EUROPEAN TRENDS IN THE FEEDSTOCK RECYCLING OF PLASTIC WASTES

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ABSTRACT

Consumption of plastic products has increased dramatically over the past few decades. This trend results in the generation of a vast waste stream that needs to be properly managed to avoid environmental damage. Increasingly stringent European legislation is setting new standards that promote the application of novel recycling technologies capable of absorbing large amounts of plastic wastes. An option with great potential is feedstock recycling, which includes a variety of processes like pyrolysis, catalytic conversion, depolymerisation and gasification, designed to transform plastic waste into hydrocarbon products for use in the preparation of recycled polymers, refined chemicals or fuels. This paper summarises the current situation regarding the generation of plastic residues in Europe and provides a general view of alternative recycling methods. Up-to-date information is also included on commercial or demonstration recycling activities currently in operation, paying special attention to the development and application of novel catalytic feedstock recycling processes.

KEY WORDS: waste plastics, plastic recycling; catalytic cracking, pyrolysis

1. INTRODUCTION

1.1 Plastic waste generation and legislative framework

Current statistics for Western Europe estimate the annual consumption of plastic products at almost 100 kg per person for a total of over 39.1 million tonnes [1]. Over 78 wt% of this total corresponds to thermoplastics (primarily low and high density polyethylene LDPE-HDPE, polypropylene PP, polyvinyl chloride PVC and polyethylene terephthalate PET) and the remaining 22 wt% to thermosets (mainly epoxy resins and polyurethane) [1]. This generates a vast waste stream, estimated at around 21.5 million tones, that needs to be effectively managed.

Despite recent advances, 61 wt% of all the waste plastics generated in Europe are still disposed of to landfill, a management alternative that generates serious environmental problems due to their low density, resistance to biological degradation and combustible nature. As illustrated in Figure 1, incineration with energy recovery represents the main alternative to landfill, absorbing on average 23 wt% of the plastic waste, while recycling takes the remaining 16 wt%. Recycling processes for waste plastics are classified into two categories: mechanical and feedstock recycling. The former covers a range of physical methods aimed at converting the polymeric residue into plastic pellets or directly into secondary plastic materials [2-3]. The latter, which currently absorbs only 1.6 wt% of the plastic waste, involves their transformation into hydrocarbon chemicals [1-3]. Information on the use of feedstock recycling in Japan [4] and the United States [5] is also available in the literature.

European regulators are setting increasingly stringent standards to reduce the impact of waste plastics in the environment. These regulations, covering a wide range of sectors, include the recently published Directive 2005/20/EC on Waste Packaging, the Directive 2000/53/CE on End of Life Vehicles (ELV) and the Directive 2002/96/CE on Waste Electrical and Electronic Equipment (WEEE). Furthermore, the Directive 1999/31/EC on the Landfill of Waste, which will require member states to reduce the amount of biodegradable waste going into landfill by 2010 to 35 % of the values reached in 1995, represents the other regulatory engine behind this transformation. Achieving these targets will require the application of a combined strategy that takes into consideration reduction at source, valorisation by energy recovery and also the application of appropriate recycling technologies for each specific case.
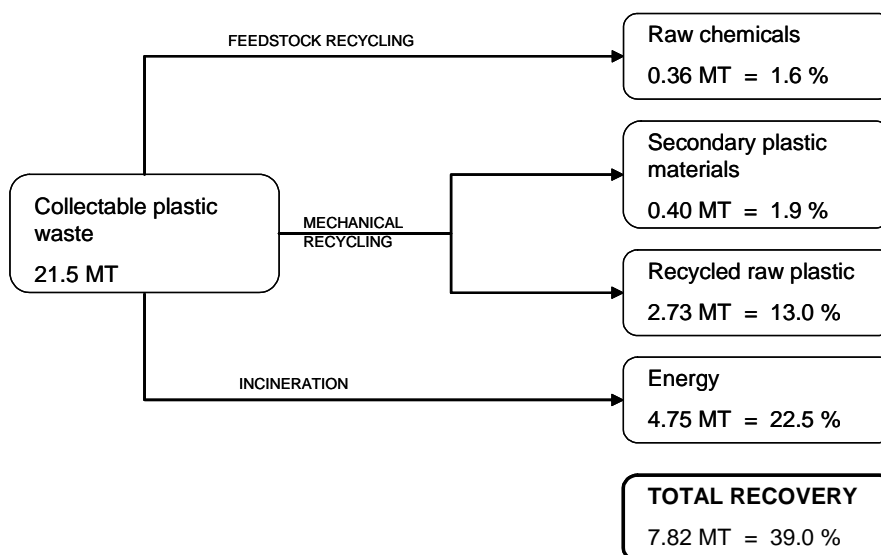

Figure 1. Management options for waste plastics in Europe in 2003. Adapted from APME [1].

