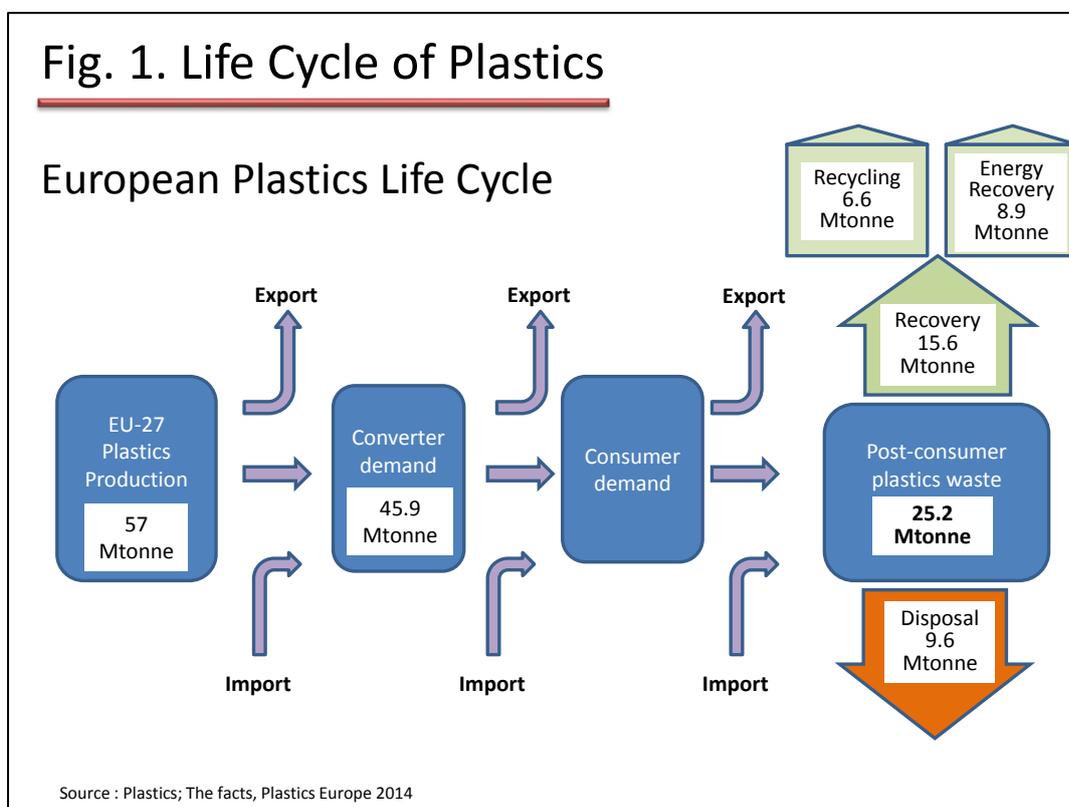


HIGH VALUE PRODUCTS FROM WASTE PLASTICS

Professor Paul T. Williams, University of Leeds, Leeds, UK

Waste plastics

Current worldwide production of plastics is around 300 million tonnes/year, with 57 million tonnes/year produced in the European Union (PlasticsEurope, 2015). Much of the plastic used in the wide variety of products will end up in the waste stream and in the EU more than 25 million tonnes of waste plastics are generated each year. Post-consumer plastic waste generation in Europe is approximately 25 million tonnes per year, of which 6.6 million tonnes are recycled mainly through mechanical recycling, 8.9 million tonnes are processed by energy recovery facilities and 9.6 million tonnes are disposed to landfill (Figure 1) (Plastics Europe, 2014).



The process options for recycling waste plastics in the EU are dominated by mechanical recycling and <5% is recycled via feedstock or tertiary recycling (Plastics Europe, 2013). Mechanical recycling involves sorting, shredding, washing drying and pelletising of the plastic producing a recyclate material. The process maintains the molecular structure of the plastic polymer and the recyclate can be used to produce new plastic products.

Feedstock recycling is an Advanced Thermal Treatment route which aims to convert the plastic into oils and gases which can be processed back into the plastics production process. Pyrolysis is one such feedstock recycling process, where the plastic is thermally degraded at moderate temperature (~500 °C) in the absence of air to produce shorter molecular chains and low molecular weight molecules to produce an oil and gas product.

Pyrolysis-catalysis

There are several waste plastics pyrolysis technologies that have been developed to commercial scale where the targeted end-product is a fuel oil to be used as an alternative to petroleum derived fuel oil. However, there is growing interest in producing higher value products from waste plastics involving the use of catalysts.

