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Technical Methods in Plastics Pyrolysis

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Abstract Plastics pyrolysis is based on thermal and sometimes catalytic breakdown of the polymer structure. The target product may be monomer (from PMMA, PTFE, PS), oil fractions ranging from petrol (C_5-C_{10}) and kerosene (C_{10} -C_{15}) to waxy fractions ($\geq C_{20}$), aromatics, synthesis raw materials formed by hydrogenation or synthesis gas (H_2, CO). The desired product determines the operating conditions required and hence the technology used. A survey is given of laboratory, pilot and industrial scale reactors, pyrolytic extruders, stirred tanks and single- or double-bed fluidized systems. Moreover, the use of plastics in oil refinery-based processes, such as fluid catalytic cracking, hydrocracking, viscosity breaking and delayed coking, and also (coal-derived) hydrogenation and gasification are briefly covered. The product distribution in a pyrolysis process has to be derived experimentally, with the operating temperature, heating rate, catalytic effects, residence time of feed material and reaction products, reaction pressure, possible supply of reactive gases (such as oxygen, hydrogen) and, of course, the chemical constitution and structure of the original plastics as major factors. Pyrolysis involves the breaking of chemical bonds and is normally endothermic. The required heat of reaction can be supplied indirectly through the reactor walls, by a circulating heat carrier, which may be the polymer content of the reactor or the sand in a dual fluid-bed system, or by partial oxidation. The reactor technology is generally determined by the temperature level required, heating method, necessary residence time and possibly the presence of a catalyst, required to rearrange linear structures to high-octane-number branched ones, to eliminate heteroatoms (Cl, N, O, S), etc. Some potential operating problems are addressed in an EU-funded project with acronym Cycleplast, a joint project of five teams from Central and Western Europe, the aims of which are briefly described.

INTRODUCTION

Plastics are a product of this century. World production has been escalating rapidly, as follows from Table 1. Originally plastics were mimicking and replacing natural products. Today they are largely synthetic materials, made from an extremely inexpensive, but non-renewable resource, crude oil (Figure 1). More complex polymers, such as polystyrene, poly(vinyl chloride) or poly(acrylonitrile), require additional raw materials (e.g., benzene, NaCl, ammonia) and synthesis or conversion processes. There is a time lag between production and end-of-life: thus, 16 000 000 t of plastics in 1995, i.e. only 2/3 of total production ended up in the Europe waste stream of that year.

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Table 1. World Production of Plastics [1,2]

Year	World Production of Plastics, t/y	Cumulated growth rate, %/y
1930	100 000	-
1950	1 500 000	14.5 % over 1930/50
1968	20 000 000	15.5 % over 1950/68
1995	100 000 000	6.1 % over 1968/95
In Europe (1995)	24 000 000	-

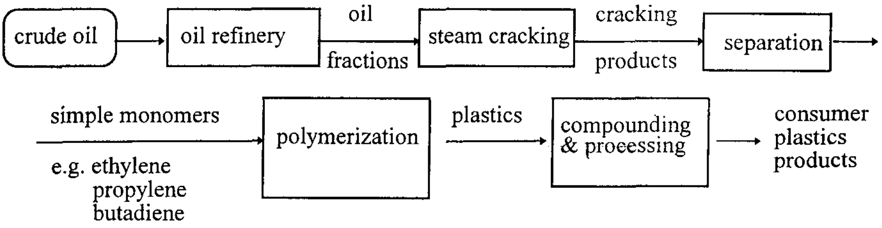


Figure 1. Actual production flow-sheet of plastics

Plastics waste management can be subdivided into the following hierarchical sequence (Figure 2):

(1) *mechanical* or *materials recycling*, preserving the macromolecular structure of plastics polymers,

(2) *chemical* or *feedstock recycling*, which converts plastics into monomers, oil refinery or petrochemical feedstock, and

(3) *energy recycling*, such as in the incineration with heat recovery of plastics contained in municipal solid waste.

Such classification, however, is only theoretical for the post-user waste since the entire system should be confronted with the much simpler energy recycling, taking into account all technical, economic, energetic and environmental factors. A life cycle analysis is an appropriate method for such an assessment. Moreover, plastics are tailor-made for each individual application, with respect to molecular weight (MW), MW distribution and specific additives. The post-consumer waste incorporates materials of various origin and specifications, with their structure and properties affected by aging, UV exposure, superficial oxidation, moisture and processing (Figure 3). Hence, mechanical recycling of the post-consumer waste is limited to simpler, undemanding applications, which can only cope with a fraction of the post-user waste, namely that of premium quality and simple to collect.

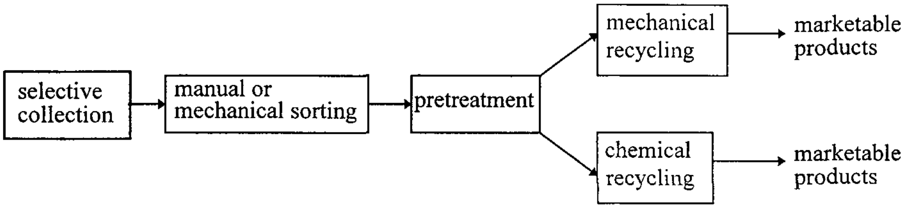


Figure 2. Mechanical and chemical recycling of post-consumer plastics

Chemical recycling may proceed by wet methods, such as hydrolysis, alcoholysis, acidolysis or transesterification on one hand, and by thermal degradation of macromolecules, or pyrolysis on the other.

