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Monomer recovery through advanced pyrolysis of waste high density polyethylene (HDPE)

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Plastic use has increased by a twenty fold since the 1950's and so has the amount of plastic waste generated. Although legislation promotes reuse and recycling, still over 50% of Europe's plastic waste are still disposed in landfills. Therefore, millions of tonnes of plastic end up in the environment provoking severe harm and wasting tonnes of resources (i.e. fossil fuels) and generating a need for advanced treatments, i.e. pyrolysis. Commonly only a small amount of monomer (i.e. ethylene, C₂H₄) but large amount of waxy products i.e. aliphatic hydrocarbons that require further refinement are recovered from conventional pyrolysis of high density polyethylene (HDPE). Therefore, direct conversion of HDPE waste into high added value products would be more desirable. In this study, experiments were carried out using cold plasma assisted pyrolysis of waste HDPE for valorisation. With the assistance of cold plasma up to 22-25 wt% ethylene was recovered from HDPE waste, up to 55 times higher than that obtained in conventional pyrolysis of waste HDPE. Catalytic cold plasma pyrolysis showed that the addition of only 3-10 wt% HZMS-5 or sulphated zirconia doubled the gas (up to 41 wt%) and subsequently the ethylene yield at low temperatures. This study opens up opportunities to valorise unsorted waste into intermediates for chemical processes via a simple process.

1 Introduction

Commodity plastics e.g. high density polyethylene (HDPE) are versatile, durable, light and cheap explaining the increasing use of plastic products and the subsequent rise in plastic waste generation during the last decade (average 9 % per year¹). In the European Union (EU), and the UK, it is estimated that plastic waste contributes up to 10-13 % of municipal solid waste (MSW)^{2,3}, of which 12.1 % (2.9 million tonnes) is HDPE⁴. HDPE, manufactured from ethylene (a petroleum-based product), along with the other commodity plastics, i.e. low density polyethylene (LDPE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS), represent around 4 % of the global fossil fuel consumption⁵. Although this percentage may appear to be low, it is also worth consider that plastic waste are mainly disposed into landfills (e.g. 83 % in the USA in 2014⁶ or 31 % in the EU in the same year⁴) within the first month of their production (approximately 40 % of plastic products are used for packaging application with an average life of less than a month)⁷. Landfill disposal of plastic waste presents several disadvantages from a sustainable point of view as it is a substantial deprivation of valuable resources and are not biodegradable over time due to their mechanical strength

and resistance to both water and micro-organisms occupying a large surface of arable land^{8,9}. They are photodegradable (i.e. are decomposed by the sunlight) into very small particles that can be transferred between ecosystems. Polyethylene is very vulnerable to be transferred by the wind or other natural forces into the sea because of the low density and weight, creating a hazard for human and wildlife^{5,9} by choking wildlife and distributing harmful organisms or toxic chemicals such as persistent organic pollutants (POP)¹⁰. Therefore, considering the latter facts and the current depletion of petroleum resources, the recovery of monomers from plastic waste to minimise landfill disposal and fossil fuel consumption is now more imperative than it has ever been.

Pyrolysis of plastic waste has been considered to recover energy and fuels due to their high volatile content (92 %) and calorific value (40 MJ/kg)¹¹. Pyrolysis is conducted in the absence of oxygen to form three fractions: gas (mainly form by light hydrocarbons - C₁-C₄-, hydrogen, CO and CO₂); a wax/oil fraction comprising of a mixture of aromatic and aliphatic compounds; and a solid residue¹²⁻¹⁶. The proportion of each fraction and exact composition varies depending on feedstock. For instance, gas contains CO and CO₂ if PET is present in the feedstock¹⁷. PS and PET yield an aromatic yield while HDPE, LDPE and PP wax is formed by aliphatic hydrocarbons in the C₁₁-C₂₀ range^{14,18}. On top of that, temperature, heating rate, reaction time and the addi-

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tion of catalysts also play an important role on product yields¹⁹. Mastral et al.²⁰ reported that HDPE pyrolysis product yield and composition varied greatly with temperature i.e. from 72.3 wt% wax and 22.1 wt% gas at 650 °C to 13.5 wt% wax and 76.16 wt% gas at 730 °C).