Despite not being used extensively, feedstock recycling is attracting increasing scientific and commercial attention as an alternative with the potential to absorb very large amounts of plastic wastes [2-6]. The application of catalysts is giving feedstock recycling a new impulse that is expected to put this technology at the forefront of plastic management. This paper provides a general view of the current situation in Europe regarding plastic waste management and includes a revision of current recovery trends and recycling options, paying special attention to the development of catalytic recycling technologies.

1.2 Alternative recovery options for waste plastics
Energy recovery involves the use of waste plastics as fuels either in purposely built incineration facilities for the production of heat or electricity, but also in specially adapted energy intensive industrial processes like cement kilns and boilers for steam or heat production [7]. Technical advances in the design and operation of incineration facilities and the application of strict regulatory measures means that energy recovery is usually regarded as an environmentally sound option. Countries with a tradition in the use of incineration for waste management like Switzerland, Denmark and France currently absorb 75, 65 and 32 %, respectively, of all their collectable plastic waste through this route. However, this activity still faces strong opposition in other countries like Ireland, Greece or the United Kingdom, where the amount of plastic valorised thought this route accounts for less than 8 wt% of the total [1].

Mechanical recycling usually involves heating the thermoplastic wastes to their melting temperatures, usually around 150ºC, followed by injection and re-moulding of the recovered polymer. Small plants based on this technology are common all over Europe for the recycling of polyethylene or polypropylene. However, owing to incomplete separation of different plastic types, the presence of additives and contaminants, and also due to the modification of the original polymeric structure during its first use (typically chain cross-linking reactions), mechanically recycled plastics only find use in lower grade applications like the production of

plastic bags, padding fibres, pipes and wood or cement substitutes in urban furniture and construction [1-2,6, 8].

Another technology under this category involves the application of selective solvents for the extraction of the polymer of interest. A commercial example of this is the Vinyloop® process, developed by Solvay for the separation of PVC [8]. The process involves an initial pre-treatment step that involves the washing, size reduction and separation of extraneous materials from the PVC waste. The resulting powdered material is then treated with the organic solvent methylethylketone that selectively dissolves the PVC fraction leaving other contaminants in suspension, which are removed via filtration. Steam is then injected into the solution, causing the PVC to precipitate into granules while the solvent is distilled off, condensed and reused. At the present time, a Vinyloop facility is already in operation in Ferrara (Italy) with a total capacity for 7500 T year^{-1} with a second plant starting operation in 2006 in Chiba (Japan).

As illustrated in Figure 1, mechanical recycling represents in Europe the second largest recovery option with 3.13 million tones per year and an annual growth estimated at over 12 % [1]. Improvements in the sorting and separation of plastic polymers are expected to facilitate an even wider application of these processes.

2. FEEDSTOCK RECYCLING METHODS

Feedstock recycling involves the transformation of plastic polymers by means of heat or chemical agents to yield hydrocarbon products that may be used in the production of new polymers, refined chemicals or fuels [2-3]. A variety of treatments may be included under this category including chemical depolymerisation, gasification, thermal cracking and catalytic conversion.

Despite its low overall contribution, currently estimated at only 350,000 tonnes per year in Europe [1], feedstock recycling is often described as an alternative capable of boosting recycling levels over the next few years. In order to achieve these expectations, it is still necessary to overcome a number of technical and economic difficulties that are discussed further in this paper.

2.1 Chemical depolymerisation

Chemical depolymerisation, or chemolysis, involves the reaction of the used polymer with chemical reagents for the production of its starting monomers [9]. Different processes have been developed which are categorised depending on the chemical agents employed, the most common being glycolysis, methanolysis, hydrolysis and ammonolysis.

Depolymerisation is restricted exclusively to condensation polymers, primarily polyesters like PET, but cannot be used with the more abundant addition polymers like polyethylene, polypropylene or polyvinyl chloride. A drawback for the widespread application of these technologies is related to their being very sensitive to the presence of impurities in the raw plastics [2-9].

