Waste Polyolefins to Liquid Fuels via Pyrolysis: Review of Commercial State-of-the-Art and Recent Laboratory Research

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Abstract

With generation of waste plastics increasing, current EU legislation dictates high recovery rates and policy favours waste management technology choices that occupy a high position on the waste management hierarchy. Pyrolysis is a thermochemical conversion technology that can be considered a 'feedstock recycling' process and may play an increasing role in integrated waste management systems of the future. The objective of this article is to present a review of current state-of-the-art commercial pyrolysis processes for the production of liquid transport fuels from waste polyolefins (polyethylenes (PE) and polypropylenes (PP)). Current plastic waste generation and management practices are briefly summarised. Waste management infrastructure in Europe is reliant on landfill, incineration and mechanical recycling, while feedstock recycling plays an insignificant role. Plastic-to-liquid (PTL) platforms including delocalised pyrolysis followed by centralised upgrading, stand alone facilities, and integrated waste management infrastructure concepts are briefly discussed. Commercial operations and their process configurations are compared. Reactor technology for cracking of plastic waste is presented. Important issues like fuel quality and contamination are also discussed. Fuel finishing operations and fuel additives required to achieve an engine ready fuel are described in the final section. Recently published laboratory research in thermal and catalytic pyrolysis and integrated and co-processing studies are also summarised in this review.

Keywords

liquefaction; pyrolysis; waste; plastic; polyolefin; waste-to-energy; waste management; feedstock recycling

Introduction

Global production of plastic has risen from 1.5 mt in 1950 to 245 mt in 2008 [1]. In 2008 in Western Europe alone, 45.3 million tonnes of plastics were generated [2]. While plastics have contributed greatly to modern society, they are also responsible for environmental nuisances. Since traditional plastics are quite resistant to degradation they persist in the environment for prolonged periods of time, and are particularly destructive to the marine environment [3]. As waste management practices are aligned with the internationally-recognised waste management hierarchy, landfill is no longer considered a sound waste management strategy. Additionally, the practice of exporting large volumes of wastes from developed countries to developing countries has created a supply chain which is highly susceptible to price fluctuations of materials [4]. Recent waste policy instruments attempt to shift waste management practices (WMPs) towards more environmentally acceptable options according to the waste management hierarchy (WMH). Furthermore, recent European legislation calls for higher recovery and recycling rates from end-of-use materials like vehicles, tyres, electrical and electronic equipment, packaging wastes etc. These waste streams must be managed in an environmentally acceptable manner. Several options for management of waste plastics are described in the next section. While technology choices should be more inclined towards those options that are more preferred on the WMH, they may not always feasible due to technical (e.g. excessive contamination) or economic considerations. Therefore solutions should be regarded on a case-by-case basis, and a combination of approaches may be applied in an integrated waste management infrastructure for maximum resource efficiency. Pyrolysis is a thermochemical conversion technology that can be employed for the production of liquid transport fuel intermediaries or finished fuel products from plastic wastes. The advantage of pyrolysis is that it can accommodate relatively contaminated feedstocks and value-added materials can, if desired, be recovered prior to conversion to fuels e.g. metals or hydrochloric acid [5]. Generally speaking, the intensity of pretreatment required of the feedstock lies somewhere between that for mechanical recycling (intensive) and incineration (non-intensive). It should be noted that the liquid energy-carrying medium that it produces is easy to store and so can be used on demand, and has a higher economic value than, for example, electricity produced via energy recovery from waste. Furthermore, pyrolysis can be employed alongside mechanical recycling and incineration in a cascaded waste management infrastructure so should be viewed as a component of a waste management system rather than a competing technology. The cascade recycling concept is illustrated in Fig 1 MSW arriving at local sorting facilities is concentrated into an MPW fraction suitable for materials recycling, while other fractions (e.g. wood, glass, paper/cardboard, aluminium and metals, organic waste, and textiles) are directed to recycling, biological treatment, incineration, landfill etc. With current mechanical recycling methods, 40-50% plastic wastes received are unsuitable for reuse as a raw material. Therefore it is proposed that this fraction would be mixed with the concentrated MPW stream and pyrolysed. The resulting pyrolysis products can then be upgraded in a refinery generating standard refinery products [6].

Fig 1 Schematic of a Cascaded Waste Management System. IW = Industrial Waste. Adapted from [6]

The first attempts to produce liquid fuels from plastic occurred during the mid 70’s and early 80’s [7]. Since then, pyrolysis of plastic has been achieved on a commercial scale, albeit to a limited extent [8]. There are several pilot and commercial plants in Japan where high plastic recovery rates are mandated by legislation. They have however struggled for viability, contending with issues arising from processing contaminated feedstock (including PVC and PET) and meeting strict product quality specifications (low chlorine content). This is highlighted by the fact that the number of companies in Japan offering plastic liquefaction dropped from 25 at the beginning of the Container and Package Recycling Law (CPRL) to 2 in 2009. The technology has also struggled for economic viability in Europe. While various processes have been technically proven, they remain unapplied in present times. In Poland 30 plants were established between 2004 and 2006 but were all shut down in 2007 due to economic challenges [9].

Pyrolysis is an extremely versatile process suitable for large scale and small scale production of an array of products. For example, pyrolysis of waste polyolefin plastics under different conditions can yield hydrocarbon waxes and oils, BTX aromatics, olefin gases (ethene, propene, butadiene). The latter two groups of chemicals are particularly interesting since they comprise of the 6 base chemicals which are used as starting feedstocks in the synthesis of a huge array of chemicals consumed by modern society [10]. Furthermore, the current trend towards integration of upstream (refining) and downstream (petrochemical production) operations in the Middle East [11] may generate new opportunities for the use of waste plastics as an alternative petrochemical feedstock.

While waste plastics are a valuable resource, the scale and delocalised nature of their generation hinder penetration of the highly optimised and competitive crude oil product market. With the average person producing 100kg of plastics per year, yielding, in the most optimistic scenario, 100 L of fuel [7], PTL applications would appear to have most potential in small scale niche markets rather than large scale ones (refinery operations). Small scale applications might include fuelling waste material transport fleets or on-site machinery at waste sorting facilities [9]. The objective of this review is to provide an overview of state-of-the-art PTL technology. A brief overview of other recycling technologies will be given. For PTL technology, the focus will be on commercially available technologies, PTL platforms, and recent (from about 2006 onwards) laboratory research.

Overview of the Plastics Sector

Global production of plastic was 1.5 Mt in 1950. Global production increased dramatically since then, surpassing steel production in 2005 at 240 Mt, and stood at 245 Mt in 2008 [1]. Europeans and Americans are the greatest consumers of plastic at about 100 kg/capita/annum with the potential to rise to 140 kg/capita/annum by 2015. The biggest potential for growth is in Asia (excluding Japan), where current consumption is 20 kg/capita/annum, and Eastern Europe [1]. The biggest demand for plastic came from the packaging sector (38%), followed by building and construction (21%) (See Fig 2**Error! Reference source not found.**). While there are over 20 different groups of plastics, each with different grades, there are five high volume plastic families: polyethylene (PE, low density (LDPE), linear low density (LLDPE), and high density polyethylene (HDPE)), polypropylene (PP) polyvinylchloride (PVC), polystyrene (solid polystyrene (PS) and expanded polystyrene (EPS)), and polyethylene terephthalate (PET), which account for over 75 wt% of European demand [1]. PEs and PPs are classified as polyolefins (PO) and are the primary focus of this review.

Fig 2 Flow diagram for plastic production and waste management in Europe. Adapted from [1]. E&E = Electrical and Electronic Sector. Note: Demand and waste production quantities differ due to import and export and varying plastic product life spans.

Some important monomers used for the manufacture of plastics include high purity ethene, propene, butadiene which are generally obtained by thermal cracking (pyrolysis) of naphtha, light gas-oil, or liquefied petroleum gas followed by purifying by low temperature high pressure distillation [5]. Globally, about 4% of crude oil production is used directly in plastic manufacture [12]. Addition polymers (e.g. PE, PP, PS, PVC) are synthesised by catalytic or peroxide initiated sequential incorporation of monomeric molecules into the growing polymer chain without the release of molecules or fragments and the reaction. During the formation of condensation polymers (e.g. PET) polymerisation proceeds with the liberation of small molecules (e.g. water). Depending on the reaction conditions used during polymerisation, structurally different forms of plastics can be formed with different properties and result in different pyrolysis products. Considering the intended application of the plastic product, additives which improve processing, stability, or mechanical specifications are compounded into the monomer resin before conversion [5,13]. Examples include plasticizers (40%), fillers (40%), flame retardants (15%), impact resistance enhancers (10%), or heat and light stabilisers (5%) [5]. These additives pose problems, especially for mechanical recycling, and can sometimes liberate hazardous species upon thermal composition [14]. Recent legislation has begun to restrict the use of hazardous additives in plastic making processes in order to facilitate easier recovery (Directive 2002/95/EC).

While the weighted average of life of all plastic is 8 years, more than 40% of plastics have a life-span of less than one-month [15,16] meaning that significant volumes of waste are generated annually. For example in the EU in 2008, 24.6 Mt of post consumer plastic were generated. Post consumer plastics make up a major portion of municipal solid waste and arise in waste streams from agriculture, distribution and packaging, construction and demolition, automotive and electrical and electronic applications [5,17]. The plastic fraction of municipal solid waste comprises 60% polyolefins (POs) like high density polyethylene, low density polyethylene and polypropylene, which is desirable from a PTL standpoint since they are the most suitable plastic candidates for quality liquid fuel production. Smaller quantities of polystyrene (generally desirable in small quantities), poly vinyl chloride and poly (ethyl terephthalate) are present. Polyolefins are long chain alkenes, with a high concentration of carbon and hydrogen with no undesirable elements e.g. halogens (e.g. Chlorine in PVC) or oxygen (in PET) in the main structure. Waste plastics are particularly suited for fuel or a liquid fuel feedstock since they don’t adsorb moisture (compared to biomass) and have high energy contents [14]. The only disadvantage of the use of polyolefins, as will be described later, is that the thermal decomposition products are fundamentally olefinic (compared to predominantly paraffinic diesel and gasoline).

In Europe the revised Waste Framework Directive (*Council Directive 2008/98/EC)* provides a legal basis for the internationally-recognised waste management hierarchy which states that it is preferable to minimise or prevent waste production, but when this is not possible waste should be re-used or recycled [18-20]. To bring European waste management practices in line with the hierarchy a number of policy instruments have been devised and implemented. These include introduction of 1) a ban on certain types of waste in landfill (*Directive 99/31/EC*) e.g. tyres; 2) a landfill levy to discourage landfilling of wastes (*S.I. 13 of 2010*, Ireland); 3) producer-responsible initiatives for the recovery of waste electrical and electronic goods (WEEE), agricultural waste plastic, and waste packaging materials (Directive 94/62/EC); 4) legally binding targets for recovery and establishment of targets for management of wastes including end-of-life vehicles (*Directive 2000/53/EC*) and WEEE (*WEEE Directive 2002/96/EC*).