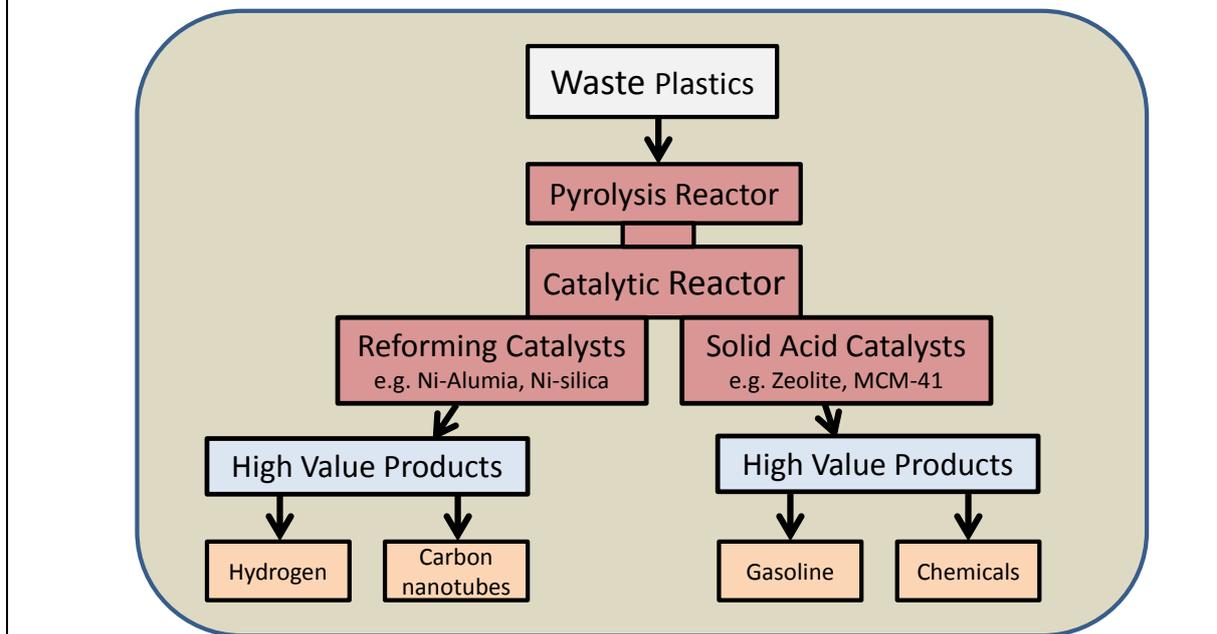
Catalysts can play a critical role in the thermochemical processing of waste plastics in terms of promoting targeted reactions, reducing reaction temperature and improving process system efficiency. The catalyst may be mixed with the waste plastic and thermally processed together, or alternatively, the catalyst may be placed downstream of the thermal pyrolysis step.

The two-step approach to catalytic pyrolysis of waste plastics has been highly recommended as a preferred option (Serrano et al, 2012) since advantages include;

- Interaction of the pyrolysis gases and catalyst improves the contact between pyrolysis products and the catalyst in the subsequent catalytic stage and minimises mass and heat transfer problems.
- The process is more controllable e.g. the temperature of each stage can be easily controlled.
- It is particularly suited to mixed plastic wastes, where any residues and dirt associated with the plastics remains in the pyrolysis unit.
- Two-stage reaction systems enable the reacted catalysts to be recovered, recycled and reused.

Using the two-stage reactor, the wide range of products of the pyrolysis of the waste plastics pass directly to the second stage and interact with the catalyst. Depending on the type of catalyst used and the process conditions, high value products can be targeted (Figure 2). For example, the hydrocarbon pyrolysis products derived from the waste plastics can be steam reformed in the second stage catalytic reactor with nickel based catalysts at typical catalyst temperatures of ~ 800 °C to produce a hydrogen rich syngas. Alternatively, solid acid catalysts such as microporous Zeolites and mesoporous MCM-41 can be used in the second stage catalytic reactor at temperatures of ~ 500 °C to produce an upgraded oil product for use as premium grade fuels or chemicals.