HDPE thermal pyrolysis at 500 °C yields mainly wax in the form of C₂₀ aliphatic hydrocarbons (67 wt%) followed by C₁₂-20 hydrocarbons (25 wt%), C₅-C₁₁ hydrocarbons (5 wt%) and around 3 wt% containing methane (0.03 wt%), C₂ (0.15 wt%), C₃ (0.57 wt%), and C₄ (2.27 wt%)²¹. The distribution of hydrocarbons in the wax fraction makes it a low quality product due to the high viscosity and high boiling point temperature range and so it is not suitable to be used as fuel without further processing. The high viscosity of the wax fraction prevents their flow downstream and may cause blockages along pipelines unless heated, therefore increasing operation costs. Since the gas fraction is also low in valuable products (hydrogen or ethylene for instance) the profitability of conventional HDPE pyrolysis is low. The addition of a catalyst i.e. HY zeolite increases the C₅-C₁₀ fraction to 44.55 wt% and the gas fraction to 24.44 wt% however only 0.62 wt% ethylene yield was obtained²².

Zeolites are well known for being an acid catalyst appropriate for hydrocarbon cracking, i.e. from heavier hydrocarbons like the plastic waste pyrolysis wax fraction into lighter compounds such as ethylene or propylene^{23,24}. However, two major issues of zeolites are: 1) the blockage of the pores by bulky compounds, such as polymers, due to the low pore size of most zeolites which deactivates the catalyst and decreases its activity²⁵, and 2) their high cost (\$30-\$120 per ton for natural zeolites depending on particle size, the smaller the higher the price²⁶). López et al.²⁷ suggested that ZSM-5 deactivation due to coke deposition in the catalyst pores occurs after one pyrolysis cycle of plastic waste at 440 °C causing a 50 % reduction in the gas yield. Although regeneration in air at 550 °C for 5 h is possible^{27,28}, it adds energy requirements to the pyrolysis process which can ultimately overcome the savings produced by the catalyst i.e. temperature reduction. Other acid catalysts have also been proposed for this application²⁹⁻³¹, including sulphated zirconia (SZ, SO₄²⁻ - ZrO₂) for polystyrene thermal cracking³² and for thermal decomposition of HDPE and coal mixtures³³. The latter was selected for this experiment since it is considered an environmentally friendly alternative: i) it does not involve the use of toxic and/or corrosive reagents and ii) it can be directly synthesised via solvent-free methods^{34,35}. Limited research has also been done in assessing the viability of SZ for catalytic pyrolysis of pure HDPE streams as a more sustainable option in comparison to other catalysts such as HZSM-5, HUSY, HMOR and silica-alumina catalysts^{24,31}. The SZ will be prepared by a direct synthesis method as proposed by Eterigho et al.³⁵, due to the enhancement in catalyst characteristics resulting in an increase in yield³⁶.

Cold (non-thermal equilibrium) plasma is characterised by the presence of charged species like energetic electrons, excited molecules and ions in which the average electron temperature is very high (10⁴-10⁵ K, 1-10 eV) whilst the bulk temperature is low i.e. near room temperature. The non-equilibrium property makes the cold plasma chemically selective and can be used for catalytic

processes. Unlike thermal plasma, a complex quenching of the electrodes is not required in cold plasma. The excited species, especially the energetic electrons, can break the C-C and C-H bonds in heavier hydrocarbon molecules to form lighter hydrocarbons. One popular method to generate cold plasma is through atmospheric pressure dielectric barrier discharge (DBD) plasma due to its simplicity and easy scaling-up³⁷. It comprises of two electrodes separated by a dielectric barrier. The plasma zone is created in the gap between two electrodes when a voltage is applied between the electrodes creating active and high energy species.

Ahmed et al.³⁸ and Deminsky et al.³⁹ reviewed the use of cold plasma for light hydrocarbon conversion into hydrogen carbon finding that cold plasma is a source of active species that can substitute the use of conventional catalysts producing high purity hydrogen streams (free of CO and CO₂) and high value carbon products. Khani et al.⁴⁰ reported the ability of cold plasma (DBD) to decompose n-hexadecane, lubricating oil (C₁₃-C₄₂) and heavy oil (C₆-C₉₈) into lighter fractions at temperatures up to 250 °C: up to 6.91 cm³/min of ethylene was recovered from liquid n-hexadecane and a 56.8 % reduction on heavy hydrocarbons into C₄-C₁₂ in the lubricating oil was achieved. Hao et al.⁴¹ also suggested the use of cold plasma (DBD operated at 200 °C) for the cracking of heavy crude oil into light crude oil increasing the light crude oil yield from 0.56 wt% to 8.5 wt%. Harling et al.⁴² found that the combination of cold plasma and catalyst could reduce the operation temperatures and energy requirements for volatile organic compounds (VOCs) decomposition. More detailed information on cold plasma and the use of DBD can be found in Meichsner et al.⁴³, Kogelschatz⁴⁴ or Kogelschatz and Eliasson⁴⁵ but it will not be discussed here as it is beyond the scope of this paper.