The implications of expanding plastic production, increasing recovery targets, and a paradigm shift in waste management practices are as follows: Firstly, waste management infrastructure must be expanded to cope with the increased volumes of waste being generated; Secondly, the choice of waste management technology made by policy makers and local authorities needs to be more technologically advanced, efficient, and environmentally responsible; and thirdly, management of composition-specific waste streams which may not have traditionally arisen (e.g. ASR (Automobile Shredder Residue), WEEE, Packaging Wastes) must be considered in the waste management infrastructure.

Technologies for Management of Plastic Waste

Overview of Plastic Waste Treatment Options

The waste management hierarchy is the cornerstone of modern waste management policy and is depicted in Fig 3. The Hierarchy states that the most preferred option for waste management is prevention and minimisation of waste, followed by re-use and recycling, energy recovery (incineration) and least favoured of all, disposal [19]. Municipal Plastic Waste (MPW) recycling technologies can be classified as primary (re-extrusion), secondary (mechanical recycling) and tertiary ((thermo)chemical), while energy recovery can be referred to as quaternary recycling [21]. Readers are referred to recent reviews by [16,21-25,14,26,27] for overviews of plastic waste management.

Figure 3 The Waste Management Hierarchy [19]

As of 2008, plastic waste treatment in Europe (EU27 + NO/CH) comprised 21.3 wt% recycling (21% of which mechanical recycling), 30% energy recovery, and 48.7% disposal [1]. In the vast majority of cases mechanical recycling is preferable to incineration [28]. While disposal of plastic by landfilling accounts for the highest fraction of MPW management, it is no longer acceptable and is being disincentivised in the form of strict landfill regulations and levies. Incineration is the most highly developed and widely used method of thermal treatment of waste but it is only considered as a viable means of waste management when material recovery processes fail due to economic restraints [21]. Grate-firing technologies are the most widely applied systems, representing 75% of the total growth in global waste management capacity (22.5 Mt) between 2001 and 2007. Another combustion option is the co-combustion of Solid Refuse Fuel (SRF) with crude-derived feedstocks or other wastes (tyres or solvents) in cement production [29]. This is being pursued by Lagan Cement in Ireland and several facilities in the UK [30]. A number of coupled ‘gasification-combustion’ processes are beginning to gain a foothold in the waste management sector. Examples include the Ebara Twin Rec and Thermoselect Processes [31]. The Thermoselect (gasification) process produces less process gas than conventional Waste-to-Energy (WTE) technologies and the cleaned and quenched gas is combusted in a power or gas turbine to produce electricity at twice the efficiency (40%) of conventional WTE technologies [26,31,27]. More information on combustion of plastic wastes can be found in [25,32,26,31,27,33]. Thermal treatment of plastic wastes by plasma technology is another topical issue at present [34,35].

Feedstock Recycling

Feedstock recycling is a form of tertiary recycling and encompasses a number of thermal or chemical processes that recover fuels or raw chemicals from plastic wastes. In Europe they currently account for just 0.3% of waste management capacity [1]. These technologies are discussed in [16,21,24,22,23,36-38,14,39].

Chemical Feedstock Recycling Processes

Chemical depolymerisation entails the breakdown of condensation polymers by reaction with chemical agents yielding the monomers from which they were originally produced [13,39]. The recovered monomers can then be used to re-synthesise the plastic. Depending on the chemical agent employed, different depolymerisation routes are distinguished: glycolysis, methanolysis, hydrolysis, ammonolysis etc. Despite being a proven technology, it is restricted to condensation polymers like PET. The only process currently being applied commercially is methanolysis of PET (Coca-Cola) [39]. The Goodyear Tire & Rubber Company and Eastman Chemical Products developed glycolysis and methanolysis technologies, respectively. A recent laboratory study on this topic has been reported [40].

Thermal Feedstock Recycling Processes

Thermochemical processes like pyrolysis (thermal cracking), catalytic pyrolysis (catalytic cracking), hydrocracking are also classified as feedstock recycling technologies. Partial-oxidation (i.e. gasification) technologies can be classified as feedstock recycling technologies when the products are used a) for the production of fuels or raw chemicals or b) as a reduction agent in the smelting process, rather than for combustion and energy recovery which would be considered a waste-to-energy process. These technologies are particularly suited for the recovery of fuels and raw chemicals from waste plastics.

Generally speaking less intensive pretreatment and sorting of the feedstock is required for these thermochemical processes compared to mechanical recycling and chemical depolymerisation (an exception is Hydrocracking, where the catalyst employed is highly sensitive to contaminants). Applied to plastic, thermal pyrolysis occurring in a reduced atmosphere yields liquids, waxes, unconverted residues, char and gas [5]. The yield structure is highly dependent on the feedstock and the process conditions employed. The use of catalysts during pyrolysis enables higher feedstock conversions at lower temperatures and reduces the carbon range of the product spectrum, thus increasing value of the fractionated products. It is also responsible for the formation of another by-product, coke. Pyrolysis is discussed in more detail in later sections. Hydrocracking differs from thermal and catalytic pyrolysis in the respect that it takes place under high hydrogen pressures [41]. The Veba Oil Process, a coal liquefaction (hydrocracking) process, was successfully applied to waste plastics. The presence of hydrogen significantly improved the quality of the products. Operation was discontinued in 1999 due to inability to compete with the Sekundärrohstoff Verwertungs Zentrum (SVZ) Schwarze Pumpe Process [5,42,43]. Degradation can also take place under partial-oxidation conditions (gasification) yielding a gas consisting mainly of H_2 and CO. Various gasification processes have been developed and proven over the years, but penetration of the waste management sector remains minimal [26,31,27,22]. SVZ have demonstrated gasification of automotive shredder residue (ASR) with coal in a fixed bed slagging gasifier followed by reforming to methanol. The current shredder residue capacity of the plant in Saxony (Germany) is 150 kt/a and it is planned to be expanded to 200 kt/a [33,44]. Enerkem (Montreal, Canada) have developed a process for fluidised bed gasification of wastes containing plastics followed by mixed alcohol synthesis. They are developing two commercial scale plants in Edmonton (Alberta, Canada), and Pontotoc (Mississippi, USA) [45]. Under the revised European Framework Directive, the use of waste plastics as a reducing agent in a smelting furnace for steel production is considered recycling [1]. Several German companies including VoestAlpine have used 300 kt of waste plastic per annum to offset fossil fuel consumption in the process [46]. Similar technologies have been developed in Japan by JFE and Nippon Steel [25,31,27]. Another option is to co-process plastics with coal (at ~1 wt %) in the coke-making process [14,47-49].

Introduction to Pyrolysis of Plastic Wastes

Thermal and Catalytic Pyrolysis of Polyolefin Waste

Pyrolysis (or cracking) can be defined as the chemical and thermal degradation of polymeric materials by heating in the absence of oxygen in an inert atmosphere e.g. nitrogen. The pyrolysis temperature is the most influential pyrolysis parameter and a values between 400-800˚C are generally employed depending on the feedstock being processed, whether or not a catalyst is used, and on the target products. Heating systems for reactors can be dynamic (e.g. some batch reactor configurations) or isothermal (e.g. fluidised bed), with isothermal systems being most frequently applied. The process yields carbonised char and volatiles that may be separated into hydrocarbon oil/wax and non-condensable gas [5]. As the pyrolysis temperature of POs decreases, increasing wax and partially converted feedstock (residue) fractions are observed in the yield structure. The pyrolysis products can be applied as fuels and petrochemicals [5]. Thermal cracking of POs are usually carried out either at high temperatures (>700˚C), to produce an olefin mixture of C_1-C_4 gases and aromatic compounds (benzene, toluene and xylene) or at low temperatures (400-500˚C) where the yield structure comprises a high-calorific value gas, condensable hydrocarbon oils and waxes [13]. For pyrolysis of plastic wastes, the majority of published studies have focused on POs, presumably due to the fact that these polymers make up the largest component of waste plastics [24] and that they are the most suited plastics for liquid fuel production [14].

Two of the main problems associated with thermal cracking of POs are 1) limited conversion of the feedstock at low pyrolysis temperatures and 2) large carbon and molecular weight distribution in the pyrolysis product, resulting in limited market value. These effects can be reduced through the use of catalysts in the cracking process. The advantages of catalytic cracking are 1) lower cracking temperature (optimum temperature range for diesel production from waste plastics is 390-425 ˚C); 2) increased reaction rate (and so smaller reactor volume); 3) increased production of isoalkanes, branched and cyclic molecules and aromatics; 4) increased efficiency; and 5) improved selectivity and quality of the product [8,50 ,51]. Reactions occurring during thermal versus catalytic pyrolysis are compared in the table below.

Table 1 Comparison of Catalytic and Thermal Cracking [51].

One of the main challenges associated with catalytic processes is loss in catalyst activity due to coke formation. Whereas char is a product of pyrolytic decomposition of carbonaceous feedstocks, coke is a carbonaceous deposit formed on catalysts during the conversion of pyrolysis products to products with higher H/C ratios. It is generated in different quantities based on the type of catalyst used: 10 wt% on USY, 5 wt% on commercial cracking catalysts, and <1 wt% with ZSM catalysts [7], and its nature and quantity vary depending on the feedstock, operating conditions, and catalyst used [52,53]. Coking reduces the cracking activity of the catalyst and thus the quality of the resulting product. Catalysts may be regenerated by combustion of the coke on the catalyst, but with reduced activities. Additionally, sensitive catalysts may be irreversibly deactivated by impurities in the feedstock.

Catalysts for Cracking Plastic Waste

Heterogeneous catalysts are the most commonly applied catalyst for plastic pyrolysis. They can influence the type of upgrading reactions that take place, the rate of reaction, and the distribution of the products [54,55]. Heterogeneous catalyst systems are those in which the catalyst is in a separate phase to the reactions and are frequently applied in pyrolysis processes. They are typically a solid material and the reaction generally occurs on ‘active sites’ on the solid surface. They can withstand severe reaction conditions (up to 1300˚C and 35 MPa), and can generally be easily separated from the gas and/or liquid reactants and products. They are typically porous materials possessing high surface areas. Since reactions take place on the surface of the catalyst, the objective is generally to maximise the surface area. Different structural features of a catalyst infer different catalytic environments. A good catalyst embodies desirable activity, selectivity (percentage of the spent reactant that forms the desired product), and stability. In the scientific community the least is known about manipulation of catalyst selectivity. Catalyst porosity and pore shape are also critical parameters. Zeolites are the most widely applied shape-selective catalysts [55,56]. They can be applied to pyrolysis, gasification, steam reforming, hydroprocessing and various other petrochemical operations. Hydroprocessing catalysts are bifunctional and possess hydrogenation and cracking functionalities [57].