Fig 2. Two-stage processing with catalysts for higher value products



Therefore combining pyrolysis with catalysis in a two-stage pyrolysis-catalysis reactor system, waste plastics can be processed to produce high value products such as;

✚ **Hydrogen**

✚ **Carbon nanotubes**

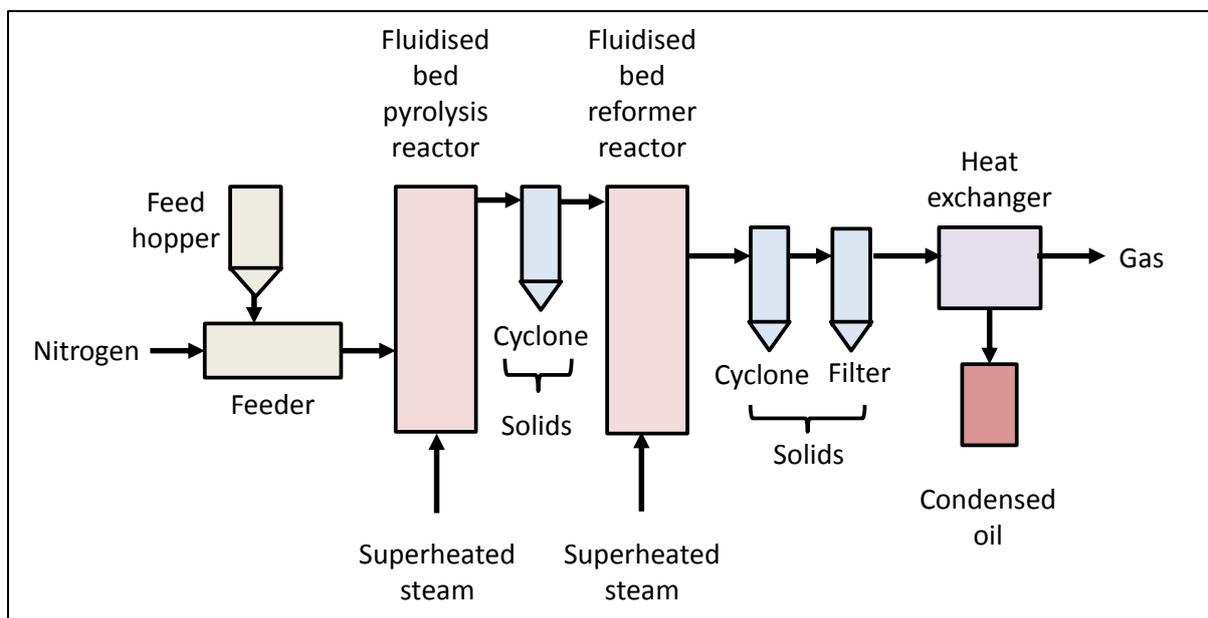
✚ **Gasoline and chemicals**

1. Hydrogen

Hydrogen is a valuable commodity with extensive use in petroleum refining, production of ammonia and methanol. In addition, with concerns related to climate change there is increasing interest in producing higher quantities of hydrogen for use as a non-polluting fuel in transport engines and fuel cells to support the projected future hydrogen economy (NRC, 2004). Hydrogen is currently produced mostly (96%) from fossil fuels, the largest source being natural gas (methane). The process involves steam reforming of methane in the presence of nickel catalysts at temperatures ~ 800 °C to produce hydrogen and carbon monoxide. Further reaction of the carbon monoxide with steam using an iron oxide catalyst at ~ 350 °C produces enhanced hydrogen yields, but also carbon dioxide via the water gas shift reaction (Spath and Mann, 2001). Producing hydrogen from waste plastics would offer an alternative feedstock and also solve a major waste treatment problem.

There are several researchers who have developed the methane catalytic steam reforming process using pyrolysis of waste plastics to produce a suite of hydrocarbons which are then steam reformed in the presence of a nickel catalyst. For example, Czernik and French, (2006) investigated the pyrolysis-steam reforming of polypropylene using a commercial Ni catalyst (C11-NK). They used a fluidised bed pyrolysis unit at 650 °C and a second stage fluidised bed catalytic steam reforming reactor at 850 °C (Figure 3). They reported a yield of $0.34 \text{ g H}_2 \text{ g}^{-1}$ polypropylene which represented 80% of the maximum amount ($0.429 \text{ g H}_2 \text{ g}^{-1}$ polypropylene) of hydrogen which could be produced if all of the polypropylene was completely converted to CO_2 and H_2 . The product gas composition consisted of ~ 70 vol.% H_2 , ~ 16 vol.% CO_2 , ~ 11 vol.% CO and lower concentrations of hydrocarbons.