Commercial examples of depolymerisation processes include the PETCORE system [10], the Eastman Chemical Company (ECC) process [11] and the DuPont process [3], all of which require a pre-treatment step aimed at separating impurities from the original plastic waste. In addition, the Japanese company Teijin Ltd. developed the ECOPET process and operates this technology at a PET recycling plant with capacity to convert 60,000 ton per year into dimethyl terephthalate (DMT). In connection to this process, Teijin Ltd. also owns another two plants in Tokuyama the first one for the conversion of DMT into high-grade terephthalic acid and the second for the transformation of this acid into recycled PET resin [12]. The German engineering company Zimmer and Lurgi has also developed another commercial process based on acid hydrolysis with phosphoric acid for the recycling of NYLON 6 [3].

2.2 Gasification

Gasification involves the partial oxidation of organic matter at high temperatures (typically between 1200-1500ºC) under mildly oxidising conditions (usually steam, carbon dioxide or sub-stoichiometric oxygen) for the production of synthesis gas (syngas). This gas, consisting

primarily of carbon monoxide and hydrogen, has application in the synthesis of chemicals like methanol and ammonia, and can be used to produce synthetic diesel or may be combusted directly as a fuel [2].

Although gasification was originally developed for the conversion of coal, the technology has been successfully adapted for the treatment of heavy petroleum fractions, natural gas, biomass and a wide range of organic materials and wastes, including plastic polymers [13]. A key advantage of this technology is that it is not affected by the presence of impurities and may even be used to treat any waste mixture with a high organic content.

From a commercial standpoint, the German company Sekundarrohstoff Verwertungs Zentrum (SVZ) runs a large commercial plant (410,000 T year^{-1}) in Cottbus (Germany) for the combined gasification of organic wastes including car oils, municipal solid wastes, residual plastics and sewage sludge [3]. Texaco has also developed an extension of its conventional fuels gasification technology called the Texaco Gasification Process (TGP) that permits its application to hazardous and other waste materials, including plastics. An operation plant based on this technology is currently in operation in Montebello (California) [14].

2.3 Thermal cracking

Thermal cracking, or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500-800ºC and results in the formation of a carbonised char and a volatile fraction that may be separated into a condensable hydrocarbon oil and a non-condensable high calorific value gas [2]. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions.

In the case of polyolefins like polyethylene or polypropylene, thermal cracking has been reported to proceed through a random scission mechanism that generates a mixture of linear olefins and paraffins over a wide range of molecular weights [15]. In other cases, like polystyrene and polymethylmetacrylate, thermal degradation occurs by a so-called unzipping mechanism that yields a high proportion of their constituent monomers [2, 15].

In pyrolytic processes, a proportion of the species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter and intramolecular reactions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.

In addition, reactor design also plays a fundamental role as it has to overcome problems related to the low thermal conductivity and high viscosity of the molten polymers. Several types of reactors have been reported in the literature, the most frequent being fluidised bed reactors [16-17], batch reactors [4, 18] and screw kiln reactors [19]. A representation of the latter is included in Figure 2.

Pyrolytic processes for the treatment of residual polymers have been extensively investigated at laboratory and pilot plant scale, and a number of demonstration plants have been in operation over the past decade. For instance, an international consortium including British Petroleum, Elf Atochem, Eni-Chem, DSM and APME developed in 1998 a pilot plant based on *Polymer Cracking Process* (PCP) technology in Grangemouth (United Kingdom) [3]. Likewise, the German company BASF developed and tested another thermal cracking process for the treatment of plastic packaging waste in Ludwigshafen. This demonstration plant, which produced hydrocarbon oil (60-70 wt%), gas (20-30 wt%) and solid char (5 wt%), was finally closed in 1999 [3]. However, the commercial success of this technology is still not a reality due to the reduced market price of the resulting products.
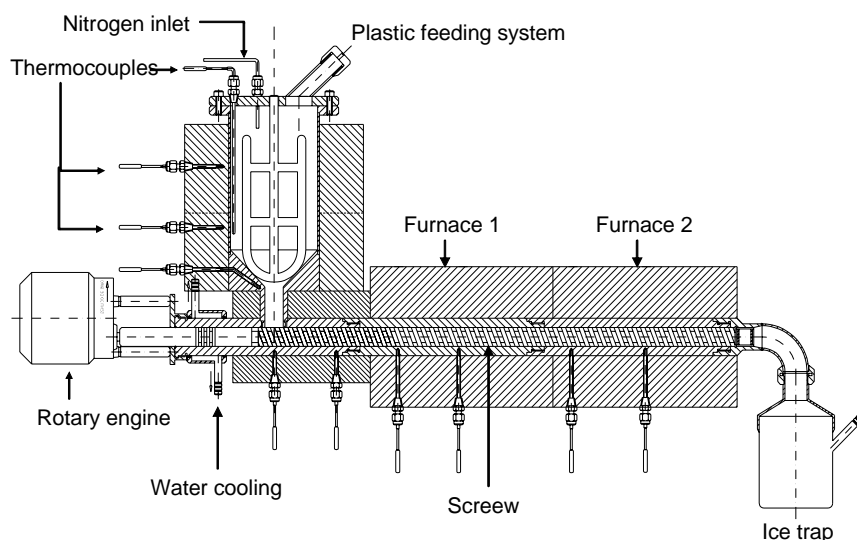
Figure 2. Screw kiln reactor developed for the thermal and catalytic degradation of plastic products [20].