Fig 4 Steps in Heterogeneous Catalysis Reactions [124]

Catalysts for cracking of polyolefin wastes are reviewed in previous publications [38,50,7,57,58,8,24]. Recent research in this area will be summarised in a later section. Zeolites, alumina, silica-alumina, FCC catalysts, and reforming catalysts have been investigated for cracking plastic waste [51]. They are frequently used in the petroleum refining sector for processing heavy hydrocarbons. While numerous catalysts have been studied, zeolites and mesoporous materials are the most important due to their porous structure and acid properties [59]. Acidic zeolite catalysts like HZSM-5 and H-ultrastable Y-zeolite (HUSY) are more effective in converting polyolefins than the less acidic amorphous silica-alumina and mesoporous MCM-41 [8]. There are considerable differences in product selectivity between catalysts [50]. Depending on the acid strength of the catalyst, cracking proceeds either by random (medium or weak acidity) or end-chain scission (strong acidity) giving rise to waxes and middle distillates (gasoil, gasoline) or light hydrocarbons (C_3-C_5 olefins) respectively. Primary cracking products can be removed from the reaction medium or undergo secondary reactions like oligomerisation, cyclisation, aromatization. The effects of catalyst on fuel properties can be seen in the table below.

Table 2 The influence of catalysts and temperature on product properties. Adapted from [57]

From a commercial point of view cheaper silica-alumina catalysts give good selectivity. Lower cracking activity can be compensated for by higher catalyst/feedstock ratio [8]. Larger pore HYs show rapid deactivation compared to more restrictive HZSM-5 and non-zeolite catalysts (alumina silica, MCM-41) because coke can form on the inside of the pore. One of its major shortcomings is sensitivity to hydrogen chloride and HCl acid, which results in destruction at concentrations above 200 ppm. Catalysts capable of handling high chlorine feedstocks have been developed. There is also considerable interest in the use of waste petrochemical catalysts for the cracking of plastics [8].

A Note on Hydrocracking

Hydrocracking is often employed in refineries to improve the H/C ratio of crude-derived residues by cracking the aromatics and adding hydrogen [60]. As previously mentioned hydroprocessing operations employ heterogeneous catalysts with bifunctional (hydrogenation/cracking) properties. High pressures and temperatures (400˚C, 8-15 MPa) and a sulfided feedstock are generally needed to activate the catalyst. For hydrocracking, the acid support supplies the cracking properties, while the metal oxide sulphite group exhibits the hydrogenation capabilities. Isoparaffins are the main product from hydrocracking. The NiREY catalyst has a gasoline selectivity of 78% and the gasoline has a RON (Research Octane Number) of 110 [58]. When compared to the thermal cracking of waste, the yields of paraffins are increased while the olefins and aromatics decrease. The boiling range and unsaturation of liquid products compared to thermal cracking and catalytic cracking are lower for hydrocracking [61]. One of the main disadvantages of this type of process is the severe reaction conditions required and the hydrogen, which is very expensive and large scales were required.

Since polyolefin plastics and their thermal degradation products are inherently olefinic (and unstable) and target components for diesel and gasoline are paraffinic, hydrogenation of the double bonds is beneficial either in a hydrocracking or fuel finishing (hydrotreatment) capacity. While the process requires high pressure process equipment, consumes significant amounts of hydrogen and the catalysts are prone to fouling, the infrastructure may already be available in a refinery and a simple thermal pyrolysis step prior to hydroprocessing can remove contaminants.

Pretreatment: Polyolefin Concentration and Dechlorination

Since commercial pyrolysis configurations are very diverse, categorising pretreatment operations would be an over generalisation. Generally speaking, the degree of pretreatment will depend on: 1) Any previous separation/treatment e.g. in a cascaded waste management infrastructure 2) The sensitivity of the process equipment and/or catalyst to contaminants 3) The quality of product required for downstream processing and any standards that must be met. The general aim of pretreatment is to remove contaminants and concentrate POs in the feedstock. Smaller quantities of PS can improve the fuel properties, and while PVC and PET may be tolerated to various degrees, they are generally undesirable [14]. Contamination of the feedstock with both PVC with PET makes cheap removal of Chlorine especially difficult due to the formation of organic chlorine compounds [62].

Separation Technology and Comparison of Sorted Plastic Fractions for Pyrolysis

In the plastic sorting sector, significant progress has been made with automated sorting technology employing detection systems (Near Infrared Systems (NIS), X-Ray and visible light) [2]. Magnetic density separation [63], x-ray fluorescence spectrometry [64], fluidisation [65,66], floatation [67], and cyclone separation [68] continue to be researched and developed. Traditional density separation is inefficient in terms of sorting plastics of similar densities i.e. POs. While this constrains further application as a mechanical recycling feedstock, no such constraints are imposed on the feed as a pyrolysis feedstock. Lee [69] investigated thermal pyrolysis of different fractions of MSW (Municipal Solid Waste) separated by density (specific gravity (SG) <1 (‘LowMPW (Municipal Solid Waste)’), SG 1-1.2 (‘MedMPW’), SG 1.1-1.2 (‘HighMPW’)). MedMPW showed the highest liquid yield with lower portions of gas and residue. It was also found that the paraffin, olefin, naphthalene and aromatic (PONA) product distribution varied significantly between the three MPW fractions. The main chemical class of chemicals in the liquid products were olefins (>75 wt %), aromatics (>95 wt %) and methylmethacrylate (>55%)/aromatic (>20 wt %) for the low, medium and high density MPW fractions respectively.

Laboratory Approaches to Dechlorination

Chlorine can be removed in a separate treatment prior to pyrolysis [62,70]. Melting plastic feedstock facilitates decholrination and also makes transportation of the waste to the cracking reactor more straightforward. When chlorine is present in the feedstock, some chlorine-derived compounds than can be expected in the decomposition products are 2-chloro-2phenyl propane, alpha-chloro-ethylbenzene and 2-chloro-2methyl pentane and 2-chloro-2methyl propane. Iron-oxide on carbon can achieve good dechlorination [62]. Miskolczi et al [71] report that the conversion of mixed plastic waste increased with the presence of PVC in the feedstock. However the desirable properties of all fractions were depreciated by the presence of PVC. Most of the original chlorine was distributed in the gas and was neutralised by a calcium hydroxide scrubbing solution. The chlorine content of the gasoline ranged from 46-2129 ppm, while that of the light oil fraction was between 132-2201 ppm. A fluidised bed pyrolysis study of brominated plastics showed that most of the bromine and antimony was distributed in the oil and char fractions, whereas <2% enters the gas phase [72]. Cho et al [73] targeted the production of low-chlorine content BTX aromatic oils from the fluidised bed pyrolysis of plastic wastes. The hot filter-employed was effective in removing the metal contaminants present in the feedstock and they were concentrated in the char. Maximum aromatics yield was achieved at 719˚C (18 wt% of organic product). Chlorine was successfully reduced (from 350-500 ppm to about 50 ppm) with various agents including calcium hydroxide, calcium oxide and oyster shells. Jung et al [74] observed that while PP and PE fractions separated from MSW had chlorine concentrations of 600 ppm and 100 ppm, concentrations of chlorine in the pyrolysis oil from fluidised bed pyrolysis were below 10 ppm and would be acceptable as petrochemical feedstock. Murata et al [75] recently reported the presence of PVC (present at 1 and 2 wt% in feedstock) decreases the decomposition rate of PE and PP, while it increases the decomposition rate of PS. The presence of PVC increased the specific gravity of the oil for PE and PS, but decreased the SG of the oils for PP.

Commercial/Pilot Approaches to Dechlorination

Sappro Plastic Recycling Co. (Japan) report their experiences with dechlorination on a pilot scale (5 tpd). They found that a single screw extruder can sufficiently dechlorinate waste plastics to meet the strict CPRL standards [6]. Nonetheless some technical challenges remain like corrosion and generation of metallic oxides which clog pipes, strainers and heat exchangers. $Ca(OH)_2$ addition can reduce corrosion problems. BASF dechlorinated plastic feedstocks in a stirred tank pretreatment unit and the HCl was recovered and subsequently used for chemical manufacturing [5]. The Zadgaonkar process uses coal (as a hydrogen-donating material) and other patented additives in a pre-pyrolysis dechlorination operation [76]. The Reentech process uses a catalyst-coated paddle to dehalogenate the feed [8]. Dechlorination can also be carried out in the pyrolysis reactor itself. The Agilyx (formerly Plas2Fuel) approach employs a thermal and vacuum pretreatment step in the batch pyrolysis reactor prior to ramping up the temperature and pressure for pyrolysis. This way moisture and HCl are ‘fractionated’ from the feedstock [77]. The Hamburg/BP process applied sorbents like limestone in the fluid bed to absorb chlorine [5]. Another interesting approach is the use of a dechlorination/cracking catalyst in the Nanofuel process [8]. The cation –donating catalyst absorbs Chlorine and sinks to the bottom of the pyrolysis reactor where it is removed. The Altis process removes hydrogen chloride from hydrocarbon vapour in a dechlorination unit post pyrolysis [14].

Liquid Transport Fuel Platforms

The Traditional Oil Refining Platform

Pyrolysis technologies are very flexible, and can be configured either to produce finished, engine-ready fuel, or intermediary transport fuel precursors from POs. Intermediaries can subsequently be upgraded in existing oil refinery infrastructure. In this vein it is logical to start by describing refining operations. There are various crude oil refinery models. A medium sized refinery typically has a crude capacity of 10,000 tpd (73,000 bpd). The most basic refinery is the *hydroskimming refinery*, comprising of a crude oil distillation unit, hydrotreatment for gasoline and gas oil, a catalytic reformer and a gas and sulphur workup section. It produces high quantities of residue (43.5 wt %) which is marketed as a heavy fuel oil. Residue conversion facilities are not present. *Cat cracking-visbreaking refineries* incorporate an FCC unit for maximum gasoline fraction production. Vacuum distilled oil is desulfurised and channelled to an FCC unit. The visbreaker unit cracks vacuum residue producing more distillates. Here the residue production is low (22.7 wt %), the gasoline yield is 33 wt%, and the middle distillates (MDs) make up 25.9 wt% of crude. In the *Hydrocracking-cat cracking refinery* FCC is combined with hydrocracking. Additional hydrogen required for unit operations is supplied by steam reforming. The net fuel oil production is 9.2 wt%, while the gasoline and MD make up 32.9 % and 39.8 wt%. The *Hydrocracking-Coking* refinery is employed to maximise MD yields (>60%), with the naphtha fraction representing 26 wt% of the product [60].

