

Waste Plastics as a Source of Petrochemical Base Materials

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In spite of numerous efforts there is as yet no technically proven and economically attractive method for the valorization of the various streams of waste plastics, as they are separated at the source from Municipal Solid Waste (MSW) or resulting from various recycling operations, such as car shredding or dismantling. Moreover, in the hierarchy of plastic waste management options there is a general support for the next classification: 1) prevention and (rarely) reuse, 2) mechanical recycling, 3) chemical or feedstock recycling, 4) use as a fuel or incineration with heat recovery, 5) safe elimination, bio- or photodegradation. Prevention is especially effective by product weight reduction and – obviously – by avoiding the use of plastic disposables. Mechanical recycling remains reserved to either premium waste sources or to the production of low grade, massive products with limited outlets. Feedstock recycling covers a wide spectrum of techniques, including 1) the chemolysis of polycondensation polymers, 2) the thermal degradation or pyrolysis of specific or of all-round plastic waste, 3) high pressure hydrogenation or 4) conversion into synthesis gas. In this paper the plastic waste streams potentially available as a source of petrochemical base materials are characterized, the processes for eventual conversion identified and the technical and economic feasibility of such ventures is briefly discussed.

Introduction

Petrochemical industry has profoundly changed the supply of raw materials in the industrialized world: synthetic products based on cheap, but finite oil resources have taken a large share out of numerous commodity markets, traditionally reserved for natural and renewable materials. For many years industry has been pressed to find adequate solutions to the resulting waste problems [1 to 9], especially those regarding highly visible plastic packaging. Pioneering work often originated in Japan [2] and was sponsored by MITI, the Plastics Waste Management Institute, or the Clean Japan Centre .

Major sectors in plastics consumption are [3]: packaging, building & construction, automotive, electrics & electronics (E & E), agriculture, and others (e.g. furniture, houseware, toys, engineering). After a short (packaging), medium (toys) or long lifetime (building) the plastic product reports to one of various waste streams, such as Municipal Solid Waste (MSW), separately collected packaging or other recyclables, shredding waste (cars, white goods), construction & demolition waste, agricultural waste, E & E-waste, etc. Such waste streams internally differ with respect to method of collection, composition and status: under environmental pressure producer responsibility has been or is being introduced, entailing separate collection and often involving mandatory recycling.

It follows that the amount of plastics' waste generated is impressive, but that only modest amounts are put to good use, whether thermally or as a secondary raw material. The waste fraction recovered is expected to increase further because of a rising importance of MSW-incineration in waste treatment, an increasing level of energy recovery in MSW-incineration as well as some gradual progress in mechanical, thermal and chemical recycling.

Plastics waste recycling indeed can be subdivided according to the following hierarchical sequence :

- (1) *mechanical* or *materials recycling*, preserving the macromolecular structure of plastics polymers,
- (2) *chemical* or *feedstock recycling*, to convert plastics into monomer, oil refinery or petrochemical feedstock and
- (3) thermal recycling, such as the use of plastics as a fuel in cement kilns or blast furnaces or incineration with heat recovery of plastics contained in MSW.

Feedstock recycling can further be subdivided into: (a) chemolytic processes, i.e. the alcoholysis or hydrolysis of polyesters, polyurethanes, polyamides, polyacetals, ... to monomers or closely related chemicals and (b) thermolytic processes, involving a thermal or catalytic breakdown of polymer structures to low or medium molecular weight products. Chemolytic processes (solvolysis) have a potential for producing high value products, but also strict requirements for sorting and cleaning the waste to be treated and for separating and purifying the resulting products. Although they qualify as petrochemical base materials, their nature is fairly specific and directly related to the parent material. Since the latter generally cannot be identified with precision in post-consumer waste, the scope of chemolytic processes is fairly limited. For a survey it is referred to [10], since the rest of this paper concentrates on thermal and (to a less extent) catalytic processes.