Fig. 3. Waste plastics to hydrogen through catalytic steam reforming (Czernik and French, 2006)



1.1. Types of catalyst

Wu and Williams (2009) investigated the two-stage fixed bed pyrolysis and fixed bed catalytic steam reforming of polypropylene using a Ni-Al catalyst with increasing Ni content. It was reported that at higher Ni:Al ratios, the theoretical hydrogen potential from polypropylene (Czernik and French, 2006) increased, from 48.8% to 57.7% producing a gas at the highest Ni:Al ratio of volumetric composition containing 66.6 vol.% H₂ and 23.9 vol.% CO. In addition, the influence of the addition of Mg and Cu into the Ni-Al catalyst was investigated. Addition of Mg has been reported to replace the Ni in the catalyst structure resulting in improved physical strength of the catalyst (Ovysyannikova et al. 1989; Koryabkina et al, 1991). Also, addition of Cu to nickel catalysts has been reported to enhance catalytic activity for the catalytic steam reforming of methane (Li et al, 2000; Chen et al, 2003) However, addition of Mg showed no major increase in hydrogen production although lower carbon deposition on the catalyst was reported. Addition of Cu produced reduced hydrogen formation

suggesting that Cu is not a suitable metal promotor for waste plastic feedstocks. Investigation of the preparation conditions of the catalyst also influenced the catalytic activity of the catalyst, with high calcination temperature (850 °C) resulting in lower catalyst surface area and reduced H₂ yield.

The use of a commercial Ru/ γ -Al₂O₃ catalyst from the pyrolysis-steam reforming of polypropylene (Park, 2010) and also of polystyrene (Namioka, 2011). Ruthenium catalysts have been reported to show higher catalytic activity towards catalytic steam reforming of methane compared to nickel-based catalysts. The reactor system used was a continuous two-stage reactor with a first stage pyrolysis unit followed by a steam reformer unit with a packed bed of the Ru/ γ -Al₂O₃ catalyst (Figure 4).