Other unit operations in a fuel refinery may include:

- *Reforming:* Conversion of normal paraffins and cycloparaffins to aromatics and isoparaffins. The octane quality of the feedstock is improved and hydrogen is liberated;

- *Catalytic Cracking:* Conducted at high temperatures in the presence of a cracking catalyst. Oil distillates are converted to gaseous components (Fuel gas and liquid petroleum gas (LPG)). LPG fractions are typically processed in alkylation and polymerisation units for the production of high octane gasoline. Fluid Catalytic Cracking is the most widely applied process for residue upgrading and is the largest process in the refinery;
- *Hydrotreating:* Employs pressures of 10-20 MPa in the presence of Co-Ni-Mo catalysts at temperatures of 200-450˚C. Represents highest capacities of all secondary refining processes worldwide. Generally used for removal of S, N, O and metals or to de-aromatise feedstocks;
- Gasoline upgrading can comprise *alkylation, polymerisation* or *isomerisation* operations;
- Residues possess a low H/C ratio. Residue conversion processes are centred on 'H-in' (Hydrogen addition) or 'C-out' (Carbon removal) approaches. H-in processes include hydrocracking. Whereas hydrotreatment aims for removal of sulfur and nitrogen (>90 %) and heavy metals at a low conversion (5-35%), hydrocracking is undertaken at higher pressure and attains higher conversion rates of between 60-90%. C-out approaches employ thermal (visbreaking and coking) and catalytic (residue catalytic cracking, like FCC) processes [60].

Transport Fuel Production

Transport fuels like diesel or gasoline are blended from various refinery fractions to produce a fuel which meets the requirements specified in standards or specifications. Gasoline is the most commonly used transport fuel in North America, while diesel is more dominant in Europe [11]. Diesel components can include various portions of straight run MD, thermally cracked gas oil, catalytically cracked gas oil, hydrocracked gas oil, kerosene, and in some cases Fischer-Tropsch diesel. On the other hand, gasoline components can comprise straight run gasoline, thermally cracked gasoline, catalytically cracked gasoline, catalytic reformate, isomerate, aklylates, polymer gasoline and oxygenates [78]. Average tax-free retail prices for diesel and gasoline in selected countries (Belgium, France, Germany, Italy, Netherlands, UK, US) in 2008 were 3.7 and 3.14 USD/gal respectively.

A Note on Petrochemicals

In a refinery the major share of the crude oil is converted to fuels. Petrochemicals are non-fuel compounds derived from crude oil and natural gas [11] and represent just 3% of crude oil consumption and 6% of refinery output (in the US) [10]. However since 90 wt% of organic chemicals consumed by modern society originate from natural gas and petroleum, the petrochemical sector is of major societal and economic importance [10]. Petrochemical plants accept base chemical precursors from crude refining (petroleum gases, naphtha, kerosene, and light gas oil) or natural gas processing plants (methane, ethane, and liquid petroleum gases), and convert them to base chemicals can be further processed or converted into a wide variety of goods used directly by consumers or industry. Base chemicals are produced by thermal or catalytic cracking, reforming, or dehydrogenation or dealkylation reactions [10].

Table 3: Summary of 6 Base Petrochemicals. PR = US Production Rank in 1995. Prices given in Euro/tonne for 2008. TC = Thermal Cracking, DH = Dehydration, CR = Catalytic Reforming, HDA = Hydrodealkylation, IP = Intermediary Product.

Profitability of petrochemical processing is highly dependent on the price of the feedstock. The weight of feedstock cost as a percentage of end product value (~70 % in Europe compared to ~15 % in the Middle East) means that, ultimately, access to low cost feedstock represents a competitive advantage. This has led to substantial expansion of the petrochemical industry in the Middle East (possessing rich gas reserves), with increasing integration between upstream (refining) and downstream (petrochemical production) operations. On the other hand, investment in Europe and the US has decreased due to poor competitiveness, with major oil companies choosing instead to invest in facilities close to major demand centres e.g. China or Korea.

PTL Platforms for Liquid Fuel Production

PTL process models include materials recycling-integrated models, stand-alone models, delocalised pyrolysis-centralised upgrading models, and refinery integrated models, with a certain amount of overlap existing between models. It was initially proposed that processing of plastic wastes could be carried out by co-processing with standard refinery feedstocks [50]. Another argument is that future

PTL technology development should target smaller-scales of application [9]. Commercial pyrolysis approaches will be discussed in more detail in a later section, but some brief examples are given here: 1) The BASF approach could be considered a refinery integrated processes because it produced gaseous olefins which could be used for the production of base chemicals in a petrochemical facility; 2) The Thermofuel, Nanofuel (Alphakat), Fuji and Reentech processes could be considered stand alone processes because they aim to produce separated engine-ready fuels in one facility from PO feedstock, while the Sappro process might be thought of as a combination of the materials recycling integrated/delocalised pyrolysis-centralised upgrading approach.

Fig 5 Schematic of a small-scale thermal pyrolysis pilot plant. [79]. 1—Transportation, 2—Selective collection, 3—Shredding, 4—Washing, 5—Drying, 6—Waste storage, 7—Catalyst storage, 8—Reactor, 9—Heating gas storage, 10—Separation unit, 11—Catalyst filter

Thermal pyrolysis of POs can yield diverse products depending on the operating conditions employed, with various strategies for integration with refineries:

1. Low-temperature cracking of POs at 500 to 600˚C to produce waxes and oils that can serve as feedstock for a steam cracker;
2. Pyrolysis of POs in an inert-gas stream at temperatures of 650 to 800˚C. A high proportion of ethene, propene, butadiene and other olefins which could be combined with the product stream from a steam cracker for joint processing;
3. Pyrolysis of POs between 600 to 800˚C using pyrolysis gas as the fluidising gas. These process conditions yield high heat content gases and BTX-rich oils, which can be transported from small regional plants to refineries or other petrochemical processing plants [80].

In the *catalytic pyrolysis* process, catalysts can significantly improve the quality of the product by narrowing their carbon distribution and increasing selectivity for desired components. Catalysts can either be mixed with the feedstocks prior to pyrolysis or the feedstock can come into contact with the catalyst in the reactor. In this mode the process is considered liquid-phase upgrading. Commercial examples of catalytic processes include the Smuda or Nanofuel processes [8]. Another variant of catalytic pyrolysis is vapour-phase upgrading. In this mode plastics are thermally cracked and the pyrolysis vapours pass through a vapour upgrading unit containing catalyst e.g. Thermofuel Process [8]. The catalyst may be continuously regenerated as with the Reentech Process [8]. These catalytic processes are capable of producing transport grade fuels from waste plastics in stand-alone facilities, with some degree of fuel finishing generally being required after vapour upgrading. When catalysts are employed under more severe reaction conditions, a high selectivity for gaseous olefins can be attained (see section on integration with refinery).

Fig 6 Integration of Plastic Waste Processing with Oil Refining Operations

Fig 6 illustrates the possibilities for integrating pyrolysis processes with existing oil refining infrastructure. In addition to the options previously discussed for thermal pyrolysis, these include 1) Direct processing of plastic wastes in FCC units 2) Co-processing of plastic wastes in FCC units; 3) Co-processing of PO-derived pyrolysis waxes/oils in FCC units; 4) Hydrocracking of plastic wastes; and 5) and Hydrocracking of pyrolysis products. These possibilities are discussed further in a later section. A drawback of using refinery infrastructure to process waste plastics and pyrolysis products derived from waste POs is that the decomposition products of contaminant plastics present in the stream e.g. PVC and PET are very corrosive to refinery infrastructure. Other types of contaminants can cause operational problems like deactivation of catalysts. Another difficulty is to transform plastics into pumpable liquid which are easily conveyed in process infrastructure. It should be realised that in the refinery, the aim of tertiary recycling is not to displace regular refinery capacity, but to use plastic waste as a very minor stream [81]. Benefits of integrating waste POs into refining infrastructure are that the infrastructure is already in place, the polyolefins have a high H/C ratio compared to heavy residues and so produce more valuable products upon thermal decomposition. Furthermore, synergistic effects can sometimes be observed upon coprocessing of POs with crude oil derivatives, producing a better quality product than what might be expected by a purely additive effect.

Reactor Technology for PTL

Bubbling Fluidised Bed

Bubbling Fluidised Beds (BFB) are characterised by excellent heat and material transfer rates, resulting in constant temperature and largely uniform products. Probably the most known Fluidised bed process the Hamburg Fluidised Bed Pyrolysis which dates to the early 1970s [80]. The Hamburg Process is reviewed in [82,83,80]. The pyrolysis temperature is one of the most critical factors determining the yield structure of polyolefinic waste materials. Three thermal modes of operation for the production of wax/oil, gaseous olefins, or high heat content gases and BTX aromatics have already been distinguished. Catalytic pyrolysis in fluidised beds has also been researched [84,85]. Other researchers have applied catalysts in fluidised bed processes, and recent studies in this area are reviewed in a later section. Supply of fresh catalyst and removal of coked catalyst from the fluidised bed would need to be considered in industrial designs. A variant of the BFB is the Conical Spouted Bed Reactor (CSBR), developed in Spain. CSBRs avoid bed defluidisation associated with BFBs through more intense mixing in the bed. This type of reactor has been applied for the thermal pyrolysis of polyolefins on a laboratory scale, and very high yields of wax are attainable (up to 80 wt %) [86,87]. Catalytic studies have also been performed with this type of reactor [88-90] with polyolefin feedstocks for the production of gasoline and diesel range products.

Fig 7 Selection of Reactors used for Cracking Plastics: a) bubbling fluidised bed b) fluid catalytic cracker c) stirred tank reactor d) screw/auger reactor. Readers are referred to Al-Salem et al [91] for classification of reactors with respect to solids and gas residence times.

Transported Bed Reactors

Fluid catalytic cracking is the most widely used process for conversion of the heavy fraction of crude oil e.g. vacuum gas oil (VGO) to gasoline and other hydrocarbons in refineries. There are two zones in the reactor; in the first a hot particulate catalyst is contacted with hydrocarbon VGO feedstock, creating cracking products and a coked catalyst. After this the coked catalyst is separated, stripped of residual oil products and regenerated by burning the coke in a regenerator. The hot catalyst is then recycled to the riser for additional cracking [56]. Feedstocks are cracked to predominantly gaseous components which are separated to fuel gas (hydrogen, methane, ethane, ethene and hydrogen sulfide) and LPG (propane-propene and butane-butene) fractions. After treatment the LPG is predominantly processed in alkylation and polymerisation units for the production of high-octane gasoline components [60]. A disadvantage associated with this type of reactor is that it has large energy requirement due to the endothermicity of the process, and very dilute feed streams [92].

The Reentech Process (Korea) employs an FCC process for the cracking of plastic wastes [8]. Also the process developed by Hunan University and Hunan Waste Management Company is a circulating fluidised bed (CFB) process which includes sand as well as catalyst [93]. The catalyst is recovered from the product stream, regenerated and returned to the system [94]. The rotating cone reactor, a variant of circulating fluidised bed technology was developed at the University of Twente (Netherlands). While generally employed for the pyrolysis of biomass (A 50 tpd plant exists in Malaysia), there are several reports in literature of pyrolysis of plastics. The main advantage with this reactor is that no fluidisation gas is necessary, good solid polymer mixing is achieved and no cyclones are necessary [95-98].