Pyrolysis also termed *thermal cracking* is a major industrial process, yielding the basic raw materials of petrochemical industry (ethylene, propylene,butadiene, aromatics) by *steam cracking* of liquefied petroleum gases (LPG), naphtha or light gasoil in tubular furnaces. In oil refineries, thermal and catalytic cracking are important in *whitening the barrel*, i.e., converting heavy distillation residues into more desirable, lighter fractions.

Oil refineries are large-scale operations with a typical capacity of 5 to 25 Mt/y for the main stream and a fraction of this capacity for the treatment, upgrading or conversion of a particular distillation fraction. Naphtha crackers typically produce 400 to 600 kt/y ethylene per unit. Even the largest ventures in plastics pyrolysis have a substantially lower capacity, e.g. 3000 to 8000 t/y. Such small-scale processing is obviously more expensive, so that integration of plastics pyrolysis into, e.g., an oil refinery, a naphtha cracker or a synthesis gas production is highly desirable.

Pyrolysis of plastics is technically a feasible process with a potential for *chemical recycling*, i.e. the conversion of high-molecular-weight materials, which can no longer be *mechanically recycled* as a plastic material, into monomer, oil refinery or petrochemical product fractions. The basic data of the process, such as the required operating temperature, the heat of reaction and the products obtained are fairly well known, due to both fundamental and applied studies, conducted in academic institutes and industry.

Specific polymers (PMMA, PTFE) are currently converted into high-value monomers by pyrolysis. However, plastics pyrolysis is only exceptionally an industrial activity because of economic reasons. In most cases, the limited value of the products obtained barely covers the variable and fixed process costs, let alone the expense of collection, sorting and grading, transport, storage, pretreatment and supply of plastics to the pyrolysis plant [3]. Hence, chemical recycling of plastics normally requires a substantial gate fee to cover the operating losses of the operation.

Polyolefins at the end of their lifetime can be used as a supplement to crude oil. This recycling method closes a *long* loop, which basically limits its efficiency, as can be derived from life cycle analysis.

Oil refining is a large consumer of oil on its own; depending on the complexity of the plant, 4 to 7 wt.-% of the incoming oil is locally consumed, in process heaters mainly. The world consumption of petrochemicals is comparable with this amount (7.0 % of the world oil production of which 4 % for plastics). Plastics manufacturers argue that oil consumed in their field serves a higher purpose than is the case if oil is directly used for heating or power generation.

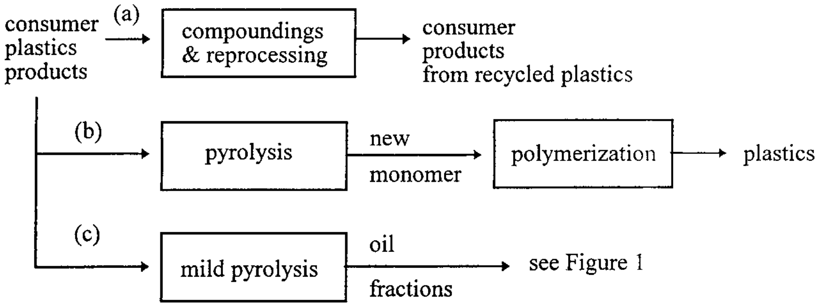


Figure 3. Three routes in recycling: (a) mechanical recycling, (b) chemical recycling by pyrolysis to monomer or (c) pyrolysis to oil fractions

PETROLEUM REFINING AND PRODUCTS

Distillation, treatment, conversion including cracking

Petroleum products are manufactured in oil refineries, according to conventional market specifications. The major treatments, applied to crude oil, are desalting, atmospheric distillation, vacuum distillation of atmospheric residue and possibly pressure distillation of lights, according to the scheme in Figure 4.

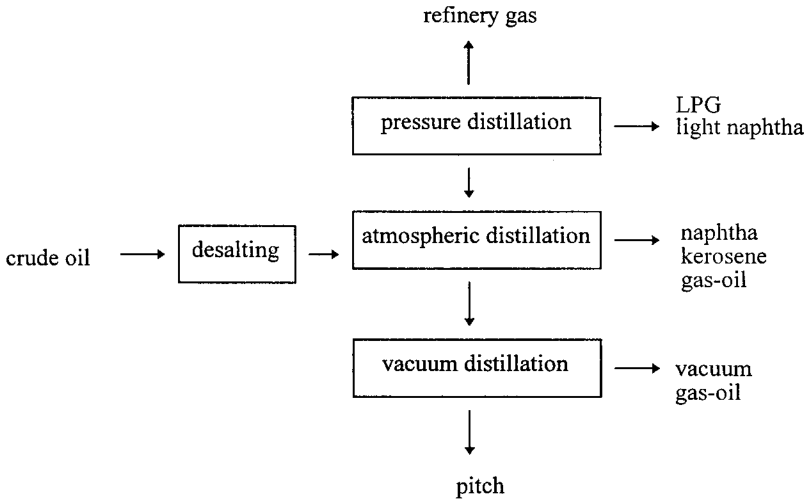


Figure 4. Crude oil distillation

Common fractions from the crude oil distillation column are thus: LPG, naphtha, kerosene, gas oil, and vacuum gas oil, some of which being possibly further subdivided into lighter or heavier fractions. These fractions are further refined or treated to improve their performance and to comply with market specifications. For this purpose, physical as well as chemical processes can be used, such as