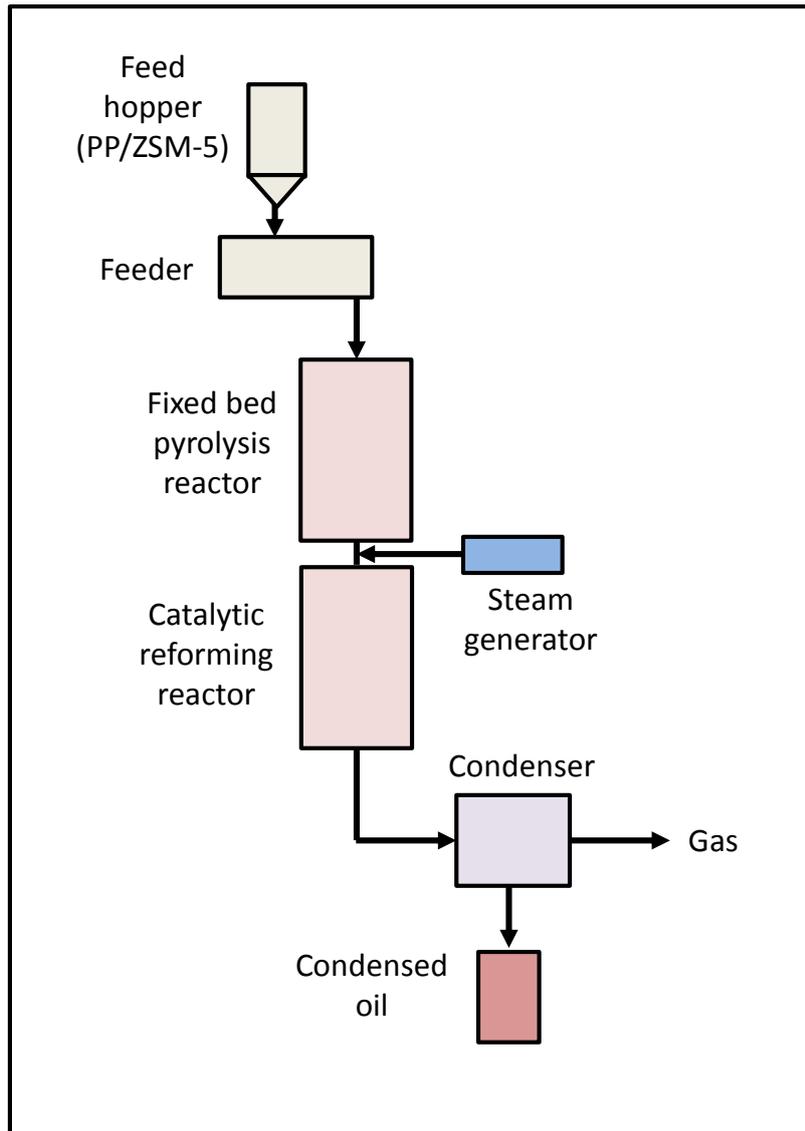
1.2. Types of plastic

Different types of plastic will produce different yields of hydrogen since the suite of hydrocarbons generated from pyrolysis which pass to the catalytic steam reformer reactor will be different. The two-stage pyrolysis catalytic steam reforming of polypropylene, polystyrene and high density polyethylene, together with a mixture of the three plastics and a real-world sample of polyalkene plastics with a Ni-Mg-Al catalyst at 800 °C has been reported (Wu and Williams 2010). Hydrogen yields of 0.266 and 0.260 g H₂ g⁻¹ plastic were obtained for polypropylene and high density polyethylene, but for the aromatic polystyrene plastic, H₂ yield was 0.185 g H₂ g⁻¹ plastic.

For the mixture (26.9 wt.% PP, 16.8 wt.% PS, 56.3 wt.% HDPE) of the three polymers, the yield of H₂ was 0.236 g H₂ g⁻¹ plastic, reflecting the high composition of the polyalkene plastics. The real-world plastic was from a process plant that produced a waste plastic mixture mainly consisting of polyethylene and polyethylene terephthalate and produced a hydrogen yield of 0.253 g H₂ g⁻¹ plastic. The composition of the product gas consisted of ~58 –

68 vol.% H₂ depending on the type of plastic or plastic mixture along with CO and CO₂ and low concentrations of C₁– C₄ hydrocarbons.

Fig. 4. Waste plastics to hydrogen through pyrolysis-catalytic steam reforming (Namioka et al., 2011)



1.3. Catalyst Deactivation

Catalyst deactivation can be caused by carbonaceous coke formation on the catalyst, poisoning of the catalyst, by trace components such as sulphur or arsenic or via metal particle sintering. Argyle and Bartholomew (2015) have undertaken a comprehensive review of the literature related to deactivation of heterogeneous catalysts. A key issue with catalytic steam reforming of a range of hydrocarbons is the formation of coke on the catalyst which lead to deactivation (Cai et al, 2008; Buffoni et al, 2009).

Sintering of the catalyst where the metal particles of the catalyst increase in size, and thereby can influence catalytic activity and coke formation on the catalyst (Sehested, 2006). Sintering of the catalyst particles can occur due to, particle migration where the metal atoms diffuse from one side of the particle to the other and the metal particle migrates across the support then coalesce to form larger particles. Sintering may also occur via Ostwald ripening where metal species are emitted from the particle into the support or gas phase followed by sorption onto another metal particle causing metal particle growth.

2. Carbon nanotubes

Carbon nanotubes have attracted a great deal of interest due to their unique characteristics and their suggested potential use in a wide variety of applications (Volder et al., 2013). Carbon nanotubes are cylindrical hollow tubes composed of carbon with nano-sized diameters (0.1-100 nm) and long length (100m>). The nanotubes may be single-walled or multi-walled. Carbon nanotubes are physically and chemically stable, with high electrical conductivity and tensile strength more than 100 times that of stainless steel (Bazargan and McKay, 2012).

The precursors used for commercial production of carbon nanotubes are pure hydrocarbons, however, pyrolysis of waste plastics produces a hydrocarbon rich suite of compounds which could be used as the precursor the carbon nanotube production. Barzagan and McKay (2012) have recently reviewed the production of carbon nanotubes from waste plastics, highlighting a range of different catalytic and thermal processes.