Stirred Tank Reactors (STRs)

STRs are one of the most frequently applied reactors for pyrolysis of plastic. These include the Thermofuel Process (Cynar Plc), Smuda (Poland), Polymer-Engineering Process (Nanofuel), Royco (Beijing, China), Reentech Process (Korea), Hitachi Zosen Process, Chiyoda Process (China) [8]. The world's largest pyrolysis plant operated by AgRob Eko (South Africa) in Poland is a stirred tank reactor based on Smuda technology. STRs can contain a heat transfer medium like hot oil (Nanofuel Process). Catalysts are frequently applied directly to the plastic waste (Smuda and Nanofuel processes) or upgrading can take place in a separate vapour upgrading tower (Thermofuel). The stirrer facilitates better heat transfer to the melt, uniform heat distribution, and scrapes char deposits from the reactor walls which act as a heat insulator [8]. Char, spent catalysts, and/or contaminants are generally removed from the bottom of the reactor (Nanofuel, Thermofuel, Royco), with the exception of the Hitachi process which vacuums char from the bottom via a vertical vacuum line [8].

While these reactors achieve good conversion of the feedstock, secondary reactions dominate, and heat gradients may exist. Depending on the target end product further processing or separation may be necessary. Since the Chiyoda, Royco and Hitachi-Zosen processes produce low quality fuel feedstocks with a large carbon distribution range, simple separation facilities like reflux or distillation towers are necessary. On the other hand the Thermofuel and Nanofuel processes aim to produce high grade liquid fuels and so require catalysts and work-up processes. One of the main disadvantages of stirred tank reactors is that they require frequent maintenance and so require an over-sized infrastructure [99]. For example the AgRob Eko facility in Poland has 6 reactors but at any one time only 3 of them are operational. On a laboratory scale, batch or semi-batch stirred reactors are frequently employed for basic research e.g. catalyst-containing basket [100,75].

Kiln-type Reactors

Rotary kiln reactors have been extensively applied for pyrolysis of waste plastics in the past, though mainly for the production of a pyrolysis vapours and residues for gasification or combustion [39]. They are applied frequently for the pyrolysis of wastes e.g. tyres. Some technologies do exist for the conversion of plastic wastes e.g. The Faulkner Process, The Conrad Recycling Process (plastic and/or tyres) [101]. The quality of the product is generally low grade. The Toshiba/Sappro process employs a rotary kiln with ceramic balls to avoid coke build-up inside the reactor [102].

Auger kiln reactors can be considered similar to rotary kilns. In this process the kiln is fixed and a centred co-axial auger conveys the material through the reactor. For example, the Haloclean Process [101] was designed for pyrolysis of plastic wastes containing more significant quantities of inert materials. Hot metal spheres transported by the auger improve the heat transfer to the plastics. Laboratory-scale auger kilns also exist and have been employed for the conversion of polyolefin wastes [103]. Catalysts can be mixed with the feedstock to improve the quality of the resulting product [104,105]. Well-defined hydrocarbon products are obtained since hydrocarbons have similar residence times in the reactor and the flow in the kiln is sufficient to avoid over cracking of hydrocarbons [43,50]. Heat transfer in the auger reactor can be improved by the use of a heat carrier e.g. sand [106]. Another variant of the auger reactor is the reactive extruder [107,108]. These reactors can be exploited on small scales (<10,000 tpd) [99].

Tube Reactors

On an Industrial scale, BASF used a tube pyrolysis reactor for the cracking of wastes. A stirred tank reactor preceded the reactor for dechlorination and depolymerisation of the plastic waste. The naphtha produced was subsequently steam reformed for the production of gaseous olefins which were used in the synthesis of virgin polymers [5]. Tube reactors also have potential for smaller scale applications [99]. This is currently being investigated in Eastern Europe, where effective small scale solutions are being developed. A 9kg/h demonstration plant in Hungary exists [109-111]. The main reactor component is a horizontal cylindrical reactor preceded by an extruder. The reactor is quite flexible and various conditions have been applied ranging between mild thermal pyrolysis of polyolefins for oil and wax production [112] to catalytic cracking for the production of liquid fuels, to fuel additive production [113]. The use of ZSM-5 at 5% with PE and PP wastes from agricultural and packaging waste increased the yield of lights (gasoline) significantly [79]. Deactivation of the cracking activity of FCC and HZSM-5 was rapid and significant >75% after one cycle. Regeneration of the catalysts proved only partially effective [114].

Another tubular reactor is presented by Dispons [115]. The tubular reactor is fed by a piston and internally offset by a cylindrical grid which does not allow plastic to touch the walls in a solid state. Molten waxes flow in an axial groove and are subsequently fractionated with superheated steam yielding 10 wt% gas, 35% light and heavy oils, 40% light fuel oil and 15% viscous products. Evidently the products would require further upgrading in a refinery.

Alternative Heat Transfer Mediums

Liquid or molten form mediums can be employed to transfer heat to pyrolysis feedstocks and are characterised by very good heat transfer rates. In the first stage of the Fuji Process incoming plastics are mixed with uncracked molten plastics returning from the main cracking reactor [93]. The Alphakat/Nanofuel process (Germany) uses hot oil as a heat transfer medium and catalyst for thermal decomposition of plastic wastes. Molten metals (tin, lead, bismuth or alloys at temperatures below 600˚C) can also be employed. Plastic waste feedstocks are cracked as they float on the hot surface of the bed. Stelmachowski [9] developed a vertical molten bed reactor design for small scale applications. A horizontal modular molten bed process was developed by T-technology (Polymer Energy outside Europe) [116,117].

Miscellaneous Reactors

Pyrolysis using microwaves has been researched but the poor thermal conductivity of plastics especially in the microwave frequency range makes the process a problem, so conductors need to be included e.g. graphitic carbon or inorganic oxides. While research is not documented in scientific literature, there are a large number of commercial patents describing microwave pyrolysis of wastes and a number of companies offering the technology [118]. Free-fall reactors have been applied to waste plastics in one [119] and two stage systems [120]. Heat transfer to the plastic may also be a problem. The Blowdec Process converts waste plastics in a centrifugal hot whirling bed of sand at 430˚C in a thermal or catalytic mode. A pilot plant exists and experimental results have been presented [121]. A novel pyrolysis system was recently patented by Agilyx [122]. The temperature and pressure of the batch reactor can be controlled. This allows pretreatment of the feedstock in the pyrolysis chamber for the removal of contaminants like water and hydrochloric acid. The pressure and thermal conditions are subsequently applied for the collection of a liquid fuel product.

Commercial Process Configurations for PTL

Commercial Thermal Processes

There are several notable thermal pyrolysis processes including those developed by BP, BASF, RoycoBejing, Chiyoda, and Hitachi Zosen. The BP process is a thermal fluidised bed process developed by a consortium of British Companies and the University of Hamburg. It was demonstrated in Grangemouth, UK in 1994, and processed mixed packaging waste. The main pyrolysis products were light and heavy wax and oil (total wax 93-99 wt%) which were suited for further refining in a naphtha cracking unit [80,13,5]. The project is no longer operational. In their 15,000 tpd plant (commissioned in 1994) BASF collected the HCl from the pretreatment step and used it for the manufacture of chemicals. Products from pyrolysis of the plastic melt at 400˚C in a tubular reactor comprised 60-70 wt% oils (naphtha, aromatic fractions, and high boiling point oils) and 20-30% gas. Subsequent cracking of the naphtha fraction yielded monomers which could be used for synthesis of virgin plastics, while the heavy oils could be coked or gasified. Operation was discontinued in 1996 due to problems with waste plastics supply and unfavourable economics [5,42]. The Hitachi Zosen process employs a stirred tank reactor for thermal cracking of plastic waste. A kerosene and gasoline fraction are recovered and the remaining non-condensable gas is burned in the furnace [8]. The Royco process [123] also known as the EZ-oil Generator^{TM} process converts waste polyolefins to fuel oil and gas which are used to generate electricity. A distinguishing feature of this process is its infrared heating system. The Chiyoda process employs a thermal pretreatment step, releasing HCl (from PVC) and terephthalic acid (from PET) which are incinerated. The plastic melt is subsequently cracked in a non-catalytic vessel yielding gas, light oil, middle distillate oil and heavy oil. The light oil is a suitable petrochemical feedstock and the pyrolysis gas is incinerated [8].

Commercial Catalytic Processes

From a technical perspective, the great majority of patented processes based on catalytic pyrolysis of plastic waste are directed towards the production of transport grade fuels (gasoline, diesel and kerosene). These can be categorised as direct catalytic cracking or thermal cracking followed by catalytic upgrading [50]. A number of processes have emerged e.g. the Nanofuel Process (Alphakat), the Zadgaonkar Process, the Thermofuel Process (Cynar Plc in Europe), the Smuda Process, the T-technology Process, Agylix (Plas2Fuel), and STEPS. Despite new and improved technologies, economic viability and issues with contaminants appear to hinder commercial application.

The Smuda pyrolysis technology employs a nickel silicate and ferrous silicate catalyst (5-10% by volume) which is charged directly to the plastic melt in the reactor to catalyse the reaction. The reactor operates at a constant level of 60%. PVC and PET can be processed without difficulty but nylons and ABS are not suitable. Like the Thermofuel process it employs a reflux mechanism at the reactor entrance to ensure sufficient degradation of heavier molecules. The paddle in the STR rotates at 30rpm.The liquid produced is 85% diesel and 15% gasoline. The gasoline is consumed in electricity production for the process. The diesel requires additives (0.01% BHT) to suppress polymerisation reactions. The largest plastic pyrolysis plant in the world is based in Zabrze, Poland, and processes 10,000 tpa of plastic in addition to other feedstocks (45,000 tpa) [99]. It is operated by Agrob Eko (South Africa) and based on Smuda technology. The crude oil produced is upgraded in a refinery [8].

The Polymer Engineering Process was developed by Alphakat GmbH [124](Buttenheim, Germany) and is also known as the KDV or Nanofuel process. Distinguishing features of the technology are a hot oil heat transfer medium and chlorine-binding cracking catalyst. The catalyst acts as an ion exchanger which dehalogenates the liquid feedstock and binds chlorine to salts which are removed from the reactor with a spent catalyst by an auger. The catalyst usage rate is 1.5% of the output diesel, and it is claimed that high concentrations of up to 100% PVC can be processed without detecting chlorine in the resulting fuel. 1000kg of LDPE/HDPE/PP yields 900L fuel in this process. Several plants based on this technology have been constructed in Germany, Mexico, Japan and Korea (500L/hr).

The Reentech process [125] is a continuous catalytic cracking process yielding gasoline, kerosene and diesel from mixed plastic wastes (polyolefins and PS). Plastic is catalytically dehalogenated (nickel/nickel alloy catalyst-coated impeller) while undergoing thermal decomposition at 350-370˚C and the resulting melt is sent to a fluid catalytic cracking unit (moving catalytic bed with continuous regeneration) where it degrades in the presence of an aluminium silicate catalyst. Fractionation of the product yields 75% fuel oil (55% gasoline, 25% kerosene and 20% diesel). The gasoline fraction requires reforming and additives [8].

