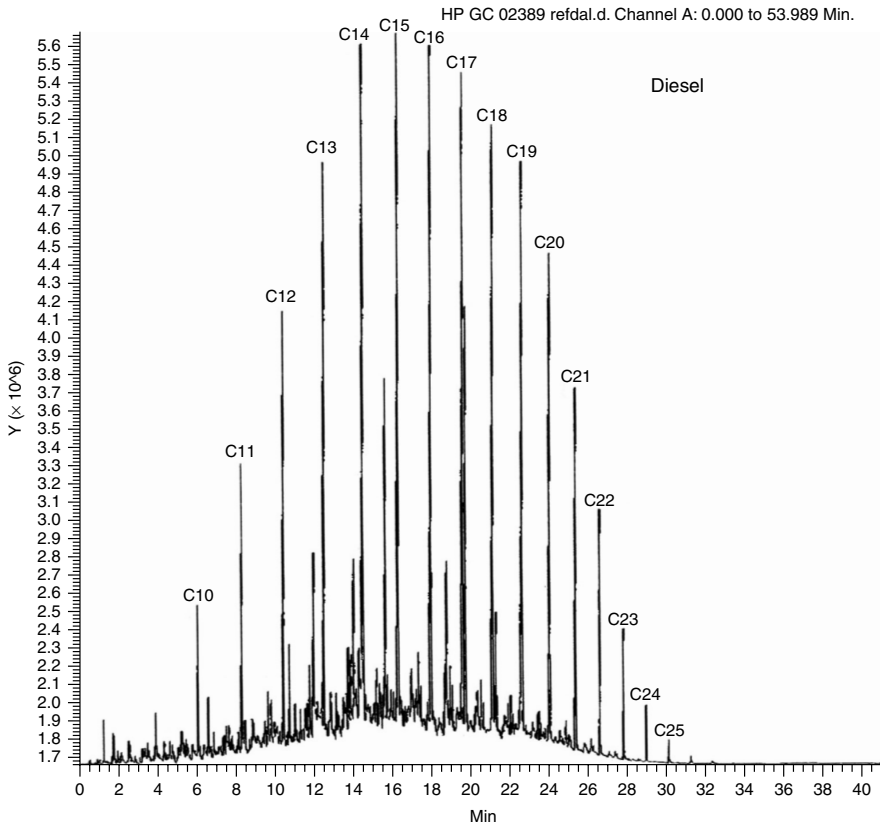
The catalyst is not consumed or poisoned, unlike zeolite type catalysts. The metal plates do however get fouled with a tar-like residue and terephthalic acid and therefore the reaction tower needs to be stripped down periodically and the plates polished back to their pristine form.

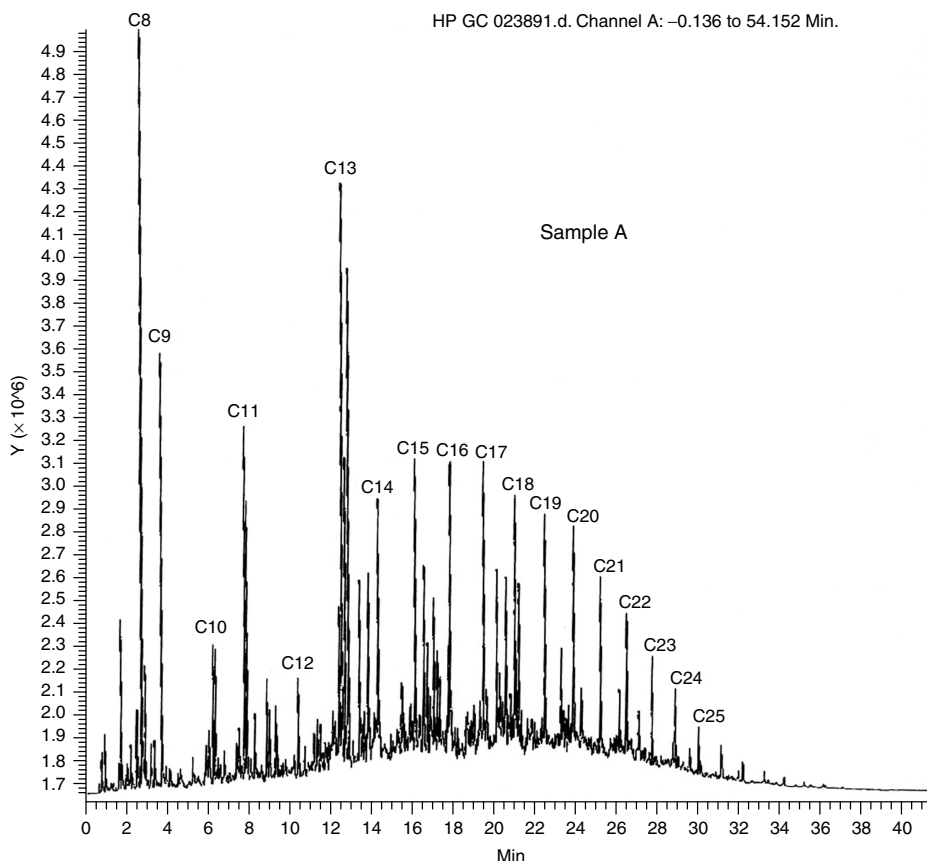


**Figure 15.6** Process flow for commercial pyrolysis plant (Thermofuel™) for converting waste plastics into diesel fuel. The plastic is heated to 375–425°C and the pyrolysis vapours are catalytically cracked and then selectively condensed. Note that the pyrolysis vessel is purged with nitrogen gas and that the hot pyrolytic vapours pass from the pyrolysis vessel to the catalytic reaction tower where they are cracked and reformed to give a high-purity diesel stream. (Reproduced by permission of Ozmotech Pty Ltd)



**Figure 15.7** Close-up of catalytic reaction tower and condensers of the Thermofuel process. (Reproduced by permission of Ozmotech Pty Ltd)





**Figure 15.8** Gas chromatogram (GC) of regular diesel (upper) and plastic-derived diesel (lower). The regular diesel exhibits a series of regular hydrocarbon with a normal distribution peaking close to C<sub>16</sub> (cetane). The plastic-derived diesel was produced by the Thermofuel process (before fractionation) from a mixture of polyethylene, polypropylene and Nylon film as feedstock. This fuel sample also exhibits regularly spaced, hydrocarbon peaks approximating a normal distribution and peaking at C<sub>16</sub> and concluding at approximately C<sub>30</sub>. Also apparent are large peaks at C<sub>8</sub> (octane), C<sub>9</sub> and C<sub>11</sub>. Collectively these additional peaks are 'light' hydrocarbons. 'Lights' are defined as paraffins or carbon chains with a length less than C<sub>11</sub>, that is, less than 11 carbon atoms long. (Reproduced by permission of Ozmotech Pty Ltd)

The catalyst chamber is the heart of the Thermofuel process and is directly responsible for the high quality of the output fuel from this process. The technology in and around this unit is highly proprietary since competitive processes do not have this type of long-life catalytic converter. Many other pyrolysis processes add zeolite catalysts directly to the pyrolysis chamber, however, these are expensive and quickly become fouled and deactivated.

A single-chamber demonstration plant in Fujioka City, used for running trials and process development, has been operational since 1996. Inspection of the inside of the

main pyrolysis chamber during a shut-down showed it to be in excellent condition with minimal scoring or corrosion.

A twin-chamber Thermofuel plant at the Totai Company in Yamanashi Province has been in operation since 2002. The plant at this site processes post-industrial plastic packaging film based mainly on polyethylene, polypropylene and nylon. The plant operation is highly automated.