- solvent extraction (of aromatics)
- paraffin wax crystallization (from gas-oil)
- asphaltene precipitation (from lubricating oil)
- mercaptan extraction (to reduce sulfur) and oxidation
- hydrodesulfurization (HDS), to eliminate sulfur (and nitrogen) from oil fractions
- catalytic reforming of naphtha to enhance the octane number by simultaneous isomerization of normal paraffins, dehydrogenation of naphthenes (cycloparaffins) into aromatics and conversion of aliphatics into aromatics
- alkylation (to produce petrol with high-octane number from propylene, isobutylene and isobutane) and isomerization of n-pentane
- thermal and catalytic cracking, hydrocracking (delayed and fluid-bed) coking.

Most important are the various cracking processes used to *whiten the barrel*, i.e., to convert heavy fractions into lighter ones. Examples are viscosity breaking, fluid catalytic cracking, hydrocracking, and delayed or fluid-bed coking. All of these operations may accommodate product flows, arising in plastics pyrolysis systems and are now briefly described.

Viscosity breaking (visbreaking)

Visbreaking is a mild thermal cracking, normally applied to crude oil distillation bottoms in order to enhance the yield of light products (gas, naphtha, kerosene) without excessive coking, which would cause a premature plant shut-down of the visbreaker.

The feed is pumped through the tube coils of a refinery furnace and reacted for a while in a soaking vessel; the light fraction is separated from the remaining feedstream and newly formed heavies (Figure 5).

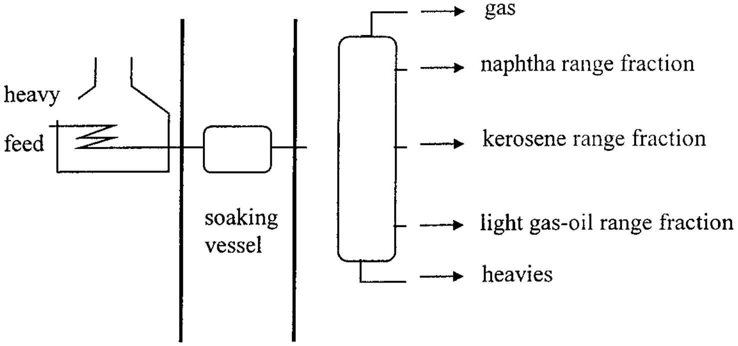


Figure 5. Flow sheet of a visbreaking unit

Plastics subjected to visbreaking should either be blended into the feed in an appropriate mixing vessel (not shown in the figure), or undergo a preliminary treatment to reduce their molecular weight and viscosity. The process is quite suitable for polyolefins, which are dissolved or suspended in the feed, because of their high hydrogen/carbon ratio and low coking tendency. Fillers will report to the heavy fraction. Halogenated polymers are not acceptable because they would necessitate the use of special alloys to prevent corrosion of heating coils and subsequent equipment as well as dehydrohalogenation of the resulting fractions, thus rendering the plant much more expensive and precluding the use of an available plant.

Fluid catalytic cracking - hydrocracking

Since the fifties, fluid catalytic cracking (FCC) has been a major catalytic conversion process to turn heavy distillates (vacuum gas oil) into a series of light and dense fractions:

- a gas fraction (mainly C_3 and i-C_4, suitable, among others, as a feedstock for *alkylation polymerization*). In an oil refinery, *polymerization* refers to the formation of oligomers (trimers or dimers) of C_3- and C_4-olefins for use as a premium petrol blending stock;
- a petrol fraction, with good octane number but strong gum-forming tendency, due to the presence of (mainly branched) olefins
- middle and higher boiling distillates, and
- cokes, either free or deposited on the catalyst.

Traditional FCC uses a cracker bed, in which the reaction is conducted at 450 °C, and a regenerator bed to burn off the cokes at 550 °C and to generate the heat required for cracking. In more recent versions, cracking mainly takes place in the feedline to the (former) reactor, in which catalyst and products finally disengage. Again a polyolefinic feedstock forms a premium supplement to the conventional feed stream; chlorine, fillers and some other additives must be removed beforehand. The main product, a FCC petrol blending stock, consists mainly of strongly branched olefins and aromatics.