Pyrolysis also termed *thermal cracking* is a major industrial process, yielding the basic raw materials of petrochemical industry (C_2H_4 , C_3H_6 , C_4H_6 , aromatics) by *steam cracking* of LPG, naphtha or light gas-oil in tubular furnaces. In oil refineries both catalytic and thermal cracking are important in *whitening the barrel*, i.e. converting heavy distillation residues into the more desirable, lighter distillation fractions.

Oil refineries are large scale operations with a typical capacity of 5 to 25 Mtonnes/annum for the main stream and a fraction of this capacity for the treatment, upgrading or conversion of particular distillation fractions. Naphtha crackers typically produce 400 to 600 ktonnes C_2H_4 /annum, unit. The largest ventures in plastics pyrolysis, on the other hand, have a substantially lower capacity, e.g. 3,000 to 80,000 tonnes/year, limited by collection, sorting and supply of feedstock. Such small or fairly small scale processing is obviously more expensive, so that integration of plastics pyrolysis and direct transfer of its products to e.g. an oil refinery, a naphtha cracker or a synthesis gas producer is highly desirable.

Plastics pyrolysis is basically a simple process: it suffices to deliver the heat required for the successive physical and chemical processes and pyrolysis will automatically occur. Depending on their structure (and the absence or presence of catalysts) polymers may decompose during pyrolysis into identical, generally monomer (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 HAC from PVAc). The resulting liquid and volatile products may undergo secondary cracking in the gas or liquid phases and eventually form thermally stable compounds, such as aromatics, the final product in the University of Hamburg pyrolysis process or - less desirably - soot and char. Finally, the plastics can also be used as a source of carbon in various gasification processes, involving an oxygen lance burner (Texaco) or a fluid bed gasifier (HT Winkler), but also there a preliminary degradation step may help in reducing melt viscosity, ensuring a steady feed to the reactor and rendering the elimination of part of the impurities much easier.

Materials and Methods

Plastic waste available for pyrolysis is generally collected by institutions such as Duales System Deutschland (D) or Fost Plus (B), responsible for the management of those waste streams subjected to mandatory separate collection and recycling, e.g. packaging waste. It is expected that more and more waste streams (tyres, electronic scrap, car, plastics fractions from white & brown goods dismantling) eventually will qualify for such separate, though expensive waste management structures.

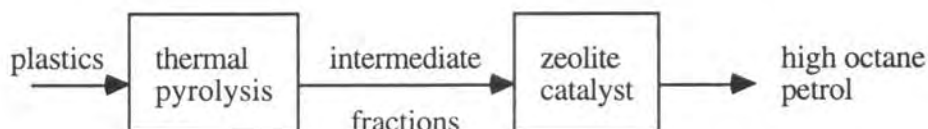
Plastics pyrolysis is based on a thermal and sometimes catalytic breakdown of the polymer structure. The targeted product may be 1) monomer (from PMMA, PTFE, or PS), 2) oil fractions ranging from petrol (C5-C10) and kerosene (C10 - C15) to waxy fractions (C20+), 3) aromatics (Uni Hamburg), 4) synthetic crude formed by hydrogenation or 5) synthesis gas (H_2 , CO) used in the production of ammonia, methanol, OXO-alcohols or Fischer-Tropsch synthetic fuel. The desired product also determines the operating conditions required in the thermal treatment and hence the technology used. A survey is given in [9] of the laboratory, pilot and industrial scale reactors, int. al. pyrolytic extruders, a single stirred tank, or a cascade of tanks, operating at a progressively higher temperature and single or double bed fluidised systems. Moreover, the use of plastics and their products of thermal degradation in oil refinery based processes, such as fluid catalytic cracking (FCC), hydrocracking, viscosity breaking and delayed coking, and also (coal derived) hydrogenation and gasification are briefly covered in the same text.