A twin-chamber Thermofuel plant at an agricultural cooperative on the island of Okinawa has been in operation since 2003 (Figure 15.9). This plant processes agricultural

**Table 15.4** Thermofuel plants in Japan

| Location | Description  | Started          |
|----------|--|------------------|
| Totai    | Dual chambers, mixed plastics                              | 2002             |
| Okinawa  | Dual chambers, agricultural film                           | 2003             |
| Nakamoto | One chamber, similar to Totai (mix plastics)               | 2004             |
| Watanuki | Dual chambers, commercial and industrial waste(recycling)  | 1993             |
| Tih-Tay  | Dual chambers, polyethylene from cables (cross-linked EVA) | 1998             |
| Nabari   | One chamber, industrial waste (packaging)                  | 2004             |
| Fujioka  | Original pilot plant                                       | Now disassembled |



**Figure 15.9** A commercial Thermofuel™ plant in Okinawa in Japan which processes agricultural plastics such as mulch and greenhouse films into diesel fuel to run greenhouse boilers for heating, tractors and other agricultural machinery. (Reproduced by permission of Ozmotech Pty Ltd)

plastics such as mulch and greenhouse film based mainly on polyethylene. The diesel fuel is used to run greenhouse boilers, tractors and other farm equipment.

Thermofuel-based fuel produces much lower sulphur oxides (SO<sub>x</sub>) than conventional diesel since sulphur levels in the fuel are typically less than 0.01% (100 ppm) as compared with conventional diesel which has sulphur around 400–500 ppm. SO<sub>x</sub> emissions for Thermofuel diesel are thus correspondingly 4–5 times lower than that of conventional diesel. Furthermore the Thermofuel incorporates an integrated desulphurization plant to ensure the sulphur content of the diesel produced is always within specification.

Nitrogen oxides (NO<sub>x</sub>) emissions from diesel engines run on Thermalysis fuels evaluated at 3000 rpm was found to vary with the load on the engine [21] (Table 15.5)

Generally, the Thermofuel fuel gives lower NO<sub>x</sub> than conventional diesel, especially at lower engine load. Particulate emissions from diesel engines run on Thermofuel diesel, also at 3000 rpm, varies with the load on the engine [21] as shown in Table 15.6.

It is apparent from the above data that Thermofuel diesel produces significantly less particulates (smoke) at all engine loadings than conventional diesel. This is environmentally significant, as the particulates formed from diesel combustion contain polycyclic aromatic hydrocarbons (PAH) which have carcinogenic potential. The hotter burning characteristic of the Thermofuel relative to conventional diesel is likely to be responsible for the better burn-out of particulates [21].

In the Thermofuel process the first reaction occurs in the pyrolysis chamber where the plastic is thermally pyrolyzed, causing random scission of carbon chain lengths. While secondary reactions occur in the catalytic converter (i.e. catalyst tower) where shorter carbon chains are reformed and further cracking of longer carbon chains occurs such

**Table 15.5** Nitrogen oxides (NO<sub>x</sub>) emissions from Thermofuel diesel as compared with conventional diesel

| Engine load | NO <sub>x</sub> (ppm)<br>(Thermofuel fuel) | NO <sub>x</sub> (ppm)<br>(conventional diesel) |
|-------------|--|--|
| 1/5         | 90   | 150  |
| 2/5         | 180  | 215  |
| 3/5         | 300  | 330  |
| 4/5         | 420  | 400  |
| 5/5         | 500  | 450  |

**Table 15.6** Particulate engine emissions from Thermofuel diesel as compared with conventional diesel

| Engine Load | Particulates %<br>(Thermofuel™ fuel) | Particulates %<br>(conventional diesel) |
|-------------|--------------------------------------|---|
| 1/5         | 0                                    | 0                                       |
| 2/5         | 0                                    | 2                                       |
| 3/5         | 5                                    | 17                                      |
| 4/5         | 22                                   | 40                                      |
| 5/5         | 43                                   | 70                                      |

that the carbon chain length distribution in the range from C<sub>8</sub> to C<sub>25</sub> and peaking at C<sub>16</sub> (cetane) is achieved.

In the Thermofuel process, carbon and coke deposits formed during the pyrolysis are continuously scraped from the pyrolysis chamber walls and reduced to a free-flowing black powder. Inorganic additives such as cadmium pigments from the plastics also end up in the char stream. The carbon matrix has a metal 'fixing' effect and binds up the metal ions so that no leaching occurs after disposal.

The noncondensable gas from the pyrolysis reactor is scrubbed of acidic gases in a water scrubber and then burnt in a noncondensable gas burner. The typical emissions from this burner are as follows:

| <i>Emission type</i> | <i>Value</i>           |
|----------------------|------------------------|
| SO <sub>x</sub>      | <5 ppm                 |
| NO <sub>x</sub>      | 198 ppm                |
| Dust density         | 0.06 g/cm <sup>3</sup> |
| Temperature          | 438°C                  |
| Water vapour         | 13%                    |

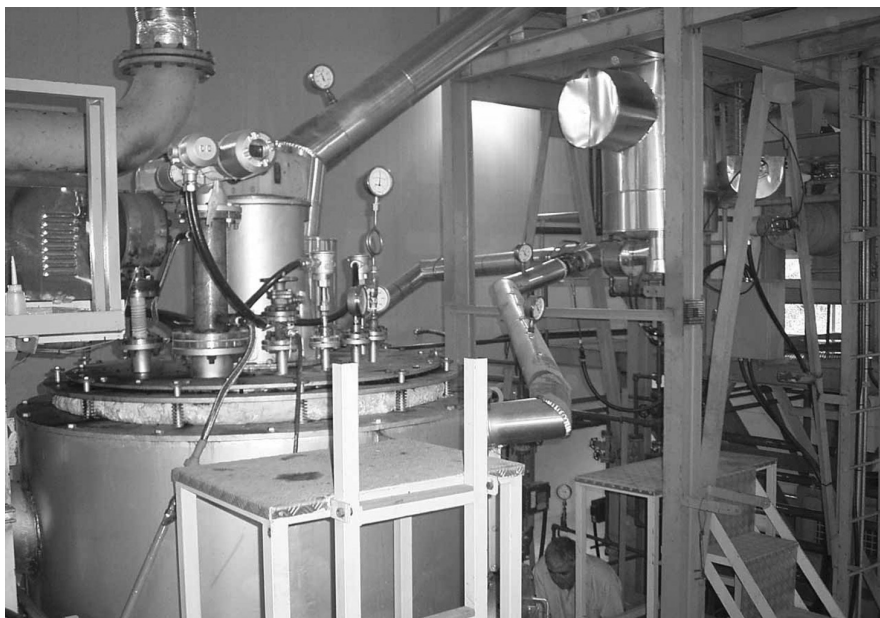
The above emissions data is for the Totai plant in Japan running a mix of PE (43%), PP (40%) and nylon (17%).

## 7.2 SMUDA PROCESS

The Smuda pyrolysis process developed by Dr Heinrich W. Smuda (Figure 15.10a) is a continuous process where the mixed plastic feedstock is fed from an extruder into a stirred and heated pyrolysis chamber [22, 23]. The extruder acts as an airlock to exclude oxygen and also to preheat and melt the polymer, so less energy input is required in the main chamber. The pyrolysis vessel operates at a constant level of 60% and the headspace is purged with nitrogen gas. A layered silicate catalyst (5–10% by vol) is added to the plastic melt to give a catalytic cracking reaction [24]. The fuel from the Smuda process is both transportation-grade diesel (85%) and gasoline (15%). The gasoline produced by the process is used in a cogenerator to produce electricity for the process. The diesel has an average olefin content of 10%, a flash point of 70°C and a pour point of –40°C. Since the diesel produced catalytic cracking contains approximately 10% olefin and inhibitor such as 0.01% BHT is required to suppress polymerization and gum formation [24].

The original Smuda Process is covered by a United States Patent entitled 'Method of obtaining liquid fuels from polyolefine wastes' [22]. The process charges a non-zeolite metal silicate catalyst directly into the main reactor which reduces the energy level required to scission the carbon chains of plastics and produces superior and stable-quality hydrocarbon products. In contrast to fluidized-bed pyrolysis processes, the Smuda process requires less capital investment and less operating cost. Pyrolytic vapours of the molten plastic are condensed in a cooler and then separated on a distillation column to give transportation-grade diesel. The diesel product (the fraction with boiling point in the range 170–300°C) shows very good low-temperature properties such as a cloud point and cold filter blocking temperature (CFPP) of –45°C and also very high cetane number of 65 [22].