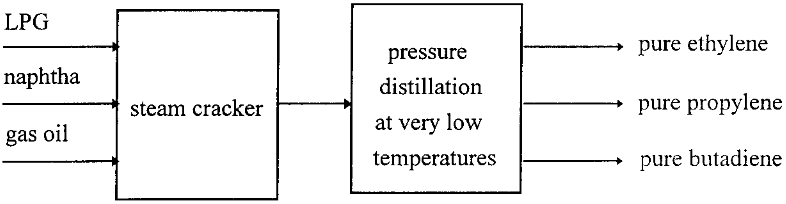
Delayed coking and fluid bed coking

Delayed coking is sometimes used in oil refineries to convert heavy residues into a wide range of products, involving cracking gas, light, medium and heavy distillates, and cokes.
The operation is conducted at more than 400 °C in batch-operated coking chambers, which in the process are gradually filled with cokes and after shut-down are cleared by cutting the cokes in the chambers to pieces. The resulting "petroleum" cokes contain almost all ash from the crude oil, including highly corrosive vanadium oxide, and are a low-grade solid fuel. The process takes residues from other refinery processes and is extremely robust, but also labour-consuming due to the periodic clearing of the coking chambers.
Fluid-bed coking is a continuous version of delayed coking, in which the cokes are formed on fluidized coke particles, which are easily circulated between the coking unit, where the endothermic reaction takes place, and the regenerator, in which the coke particles are reheated by partly burning-off. The process is quite robust and pyrolysis residues are incorporated into the cokes, but here again halogens are undesirable.

BASIC PETROCHEMICAL PROCESSES

Ethylene, propylene, butadiene and, to some extent, BTX (benzene, toluene, xylenes) aromatics, are obtained by steam cracking of inexpensive oil fractions, mainly naphtha (Western Europe, Japan), LPG (USA) and light gas oil. These oil fractions are very rapidly heated in tubular coils, exposed first to convective flue gas heat and then to radiant heat in a gas- or naphtha-fired furnace. Some steam is admixed to the feed to reduce coking. Heating, up to about 860 °C, is extremely fast and breaks down parent molecules to form a very complex mixture of light gases containing H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, etc., and condensable C_5 and higher fraction (pyrolysis gasoline). The hot gas is quenched in a waste heat boiler, the water vapour and gasoline condensed and the resulting gas is separated under pressure at very low temperatures, yielding as major product streams of very pure ethylene, propylene and butadiene fractions.

The process scheme can be simplified as follows :



The major building blocks in petrochemical processes are ethylene, propylene, butadiene, and BTX aromatics. They are used extensively as monomers (ethylene, propylene, butadiene), starting material for reactive intermediates (e.g. ethylene and propylene oxides), solvents, detergents, raw materials for the manufacture of pharmaceuticals, biocides, etc.

Polyolefins may serve as a cracker feedstock only after conversion to liquids with an appropriate boiling range. As an alternative to steam cracking in a coil furnace, the same basic products can be obtained by direct thermal cracking of crude oil in a double fluid-bed system, as developed in the sixties in Japan (Professors Kunii and Kunugi, University of Tokyo). Such fluid-bed thermal cracking has the potential of accommodating various plastics streams, but unfortunately it is not practised industrially.

GASIFICATION

Gasification has been a major industrial process, especially in time periods and countries where the economy relied on coal extraction as a source of fuel (and reactive carbon) supply.

The basic purpose of gasification is (1) to convert solid fuels, such as coal, lignite, peat, wood and other biomass, into a gaseous fuel, for use in street lighting (ca. 1900), industrial and domestic heating and cooking, powering of spark-ignition and internal-combustion (Diesel; operating in the dual-fuel mode) engines, etc.; (2) to provide chemical industry with *synthesis gas*, i.e., a gas with a tailored composition for manufacture of:

- *hydrogen;*
- *ammonia* and derived products (nitric acid, urea, nitrogen fertilizers) from a synthesis gas composed of 75 vol.-% of hydrogen, 25 vol.-% of nitrogen, with minimum of impurities (CH_4) or catalyst poisons (sulfur compounds);
- *methanol* (from which formaldehyde, methyl esters, acetic acid, and others are derived) from a synthesis gas containing two parts of hydrogen per one part of carbon monoxide (some CO may be replaced by CO_2, at a cost of additional hydrogen):
- *aldehydes* and *alcohols*, by hydroformylation of olefins;
- Fischer-Tropsch *hydrocarbon fuels*;
- *syngas* (synthetic natural gas).

The basic reactions in gasification are:

$C + {}^1/_2\, O_2 \rightarrow CO + \text{heat}$ (1) $C + H_2O + \text{heat} \rightarrow CO + H_2$ (2)

or, for a hydrocarbon feedstock, e.g. methane:

$CH_4 + {}^1/_2\, O_2 \rightarrow CO + 2H_2 + \text{heat}$ (1a) $CH_4 + H_2O + \text{heat} \rightarrow CO + 3H_2$ (2a)

The process is also termed *partial oxidation.* It is normally conducted at pressures, ranging from 3 to 7 MPa to save compression costs for the gases produced (both their purification and ultimate conversion take place at high pressure).

Ammonia, methanol and oxo alcohols are still important basic chemicals, the manufacture of which was originally linked to coal coking batteries and coal chemical industry, but has shifted today towards natural gas, oil fractions or inexpensive (open pit-mine) coal, lignite, peat or even wood. In principle, the process can accommodate any source of carbon as a raw material, but the use of inexpensive natural gas considerably simplifies feed handling and downstream processing as well as cleaning of the crude gas. Coal or pitch are used whenever they have a marked cost advantage over easier-to-process fuels. The use of biomass as a raw material has been explored in numerous pilot and demonstration projects, but its use requires a more complicated fuel handling and a pretreatment plant, and approximately doubling the cost of manufacturing. chemicals, such as methanol, from synthesis gas.