Fig 8 Flowchart of Reentech catalytic cracking process. From [8]

The Thermofuel process is offered by Cynar Plc. in Europe. It involves thermal degradation of plastic extrudate in a stirred tank (350-425˚C) followed by vapour-phase upgrading in a catalyst tower at 220˚C. The Raney Nickel/Adams catalyst is coated on metal plating. The hydrocarbon distillate obtained is made up of aliphatic and aromatic hydrocarbons. A number of plants in Japan operate on this technology [8] and a 5,000 tpa plant was recently commissioned in Ireland. SITA UK have announced plans for the construction of 10 plants based on the Thermofuel technology across the UK with a combined capacity of 60,000 t [126].

In the Fuji Process, plastic waste enters a molten plastic bath via an extruder, and it is mixed with uncracked plastic residues which have been returned from the thermal cracking reactor. The molten bath is at a temperature of 180 to 300˚C and volatilises HCl (from PVC). Molten plastic is transferred to the thermal cracking reactor maintained at a temperature of 350 to 400˚C. Pyrolysis vapours subsequently pass to a catalytic reforming reactor, yielding gasoline, kerosene and a diesel oil [8].

A 5 Mt plant based on technology by Zadgaonkar has been operating in India since 2005 [76]. Extensive mechanical pretretreatment separates undesirable contaminants from the plastic feedstock. The dechlorination occurs in the presence of patented additives and coal. Pyrolysis takes place in a fixed bed reactor (350˚C) over coal and other additives. Liquid product fractionation yields diesel, kerosene, gasoline, heating oil and petrochemical feedstock. The process can handle a wide range of plastics including PE, PP, PET, PC and ABS. The rights to this technology have since been sold to Asian Electronics [127].

Another catalytic process is offered by T-technology. The cracking reaction takes place in a sealed reactor at atmospheric pressure and a temperature of 390-420˚C. The resulting product has a carbon distribution between C_8-C_{34}. Fractionation of the product yields 15-20% wax, 60-70% light oil, fuel oil and diesel, and 15-20% gasoline. Uncracked residue may be re-circulated through the system a number of times to achieve higher conversion efficiencies. The products may be suitable for energetic applications or further refining. As of 2010, it is claimed that 11 plants with a capacity of 10 Mt are operational in Poland, India, and Thailand [128].

Table 4 Summary of Some Commercial PTL Processes

Summary of Recent Laboratory Research

Comparison of Feedstocks

Encinar and González [129] present a study on the isothermal and dynamic pyrolysis of plastic including polyethylene and polypropylene in a thermobalance reactor. The influence of the nitrogen sweep gas flow rate and initial mass sample was found to be negligible, while the influence of temperature was significant. The authors also developed a kinetic model to describe the decomposition. Marcilla et al [59] report that cross-linked polyolefin feedstocks have improved decomposition behaviour compared to normal polyethylene but require an increased temperature for catalytic cracking.

On Interactions in Mixed Plastic Waste Pyrolysis

Williams and Slaney [130] compared thermal pyrolysis and liquefaction of authentic mixed waste plastics and simulated mixtures of waste plastics. It was evident from the composition of the liquids that there was significant interaction between mixed plastics pyrolysed or liquefied when they were compared to the additive effects of the pyrolysis or liquefaction of single plastic feedstocks. Chowlu et al [131] observed synergistic interactions between LDPE and PP blends during decomposition on a TGA when the PP composition of a binary blend was greater than 40 wt%. The yields of hydrocarbons were greater when the ratio of PP in the blend was increased and was maximised at 65 wt%. Hujuri et al [132] developed a predictive model for thermal decomposition of binary and tertiary mixtures of PET, LDPE and HDPE on a TGA and correlations were similar.

Pyrolysis of Mixed Plastic Waste/Co-pyrolysis

Polystyrene may be present in the feedstock and is generally desirable in small portions since it enhances the quality of the fuel. Generally speaking thermal pyrolysis of polyolefins results in conversion of the polyolefin at lower temperatures (350˚C) to wax [133]. When PS is present the liquid/wax yields increase since higher liquid yields from polyaromatic plastics are possible [51,8,134]. The compounds in the liquid are a mixture of the thermal decomposition products of both plastics. Angyal et al [110] found that in the liquid fractions produced from cracking PE and PS, aromatics were only detected when PS was present in the feedstock, and was mainly distributed in the naphtha boiling point range fraction [57]. Buah et al [135] observed that the aqueous and oil phase were recovered from the pyrolysis of RDF and biomass was highly oxygenated due to the presence of biomass derivatives (from paper, cardboard etc.) and had a heating value of about 35 MJ/kg. Koç and Bilgesü [136] performed thermal oxidative pyrolysis of LDPE and catalytic MoO_3/SIO_2. Liquid yields decreased from 102 wt% for thermal pyrolysis to 75 wt% for catalytic pyrolysis, while oxygenated compounds detectable by GCMS decreased from 50 wt% to 27 wt%.

Catalyst Deactivation and Regeneration

Marcilla et al [137] studied deactivation of HZSM-5 with LDPE and HDPE feedstocks. With LDPE, the coke production increased until the 5th cycle, when the products obtained were characteristic of thermal cracking, whereas HDPE deactivated the catalyst in the first or second cycle. It was also found that spent catalyst from LDPE cracking could be used to crack HDPE effectively. Marcilla et al [138] report an interesting study into coking behaviour of catalysts in catalytic pyrolysis. It was found that the polyaromatic nature of coke increases for zeolites as temperature increases. Relative portions of soluble and insoluble coke were compared. Soluble coke from HZSM-5 comprises mainly naphthalene derivative compounds. The early deactivation of polymers in the presence of catalysts was examined by applying heating and cooling regimes to plastic and catalyst mixtures in a thermobalance [52]. It was found that polymer-catalyst systems with low steric hindrances (PE-MCM-41) caused a noticeable decrease of the catalyst activity for the main decomposition step in comparison with polymer-catalyst systems with higher steric restrictions (EVA-MCM-41). Marcilla et al [137] studied early deactivation of catalysts during cracking. It was found that PE induced deactivation more quickly than PP.

Comparing Catalysts

Micro-scale Studies

Obali et al [139] perfomed catalytic pyrolysis of PP with synthesised MCM-14 catalysts (with varying Aluminium concentrations) on a TGA balance. The initial decomposition temperature and the activation energy value for degradation dropped significantly from 172 kJ/mol to 24-28 kJ/mol. Agullo et al [140] compared various catalysts for cracking LDPE in a TGA. Catalyst with larger pores (H-B-25 and H-B-75) exhibited more activity than smaller ones (H-Mor and H-Ferrerite). However coke formation in catalysts with large pores was a problem. Coelho et al [141] investigated catalytic degradation of LDPE and HDPE with zeolite-based ethene polymerisation catalysts in a TG/DSC. The gaseous products were routed to a GC. The catalysts were found to have good potential though some deactivation was observed. Aguado et al [142] achieved gaseous yields of 73.5 wt% during pyrolysis at 400˚C with nanosized HZSM-5 and Al-MCM-41 catalysts. The liquids contained aromatics and branched species which would be a good blendstock. The MCM catalyst produced less gas and more liquid. The aromatic composition was less compared to HZSM-5 but possessed a good combination of olefins and n-paraffins.

Batch/Semi Batch Studies

Renzini et al [143] present a study on the catalytic conversion of LDPE in a semi-batch reactor. The product from H-ZSM-11 yielded more gas and less liquids compared to the other catalysts. Zn-ZSM-11 produced a highly aromatic liquid (C_6-C_9 aromatics were 52.98 wt% at a reaction time of 60 minutes compared to 26.88 wt% for HZSM-11. Aguado et al [144] investigated semi-batch pyrolysis of LDPE with mordenite catalysts. A significant improvement in C_6-C_{12} was observed for MO-15 (21.2 wt %) compared to MO-T. Pressurised catalytic pyrolysis was carried out in a batch reactor [145]. At higher temperatures aromatics prevailed. Longer residence times increased volumes of straight chain hydrocarbons. Marcilla et al [53] compared different cracking catalysts for LDPE on a batch and TG reactor. Nano-Hβ yielded a saturated product at lower temperatures. HZSM-5 produced a gas richer in C_3, while the gas from Hβ was richer in C_4-C_5. The isobutene/butene ratio was higher for Hβ. Rasul Jan et al [146] obtained 92 wt% liquid fraction from catalytic degradation of HDPE in a batch reactor with $MgCO_3$ which consisted of heavy naphtha (C_8-C_9), gasoline (C_8-C_{10}), and diesel (C_{10}-C_{20}), with about 50 wt% in the gasoline and 50 wt% in the diesel range. Lee [147] presents a study on thermal and catalytic cracking of pyrolysis oils obtained from a commercial rotary kiln pyrolysis with a FCC catalyst in a batch reactor. Inclusion of the catalyst in the process improved the liquid and gas yield but a high fraction of heavy hydrocarbons in the oil product resulted due to increased cracking of the residue. Gulab et al [148] catalytically cracked polyethylene with US-Y zeolite in a semi-batch reactor. Liquids in the boiling point range of gasoline and diesel were obtained. A polymer/catalyst ratio of 8:1 was sufficient to achieve complete conversion with reduced coke and more liquids. Park et al [149] applied ferrerite catalyst to the catalytic pyrolysis of polyethylene in a fixed bed batch reactor. The activation energy of the reaction significantly decreased. The catalyst was resistant to coking and showed good selectivity for the production of olefins which peaked in the C_6-C_{10} range. Lee et al [150] obtained a very high liquid selectivity (80 wt %) with a form of nanocrystalline beta-zeolite (Si/Al ratio of 10.7 and crystal size of 10nm). The carbon distribution was in the C_7-C_{12} range. Lee [151] investigated the catalytic degradation of PE and PS blends in a stirred tank reactor with spent FCC catalyst. While the formation of aromatic products (styrene and ethylbenzene) depended on the portion of PS in the feed, it also depended significantly on the reaction time. Achilias et al [152] performed chemical recycling and catalytic pyrolysis of waste polyolefins with an acid waste catalyst. Low conversions were observed due to the low pyrolysis temperature and reaction time (450˚C and 17 mins). The residue increased for PP<LDPE<HDPE. There were high quantities of isoalkanes and isoalkenes in the gasoline-range product, with few aromatics. Marcilla et al [153] compared various catalysts for cracking of single plastics. They report that the catalytic pyrolysis process depends on a) the chemical and physical characteristics of the catalysts and b) the chemical and structural nature of the polymers. MCM-41b and MCM-4a were both found to be more active than HZSM-5 for the degradation of LDPE, PP and EVA. MCM-41 showed more activity for cracking of PP>LDPE>EVA>PS, while HSZM-5 showed more activity for the cracking of LDPE>PP>EVA>PS.