In cold plasma, reactive species and excited molecules and atoms are generated by energetic electrons rather than by high temperatures as occurs in conventional thermal decomposition. Therefore, some thermodynamically unfavourable reactions can be realized in cold plasma⁴⁶. Cold plasma may influence or add additional reactional channels/pathways to conventional pyrolysis, which can improve the reaction activity and product selectivity. In this work cold plasma assisted/promoted pyrolysis of HDPE was carried out over a range of temperature and heating rate to directly crack heavier hydrocarbons formed from plastic waste during pyrolysis into lighter hydrocarbons. SZ catalyst was used and compared with commercial zeolite HZSM-5 in terms of gas yield maximisation. The synergistic effect of catalyst and cold plasma was also exploited to increase the ethylene yield for monomer recovery to valorise plastic waste.

2 Materials and Methods

2.1 Materials

HDPE waste obtained from O'Brien Recycling Solutions (Wallsend, UK) were washed with soap and water to eliminate any external contamination that could alter results and cut into 1.5x1.5 cm particles. Samples were characterised by proximate analysis, ultimate analysis, calorimetry, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Table 1 waste HDPE samples had high volatile content (77.70

wt%) and calorific value (44.81 MJ/kg) as expected. The main component in waste HDPE was carbon (73.33 wt%) followed by hydrogen (13.28 wt%) with no trace of nitrogen. Although HDPE is polymerised from ethylene ($\text{CH}_2=\text{CH}_2$) to form a straight chain of aliphatic hydrocarbons, the mass balance from the ultimate analysis presented an oxygen content of 13.40 wt%. This presence could be due to the additives (adhesives, paint, etc.) used to alter the plastic product quality when it was manufactured. As a result, the ash content was also higher than expected (around 10 wt%). This additives also affect waste HDPE reaction kinetics (higher activation energy than pure HDPE, 233 kJ/mol⁴⁷) and could vary the composition of HDPE pyrolysis products if the oxygen is released from the structure producing small amounts of CO_2 and CO .

However, not all HDPE waste presented this high oxygen content. It was only observed when waste HDPE plastic bags were used as feedstock. Other products such as milk or bleach bottles did not have this behaviour due to the considerably lower amount of oxygen present ($5.30 \pm 0.54\text{wt}\%$) and therefore were used as feedstock in all experiments. In addition to the previous analysis, X-ray Photoelectron Spectroscopy (XPS) conducted in a Thermo Scientific K-Alpha and XPS System at the National EP-SRC XPS Users' Service (NEXUS) at Newcastle University showed that waste HDPE only comprised of carbon and a small amount of oxygen and no other elements were found.

Table 1 Waste HDPE characterisation by proximate analysis, ultimate analysis, calorimetry, TGA and DSC. "Obtained by mass balance.

Waste HDPE (plastic bag)	
Proximate Analysis	
Volatile matter/[wt.%]	77.70 ± 1.64
Ash/[wt.%]	10.36 ± 0.30
Fixed Carbon/[wt.%]	11.94 ± 1.67
Moisture/[wt.%]	0.10 ± 0.07
Ultimate Analysis	
Carbon/[wt.%]	73.33 ± 0.38
Hydrogen/[wt.%]	13.28 ± 0.37
Nitrogen/[wt.%]	0.00 ± 0.30
Oxygen ^a /[wt.%]	13.40 ± 0.44
Calorimetry	
High Calorific Value/[MJ/kg]	44.81 ± 0.36
TGA	
Decomposition Temperature/[°C]	425-565
Activation Energy/[kJ/mol]	375.59 ± 39.69
Order of Reaction/[-]	1.70
DSC	
Melting Temperature/[°C]	126.66 ± 0.25