The product distribution in a pyrolysis process has to be derived experimentally, with as major factors the operating temperature, the heating rate, catalytic effects, residence time of feed material and reaction products, reaction pressure, possible supply of reactive gases (oxygen, hydrogen) and, of course, the chemical constitution and structure of the original plastics. Pyrolysis is slow below 350 °C, but allows the bulk of HCl to be driven off from PVC prior to the decomposition of the main, polyolefinic fraction. Pyrolysis of PE and PP becomes fast around 450 °C, and yields lighter products at rising temperatures and also when heavy product fractions are condensed and recycled to the pyrolysis process, e.g. to preheat or melt and dissolve the feed materials. Light products (< C10) are obtained at high temperature (> 600 °C), aromatic fractions require high cracking severities (> 700 °C, adequate residence time). The heating rate in liquid phase processes is limited by viscosity, so that operation at relatively high temperature, dilution with or dissolution in less viscous fractions and intense stirring may all be required. In fluid bed processes the plastics coat the bed particles and are rapidly dispersed, so that pyrolysis rates are no longer limited by heat or mass transfer considerations. Catalysts may be used to lower the pyrolysis temperature or to rearrange the structure of the volatile products, e.g. enhancing the Octane Number. Reaction pressure and the supply of hydrogen are a means to control the hydrogenation/ dehydrogenation equilibrium and influence upon the saturation level of the fractions obtained.

Pyrolysis involves the breaking of chemical bonds and is normally endothermic. The required heat of reaction can be supplied 1) indirectly through the reactor walls, 2) by means of a circulating heat carrier, which may be either the reactor polymer content in a liquid phase system or the sand in a fluid bed gas phase system, or 3) by partial oxidation. Reactor technology is generally determined by the temperature level required, the heating method, the necessary residence time and possibly by the presence of catalyst, required to lower the process temperature, rearrange linear structures to high octane number branched ones, or to eliminate heteroatoms (Cl, N, O, S).

Mixed plastics from household refuse are largely composed of polyolefins; singled out, the latter are a premium steam cracking feedstock once their molecular weight is sufficiently

degraded to allow their introduction into a steam cracker. As an alternative the paraffin/olefin mixture resulting from polyolefin pyrolysis can be further treated on int. al. zeolite catalysts to yield light fractions with a superior octane number:



In actual practice it is impossible to feed such pyrolysis products directly into the system, for logistic as well as technical reasons. Commercial polyolefins contain various additives and also finely dispersed fillers and pigments, that must be eliminated prior to further use. Also, it is very difficult to eliminate completely any extraneous materials, ranging from stones, dirt or paper, to other plastic resins, such as PVC. The latter generates HCl, causing a contamination of all product streams with chlorinated organics, as well as in the creation of corrosion problems that can only be avoided by specifying expensive construction materials and/or a thorough neutralisation of the various effluent streams.

Polyolefins of various origins are a desirable pyrolysis feedstock and the required levels of feed purity depend on the extent of further processing, including the ability to eliminate or bind the various extraneous and inherent impurities.

A survey of the various other possibilities is given in table 1.

Table 1. Pyrolysis Products, associated Feedstocks and Production Processes

Product	Feedstock	Production process
Monomer	PMMA, PTFE, PS, PA 6	thermal cracking
alfa-olefins	PE	thermal cracking
Polyethylene Wax	pure PE	thermal cracking
Aromatics	mixed plastics (*)	high severity thermal cracking
High octane petrol	mixed plastics (*)	fluid catalytic cracking,
Blending stock		hydrocracking, delayed coking
Synthesis Gas	any carbon bearing material	Gasification

(*) the presence of heteroatoms in the molecular structure may be a problem with respect to product purity (especially the chlorinated compounds)

The value of all such products is determined by market conditions, i.e. offer and demand. Obviously, there is added value in the series:

crude oil < oil distillation products < cracking products < monomers < polymers

which unfavourably influences the economics of plastics pyrolysis! Normally, oils derived from biomass, coal or plastics are unable to compete economically with that, pumped from an oil field !

Streams entering or leaving an oil refinery or indeed a petrochemical plant must satisfy to a long series of specifications. The latter have often an empirical origin and are still largely

determined by standardised testing methods; the resulting values determine whether a product stream is fit for a given purpose or not.