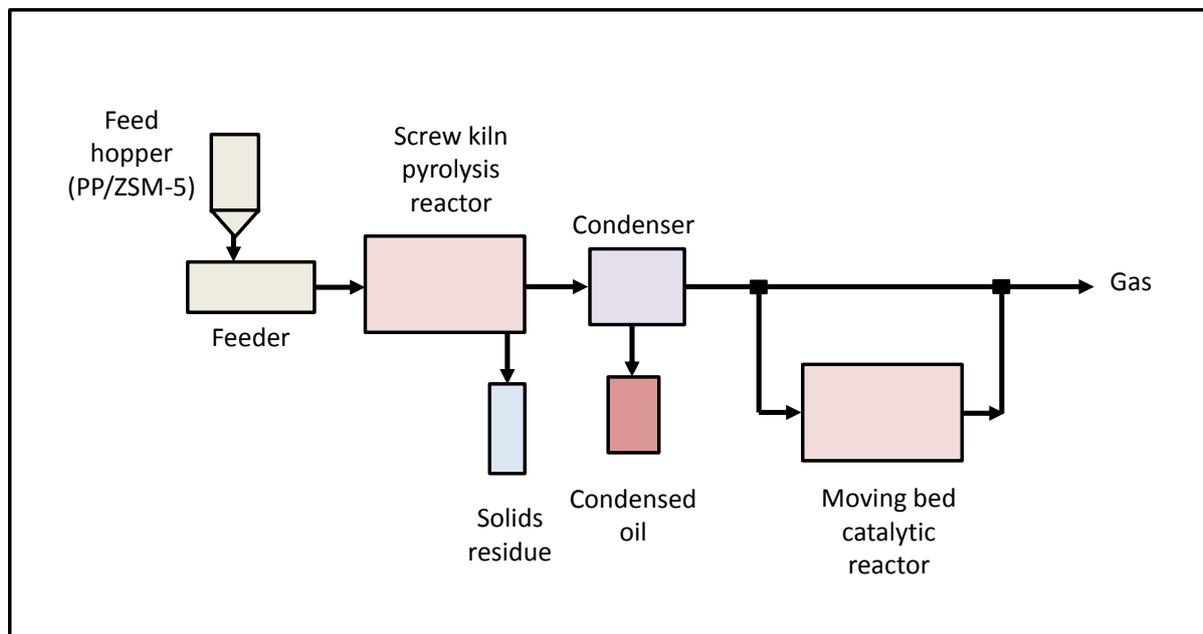
Yang et al (2015) used a mixture of polyethylene and polypropylene as feedstock for production of carbon nanotubes. The waste plastic was gasified in a fluidised bed reactor with sub-stoichiometric air and the product gases were passed to a catalyst reactor containing Ni-Al₂O₃ catalysts prepared by different processes (calcined in air, N₂ or H₂/He)(Figure 14). The Al₂O₃ catalysts prepared in a H₂ calcination atmosphere produced nano-sized nickel particles which produced the optimal production yield and quality of carbon nanotubes. They investigated the influence of catalyst temperature on carbon yield and found that the carbon nanotube yield at 600 °C was 20.0%, 24.3% at 680 °C and

30.5% at 750 °C. However, the highest quality carbon nanotubes were produced at 680 °C with a higher degree of graphitisation.

Polypropylene has been used for the production of carbon nanotubes. Gong et al (2012) pyrolysed polypropylene at temperatures between 720 °C and 920 °C with metal catalysts together with activated carbon. The metal catalysts consisted of Ni_2O_3 , Fe_2O_3 and Co_2O_3 and were mixed with the activated carbon and polypropylene and heated in a quartz tube reactor. The carbon residue left in the quartz tube after reaction contained the carbon nanotubes. It was suggested that the addition of activated carbon produced an increase in the cracking of the polypropylene and also the formation of aromatic and/or polycyclic aromatic compounds from the light hydrocarbon pyrolysis products. Also, the activated carbon promoted hydrogenation and aromatisation reactions which led to an increase in carbon nanotube production.

Liu et al (2011) used a two stage pyrolysis-catalytic reactor for the production of carbon nanotubes from polypropylene. The first stage pyrolysed the polypropylene in the presence of a zeolite catalyst in a screw kiln reactor, the liquid products were condensed and the gases passed to the second stage consisting of a moving bed reactor containing a NiO catalyst (Figure 5). The influence of varying the pyrolysis temperature showed higher polymer decomposition at higher temperature leading to higher gas yield and consequent higher carbon nanotube yield. Increasing the catalyst temperature led to an improvement in the quality of the product hydrocarbons. The yield of carbon nanotubes was optimised at a pyrolysis temperature of 650 °C and a catalyst temperature of 700 °C at 37 wt.% of carbon nanotubes from the polypropylene

Fig. 5. Carbon nanotube production from waste plastics (Liu et al., 2011)



Polystyrene as an aromatic based polymer has also been investigated for the production of carbon nanotubes in comparison with polypropylene (Chung and Jou, 2005). The polymer was mixed with xylene or toluene in the presence of an iron nanoparticle catalyst and coated onto a silicon wafer substrate. The samples were heated to between 500 and 900 °C, with 700 °C producing the most suitable carbon nanotubes. The product carbon nanotubes from polystyrene were between 7.5 and 25 nm but had thick walls compared to those produced with polypropylene which was attributed to secondary pyrolytic deposition of carbon with the polystyrene precursor.