2.2 Experimental set-up

Figure 1 shows a diagram of the experimental set up (a) as well as a diagram of the DBD reactor (b) used to generate the plasma. The DBD reactor (Figure 1b) comprised of two coaxial quartz tubes with a gap of 1.5 mm. The outside of the outer tube was covered with a 316L stainless steel mesh and the interior of the inner tube with a stainless steel sheet acting as the two electrodes to create a cold plasma zone 12 cm long and with a volume of 7.6

cm^3 . The DBD reactor was connected to the pyrolysis, consisting of a 25 cm long x 32 mm OD quartz tube (1.5 mm wall thickness). HDPE samples were placed inside the pyrolysis reactor and were heated by the electric furnace to a set pyrolysis temperature (500-700 °C) at a set heating rate (30-75 °C/min) and then hold at that temperature for 15min in a nitrogen atmosphere (20 mL/min). The cold plasma was generated using an AC power supply (0-240 V, 50 Hz). The input specific energy density (SED), i.e. the discharge power supplied to the cold plasma reactor per unit of gas volume, varied between 90 J/mL (30 W supplied) and 180 J/mL (60 W supplied). The different SED were kept constant during the whole experiment and were obtained by adjusting the input voltage between 0-240 V. The effect catalyst (HZSM-5 and SZ) was also studied by addition of 0-3 wt% (catalyst to plastic mass ratio) into the gap in the DBD reactor. Cold plasma catalytic pyrolysis experiments were carried out at 55 °C/min, 500 °C and 135 J/mL (45 W supplied).

Fig. 1 Experimental set-up: a) Pyrolysis and plasma experimental set up and b) Detail of pyrolysis-DBD plasma reactor

2.3 Catalyst characterisation

A commercial zeolite HZSM-5 was obtained from Sigma-Aldrich (surface area = 211 m^2/g and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 312$) and SZ was prepared following the method proposed by Etherigo et al.³⁵ by direct mix of zirconium (IV) oxychloride octahydrate (Sigma Aldrich) and ammonium sulphate (Sigma Aldrich) at a 1:6 molar ratio followed by 18 h aging at room temperature (25 °C) and finally calcined at 500 °C for 6 h.

Surface area of SZ was obtained by N_2 physisorption isotherms determined at 77 K using a Thermo Scientific Surfer and Brunauer-Emmett-Teller (BET) equation with samples outgassed at high vacuum for 12 h at 150 °C prior to analysis. BET results showed that fresh SZ presented a high surface area ($277 \pm 15\text{m}^2/\text{g}$), which was higher than others reported at 108 m^2/g (Etherigo et al.³⁵) or 119.3 m^2/g (Tangchupong et al.⁴⁸). The difference could be due to the variation in the preparation conditions, e.g. slightly different aging time and temperature during aging can vary the surface area from 19 m^2/g (no aging) to 104 m^2/g (1 day aging at 150 °C)^{49,50}. Used SZ presented a much lower surface area of just 10.83 m^2/g suggesting that catalyst pores are covered with coke after reaction causing catalyst deactivation.

X-ray diffractograms (XRD) were obtained in a Panalytical X'Pert Pro Multipurpose Diffractometer (MPD) fitted with an X'elerator and a secondary monochromator ($\text{Cu-K}\alpha$ radiation, wavelength (λ) = 1.54 Å generated at 40 kV and 40 mA) over a 2θ range of 2° to 80° from 2 °C to 100 °C. Figure 2 shows

the X-ray diffraction spectra of fresh and used SZ. Results for the fresh catalyst showed that the sample was mainly amorphous with relative low tetragonal and monoclinic phase crystalline fractions formed during calcination of SZ prior to experiments via the following reactions: $\text{Zr}(\text{SO}_4)_2 \rightarrow \text{ZrO}_2 + \text{SO}_3$ and $\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2$ ⁵¹. Results were similar to those showed by Eterigho et al.^{35,36} although the crystalline fraction of SZ was slightly higher in this case. The latter can also explain the difference found in the surface area which confirms that preparation conditions affect SZ characteristics. The used SZ catalyst showed a new crystalline phase i.e. orthorhombic zirconium bisulphate (VI) ($\text{Zr}(\text{SO}_4)_2$) not present in the fresh SZ catalyst and therefore caused by the effect of cold plasma (Figure 2). This zirconia polymorph only forms at elevated pressure but the high energy environment of cold plasma mimicked those conditions.