Gasification processes, developed for solid fuels, were based on three types of plant:

- vertical shaft or moving-bed gasifiers, using air or oxygen and steam as a gasifying agent, e.g. the Lurgi pressure gasifiers operated by SASOL (South Africa);
- fluid-bed gasifiers, such as the Winkler HT (high-temperature) process;
- entrained flow or Koppers-Totzek gasifiers.

Molten slag or metal processes never found industrial acceptance.

Oil products are much simpler to gasify: basically, it is sufficient to feed the raw material through a burner, operating with a large oxygen deficit, then to maintain the gas for a sufficient soaking time period to (almost) establish thermodynamic equilibrium. A typical operating temperature is 1200 - 1500 °C. The resulting gas stream is quenched in a high-pressure waste-heat boiler and further purified in a well-established sequence of scrubbing, adsorption and chemical conversion processes. Oil gasification processes were developed by Montecatini, Shell and Texaco. The same process has been applied to pulverized coal and, more recently, to waste plastics (Texaco process).

Waste plastics have been partially burnt to generate the heat and reducing gas, required to produce pig iron from ore in a blast furnace (Klöckner, Bremen).

Natural gas and a light naphtha are usually converted to synthesis gas, following an alternative route, namely by *steam reforming* according to reaction (2a), conducted in externally heated tubes filled with a nickel-based catalyst.

In principle, a light fraction, derived from polyolefins, could serve as a feedstock. This avenue has remained unexplored because feed specifications are quite stringent with respect to carbon number and sulfur content.

Synthesis gas can be converted into synthetic natural gas (a process that makes sense only if solid fuel is available) or into synthetic oil by the Fischer-Tropsch catalytic conversion. This high-pressure process was used in Germany and Japan before and during the World War II and later in Sasolburg (South Africa).

$$\text{coal gasification} \longrightarrow \text{synthesis gas} \xrightarrow[\text{synthesis}]{\text{Fischer-Tropsch}} \begin{array}{l}\text{high-grade, sulfur-free}\\ \text{synthetic oil}\end{array}$$

An alternative route, oil from methanol, has been demonstrated by Mobil in New Zealand:

$$\text{natural gas} \longrightarrow \text{synthesis gas} \longrightarrow \text{methanol} \xrightarrow[\text{process}]{\text{Mobil}} \text{synthetic petrol}$$

Texaco and Shell proposed processes to convert plastics waste into synthesis gas.

COAL LIQUEFACTION - HYDROGENATION

An alternative coal-to-liquid fuel route was developed by Bergius: pulverized coal was suspended in a recycle oil and the resulting slurry hydrogenated using an inexpensive catalyst, discharged together with the coal ash. Hydrogen is also extensively applied to oil fractions (dehydrosulfurization, DHS) in order to eliminate heteroatoms, such as S and also N, e.g., $R\text{-}SH + H_2 \rightarrow RH + H_2S$. The hydrogen sulfide is easily scrubbed out of the main gas stream (hydrogen), which is recycled. Hydrogen can also be used to eliminate halogens from plastics fractions.

In Bottrop, a hydrogenation plant, used for the upgrading of oil residues, has been used to demonstrate plastics liquefaction. Due to the high operating pressures, however, the residual chlorine content in the liquid products is fairly high.

PLASTICS PYROLYSIS FEEDSTOCK STREAMS

A survey was given of the major basic operations used in oil refineries, ethylene plants, and synthesis gas units. Each of these are well-known, high-volume operations, with some connection to the raw materials from which plastics are made. Conversely, plastics waste *can* be converted back into the specific feed or product streams mentioned above, provided extraneous matter (e.g. non-plastics, fillers) can be discarded, halogens removed and the plastics brought down to such a viscosity that they may blend into usual feed streams.

Typical specifications for a refinery, petrochemical feedstock or plastics pyrolysis unit include:

- a pumpable oil or gas, or else, free flowing solids (e.g. pellets, not film, fluff, plastics of variable size or form);
- a halogen content limit, e.g. below 20 ppm;
- heavy metals below 0.1 % to avoid deposits, coking and, possibly in some processes, catalyst fouling;
- condensable additives, that may separate and plug ducts;
- filler materials, that may foul heat exchange surfaces and plug ducts.

Polyolefins are desirable pyrolysis feedstock components because of a high hydrogen/carbon ratio (equal to 2) and negligible coking tendency. Polystyrene generates mainly monocyclic aromatic compounds, such as styrene, ethylbenzene and BTX aromatics. PVC loses HCl and some benzene in a first decomposition step, substituted aromatics in a second, leaving a carbonized residue. Thermosets gradually decompose over a wide range of temperatures. Mixtures of plastics may behave differently than predicted on a basis of simple additivity; PVC, for example, generates HCl which inhibits radical depolymerization and cracking reactions, yet promotes hydrolysis of condensation-type polymers [4].