There are few reports on the use of real-world waste plastic feedstocks for the production of carbon nanotubes. The presence of impurities potentially influencing the yield and quality of the carbon nanotubes. Wu et al (2014) reported on the pyrolysis-catalysis of several different waste plastics, including

plastics from a motor oil container (MOC), waste commercial high density polyethylene (HDPE) and regranulated HDPE waste containing polyvinyl chloride (PVC). The plastics were pyrolysed and the product gases passed to a catalytic steam reforming reactor using a Ni-Mn-Al catalyst, where the carbon was deposited on the catalyst. All of the plastics produced carbon deposits which consisted of amorphous and filamentous carbons which were shown to be mostly multi-walled carbon nanotubes. The carbon nanotubes had average diameters of 30 nm with 10 nm thick walls and up to 10 μm in length. The HDPE containing PVC produced less carbon nanotubes which was attributed to the chlorine which poisoned the catalyst.

3.0 Gasoline and Chemicals

The production of gasoline from waste plastics involves the use of solid acid catalysts, such as HZSM-5, MCM, NH_4Y , NaY since these are used in petroleum refineries for upgrading crude oil through catalytic cracking (Bagri and Williams, 2002; Serrano et al, 2003; Serrano et al, 2012). In addition to the catalysed process for the production of gasoline, the product oil is highly aromatic. Consequently, the use of solid acid type catalysts can generate aromatic chemicals such as benzene, xylenes, toluene and ethylbenzene in high concentration, therefore the product oil becomes a source of high value chemicals for the chemical industry rather than a gasoline type fuel. For example, Keane (2009) has suggested that the shape selectivity micropore-size properties and surface acidity of zeolite catalysts can be manipulated to produce narrow ranges of hydrocarbons. It has also been recently suggested that using mesoporous catalysts such as MCM-41 can also allow the manipulation of the product slate to produce targeted aromatic chemicals (Serrano et al, 2012). Catalytic cracking occurs on the catalyst acidic surface on Lewis or Bronsted

acids sites, where the polymer is cracked to form a range of carbon cations. The carbocations react through isomerisation, oligomerisation, cyclisation, aromatisation and cracking reactions on the solid acid catalyst sites to produce increased branched, cyclic and aromatic hydrocarbons (Corma, 1995; Serrano et al, 2012).

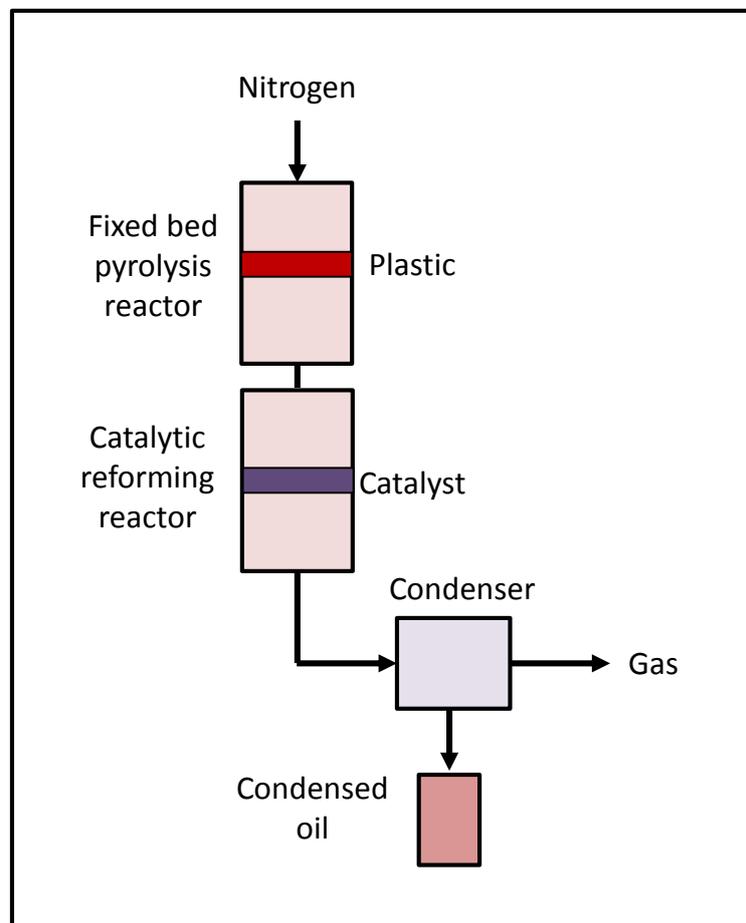
Kumar et al (2011) have highlighted the characteristics of catalysts for plastics processing to produce premium grade fuels; catalyst acidity, in the form of Lewis acid and Bronsted acid sites which promote catalytic cracking; the Si:Al ratio of the catalyst which influences acid site density with lower ratios producing an increase in the surface acidity of the catalyst which promotes catalytic cracking of hydrocarbons; catalyst properties of surface area and porosity which influence catalytic activity and product selectivity.