Fig. 2 X-ray diffraction spectra of fresh (solid line) and used (dashed line) SZ (T = tetragonal crystal, M = monoclinic crystal and ZBS = zirconium bisulphate (VI))

Fresh and used SZ catalyst were scanned from 4000-600 cm^{-1} on an Agilent Cary 630, using KBr as background reference to obtain Fourier Transform Infrared (FTIR) spectra. Figure 3. The fresh SZ spectra (solid line in Figure 3) showed bands at 992 and 1119 cm^{-1} characteristic of the S-O stretching vibration modes of SO_4^{2-} species on the catalyst surface. The band at 1425 cm^{-1} corresponds to the stretching vibration of S=O bonds in the sulphate groups. The bands at 1635 and 3207 cm^{-1} were caused by the $\delta_{\text{O-H}}$ bending frequency and the O-H stretch of the water molecules in the sulphate groups. These results agreed well with previous studies of SZ catalyst⁵². The used catalyst spectra (dashed line in Figure 3) after 4 cycles in the presence of cold plasma showed a considerable reduction on the bands at 1635 and 3207 cm^{-1} suggesting the water is removed during experiments. There is also a decreased in the intensity of the 992 and 1119 cm^{-1} bands which suggest a certain alteration of the S-O bond in the sulphate groups.

Fig. 3 FTIR spectra of fresh (solid line) and used SZ

3 Results and discussion

3.1 Comparison of cold plasma pyrolysis with conventional and catalytic pyrolysis

The main difference when cold plasma was applied to pyrolysis of HDPE was a considerable increase in the gas yield i.e. from 15 wt% to 44 wt% at 600 °C when the SED increased from 0 J/mL to 90 J/mL as shown in Figure 4. According to Bagri and Williams⁵³ conventional pyrolysis of HDPE at 500 °C produces high wax (95 wt%) and low gas yields, showing similarity to those reported in Figure 4 (92 wt% wax yield and 6 wt% gas yield). They also reported an increase in the gas yield with the addition of both Zeolite Y and ZSM-5. The gas yield for the cold plasma (44 wt% at 600 °C and 90 J/mL) approached more the amount of gas recovered through catalytic pyrolysis (77 wt% at 600 °C and 5 wt% of HSZM-5) than that of conventional pyrolysis (15 wt% at 600 °C). Gas yield result from this study could not be compared to literature as no studies on the use of cold plasma for plastic waste pyrolysis were found at the time this manuscript was written.

Cold plasma provides higher energy species (excited electron = 0 - 10eV⁵⁴) than the bond dissociation energies present in HDPE (C-H = 415kJ/mol and C-C = 331kJ/mol⁵⁴) easing the reach of the activation energy and therefore promoting cracking and gas products. Along with other active species such as N_2^+ , excited electrons collide with the volatiles released from HDPE pyrolysis leading to the formation of carbenium-like ions and radicals along hydrocarbons chain promoting reaction pathways similar to secondary β -scission reactions mimicking the mechanism of thermal decomposition of hydrocarbons in the presence of acid catalysts i.e. HSZM-5 as explained later.

As shown in Figure 4, it is obvious that to maximise the gas yield in conventional pyrolysis temperatures have to be high (700 °C). The addition of only 5 wt% HSZM-5 slightly decreased the pyrolysis temperature from 700 °C (59 wt% of gas yield in conventional pyrolysis) to 600 °C (77 wt% of gas yield in catalytic pyrolysis). This is due to the different mechanism between conventional (random chain scission as shown in Figure 5)⁵⁵⁻⁵⁷ and catalytic (carbocation mechanism pictured in Figure 6)⁵⁷⁻⁵⁹. In the latter, the β -scission step is dominant and promotes the forma-

Fig. 4 Comparison between conventional pyrolysis of waste HDPE at temperatures between 500–700 °C and 45 °C/min (columns 1–3), catalytic pyrolysis of waste HDPE at 600 °C, 45 °C/min and 5 wt% HZSM-5 (column 4) and cold plasma pyrolysis of waste HDPE at 600 °C, 30 °C/min and SED = 90–180 J/mL (columns 5 and 6). Legend: Temperature (°C)/SED (J/mL)/Catalyst weight (wt.%)

tion of smaller chains thereby enhancing the formation of lighter compounds, i.e. increases the gas yield^{58,59}.