Vapour Upgrading Studies

A batch vapour-phase upgrading system was applied to catalytic cracking of polyethylene [154]. A temperature of 450˚C was required to achieved >90 wt% conversion in the thermal control experiment. Reforming with HZSM-5 catalyst induced a shift to gaseous olefins (73.5 wt% a 450˚C) and aromatic/branched liquids. Al-MCM-41 was a less effective catalyst. San Miguel et al [155] investigated two stage thermal (450˚C) and catalytic (425-275˚C) pyrolysis of agricultural plastic waste. The conversion and product distribution was constant regardless of reforming temperature. The HZSM-5 catalyst yielded 53 wt% lights (C_3-C_4). The C_5-C_{12} fraction contained 12.7% aromatics, 8.9 wt% isoparaffins and 4.0 wt% naphthalene. The Beta and Al-MCM catalyst exhibited inferior reforming capacities.

Continuous Systems

Miskolczi et al [111] pyrolysed a HDPE and PS blend (90/10) in a semi-batch reactor with a FCC and ZSM-5 catalyst. The FCC and clinoptillilite showed good catalytic activity for the production of light liquids. The carbon distribution became wider with increasing temperature, possibly due to deactivation of the catalyst by coking. The liquid products were fractionated to diesel and naphtha fractions. The naphtha fraction had one-third aromatics. Neither catalyst type or grain size appeared to significantly affect the product distribution, though crushed catalyst products appeared slightly more branched product. Miskolczi and Bartha [156] applied various cracking catalysts to the degradation of polyethylene. An array of chemical analysis techniques were used to characterise and analyse the products (GC, FTIR, SEC, energy-dispersive X-ray fluorescence spectroscopy and other methods). The catalysts employed (equilibrated FCC, HZSM-5 and clinoptilolite) yielded a liquid with a carbon distribution in the C_5-C_{23} range. The catalysts induced carbon chain isomerisation and switching of the position of the double bonds in the liquid product.

Elordi et al [89] pyrolysed HDPE with HZSM-5, Hγ and HB in a conical spouted bed reactor. HZSM-5 was light olefin selective (58 wt %) and Hγ and HB were highly non-aromatic C_5-C_{11} selective. Catalysts with larger pores (HZSM-5<Hβ<Hγ) produced more butenes, whereas smaller pores yielded more propene. Coke formation on Hβ and Hγ were problematic, but not for HZSM-5. The single ring aromatics increased with catalyst strength (HZSM-5>Hβ>Hγ). Zorriqueta and Kaminsky [157] investigated catalytic pyrolysis of PP in a fluidised bed reactor with $TiCl_4/AlCl_3$. Good contact was achieved with the catalyst which was soluble in the plastic melt and the reaction could be carried out without collapse of the bed. Del Remedio Hernández et al [158] scrutinised cracking mechanisms of HZSM-5 with HDPE on a pyroprobe and fluidised bed reactor. HZSM-5 was most significant in primary cracking reactions rather than secondary reactions. It is highly propene selective (30.6 wt %). HUSY yielded more aromatics and branched alkanes and the product had a lower narrower product distribution. The gas yield was independent of temperature. HUSY produced more liquids compared to HZSM-5. Triplets were not formed with catalytic pyrolysis. Elordi et al [88] obtained a gasoline which was very close to EU specifications by fluidised bed pyrolysis of HDPE with Hγ zeolite. At 500˚C, 44.6 wt% C_5-C_{10} non-aromatics were obtained. This comprised 75 wt% paraffins, 26 wt% olefins, and 1.5 wt% naphthalenes. The main compounds present were isopentane (7.26 wt%), 2-methyl-pentane (4.10 wt%), and 2-methyl-butene; There were 24.9 wt% aromatics (>95 wt% of which were C_5-C_{10} aromatics, no benzene). Olzar et al [90] examined steaming as a catalyst pretreatment. Severe steaming of the FCC catalyst (reducing the acidity and surface area) changed the yield structure. The non-steamed catalyst produced 52 wt% gas, 35 wt% light liquid and 13 wt% C10+. The steamed catalyst yielded 8 wt% gas, 38 wt% aromatics, 18 wt% paraffins and isoparaffins. The diesel fraction contained a significant portion of naphthalenes (54 wt%).

Cracking under 'FCC Conditions'

Lin and Yang [159] performed catalytic fluidised bed pyrolysis in a reactor simulating FCC conditions. Valuable olefins and isoolefins were obtained from a HDPE/LDPE blend at 290-430˚C and various catalysts (HSM, HUSY, HMOR, MCC-14, SAHA). Acidic zeolites produced more volatile hydrocarbons compared to non-zeolites. MCM-14 and SAHA yielded a highly olefinic product with a wide carbon distribution. HUSY yielded a saturate rich product with wide carbon distribution and a significant quantity of coke. HZSM-5 and HMOR exhibited the highest selectivity (60 wt %) for C_3-C_5 olefins, with HMOR having the highest C_1-C_4 yield of all. Lin et al [160] simulated FCC conditions in a fluidised bed for catalytic pyrolysis of mixed plastic waste. The volatile yields achieved with ZSM-5 and USY were higher than for non-zeolite catalysts

(SAHA) and zeolite-based FCC catalysts. The highest yield of 88 wt% was obtained ZSM-5, with a C_1-C_4 fraction of 53.7 wt%. The gasoline yield (C_5-C_9) achieved with catalysts was in the order FCCR1>SAHA>HUSY>ZSM5>FCC-S1. Yang and Lin [161] simulated FCC conditions for a HDPE/PE blend. USY exhibited a high selectivity for C_5 (> 35 wt% i-C_5) but had the most significant coke yield (4.6 wt%). The products obtained from MCM-41 and ASA were highly olefinic. Lin [162] reports catalytic pyrolysis of mixed waste plastic in a fluidised bed. Liquid range gasolines were 52.3 wt% (USY)>50.9 wt% (MCM-41)>48 wt% (ASA)>32.3 wt% (FCC-E1)>31.9 wt% (ZSM-5). USY yielded the most coke (4.6 wt%) but exhibited the most paraffinic selectivity (25 wt% in the C_5 fraction, 13% of which isobutane). A similar study is reported where HDPE and PP were cracked in a fluidised bed simulating FCC conditions [163]. Good olefin gas yields were obtained (58.6 wt %) with RCat-C1. The silicate catalyst achieved poor conversion. Olefins and isoolefins were maximised at lower temperatures and short residence times. Lin and Yang [164] obtained a higher yield of gas and liquid hydrocarbons at 390˚C with spent FCC compared to silicate. The used FCC catalyst yielded 61 wt% olefins in the C_3-C_7 range and so was very selective. A waste (RCat-C1) FCC catalyst was also used at this temperature to catalytically crack PE/PP blends [165]. In this case 53 wt% olefins in the C_3-C_6 range were yielded. Salmiaton and Garforth [166] report catalytic fluidised bed pyrolysis at 450˚C with two deactivated FCC catalysts. Inactivity due to metal contamination was minimal. The catalysts yielded mostly C_5-C_9 gas, coke and residue. Volatile yields from fresh catalysts was greater than steamed FCC catalysts. Used FCC catalysts yielded about the same volatiles as steamed FCC catalysts.

Catalyst Contact Mode

Murata et al [100] investigated catalytic pyrolysis in a continuous batch reactor with a novel catalyst cage on the stirrer. The mode of contact (liquid phase versus catalyst cage) did not have a significant effect on the reaction rates, but yielded lower molecular weight volatile products. The yield of aromatics with a SA-1 catalyst was 10.8 wt% compared to 0.2 wt% for thermal studies. Marcilla et al [167] investigated slow, fast, thermal and catalytic pyrolysis, and catalyst contact method. Fast pyrolysis yielded a mix of thermal and catalytic degradation products, while those from slow pyrolysis were aromatic. Melting the blend achieved a better contact than dry contact and more methane, ethane and ethene was observed in the gaseous product.

Comparing Thermal and Catalytic Pyrolysis

Marcilla et al [168] performed catalytic cracking of HDPE and LDPE in a semi-batch reactor with HZSM and USY catalysts. Thermal pyrolysis produced more liquids than gases (mainly olefins and n-paraffins). LDPE produced more 1-olefins than HDPE. The 10 major compounds from thermal pyrolysis were 1-olefins. LDPE and HUSY yielded aromatics, n-paraffins and olefins, while HDPE and HUSY yielded isoparaffins and olefins. A narrower product distribution was achieved for HZSM compared to USY. Ju Park et al [169] cracked PP with Al-MCM-48 and Si-MCM-48. Al-MCM-48 yielded the most oil (76.5 wt %) compared to just 2.1 wt% for thermal pyrolysis. Also the carbon distribution was narrower for Al-MCM-41 (C_7-C_{10} versus C_7-C_{14}). Marcilla et al [170] compared thermal and catalytic pyrolysis of HDPE and LDPE over HZSM-5 and HUSY in a batch reactor. Thermal pyrolysis of PE under dynamic conditions yielded liquids and gases mainly composed of 1-olefins and n-paraffins with smaller quantities of olefins, isoparaffins and aromatics. LDPE yielded a comparatively higher portion of 1-olefins. The 10 major products yielded from thermal degradation were 1-olefins with a distribution between 16-28 carbons. The high activity of the catalysts meant that more gases were liberated. The composition of the catalytic liquid products depended on the type of plastic employed. The main compounds were aromatics>n-paraffins>olefins for LDPE and iso-paraffins and olefins for HDPE-USY.

Recent Integrated Processing Studies

Co-processing of plastic wastes in FCC units

There are two main strategies using FCC for cracking of wastes. One possibility is including the polymer in crude stream into a standard FCC unit. Another is to develop a similar independent process, where polymer-oil blend contains as much polymer as is technically possible. The products of the separate unit could be then treated if necessary and mixed with those from a standard FCC unit, following conventional path in the refinery. While it is possible to directly process plastics in a FCC unit, the main disadvantage is that contaminants in the feedstock can damage the catalyst. Marcilla et al [171] investigated the rheometry of LDPE and VGO blends to determine the technical feasibility of co-processing operation. While the melting temperature of blend is not affected (0-10 wt% LDPE), increasing polymer concentration resulted in more pronounced effects at lower rather than higher shear rates. Mominou et al [172] investigated thermal decomposition of plastic and vacuum residue blends on TGA. Higher initial weight loss of PE decreased significantly by addition of vacuum residue. Significant synergistic effects appear to take place at higher temperatures.

Marcilla et al [173] investigated catalytic cracking of PE and VGO with HZSM-5, HUSY, HB zeolite, FCC and AL-MCM-41. The order of activity of the catalysts was Hβ/Al-MCM-41>HUSY>HZSM-5>FCC catalyst. The amount of coke formed decreased with a binary mixture of PE and VGO alone as there were less aromatics in the feedstock (VGO contains 40% aromatics compared to none in PE). The dry gas fraction decreased while the LPG yields doubled. The presence of the catalyst inverted the composition of the gas compared to thermal pyrolysis: increasing quantities of compounds which are generally low for thermal pyrolysis were observed (propane, n-butane, isobutane ad isopentane and cis-2-butene, and C_3-C_5 paraffins), while compounds which are usually present in significant quantities for thermal pyrolysis were reduced (ethene, propene, and 1,3, butadiene).