**Figure 15.10** (a) Photograph of the inventor of the Smuda Process, Professor Heinrich Smuda (right) and the editor Dr John Scheirs (left). (Copyright © J. Scheirs). (b) Photograph of Smuda stirred-tank reactor (left) and bottom of distillation column (right). (Copyright © J. Scheirs)

Nickel silicate and ferrous silicate are the preferred catalysts in the Smuda process. The Smuda catalyst is a layered silicate clay framework with ordered nickel (or iron) atoms inside. The catalyst is charged at 10 wt% ratio of the plastic feedstock. The catalysts are based on layered silicates with Lewis acid activity [24]. Catalytic cracking results in very little noncondensable gas (<1%) and minimal carbonaceous char. The life of the Smuda catalyst is approximately 1 month [24].

Natural minerals and ores containing transition metal ions, steelmaking slags or metal plant wastes can be used as catalysts or sensitizers in the plastic material cracking. These materials include  $\text{Ni}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_4$  and  $\text{Co}_2\text{O}_3$ .

A number of low-grade transition metal ores (for example, minerals containing nickel oxides) can be used as catalysts. Smuda has demonstrated that microwave or radiofrequency irradiation of a mixture of such ores with a carbon source initiates reduction of the oxide to metal. With this approach, poisoning the active sites of the catalyst will not be critical for the process since there will be a constant supply and generation of active catalyst with the feed material. In addition to well-known catalytic properties of nickel in organic reactions, it was also shown that Ni on carbon and other supports, catalyzes hydrodechlorination and dehydrochlorination of chlorinated organic waste streams [22–24].

The Smuda process also uses new cracking catalysts based on cobalt resins which are cobalt salts of resin acids (mainly abietic acid) such as cobalt abietate and cobalt linoleate (these are commonly referred to as driers in the coatings industry) and preferably with admixtures of heavy metal silicates. Smuda has also explored the use of manganese resinate deposited on an aluminium oxide support to maximize active surface area [23].

In the Smuda process the pyrolysis reactor temperature is  $350^\circ\text{C}$  and the operating pressure is 4–5 psi. The pyrolysis gases from the pyrolysis vessel are sent directly to a distillation column. The distillation column has a typical temperature profile as follows: top  $140^\circ\text{C}$ , Sulzer 250Y; middle  $322^\circ\text{C}$ , Sulzer 350Y and bottom  $331^\circ\text{C}$ .

The melt is stirred with an agitator running at 30 rpm to keep the catalyst in suspension. The torque on the agitator is monitored to determine the level of inorganic impurities and carbon residues that have accumulated. At a preset torque level the polymer melt is completely pyrolyzed and the carbon residues and impurities are then evacuated from the chamber using an auger positioned in the base of the vessel. Char removal is only activated when the vessel is cooled.

The Smuda catalysts, due to their acidic nature, have a low tolerance to alkaline compounds. Accordingly Nylons (which form ammonia) and ABS (which form amines) are not suitable since these polymers form by-products which are alkaline in nature. PVC does not pose a problem since the acidic by-products do not deactivate the catalyst [24].

Due to the sensitivity of the catalyst, the Smuda process requires that the plastic feedstock be pre-processed and cleaned by mechanical processing (i.e. other than washing). In this way dirt, food impurities, etc. can be removed before they deactivate the catalyst [24].

An additional problem with the powdered silicate catalyst in the polymer melt is that carryover (i.e. entrainment) of fine catalyst particles into the diesel stream can occur.

Advantageously, the Smuda Process can tolerate high levels of PET. In catalytic pyrolysis the terephthalic acid is decarboxylated to give benzoic acid and benzoates [24] (see also Figure 15.3). PET gives fuel with appreciable aromatic content (e.g. level of 10% or higher). In other competitive processes PET proves problematic due to the formation of troublesome terephthalic acid (TPA) deposits in the downstream pipework and condensers.

The Smuda process uses a reflux return where longer paraffin chains that condense shortly after exiting the main chamber are allowed to flow back to the main chamber (the 'reflux effect'). Also the heavies from the bottom of the distillation column flow back to the pyrolysis chamber for re-cracking (Figure 15.10b).

In 1997, the world's largest catalytic cracking plastics recycling plant began operation by AgRob EKO, S.A. in Zabrze, Poland. The plant has six cracking reactors each with a volume of 20 m<sup>3</sup> and equipped with agitators and internal heat exchangers. The reactors are run in a semi-continuous mode and after cracking approximately 60 tonnes of waste plastic and spent lubrication oil, they are stopped for cleaning and coke removal by scraping the internal heat-exchanging surfaces of the reactor. Since the plant runs a catalytic cracking process with silica alumina catalysts, coke formation is minimized (as compared with thermal cracking). In 2000, Dr Smuda began an association with a South Korean company to develop the Smuda Process, - an integrated process for catalytically converting post-consumer plastics into gasoline and low-sulphur diesel fuel.

### **7.2.1 Specific Advantages of the Smuda Process**

- The process is continuous.
- Vessel is filled with 60% plastic melt and the level is maintained there using a level sensor.
- Excellent temperature uniformity and control of pyrolysis vessel (chamber is heavily insulated).
- Solid residue (coke) removal is automatic (by auger).
- Fractionation column ensures the boiling point range of liquid outputs.
- Liquid yield is high (95%) due to low temperatures used (350–370°C).
- Heavies from fractionation column are re-fed to reactor.
- Process also incorporates a diesel side-stripper, gasoline stabilizer and fuel dechlorinator.
- The process uses a 'catalytic isomerization dewaxing' step to preferentially isomerizes the paraffins, thus reducing the diesel pour point and cloud point while keeping the high-cetane components in the diesel product.
- Rapid stirring of the melt (30 rpm) ensures proper catalyst distribution and dispersion as well as satisfactory heat distribution

### **7.2.2 Specific Shortcomings of the Smuda Process**

- Catalyst is consumable and hence has an associated operating cost (~ US\$20/kg).
- Impurities and dirt in feedstock dramatically shorten catalyst life.
- Process requires feedstock pre-processing in order to remove impurities.
- Catalyst is charged into reactor monthly with catalyst activity decreasing over time.
- Catalyst is acidic and is especially deactivated by Nylons and other polymers that produce alkaline (i.e. basic) by-products.
- Catalyst type (there are some 20 to choose from) is determined by the composition of the feedstock.
- The only indication of catalyst deactivation is a gradual deterioration in diesel quality.

- The above situation necessitates frequent quality control checks on the diesel.
- There is no centrifuge in the process to remove water and carbon residues from the diesel.
- Close proximity of multiple heating pipes in larger reactors renders them prone to coking and fouling.
- The diesel fuel has 10%  $\alpha$ -olefin content (i.e. terminal unsaturation or double bonds) which make the fuel unstable and prone to polymerization (i.e. sludge formation).
- There is no proven track record for producing transportation-grade diesel from the Smuda Process (Poland plant produces crude oil from plastics which is subsequently sent to a refinery).

### 7.2.3 Similarities of the Smuda Process and the Thermofuel Process

- Both use a stirred tank reactor.
- Both use a paddle agitator that also serves to prevent coking.
- Both are fed with molten plastic from an extruder.
- Both use nitrogen purging before the pyrolysis begins.
- Both use low temperature pyrolysis (350–425°C).
- Both employ a reflux philosophy where 'heavies' are sent back to the reactor for further cracking.
- Both produce predominantly diesel, along with gasoline, some LPG and a coke residue.