If logistically, technically and economically feasible, pure plastics are normally recycled as materials in mechanical recycling processes. Only unidentified, soiled, burnt (thermally degraded) and composite wastes are normally not recyclable by such methods [5], so that pyrolysis may provide a suitable method of recycling.

Post-consumer plastics are often commingled and contaminated with extraneous materials (soil, metals, rubble, food remnants) or composites. Soil can be eliminated by washing, but this is a fairly expensive operation, leading to secondary waste streams (wastewater, sludge, residue). On the other hand, sink/float separation is an elegant way to separate a floating polyolefinic fraction from denser PET, PVC, PS resins. Foams, composites and floating organics may contaminate the polyolefin fraction. Metals and rubble generally need to be eliminated before plastics are melted and/or pumped. Their elimination from a fluid bed reactor, on the other hand, is fairly straightforward.

Literature on pyrolysis projects lists a variety of *typical* compositions for a polyolefinic (after sink/float separation) or mixed plastics stream. Examples are given in Table 2.

Table 2. Typical compositions of a polyolefinic or mixed plastics stream

	University Hamburg	APME[a]	[6]	BP
Polyolefins (HDPE, (L)LLPE, PP)	66.9	66.9	77	80
Polystyrene (PS)	13.3[b]	13.3	12	15
Poly(vinyl chloride) (PVC)	10.3	10.3	5	2
Poly(ethylene terephtalate) (PET)	5.3	5.3	–	3
Others	4.2	4.2	6	–
	100	100	100	100

[a] Association of Plastic Manufacturers Europe; [b] including expanded PS

APME distinguishes the following sources of plastics waste (in the order of decreasing tonnages) [7]:

- municipal solid waste (of which typically 7-8 wt.-% consists of plastics),
- distribution waste (foils, shrinking film, expanded polystyrene),
- automotive and car shredding waste,
- electrical/electronic waste (cable scrap, printed boards, often involving flame retardants),
- agriculture (solid film),
- building and construction plastics (pipes, sheets, foils, profiles, thermal insulating foams).

An important consideration in the selection of a plastics pyrolysis process is its robust character, i.e., how well it copes with the almost inevitable impurities, due to errors in collection and classification or to the numerous products added to plastics to improve properties or facilitate processing. Table 3 lists the most important of such additives, which are blended into the plastics prior to processing.

Table 3 List of the most common additives

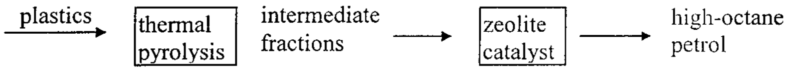
Additives
Antiblocker agents
Antifogging agents
Antioxidants
Antistatics
Biostabilizers
Chemical blowing agents
Colorants
Crosslinking agent
Dyes
Flame retardants
Fillers and reinforcements
Light stabilizers
Lubricants
Metal deactivators
Mold-release agents
Heat stabilizers
High-polymeric additives for improving impact strength
High-polymer processing aids
Nucleating agents
Optical brighteners
Plasticizers
Property modifiers
Smoke and afterglow suppressants
Wetting agents

If plastics are heated, the additives may decompose even before the associated plastics, they may evaporate, or remain as a residue after pyrolysis. Their possible interaction with primary pyrolysis or impact on subsequent processes (coking, fouling, clogging) is still incompletely documented.

PRODUCTS FROM PLASTICS PYROLYSIS

Polymers during pyrolysis may decompose into identical, generally monomeric (or oligomeric) units (unzipping), into chain fragments of variable length (random cracking) or into a carbon chain that gradually loses its substituents (elimination of HCl from PVC or of acetic acid from PVAc). The resulting liquid and volatile products may undergo secondary cracking and, eventually, form particularly stable compounds, such as aromatics, the final product in the University of Hamburg pyrolysis process or, less desirably, soot and char. Plastics pyrolysis may serve as a pretreatment to yield a stream to be blended into a refinery or petrochemical feed stream.

Mixed plastics from the household refuse are largely composed of polyolefins; the paraffin/olefin mixture resulting from pyrolysis can be further treated on zeolite catalysts to yield light fractions with a superior octane number.



Finally, the plastics can be used as a source of carbon in various gasification processes, involving an oxygen lance burner (Texaco) or a fluid-bed gasifier (HT Winkler).

A survey of the various possibilities is given in Table 4.

Table 4. Pyrolysis products and associated feedstocks and processes

Product	Feedstock	Process
Monomer	PMMA, PTFE, PS, PA 6	thermal cracking
α-Olefins	PE	thermal cracking
Polyethylene wax	pure PE	thermal cracking
Aromatics	mixed plastics [a]	high-severity thermal cracking
High-octane petrol blending stock	mixed plastics [a]	fluid catalytic cracking, hydrocracking, delayed coking
Synthesis gas	any carbon-containing material	gasification

[a] heteroatoms may be a problem with respect to the product purity (e.g.. chlorinated compounds)

The value of all such products is determined by market conditions, i.e., offer and demand. Obviously, the added value **increases** in the series crude oil < oil distillation products < monomers < polymers, which unfavourably influences the economics of plastics pyrolysis. Normally, oils from biomass, coal or plastics are unable to compete economically with the oils pumped from an oil field.