The pore size of zeolite catalysts controls the molecular size of the hydrocarbon products from pyrolysis of the waste plastics from entering the pore structure for catalytic cracking and reformation reactions to take place (Venuto and Habib, 1979). The larger molecular weight pyrolysis products would need to first decompose to lighter, smaller hydrocarbon products on the surface of the catalyst before they could enter the small pore size of the catalyst.

Serrano et al (2012) highlighted the importance of the porosity of solid acid catalysts. Zeolite type catalysts with micropore structure can inhibit catalytic cracking of the larger molecules produced from the pyrolysis of waste plastics during pyrolysis-catalytic cracking processes. Therefore, larger pore sized mesoporous catalysts such as MCM-41 or Al-SBA-15 have been investigated which more easily can crack the polymeric fragments from pyrolysis, leading on to the application of combined microporous and mesoporous materials as hierarchical type catalysts.

Muhammad et al (2015) investigated the two-stage pyrolysis-catalysis of different plastics (polyethylene, polypropylene, polystyrene, and polyethylene terephthalate) using a HZSM-5 catalyst. The reactor used consisted of pyrolysis of the plastics in the first stage followed by catalysis in a separate second stage reactor (Figure 6). The pyrolysis of the plastics in the absence of the catalyst produced between 81 - 97 wt.% of a oil/wax product, with the HZSM-5 catalyst a wholly oil product was produced between 44 and 51 wt.%, depending on the type of plastic. However, the product oils from pyrolysis-catalysis had a high proportion of C₅ - C₁₅ hydrocarbons with a high content of single-ring aromatic compounds and there was also an increase in gas yield. Muhammad et al (2015) also reported benzene yields of more than 30% of the product oil for the pyrolysis-catalysis of polyethylene terephthalate using a HZSM-5 catalyst. The product yield from pyrolysis-catalysis of polystyrene reduced the styrene yield compared to thermal pyrolysis, but significantly increased benzene yield to more than 20%. In addition, a real-world plastic waste sample obtained from a commercial processing plant consisting of mostly polyethylene, polypropylene and polyethylene terephthalate was subject to pyrolysis-catalysis. The yield of product oil was ~50 wt%, with gas yield ~40 wt.%, and the oil consisted of benzene, toluene, ethylbenzene, xylenes and styrene which comprised about 50% of the product oil composition.

Fig. 6. Gasoline and chemicals from plastics using a pyrolysis-catalysis reactor (Muhammad et al., 2014)



Catalytic pyrolysis of polyethylene with Zeolite ZSM-5 carried out by Mordi et al (1994a) also reported a high content of aromatic compounds in the product oil, comprising mostly single ring benzene, toluene and xylenes. Additional work by Mordi et al (1994b) investigated a range of different catalysts including H-mordenite, H- θ -1, and HZSM-5 zeolites for the catalytic cracking of polyethylene in a batch reactor. HZSM5 was found to produce higher yields of gas and aromatic content in the product oil. Sakata et al. (1999) investigated the pyrolysis and catalytic pyrolysis of polyethylene and polypropylene for several

different solid acid catalysts, including silica–alumina (SA-1, SA-2), zeolite ZSM-5 and non acidic mesoporous silica catalysts (silicalite, mesoporous silica gel and mesoporous folded silica (FSM) where the catalyst and polymer were mixed in the same reactor. With the Zeolite ZSM-5 catalyst the strong surface acidity resulted in a high conversion to hydrocarbon gases and low oil yield.

Mertinkat et al (1999) used a 1 kg h^{-1} fluidised bed reactor to investigate the catalytic pyrolysis of polyethylene and polystyrene using fluid catalytic cracking catalysts as bed material at temperatures between 315 and 515 °C. The thermal pyrolysis of polystyrene produced an oil with 61 wt.% styrene, but in the presence of the catalysts a range of single ring aromatic compounds were obtained in high concentration, with maximum concentrations of 26 wt.% ethylbenzene, 22 wt.% benzene, 7 wt.% styrene and 5 wt.% benzene. Catalytic pyrolysis of polyethylene produced mainly alkylated compounds in the product gas (28–52 wt.%) and product oil (38–39 wt.%) and the yield of waxes was negligible. The main products were C_3 and C_4 hydrocarbon gases. Kaminsky and Zorriqueta (2007) used a fluidised bed with in-bed solid TiCl_4 , AlCl_3 catalysts to pyrolyse polypropylene. A marked increase in the amount of C_1 - C_6 hydrocarbons was reported.

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