2.4 Catalytic conversion

Catalytic conversion of plastic wastes implies several advantages over conventional pyrolytic methods. The most evident relates to the lower degradation temperatures at which degradation reaction takes place, which results in lower energy consumptions and higher conversion rates. However, an even more important aspect is the shape selectivity exhibited by some microporous catalysts, which allows the process to be directed towards a narrow distribution of hydrocarbon products with a higher market value [20-23]. Another advantage mentioned in the literature resides with the inhibition effect of catalysts in the formation of some undesired species, particularly chlorinated hydrocarbons, an aspect of particular interest in plastic wastes contaminated with PVC residues [2].

Catalytic recycling may be carried out in one of two ways. The simplest one involves having the polymer and the catalyst in close contact inside the reactor [4-5]. The other is a two-stage process involving an initial thermal degradation of the plastic followed by a catalytic reforming of the resulting vapours [6, 24]. Figure 3 includes a representation of a two-stage discontinuous laboratory reactor developed for the catalytic conversion of plastic products.
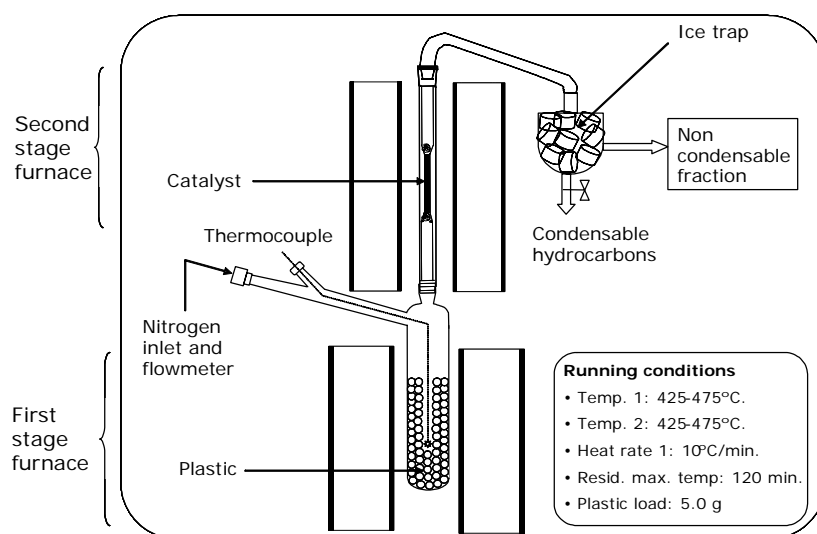

Figure 3. Discontinuous two-stage reaction system for the catalytic conversion of plastics.

A key limitation of direct catalytic cracking relates to the accessibility of bulky polymeric molecules into the micropores of acid catalysts like zeolites. Furthermore, it has been

reported a significant reduction in the activity of the catalysts when used on residual plastics [20-21]. This deactivation has been related to various factors including the poisoning effect of sulphur and nitrogen containing species on aluminium acid centres and also to the dealumination capacity of acid vapours (acetic acid or hydrochloric acid) that may be released from the thermal degradation of polymers like PVC or ethylene vinyl acetate (EVA). Furthermore, modifications in the chemical structure of the waste plastics during their first use, due to the occurrence of cross-linking reactions, may also have a negative effect on the reactivity of the plastics, on their visco-elastic properties and also on their ability to char, thus affecting the efficiency of the catalytic reaction.

Despite these inconveniences, several processes have been described in the literature for direct catalytic cracking using different reactor types including stirred batch [20], fluidised bed [25], a cycled-spheres [26] and screw kiln [19, 21]. Most of these systems are not operational at commercial scale and are employed for testing or research purposes. The two-stage process benefits from a better control of the catalytic conversion reaction, as it takes place in an independent reactor. Furthermore, in practical terms, this alternative would permit the removal of unwanted species previous to the catalytic treatment, thus reducing their deleterious effects on the catalysts.