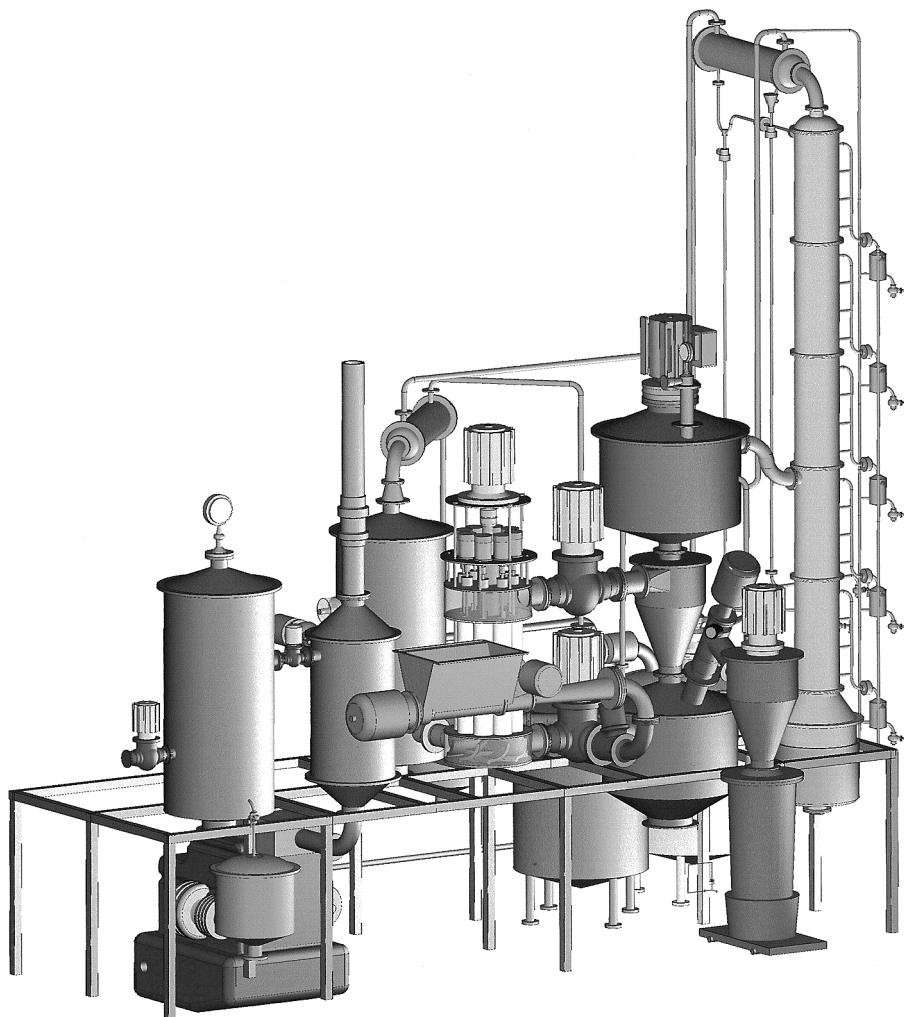
### 7.3 POLYMER-ENGINEERING PROCESS (CATALYTIC DEPOLYMERIZATION)

A catalytic diesel process (Figure 15.11) is being offered by a German company called Polymer-Engineering (Bielefeld, Germany). The process was developed by Alphakat GmbH (Buttenheim, Germany) and Siemens and is described in German Patent DE 100 49 377 C2 by the inventor Dr Christian Koch. The process which has been trademarked as NanoFuel<sup>®</sup> Diesel produces high-grade stabilized diesel fuel from waste plastics. Further information can be found at <<http://www.globalfinest.com/tech/>>. The process converts waste plastics by catalytic depolymerization at 270–370°C in the presence of an ion-exchanging catalyst (disclosed as a crystalline, highly active Y sodium aluminosilicate zeolite catalyst). The composition of the end products of the catalytic depolymerization is:

- liquid fuel (diesel)      93–95%
- noncondensable gas      4–5%
- residue                      <1%

The process uses hot oil (high boiling bunker oil) as the pyrolysis medium to ensure good thermal conductivity and eliminates the need for an expensive hot melt extruder, as the plastic flakes melt instantly on contact with the hot oil. The heat required for melting the mixed thermoplastics is quoted at 0.28 kW h/kg [25].

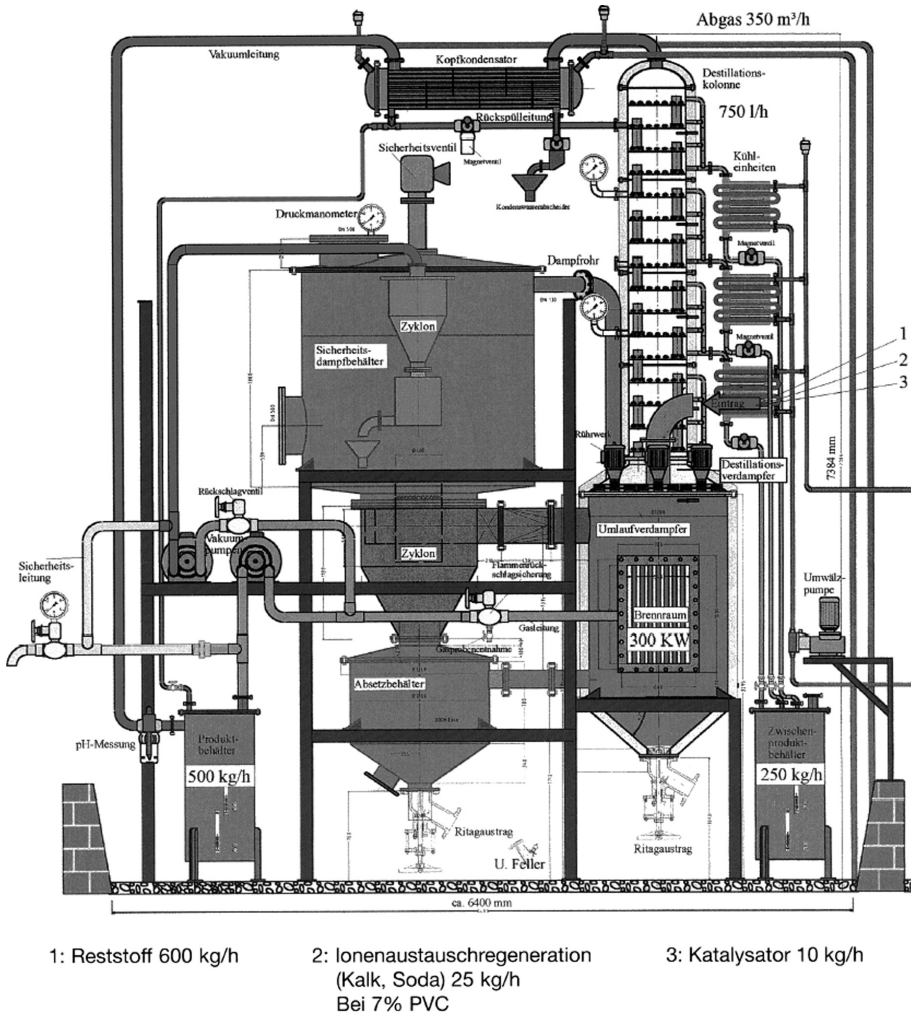
The catalytic pyrolysis process is characterized by the very high liquid fuel yield and the low noncondensable gas and solid residue yields in contrast to thermal pyrolysis. The diesel product from the NanoFuel<sup>®</sup> Diesel process has a cetane number of >56, is completely desulfurized and the chain-end double bonds are saturated in the process,



**Figure 15.11** Overview of the NanoFuel<sup>®</sup> catalytic diesel process process developed by Dr Christian Koch. The process converts waste plastics by catalytic depolymerization at 270–370°C in the presence of an ion-exchanging catalyst based on a highly active Y sodium aluminosilicate zeolite catalyst. (Courtesy of Polymer-Engineering, Bielefeld, Germany)

thus stabilizing the diesel fuel. The diesel fuel is intended for use as substitute diesel for transportation. The desired boiling range for the diesel fuel is achieved by the use of a distillation column above the pyrolysis reactor. The process can convert an input stream of 1000 kg of mixed polyolefins (LDPE/PP/HDPE) into >900 L of low-sulphur diesel fuel [25].