Typical examples of such specifications for a refinery stream are: vapour pressure, boiling range, viscosity and viscosity index, chemical characterisation (PONA = Paraffins, Olefins, Naphtenics, Aromatics), sulphur, nitrogen and oxygen content, actual and potential gum, octane number (petrol), cetane number (diesel oil), pour point, anilin point, Conradson carbon index, etc. Depending on their origin, composition (resin + additives !) and pretreatment waste plastics have a different composition and potential for feedstock recycling. Polyolefinic streams have a high potential for yielding a desirable steam cracker or FCC feedstock. The presence of heteroatoms (Cl, Br, F, N, S, O) of additives, fillers and pigments should be considered when developing a pyrolysis project.

When products derived from plastics pyrolysis are proposed as a feedstock, however, they suffer from having unusual composition and characteristics, when compared to conventional oil fractions and products. Especially the presence of the element chlorine, of finely divided pigments and fillers (particle size in the range 0.2 to 2 μ) and of a host of possible additives may create unexpected problems. Introducing the element chlorine invariably leads to a partition over all products streams, whether gaseous, liquid, or solid, severely compromising their eventual utilization. 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.

Table 2. Some relevant Factors in Technical Processes

Factor	Problems, Solutions
Feeding	Special, densifying feeders are required for loose plastics; melt feeders are often preferred;
Heat Transfer	Fouling of Surfaces. To avoid coking, feed impurities can be removed;
PVC	HCl in flue gases, some chlorine in pyrolysis products. Material selection, moisture avoidance, Cl-elimination with suitable reactives, Cl-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.

Results and Discussions

Early ventures in plastics pyrolysis were very popular in Japan in the early seventies [2]. In Europe Prof. Kaminsky pioneered fluid bed pyrolysis of plastics and his work served in the design of a full-scale plant at Ebenhausen, which was taken-over and eventually dismantled by ABB.

A second generation of plastics pyrolysis projects was launched in the eighties under political pressure (EU Packaging Directives) requiring higher recycling rates than is achievable by mechanical recycling alone. Material was collected by Duales System Deutschland (Germany), Fost Plus (Belgium) and the Packaging Industry (Holland). Processing took place in demonstration units at lab, pilot and/or semi-industrial scale, e.g. :

BASF built and operated a 15,000 tonnes/year pilot plant (Investment Cost: 40 M DEM) to evaluate and optimise technology for producing feedstock for its Ludwigshafen complex from DSD-plastic waste. After metal separation the plastics are locally densified by a Zerglomat sintering step and transported to Ludwigshafen using bulk trucks. The pyrolysis plant used a cascade of CSTR, a first for dissolving the feed operating at 300 °C, a last operating at about 450 °C. A full-scale unit, with a capacity of 300,000 tonnes/year and requiring a plant investment of 300 M DEM (or 400 M DEM, including auxiliaries) was never constructed, since the supply of waste and the concomitant dumping fee were all but guaranteed;

VEBA OEL linked a feeder step for converting plastics waste into feedstock to its pre-existing high pressure coal hydrogenation demonstration plant at Bottrop and since 1992 converted selectively collected and manually separated plastics into Syncrud-Oil; on last Aug. 25, 1999 Veba Oel suspended its contract with DSD arguing a production cost of 60 to 70 US \$/bbl., to be compared with a market value of only slightly more than 20 US \$/bbl at present and only half that amount a year ago !

Laubag, a RWE subsidiary, uses waste plastics in a lignite gasification process; also in Poland and the Czech Republic there is interest in blending coal and waste plastics in various process applications;

Klöckner Stahl tests blowing in finely-divided plastics as a reducing agent into a blast furnace at Bremen;

Texaco in Holland proposes to melt and decompose plastics, prior to their gasification in a synthesis gas plant;

a Consortium led by BP-Chemicals successfully tested fluid bed technology for plastics pyrolysis, conversion of the resulting products in steam cracking and FCC-units and gathered design and operating data on the process. The project will be presented at this conference.

A project, named Cycleplast and, prepared by Dr. Blazso (Hungarian Acad. Sci.), Prof. Bockhorn (Karlsruhe Univ.), Prof. Buekens (Brussels Univ.), Dr. Kovarova (Czech. Acad. Sci.) and Prof. Vergnaud (St. Etienne Univ.) on the pyrolysis of plastics has been financed by DG XII of the European Union in the framework of *INCO-COPERNICUS*.