REACTOR TYPES [8,9]

Several studies and preliminary investigations were conducted on *extruder-type reactors*. The latter are fairly conventional units, equipped with electric or thermal oil heating, and a single or a double screw for material transport and mixing. Extruders may be used for supplying a molten feed into a pyrolysis unit, to effect a mild pyrolysis and eliminate HCl or to convert molten plastics into volatile hydrocarbon fractions. Extruders may be used for supplying a molten feed into a pyrolysis unit, to effect a mild pyrolysis and eliminate HCl or, as a second step, to convert molten plastics into volatile hydrocarbon fractions. In contrast to usual extrusion, there is no need to build up large pressure and force the material through a die. On the contrary, it is desirable to promote the release of the vapours arising in the decomposition of polymers and additives. Optionally, the decomposing liquid polymer can be discharged into a soaking vessel in which the pyrolysis is completed. Conventional extruders are built for capacities of up to 1 - 1.5 t/h, so that extruders are suitable for a low to medium throughput and an operating temperature generally limited to 350-400 °C. Free-flowing material is conveyed pneumatically or mechanically to a feeder hopper; for film or fibre recycling, a densifying, positive-action feeder is required. Mixed scrap will normally require mechanical pretreatment, such as sintering or regranulation, for easier handling, feeding and metering.

A now obsolete technology makes use of a *molten metal bath* (lead or tin) to supply the required heat indirectly. Operation may be in weekly cycles; obviously, the contact with the molten metal gradually degrades as more cokes and residues accumulate on the metal surface.

Discontinuous (batch-operated) and continuous (single or cascade) stirred tank reactors have both been used in large-scale melt-phase pyrolysis. The units are relatively simple, basically consisting of a large vessel with indirect heating, a large stirrer and possibly internals, such as baffles to enhance mixing, and internal heat exchanger surfaces. Internals, however, may gradually be coated with cokes, fillers or other impurities and are generally avoided; heat is supplied through a more accessible, easier-to-clean external heater. Provisions allow to discharge settling solids from the bottom of the reactor. If possible, the feed is melted and preheated prior to feeding, or dissolved in a hot recycle stream.

Fluidized-bed reactors provide homogeneous and isothermal operating conditions, as well as a well organized release and evacuation of the volatiles generated. Circulation of the bed material (usually sand) allows to heat the bed material in a second fluidized bed, heated by burning off the carbon deposited on the bed material. The Hamburg pyrolysis process, as applied in Ebenhausen, features immersed refractory steel heaters, internally heated by firing (pyrolysis) gas, as well as a settling zone underneath the fluidized bed.

Rotary kiln reactors have been extensively used in the pyrolysis of composite waste streams, e.g., car shredder waste, rubber tyres, and industrial waste. The waste is heated while tumbling in the kiln, in contact with an externally heated wall and, sometimes, heating internals. The process generally addresses high calorific industrial waste streams, of which various plastics and tyres are a part. Examples are the Pyrocal (BKMI), Kiener, Siemens, Odapyr (Dr. C. Otto & Co.) and Rotopyr (MVU) processer.

TECHNICAL FACTORS

Pyrolysis is basically a simple process: it is sufficient to deliver the heat required for the successive physical and chemical processes (evaporation of moisture and some additives, melting and other phase changes, bond breaking and evaporation of the resulting pyrolysis products) and pyrolysis will automatically occur.

Operating problems are often mechanical in nature and related with feeding and residue extraction problems, fouling and coking of heat transfer surfaces, corrosion by aggressive products, clogging of heat exchangers and ducts by waxes and other solidified products. In the Ebenhausen plant, severe clogging problems arose as a consequence of the addition of lime to neutralize HCl: the resulting $CaCl_2$ (melting at 772 °C) deposited in the ducts and clogged them (Table 5).

Table 5. Some relevant factors in technical pyrolysis

Factor	Problems, solutions
Feeding	special, densifying feeders required for loose plastics; melt feeders often preferred
Heat transfer	fouling of surfaces; to avoid coking, feed impurities can be removed;
PVC	HCl in flue gases, chlorine in pyrolysis products; material selection, moisture avoidance, chlorine elimination with suitable reactives, chlorine dilution in feed and product fractions
Polyolefins, PET	some reaction products solidify upon condensation, causing clogging problems
Coking polymers	fouling of heat transfer surfaces by coking.

PYROLYSIS PROJECTS

In the early seventies, a variety of plastics pyrolysis projects were already developed in Japan. In Europe, the Universities of Hamburg (Profs Sinn and Kaminsky), Aachen (Prof. Menges) and Brussels were particularly active. Some of these early projects were transformed into the industrial reality, for example in the Stardust project in Yokohama, a double-fluidized bed pyrolysis addressing a non-shreddable fraction surviving a semiwet pulverizer pretreatment (Figure 6).