The plastic flake and catalyst are fed into the stirred reactor *via* a feeding chute. The diesel vapours are produced in the evaporator and sent to the distillation column for diesel fractionation (Figure 15.12). In the lower part of the reactor the chlorine-bound salts and

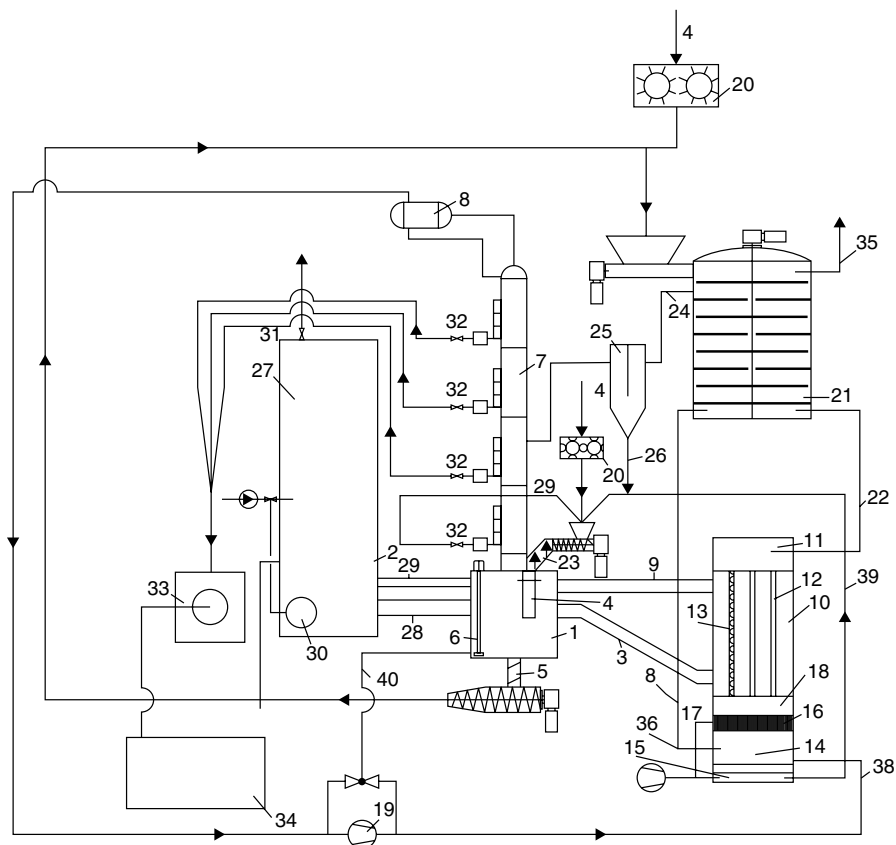


**Figure 15.12** Schematic of the NanoFuel<sup>®</sup> catalytic diesel process developed by Dr Christian Koch. (Courtesy of Polymer-Engineering, Bielefeld, Germany)

spent catalyst are removed from the reactor by an auger positioned at the outlet [25]. An annotated schematic of the NanoFuel<sup>®</sup> Diesel process is shown in Figure 15.13.

The depolymerization catalyst possesses cations that make it act as an ion exchanger. Before the hydrocarbon plastics begin to thermally crack, they are dechlorinated and dehalogenated by neutralization by the ion exchanger.

The ion-exchange catalyst dechlorinates the plastics (e.g. PVC) and therefore avoids issues with HCl generation and chlorine contamination of the diesel. The company claims to have processed cable waste consisting of almost 100% PVC and the catalytic depolymerization process produced diesel fuel with a chlorine content below the detection limit. The catalyst needs to be activated before use via ion exchange using soda (sodium carbonate) and lime (calcium hydroxide) in order to insert the sodium and calcium ions



**Figure 15.13** Schematic of the NanoFuel<sup>®</sup> catalytic diesel process plastic-to-diesel plant from German Patent DE 100-49-377-C2

**Legend:**

1 reactor; 2 pressure-free tank; 3 oil; 4 inlet; 5 waste catalyst gate; 6 mixer; 7 distillation line; 8 condensor; 9 connecting pipes; 10 cycle vaporizer; 11 tank; 12 exhaust pipes; 13 swirl spiral; 14 combustion; 15 burner; 16 honeycomb catalyst layer; 17 temperature control; 18 honeycomb layer; 19 vacuum pump; 20 shredder; 21 regenerator; 22 connecting pipe; 23 inlet gate; 24 smoulder exhaust; 25 seperator; 26 water treatment; 27 release tank; 28 pipes to release tank; 29 pipes from release tank; 30 fluid level indicator; 31 pressure release valve; 32 cooler with outlet (withdrawal); 33 liquid separator; 34 tanks; 35 smoke gas exhaust; 36 connecting pipe between catalyst dryer and combustion chamber; 37 ash exhaust pipe; 38 gas pipe from vacuum pump to combustion chamber; 39 oil pipe from lowest level to entry; 40 return pipe from lower line to reactor. (Courtesy of Polymer-Engineering, Bielefeld, Germany).

into the zeolite catalyst. The usage rate of catalyst is stated to be 1.5% of the output of diesel (which is 12 000 L/day) and this equates to 180 kg of catalyst usage per day. It is the ion exchange capability of the catalyst that enables the considerably lower cracking temperatures compared with conventional catalysts [25].

The acid cracking catalysts produce carbonium ions by the addition of protons to polyolefin chains or by abstraction of hydride ions from hydrocarbon molecules. This is followed by chain scission, which yields  $C_{30}$ – $C_{50}$  oligomeric hydrocarbons. Secondary cracking by  $\beta$ -scission of the  $C_{30}$ – $C_{50}$  hydrocarbons yields liquid ( $C_{10}$ – $C_{25}$ ) hydrocarbon fuel.

Specific advantages of the Polymer-Engineering Process include:

- Molecular depolymerization at low temperatures (270–370°C) and under virtually pressure-free (<0.1bar) conditions.
- The ion exchanger catalyst binds the chlorine in the waste plastic to form neutral salts. The catalyst splits the long-chain hydrocarbons into shorter chains at a maximum temperature of 390°C.
- Virtually no carbon is formed during catalytic depolymerization and therefore no carbon residue accumulates on heat exchanging surfaces.

Catalytic depolymerization plants (KDV 500) with a capacity of 500 L/h have been constructed for Germany, Mexico, Japan and Korea while a KDV 150 B plant with a capacity of 1 500 000 tonne/yr is under construction for Bayern Oil in Germany to treat vacuum residue [25].

The Polymer-Engineering process is very similar to the Thermofuel system design, except that the main chamber contains a heavy thermal oil with a high boiling point. The waste plastic is continuously added as flake and it quickly melts in the thermal oil and pyrolyzes. The heavy oil is held at 390°C and the plastics quickly pyrolyze since it is an excellent heat transfer medium.

In a related process Arandes *et al.* [26] dissolved polyethylene and polypropylene in light cycle oil (LCO) and then catalytically cracked the polymers using a mesoporous silica (pore size between 3 and 30 nm) in a commercial fluid catalytic cracking (FCC) unit at 450°C. This strategy for upgrading plastics and oils together avoids heat transfer limitations and other problems inherent to the cracking of molten plastics. The polyolefins gave fuel with increased content of paraffins and iso-paraffins.

#### 7.4 ROYCO PROCESS

The Beijing Roy Environment Technology Co., Ltd (also known as Royco) has developed a commercial pyrolysis process for turning waste plastics into oil known as the EZ-Oil Generator™ process.

The EZ-Oil waste plastics cracking unit converts waste plastics (e.g. waste plastics including PP, PE, PS mixed plastics) into oil by low-temperature thermal cracking in the absence of air and utilizes the output to produce electricity. The system includes a feeding unit, reaction vessel, distillation tower, solid residue extractor/drying unit, circulation water unit, oil storage unit, wastewater treatment unit, a scrubbing unit, and power-generating unit. The company's Web site is at [www.roycobeijing.com](http://www.roycobeijing.com).

A 20 t/day plant (6000 t/yr) is equipped with two pyrolysis vessels (with dimensions of 2800 mm ID and 2000 m height). The vessels are fed with molten plastics by four extruders each with a capacity of 250 kg/h. The plant runs continuously and can feed waste plastics and discharge the solid residue while the plant is running. The liquid fuels are fractionated in a fractionation tower. The plant produces a liquid fuel yield of up to 80% (by weight), depending on the nature of the feedstock.