Attention is focussed on int. al. 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, a first step featuring HCl, H₂O, ... elimination, a second operating in a HCl lean environment;
- (3) evaluation of pyrolysis product quality;
- (4) study and evaluation of carbon formation and condensing product 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 APME.

Conclusions and Outlook

The pyrolysis of plastics is technically a feasible process for *chemical recycling*, i.e. the conversion of high molecular materials, that can no longer be *mechanically recycled*, into monomer, oil refinery or petrochemical feedstock or product fractions. The basic data of the process, such as the required operating temperature, the heat of reaction and the products obtained under various experimental conditions are fairly well known, thanks 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. Plastics pyrolysis is only exceptionally an industrial activity, however, because of economic and logistic reasons. In most cases the limited value of the products obtained barely covers the variable and fixed process costs of thermal processing, let alone the expense of collection, sorting & grading, transport, storage, pretreatment and supply of plastics to the pyrolysis plant. Hence chemical recycling of plastics normally requires a substantial gate fee (some 150 EURO/tonne) to cover the operating losses of the last step in the recycling operation.

Polyolefins at the end of their lifetime can be used as a premium (low S, fully paraffinic) supplement to crude oil. This recycling method closes a **long** loop, which basically limits its efficiency. The latter can be derived from a Life Cycle Analysis, a most useful instrument in evaluating system efficiencies, in particular in cases in which the operation is to be justified on a basis of sustainability rather than market forces. Plastics pyrolysis may serve as a stand alone operation or (preferably) as a pretreatment to yield a stream to be blended into a refinery or petrochemical feed stream. There is a sufficiently dense network of refineries and petrochemical units throughout the European Union for processing all waste plastics separately collected and feeding the resulting pyrolysis products into such larger scale units [11].

References

1. A.G. Buekens, "Some observations on the recycling of plastics and rubber, Conservation and Recycling", (1), p. 247-271, 1977
2. A.G. Buekens, "Resource Recovery and Waste Treatment in Japan. Resource Recovery and Conservation", (3), p. 275-306, 1978
3. A.G. Buekens, "Opportunities in the Sorting of Waste Plastics, Recycling Berlin", 531-541, 1984
4. A.G. Buekens, G. Patfoort, A. Vandermeersch; "Les systèmes de collecte et de tri des déchets des matières plastiques et les problèmes à résoudre pour optimiser ces technologies, Colloque International sur le recyclage des déchets de matières plastiques"; Paris, March 1988 In : Le recyclage des déchets de matières plastiques, EUR 11717, p. 96-121.
5. A.G. Buekens; "Kunststoffe einschliesslich PVC und Abfallverbrennung", Fachkolloquium KABV Saarbrücken, Saarbrücken, April 1989.
6. A.G. Buekens; "Environmental Considerations and Ecologically sustainable Development in Plastics and Plastics Waste Recycling", US/CPR/86/130 "Recycling of solid waste", April 1991. Presented in Copenhagen at the UNIDO Conference, and as a Summary at the Conference of Head of States of Mediterranean Nations, Athens.
7. A.G. Buekens, J.G. Schoeters; "Technical and Economic Appraisal of Plastics Pyrolysis, 10th International Conference of Fundamental Aspects, Processes and Applications on Pyrolysis", University of Hamburg, Hamburg, 28 September - October 1992

8. A.G. Buekens, J.G. Schoeters; "Technical and economic appraisal of plastics pyrolysis". Körber Foundation, January 1995.
9. A. Buekens, J. Schoeters; "Technical Methods in Plastics Pyrolysis", 38th Microsymposium of PMM", Inst. of Macromolecular Chemistry, Praag, July 97.
10. L. Bontoux, Preliminary survey of current projects on plastics recycling by chemolysis. Project i.l.a, a Study for DG XI B1, May 1995
11. Ph. Huybrechts, Fina, Private communication, 1999

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