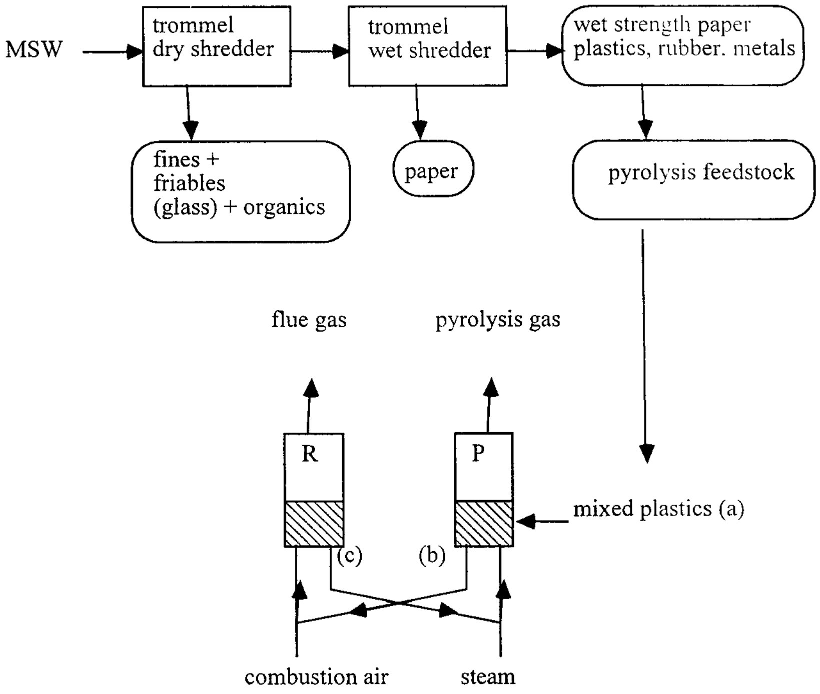


Figure 6. Double-fluidized bed pyrolysis (Stardust project, Yokohama)

Mixed plastics (a) are fed into the pyrolysis bed P, which is fluidized with steam. Sand, coated with char (b) is discharged and regenerated in the regenerator bed R. Hot, clean sand (c) is recirculated to the pyrolysis bed and supplies the required heat to operate the system.

Dual fluid-bed pyrolysis was applied succesfully by Ebara Co. (Stardust project, Yokohama) and, with more difficulties, by Tsukishima Kikai (Funabashi City). Both demonstration projects were eventually halted, for both economic and technical reasons. The Ebenhausen project was launched by Deutsche Reifen Pyrolyse and taken over for a short while by ABB. The technology was based on developments at the University of Hamburg, using a single fluid bed unit, indirectly heated by closed, gas-fired pipes.

A second generation of plastics pyrolysis projects was launched in the eighties under political pressure (EU Packaging Directives) requiring higher recycling rates. Material was collected by the Duales System Deutschland (Germany), Fost Plus (Belgium) and Packaging Industry

(Netherlands). Processing took place in demonstration units on laboratory, pilot-plant and/or semi-industrial scale, e.g.:

- BASF built and operated a pilot plant producing feedstock for its Ludwigshafen complex.The plant used a cascade of continuous stirred-tank reactors;
- VEBA OEL linked a feeder step converting plastics into feedstock for its high pressure hydrogenation demonstration plant at Bottrop;
- Laubag, a RWE subsidiary, uses waste plastics in their lignite gasification process;
- Klöckner blows finely divided plastics as a reducing agent into a blast furnace at Bremen.

A *two-step pyrolysis* concept was adopted by BASF, Shell, Professor H. Bockhorn and other process developers. The process

- dissolves or melts plastics in a first step, operating at 250-400 °C, which allows to eliminate the bulk of HCl without extensive decomposition, thus avoiding the formation of chlorinated by-products in various product streams;
- in a second step, the molecular weight and viscosity are further reduced; gas, liquids and some cokes are produced, like in conventional visbreaking, or liquid-phase and fluid-bed plastics pyrolysis.

CYCLEPLAST PROJECT

A project, named Cycleplast and, prepared by Dr. Blazso, Prof. Bockhorn, Prof. Buekens, Dr. Kovářová, and Prof. Vergnaud, of the pyrolysis of plastics has been financed by DG XII of the European Union in the framework of the INCO-Copernicus programme.

Attention is focussed on the following factors :

(1) effect of polymer mixtures, composites, additives, and superficial oxidation of post-consumer plastics on the pyrolysis process;

(2) further development of a two-step pyrolysis process, the first step featuring HCl and H_2O elimination, the second step operating in a HCl-poor environment;

(3) evaluation of pyrolysis product quality;

(4) study and evaluation of carbon formation and product condensation phases as a function of operating conditions;

(5) mechanical recycling of plastics mixtures in the presence of compatibilizers.

The studies make use of various laboratory and pilot set-ups and are accompanied by an economic, technical and logistic evaluation of the pyrolysis system, prepared in close collaboration with the Association of Plastic Manufacturers Europe.

CONCLUSIONS

Plastics pyrolysis is a form of materials recycling, in which plastics are converted into monomers, chemicals, or gaseous or liquid fuels, rather than to be tipped or incinerated directly. Although the process is uneconomic under present market conditions, considerable pressure is exerted by public opinion to try and demonstrate this route. At present, there is adequate pilot-plant information available for testing and demonstrating the process. However, the very high costs of plastics collection, sorting and pretreatment form an unsurmountable barrier to the introduction of the process.

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