The majority of waste plastic to oil processors utilize flue gases and other means to heat their systems indirectly thereby having loss of heat energy. By so doing, these other systems face problems with costs of operation, coking and inefficient processing of the waste plastics. The Royco system utilizes a novel heating system based on far infrared inner heating which dramatically reduces costs, virtually eliminates coking and is most efficient compared with traditional heating methods. The major advantage of the far infrared system is that it heats the waste plastics much more quickly and more thoroughly, thereby shortening the time needed to melt the plastics to the stage where the hydrocarbon vapours are released. Another significant advantage is that with the inner heating system, the amount of heat loss is greatly reduced so that the unit runs more economically and efficiently than other units who use indirect heating sources.

Notable features of the process are:

- The sediments like sand, mud, sludge, etc. are discharged out of the bottom of the reactor while the plant is running.
- The molten plastic flows into the noncatalytic cracking unit where the liquid is cracked into gas and fuel oil vapour and then leaves out of the top of the unit to go to the condenser and fractionating tower.
- A 'reflux' is used where 'lighter' liquid is injected at the top of the distillation column and this "strips" by counter-current absorption the heavy components from the rich vapour rising up the packing inside the column.
- The noncondensable gas from the top of the tower is compressed into liquid gas (LPG) and dry gas. The liquid gas is high quality.
- The fuel oil mixture from the cracking process is sent through the extraction and fractionation process where high-grade fuel oils are obtained.

The technology is covered by the following patents:

- WIPO PCT/IB2004/000306 (Pending) 'Enhanced Oil Recovery From Waste Plastics Reactor' (February 2004)
- US 60481826 (Pending) 'A Reactor and Process for Converting Waste Plastics into Oil with the FIR Heater' (December 2003)
- Japan 2002-145569 (Pending) 'Movable Apparatus and Method for Extracting Fuel from Waste Plastics and Waste Oil' (May 2002)

### 7.5 REENTECH PROCESS

Reentech Limited (Korea) has developed a patented catalytic cracking process (Figure 15.14) which converts mixed plastics (e.g. PE, PP, PS) into gasoline, kerosene and diesel fuel [27–31].

The Reentech moving-bed catalytic cracking process enables the continuous preparation of gasoline, kerosene, and diesel oil from waste plastics. The method comprises the steps of subjecting a melt of the waste plastics to a first catalytic reaction in which the waste plastic melt is in contact with a nickel or nickel alloy catalyst to be dehydrogenated while being thermally decomposed, then subjecting the dehydrogenated and decomposed waste plastic melt to a fluid catalytic cracking (moving-bed catalytic cracking), fractionating the cracked material into a gasoline-based fraction, a kerosene fraction, and a diesel oil fraction; and reforming the gasoline-based fraction to produce a high octane number gasoline [27–31].



**Figure 15.14** Photograph of the Reentech catalytic cracking process in Korea. The Reentech process converts mixed plastics (e.g. PE, PP, PS) into gasoline, kerosene and diesel fuel. (Courtesy of Reentech, Korea)

The incoming waste plastic melt is brought into contact with a catalyst impeller (preferably made of nickel or nickel alloy) at a temperature of 350°C. to 370°C., thereby being dehydrogenated and decomposed. The downstream process consists of a moving-bed catalytic cracker, in which a melt of the waste plastics and an alumina silicate solid acid catalyst particles are introduced downward from the upper portion thereof, and cracked and isomerized, and into which steam is injected through its lower portion to vaporize nonvaporized gaseous oil present on the catalyst surface. The cracked gases are sent to a fractionating column to give various hydrocarbon fractions. The fractionating column is an Aspen fractionating column having a bubble cap tray type [29].

A cyclone outside the moving-bed catalytic column serves to sort only catalyst particles of a desired size among the catalyst particles dropped to the lower portion. A nickel–molybdenum catalyst regenerator with an air injector serves to regenerate the catalyst transferred from the cyclone and the regenerated catalyst is then returned to the moving-bed catalytic cracker [29].

The process yields the following products:

- 75% fuel oil (comprising 55% gasoline, 25% kerosene and 20% diesel);
- 15% noncondensable gas (used as energy in the plant);
- 10% carbon (coke).

The annual capacity of the Reentech plants is 6000 tonne/yr of plastic input yielding some 4.2 million litres of fuel oil [27].

The gasoline fraction has the following property profile:

- |                              |         |
|------------------------------|---------|
| • iso-C4, C5                 | 25%     |
| • Aromatics                  | 13%     |
| • olefins                    | 8.6–10% |
| • benzene                    | 1.4%    |
| • octane number (RON)        | 91–94   |
| • Reid vapour pressure (RVP) | 144 kPa |

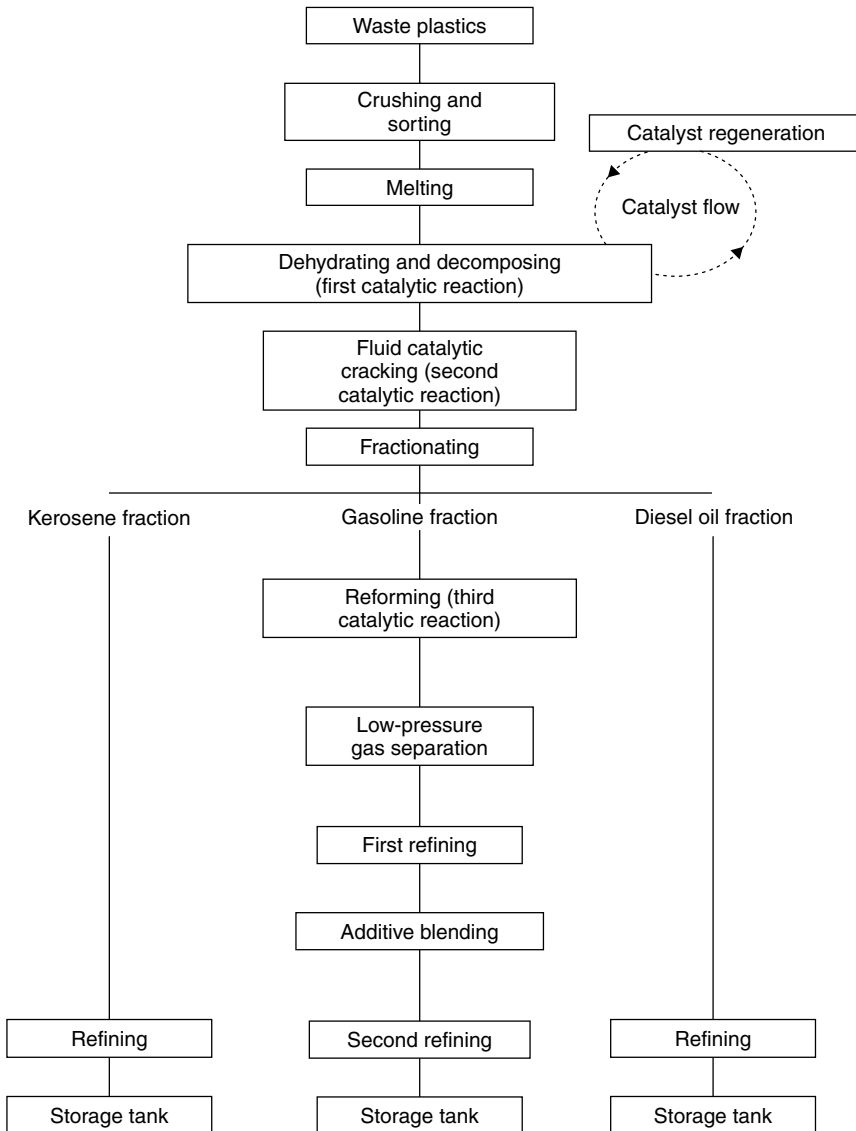
The Reentech process incorporates the following key process steps:

- melting;
- dehydration and polymer decomposition (first catalytic reaction);
- contact catalytic cracking (second catalytic reaction);
- fractional distillation;
- refining of gasoline fraction;
- addition of additives.

A process flowchart for the Reentech process is shown in Figure 15.15.