A commercial plant based on this technology is in operation in Zabrze (Poland) since 1997. The plant is operated by AgRob EKO, S.A. and has a capacity to treat 145,000 tons of plastics per year for the production of diesel fuel. A similar facility is operated by Nippon Steel Corporation (Japan) for the treatment of automobile plastic refuse [3].

2.4.1   Catalysts for plastic cracking and reforming

Acid conditions are known to catalyse the cracking of plastic polymers. Initial investigations were conducted using homogeneous Friedel-Craft systems ($AlCl_3/HCl$), although they never found commercial applications due to corrosion and environmental problems associated with these chemicals [2].

Heterogeneous catalysis has been investigated extensively using solids with acid properties like the ones conventionally used in the catalytic cracking of hydrocarbon feedstocks (zeolite Y, ZSM-5, Beta) [22, 27-28] and other modified versions like nanocrystalline ZSM-5 [29] or ultra-stable Y zeolite [27]. Other acid solids like silica-alumina, alumina, aluminium pillared clays, mesostructured solids (Al-MCM-41, Al-SBA-15) [19-22], super-acid solids (ZrO_2 / SO_4^{2-}) and metals supported on activated carbon have also been investigated for this purpose [2].

Acid strength and textural properties are the key parameters dictating the performance of these solids in the catalytic cracking of polymers, although other aspects like thermal stability, regeneration potential, resistance to deactivation and production costs need to be taken into consideration. The acid character of these solids originates primarily from the charge imbalance created due to the incorporation of aluminium into a silicate framework. Porosity, surface area characteristics and particle size determine to a large extent the accessibility of bulky polymeric molecules to the internal catalytic acid sites of the solids. Thus, acid solids exhibiting larger pores (mesoporous catalysts, pillared clays) or an extensive external surface (nanocrystalline zeolites) have proven to be particularly effective in polymer cracking experiments [20-22]. These steric hindrances are less notable in the abovementioned two-stage processes, as the molecules reaching the catalytic step are significantly smaller.

On the other hand, product shape selectivity is more intense in microporous catalysts, where space limitations facilitate the formation of specific molecules on the basis of their capacity to exit the narrow pore system of the catalyst.

2.4.2   Products from the catalytic conversion of plastic polymers

Most of the catalytic processes designed for feedstock recycling of plastic are intended for the production of higher quality fuels, primarily gasoline and diesel fractions. Other interesting products include gaseous olefins and aromatic species (toluene, benzene, xylene) for use as raw chemicals. Alkylaromatic compounds find applications as transmission fluid, detergents, improvers of cetane number in diesel fuels and lubricating oils [2].

The presence of acid catalysts during the cracking of plastic polymers always increases the formation of lighter hydrocarbon products. Experimental work has shown significant shape selectivity in microporous acid solids like zeolites (Y, Beta, ZSM-5) towards the production of aromatic species, a result that is usually enhanced when using higher conversion temperatures and catalyst to polymer ratios. On the contrary, solids with a larger pore size distribution like mesostructured materials (Al-MCM-41. Al-SBA-15) typically exhibit strong alkylation properties but reduced aromatic capacities [20-22].

3. CONCLUSSIONS

The management of plastic wastes is currently seeing a profound transformation, with a need to redirect a large proportion of this waste stream towards more environmentally friendly recycling and recovery options. Legal requirements included in recently enacted European legislation is forcing member states to reduce the volume of used plastics disposed of to landfill and promoting alternative activities.

In this direction, catalytic feedstock recycling represents an area of intense scientific and technological research with great potential to absorb large volumes of plastic wastes. Although the viability of existing processes has historically been questioned, this situation has started to change, with several plants being in operation based on the use of catalytic processes for converting plastic wastes into fuels and chemicals. This progress can be considered the result of better sorting procedures, regulatory pressure and most importantly, scientific progress in the development of catalytic technologies.

Significant advances have been carried out in the field of catalysts development with materials exhibiting stronger acid properties, reduced diffusional/steric hindrances, and improved catalytic activities for the conversion of a wider range of plastic wastes. Novel catalysts are also being designed to deal with heterogeneous plastic waste and exhibit increased resistance to deactivation. Furthermore, improvements in the shape selectivity of catalysts towards the formation of valuable raw chemicals (light olefins and aromatics) are expected to make this type of technologies increasingly attractive.

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