Co-processing of pyrolysis waxes in FCC units

Problems with contamination of the FCC catalyst during co-processing can be avoided by subjecting the feedstock to a thermal pyrolysis prior to FCC. Waxes can be fed to the FCC reactor mixed with standard FCC feed (VGO). The first step could be carried out at small scale plastic collection and classification facility and second step at refinery. The wax is easy to transport and can be directly fed and no additional equipment needed [174]. There are several reports of the catalytic cracking of polyolefin-derived waxes with residues in FCC simulators in literature [175-177,174]. Generally speaking, conversion of the wax is higher than the residue, and the waxes produce more of a gasoline fraction than residues. Maximum LPG production was observed at 550˚C. The C_3 and C_4 components of the products had higher oelfinicity. The gasoline from wax has higher olefinicity, more naphthalenes, paraffins, and isoparaffins with a lower content of aromatics than VGO. RON of the gasoline obtained was high >95%. Less coke is also observed. Olefinicity and molecular weight of the gasoline increased with temperature. Cracking at a higher temperature increased the paraffinic content and reduced the aromatic content.

Steam reforming of thermal pyrolysis waxes

The BP process envisaged steam reforming of polyolefin-derived wax in a naphtha reformer on an industrial scale. Hájeková et al [178] investigated an upgrading process which involved thermal pyrolysis followed by steam reforming (780-820˚C) with naphthalene blends in a tube reactor. Binary and tertiary mixtures (10 wt% PE/PP in Naphtha) with Naphtha yielded more gas than single PE/PP feedstock. Angyal et al [112] thermally cracked and reformed PE/PP and PE/PS blends in a pilot tubular reactor (75 tpa) and steam reformer. The reformer was operated at 860˚C for light distillate, with a residence time 0.3s with a steam/raw material ratio of 0.54 wt%. For the middle distillate fraction the temperature was 830˚C, with the same residence time and a steam/material ratio of 0.85 wt %. About 40-60 wt% of the original feedstock could be converted to light and middle distillate fractions (depending on the raw material) which could in turn be applied as steam cracking feedstocks.

Hydrocracking of Waste Plastics

Tiikma et al [179] investigated co-pyrolysis of heavy oil with waste plastics. This resulted in an increase in the percentage of aliphatic hydrocarbons (by a factor of 6), a decreased quantity of heteroatoms and a drop in the oil viscosity. The addition of catalysts (Estonian Dictyonema and Al-Co-Mo) enhanced cracking but resulted in the production of unstable oil, which was solved by addition of hydrogen. In addition to cracking, some catalysts have another function e.g. hydrogenation. Siddiqui and Redhwi [180] present a study into co-hydroprocessing of waste plastics (PE, PP, PS) and light Arabian Crude oil at 400˚C with ZSM-5, FCC (Y-zeolite), NiMO, and NiW. Synergistic effects were observed by increased conversion of plastics. The residue contained significant aromatic content and aliphatic structures, which on mixing provides an aquatic phase for further dissolution. Polystyrene produced a higher amount of material boiling below 500˚C. The best conversion was observed with an NiMo catalyst at 3 wt%, 90 mins reaction time, 1200 psi and 430˚C with a 3:2 residue/plastic blend. Ali et al [181] report similar findings, though the optimal conditions in this case were 1 wt% catalyse, 60 mins reaction time, 8.3 MPa and 430˚C. They concluded that co-processing is a feasible process.

Fuel Finishing Operations

Fuel Requirements

This section summarises typical fuel finishing operations in a refinery. Extra considerations for polyolefin-derived liquids compared to crude-derived fuels are that they may require additional treatment for their highly olefinic nature. For gasoline, the most critical fuel quality criteria are resistance against autoignition (octane quality), evaporation properties (for provision of an ignitable air-fuel vapour in the combustion chamber), environmental acceptability and low toxicity. While these properties are mainly determined by the fuel components (previously summarised) they can also be improved by the addition of organic additives at the end of the production processes before delivery to service stations. Benzene, a toxic compound, was previously used to improve the octane quality. European Legislation has restricted its concentration in gasoline to <1% since 2000. Instead, isomerates, higher aromatics, ethers and alcohols are used to improve the octane quality. The 2005 European Limits for aromatics, benzene, olefins, and sulfur were 35 vol%, 1.0 vol %, 18 vol %, and 10 ppm. On the other hand, the main criteria for diesel is ease of ignition. Other important parameters for diesel are density, cold flow performance, fuel lubricity, viscosity and stability.One issue with diesel is that n-paraffins which have a high ignition quality are particularly prone to crystalisation at low temperatures, leading to clogging of fuel filters. This applies especially to polyolefin-derived fuels which can contain significant quantities of n-paraffins [78].

Finishing Operations

Fractionation

The most simple and commonly applied technique to improve the definition of the pyrolysis product is fractionation of the products, thus limiting the carbon distribution range and increasing the value of the separated fraction. Most commercial PTL processes continuously fractionate the liquid product [14]. When fractionation is applied in conjunction with catalytic techniques and/or hydrogenation, well defined, high quality fuels can be obtained i.e. diesel or gasoline.

Blending

Diesel fuels are very susceptible to clouding, which can cause clogging of engine filters. In this respect, the cloud point, pour point, and cold filter plugging point are critical parameters. Blending can be employed to improve the low temperature properties of the diesel [78]. For example, mixing diesel oil with heating fuel ((1:4), or kerosene (1:4) will reduce the cloudpoint by 2˚C and 8˚C respectively [8].

Hydrotreating

A mild hydrotreatment step (as opposed to hydrocracking) may be required to reduce the high concentration of olefins (especially alpha-olefins) in the product this technique is frequently applied to FCC gasoline in oil refineries [8].

Dewaxing

Catalytic and isomerisation dewaxing may be required to reduce the concentration of highly paraffinic oils which originate from PE –rich feedstocks. In the past solvent removal techniques were applied e.g. propane dewaxing and MEK dewaxing, both of which are time consuming and costly. Catalytic dewaxing is a more economic process which selectively cracks the longer chain n-paraffins, reducing the diesel pour point while keeping high cetane components. In isomerization dewaxing the n-paraffins are isomerised to iso-paraffns, forming liquids with low viscosities and pour points. It is more expensive than catalytic dewaxing but achieves a better treatment [8].

Fuel Additives

Additives are described as agents added to fuels in concentrations of <1% [78]. Additives are frequently added to crude-derived gasolines and diesels depending on the characteristics of the fuel and the required standards. One of the main issues with polyolefin derived diesel is the high concentration of n-paraffins in the oil which can cause clogging of filters.

Some additives are summarised:

- Detergents and dispersants (ethyloxated products of alkyl phenols) keep oil-insoluble fractions suspended in the fuel and prevent agglomeration;
- Metal deactivators prevent precipitation of metal ion oxidation reactions and precipitation of metal insoluble compounds;
- Ignition improvers (e.g. alkyl nitrates – 2-ethylhexyl nitrate (EHN)) improve the cetane number and ignition properties of the fuel;
- Detergents (amines, imidazolines, amides, succinimides, polyalkyl succinimides or amines, and polyetheramines) form a protective film and induce a dispersion effect which avoids deposit formation and may also improve storage stability and infer protection against corrosion.
- Flow improvers (ethene-vinyl acetate (EVA) copolymers) reduce the wax crystal size and the tendency to agglomerate.
- Wax antisetting additives (WAAS) keep small wax crystals in suspension and inhibit the formation of wax layers (modified ethene-vinyl acetate copolymers).
- Cloud point depressants (ethene-vinyl acetate based polymers, unsaturated esters, imides or olefins) irreversibly decrease the crystallisation temperature. The styrene monomer derived from pyrolysis of polystyrene is also known to depress the cloud point [8].
- Lubricity additives (fatty acid derivatives) ensure lubricity is sufficient to avoid injection pump wear;
- Diesel fuel produced via pyrolysis is highly unstable and can repolymerise within days of being produced forming a sludge [8,182,183]. Stabilisation diesel fuel additives may be required which inhibit polymerisation and oxidation reactions. Antioxidants (sterically hindered phenols and phenylenediamines and trialkylamines) avoid oxidation and radical polymerisation reactions which result in corrosion effects and the formation of a darkening layer which later results in sediment. The Smuda process yields a liquid product with 10% olefin content, so BHT (bythlated hydroxy toluene) a polymerisation suppressant is added at 0.1 wt%. Corrosion inhibitors and detergents also have an antioxidant effect.
- Other additives include antifoamers, dehazers, biocides and re-odourants [78].

Conclusions and Outlook

Waste management infrastructure needs to be expanded to cope with increasing volumes of plastic wastes and legally binding waste recovery targets and environmentally conscious waste management. In this vein, there appears to be a role for pyrolysis of plastics wastes in future waste management systems e.g. in a cascaded waste management system. Polyolefins (HDPE, LDPE and PP) are the most ideal waste plastic feedstocks for diesel and gasoline production and are present in significant quantities in plastic wastes. Smaller quantities of PS are allowable, and generally desirable. With polyolefin feedstocks it is not generally possible to produce a well defined transport grade fuel without the use of catalysts. Fuel additives may also be required. Laboratory research shows that catalysts can be tailored for high selectivities of target products. However catalyst coking remains an issue, and needs to be further investigated. The use of waste (e.g. FCC) catalysts appears to have potential. At present two of the main barriers to commercialisation appear to be contamination of polyolefin feedstock with PVC and PET and the strict standards required of the pyrolysis products, and the high correlation between PTL viability and the price of oil. Accordingly, market instruments e.g. tax exemptions on plastic-derived liquid fuels or for refiners accepting plastic degradation products at the refinery may be beneficial. Another approach might be to target the production of higher value products e.g. gaseous olefins through the FCC process.

In terms of reactors and commercial processes, a wide range of configurations exists. That said, there is no one successful and widely licensed technology presented in literature. While some configurations produce a good quality fuel, intensive processing is generally required. Another point to consider is that while extensive processing required to produce an acceptable fuel may be feasible on a refinery with large throughputs, it may not be feasible on a small scale. Furthermore, it is difficult for newer technologies like pyrolysis to compete with incineration and to a lesser extent gasification in the waste management sector since the other two have a longer history of development. When comparing pyrolysis to incineration or combustion, it is important to consider the value of the liquid fuel produced from pyrolysis. For example, the production of a transport-grade liquid transport fuel via catalytic pyrolysis has a higher economic value than, for example, incineration of waste for electricity.

In summary, not all of the problems have been solved and the technology needs more development. Small scale applications seem to have potential. Large scale co-processing applications should be technically feasible once the contaminants can be removed but this is not likely to be a financially rewarding exercise. If pyrolysis processes are to be used as part of a cascaded waste infrastructure, they will need to be very robust and capable of dealing with significant amounts of contamination.

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