The Reentech process uses a moving-bed catalytic cracking step, which is fundamentally the same concept as a refinery fluid catalytic cracking unit (FCCU). The FCCU converts high-boiling hydrocarbon pyrolysis gases to high-value high octane gasoline and kerosene/diesel mixture. The FCC unit utilizes a microspheroidal catalyst that fluidizes when properly aerated by vaporized feed in the reactor riser. The term ‘fluid’ catalytic cracking unit is derived from this characteristic property. The gas–oil feedstock is vaporized by hot catalyst and thermally and catalytically decomposes in the reactor riser to produce various products. These products undergo additional processing and separation in the FCCU main fractionator and other vessels downstream of the FCCU reactor. As a result of the cracking process, carbon (or coke) is deposited on the catalyst. The spent catalyst is sent to the regenerator, where it is regenerated by burning off the carbon, utilizing atmospheric air. The regenerated catalyst is then circulated back to the reactor, where the process is repeated [27–31].

Reentech has adapted fluid catalytic cracking (FCC) for the small-scale refining of PE, PP, and PS scrap. In FCC, a catalyst is used to accelerate the thermal cracking process. In this form of cracking, the fractions are heated and then passed over zeolites, certain types of clay, or other catalysts. FCC is more widely used than thermal cracking because it requires less pressure and produces higher-octane gasoline. Also FCC can convert the heavy fractions of the distillation process more efficiently than thermal cracking. In theory, FCC is particularly suited for the recovery of the fuel value contained in plastic scrap as gasoline, kerosene and diesel oil. The key to Reentech’s technology is a *continuous* catalytic cracking process that Reentech calls *contact catalytic cracking* that continuously regenerates the catalyst stream and thus delivers freshly activated catalyst to the catalyst cracker (Figure 15.16). In contrast, the spent catalyst in a full-scale refinery must be removed and replaced when the catalyst degenerates. The continuous regeneration of the catalyst increases the efficiency of the processes, allowing the process to be run economically on a relatively small scale [27–31]. Figure 15.16 illustrates the principle of continuous regeneration combined with catalytic cracking.

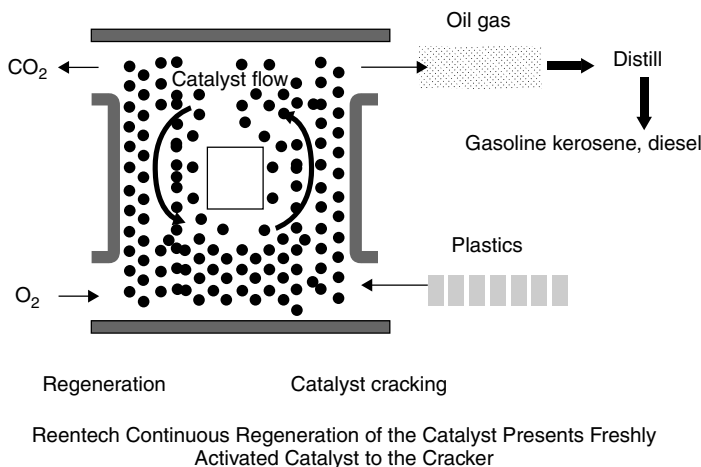


**Figure 15.15** Flowchart of Reentech catalytic cracking process. (Courtesy of Reentech, Korea)

The catalyst flow process is as follows:

- regeneration at 700°C;
- transport to cracking reactor;
- vaporization of cracking gasoil;
- lifting up to regeneration tank.

The carbon residues of catalytic cracking are separated by a cyclone.



**Figure 15.16** Schematic of Reentech continuous regeneration of the catalyst which supplies freshly activated catalyst to the cracker. (Courtesy of Reentech, Korea)

The noncondensable gas separated in the distillation tower is passed through a water scrubber to remove HCl if PVC is present. Then the NCG is contacted with refrigerated gasoline to condense some light fractions and finally the gas is passed through a flame arrestor to a burner in the flame stack.

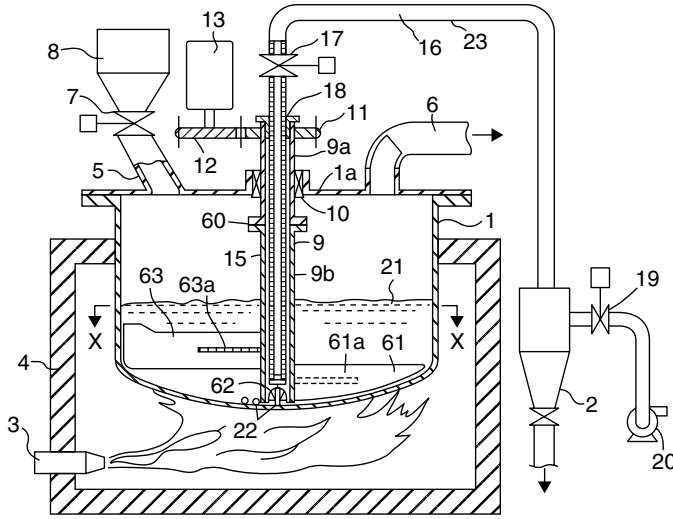
## 7.6 HITACHI PROCESS

Hitachi Zosen have developed a stirred tank/kettle pyrolysis process for waste plastic (Figure 15.17) that is characterized by the following features [32, 33]:

- the ability to handle mixed plastic waste;
- a relatively low pyrolysis temperature;
- the automatic removal of char and extraneous matter;
- double (or triple) condensers;
- production of kerosene and gasoline fractions.

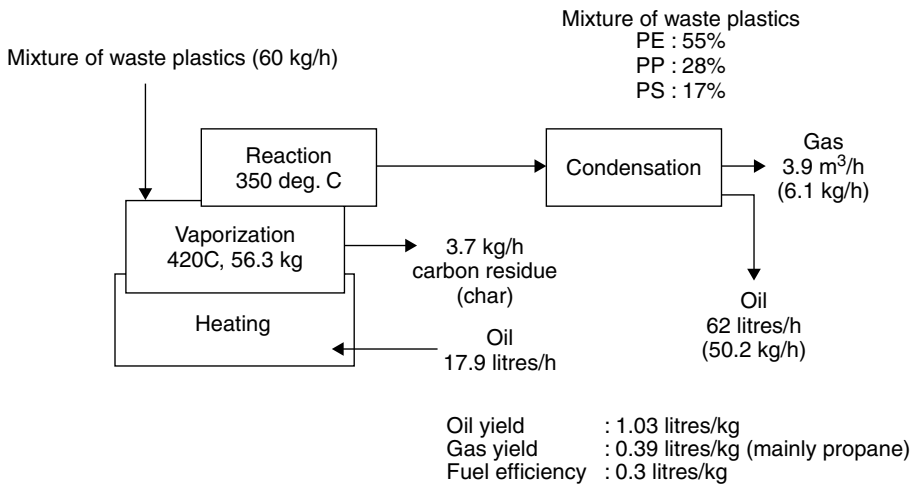
Hitachi Zosen have filed two US patents on their plastic-to-oil technology. The relevant US patent numbers are US 5,584,969 and US 5,597,451 [32, 33]. The first patent (5,584,969) 'Apparatus for thermally decomposing plastics and process for converting plastics into oil by thermal decomposition' embodies a two-condenser system with an option for a third.

In the Hitachi Process the low-boiling component of the gas flowing out from the top of the column of the pyrolysis chamber is cooled and condensed initially in the primary condenser, whereby kerosene is recovered. The low-boiling component of the gas passing through the first condenser without condensation is transferred to the second condenser where it is cooled for condensation, whereby gasoline is recovered. The decomposition gas portion remaining uncondensed from the second condenser is then sent to the gas combustion furnace by way of the water seal device and burned in the furnace [32, 33]. A mass



**Figure 15.17** Schematic of the pyrolysis vessel of the Hitachi Process. A notable feature of the Hitachi Process is that the solid residue (char) is evacuated from the bottom of the pyrolysis vessel via a suction pipe running down the centre of the hollow agitator shaft. Legend: 1 pyrolysis vessel; 2 cyclone for solid residue; 3 burner; 4 furnace; 5 feed inlet to pyrolysis chamber; 6 outlet for pyrolysis gases; 7 slide gate valve; 8 hopper for plastic flake; 9 agitator shaft; 10 packed seal; 12 agitator drive chain; 13 drive motor for agitator; 15 suction pipe for solid residue; 16 vacuum pipe; 17 vacuum cut-off valve; 18 sealing agitator paddle; 19 valve; 20 suction fan; 21 molten plastic; 22 burner flame; 61 char scraper; 63 agitator paddle [32]. (Courtesy of Hitachi, Japan)

**Reclaiming Oil from Waste Plastic (Hitachi Zosen Corp.)**



**Figure 15.18** Mass balance for Hitachi plastic-to oil pyrolysis process. (Courtesy of Hitachi, Japan)

**Table 15.7** Characteristics of the fuel produced by the Hitachi Zosen pyrolysis process

| Property         | Typical value  |
|------------------|----------------|
| Specific gravity | 0.8            |
| Cetane number    | 48             |
| Flash point      | 37°C           |
| Aromatic content | 23%            |
| Sulphur content  | 110 ppm        |
| Viscosity        | 1.50           |
| Calorific value  | 10 800 kcal/kg |

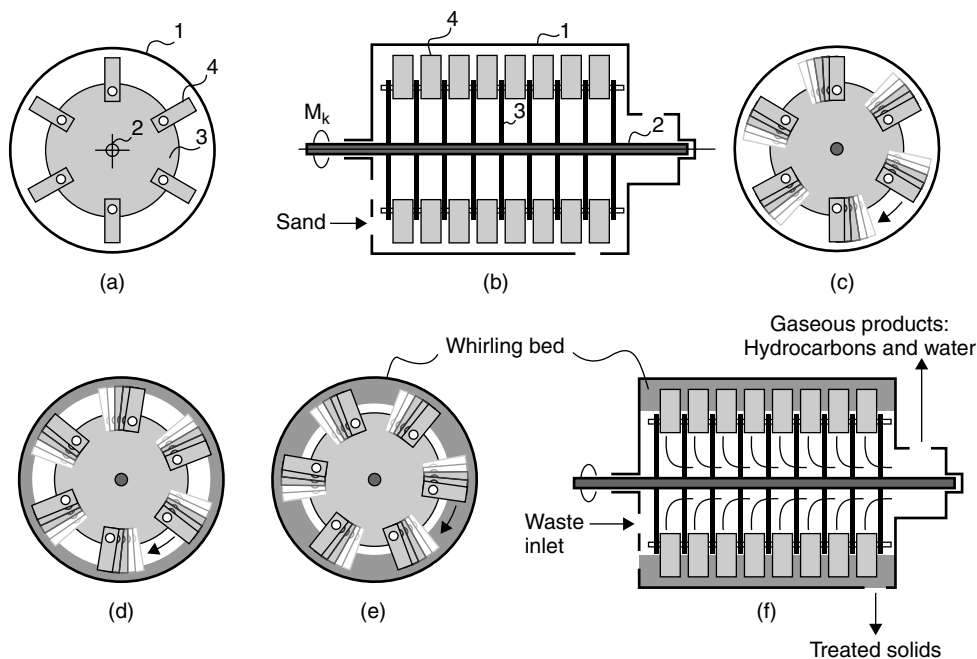
balance for the process is shown in Figure 15.18. The characteristics of the fuel produced by the Hitachi Zosen pyrolysis process from mixed waste plastics are shown in Table 15.7.

### 7.7 CHIYODA PROCESS

Chiyoda Corp., Japan, has developed a next-generation technology for liquefaction of plastic wastes. The new process facilitates reuse of plastic wastes from household refuse into liquid fuel. In the new method, crushed plastic waste is fed to a dechlorination unit where PVC and PET are thermally degraded into hydrogen chloride, terephthalic acid, etc. These gaseous components are separated from the melted liquid plastic and sent to an incinerator for safe disposal. The melted plastic waste is transferred to a thermal cracking reactor where it is further heated and converted to vapour-phase hydrocarbons and residue. The vapour-phase hydrocarbons are charged to a distillation column and separated as cracked gas, light oil, a middle distillate and heavy oil. A portion of the middle distillate is recycled to the thermal cracking reactor as vapour phase through the heating furnace. The heavy oil is mixed with residue from the bottom of the thermal cracking reactor and the mixture is used as a fuel. The separated light oil can be used as a feedstock for petrochemical plants or as fuel oil. Cracked gas obtained at the top of the distillation column is cooled and separated from the light oil and transferred to the incinerator [34].

### 7.8 BLOWDEC PROCESS

The Blowdec depolymerization process from Slovakia converts waste plastics into low-sulphur diesel fuel [35]. The main principle is the processing of waste plastics in a hot whirling bed of hot sand in the BLOWDEC reactor (Figure 15.19). The plastic is heated to 430°C. The process allows for simultaneous cracking of hydrocarbons and inhibition of coke formation. The fluidized sand bed products three types of cracking reactions: mechano-activation; thermal; and catalytic (SiO<sub>2</sub>/aluminosilicates). The process is covered under the US Patent 6,165,349. The process enables the economical conversion of mixed waste plastics into liquid hydrocarbons, mainly low-sulphur (25 ppm) diesel



Principle of the process.

- a, b – Basic scheme of the reactor's construction
- c – Start up (movement of the reactor rotor)
- d – Creation of the whirling bed (sand filling)
- e – Heating of the reactor
- f – Process run

Description: 1-process chamber, 2-shaft, 3-arm of the blade, 4-blade,  $M_k$ -torque

**Figure 15.19** Schematic of the reactor of the Blowdec depolymerization process from Slovakia which converts waste plastics into low-sulphur diesel fuel in a hot whirling bed of hot sand. The plastic is heated to 430°C by the hot sand which also exerts a catalytic effect that enables simultaneous cracking of hydrocarbons and inhibition of coke formation [35] (Reproduced by permission of Slovnaft Virup)

with Pensky–Martens flash point of 62°C and pour point of –15°C, and has the added advantage of the lack of formation of coke residues on heat transferring surfaces [35].

## 7.9 CONRAD PROCESS

Conrad Industries (Chehalis, Washington) have demonstrated the pyrolysis of post-use plastics into petrochemical feedstocks. The plastic most studied was a mixture of 60% high-density polyethylene, 20% polypropylene, and 20% polystyrene. Yields of liquid products were in the range 65–75% at 482–510°C. Other studies examined the effects of PET and PVC on the liquid yields. The liquid products were determined to be suitable feedstocks for further refining, but the economics were not competitive with conventional petroleum refining in 1994 [36].



### 7.10 OTHER PROCESSES WITH SEPARATE CATALYST BEDS

The Likun Process (China) uses a two-stage cracking process under normal pressures where the waste plastics are first pyrolyzed at 350–400°C in the pyrolysis reactor and then the hot pyrolytic gases flow to a catalyst tower where they undergo catalytic reforming over zeolite at 300–380°C. By having the catalyst in the second stage this overcomes the problems of rapid catalyst deactivation from coke deposits on the surface of the catalyst.

The Fuji Process also uses a two-stage cracking process comprising a main cracking reactor and a reforming reactor. In the reforming reactor the pyrolysis oil is upgraded to gasoline, kerosene and diesel.

Such two-step processes are also referred to as cracking–catalytic reforming (CCR) processes. The catalytic reforming stage of the primary oil product ensures high-quality diesel or gasoline products are obtained. The catalytic reforming step improves the RON and the contents of isomer, cycloparaffins and aromatics.

## 8 CONCLUSIONS

A major advantage of plastics pyrolysis is its ability to handle unsorted, unwashed used plastic. This means that heavily contaminated plastics such as mulch film (which sometimes contains as much as 20% adherent dirt/ soil) can be processed without difficulty. Other normally hard to recycle plastics such as laminates of incompatible polymers, multilayer films or polymer mixtures can also be processed with ease, unlike conventional plastic recycling techniques. In fact, most plastics can be processed directly, even if contaminated with dirt, aluminium laminates, printing inks, oil residues, etc. The viability of pyrolysis is assured by the lack of other recovery options for such waste plastics besides landfilling and incineration. The increasing pressure on companies to adopt sustainable outlets for their end-of-life plastics, the introduction of extended producer responsibility and product stewardship directives, together with the implementation of legislative measures to deal with waste plastics are significant drivers which will further increase the interest and adoption of the pyrolysis route for waste plastics.

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