Fig. 5 Schematic representation of random chain scission mechanism^{57,60,61}

Conventional pyrolysis of HDPE occurs by random chain scission as shown in Figure 5, consisting of three steps: initiation (i.e. formation of a radical), propagation (by intramolecular and intermolecular hydrogen transfer) and finally termination through recombination of the free radicals to form alkanes, alkenes and dienes. In the case of HDPE and other polyolefins, the amount of monomer formed is governed by the substituent groups or atoms of the carbon alpha (i.e. the one with the unpaired electron), i.e. hydrogen atoms for HDPE. If the substituent groups

of the carbon alpha are large, e.g. methyl group in polypropylene or phenyl group in polystyrene, the intermolecular hydrogen step is hindrance (steric hindrance) and the reaction occurs through reverse polymerisation or unzipping increasing the monomer yield⁶¹. The weakest C–C bond in a linear hydrocarbon chain tends to be the 4th carbon (bond dissociation energy of 282.4 kJ/mol compared to 335 kJ/mol for terminal C–C bond⁶²). As hydrogen atoms are small they do not interfere in the transfer of hydrogen from carbon four to the unpaired electron in the carbon alpha (Figure 5). This implies that the chain will broke far away from the end and, therefore, the molecules formed will be larger. This phenomena explains the low gas yield obtained with conventional pyrolysis unless the temperature is increased to promote secondary cracking.

When HZSM-5 is added HDPE pyrolysis occurs through a carbocation formation (Figure 6). First, the Lewis acid sites of the zeolite extract a proton (H^+) from the HDPE chain creating a carbocation (i.e. carbon ion with positive charge) in the chain⁵⁸. Then, the carbocation can either: i) accept a proton (H^+) from the Brönsted acid sites of the zeolite (termination to form another long alkane); ii) undergo propagation as described in the random scission mechanism; or, more frequently, iii) a β -scission reaction can occur where the C–C bond between the beta carbon (i.e. the one next to the carbocation) and the following one is broken resulting in a smaller carbocation and a shorter olefin. This step enhances the formation of shorter hydrocarbon chains explaining why the gas yield increased from 15 wt% to 77 wt% at 600 °C at 3 wt% of HZSM-5 (Figure 4). Detailed mechanism of reaction are not shown in Figures 5 and 6, only a schematic representation to illustrate and ease the comprehension of the discussion. More detailed information can be found elsewhere⁶³ but it will not be

Fig. 6 Schematic representation to illustrate carbocation mechanism of HDPE over zeolites^{57,58}

discussed here as it falls out of the scope of this work.

Figure 4 implies that in the presence of cold plasma system, the longer volatile chains released as HDPE was heated above 410 °C could also create carbocations as a result with collisions with high energy species and could then underwent a β -scission reaction. The active species in the cold plasma (e.g. N_2^+) also generate radical species as a result of their collisions with volatiles released during pyrolysis. These radical species enhance the cracking of heavier hydrocarbons⁶⁴, thereby increasing the gas and C_1 - C_4 yields compared to conventional pyrolysis. The lower gas yield in cold plasma than in HZSM-5 at the same temperature indicated that collisions between radical hydrocarbons and active hydrogen atoms released during cracking occur more frequently than β -scission causing the formation of longer alkanes, alkenes and dienes⁶⁴.

3.2 Effect of cold plasma on HDPE pyrolysis

3.2.1 Product Yields

The effect of the temperature (600-700 °C), heating rate (30-75 °C/min) and SED (90-180 J/mL) was studied and it is summarised in Figure 7. Increasing the SED increased the gas yield at all tested temperatures and heating rates as expected. High SED, i.e. high discharge power, enhances the electric field, electron

density and gas temperature in the discharge^{65,66}. This translates into a more reactive environment with more energetic electrons⁶⁷ increasing the formation of carbocations and radicals in the hydrocarbon chains and enhancing the cleavage of C-C and C-H bonds and therefore promoting the formation of light hydrocarbons i.e. higher gas and ethylene yields.

The effect of temperature or the heating rate was less than that of SED, e.g. at constant SED = 90 J/mL, the gas yield decreased by 15 % (44.4 wt% to 37.8 wt%) at 600 °C and increased by 30 % (33.3 wt% to 43.5 wt%) at 700 °C when the heating rate was changed from 30 °C/min to 75 °C/min. However, it increased by 94 % (32 wt% to 62 wt%) when the SED was increased from 90 J/mL to 180 J/mL at 700 °C and 30 °C/min. As it is shown in Figure 7 low heating rates favour the formation of wax over gas while high heating rates enhance the formation of gas as secondary cracking reactions of the longer volatiles released occur⁶⁸. Therefore in order to maximise the gas yield for monomer recovery high heating rates should be used. Thereby, subsequent experiments testing the effect of a catalyst in the cold plasma were all performed at high heating rate only i.e. 55 °C/min. The yield of solid residue did not vary with neither temperature, heating rate nor SED and remained below 1 wt% in all cases due to the low ash content already mentioned in section 2.

3.2.2 Gas composition

Waste HDPE pyrolysis gas fraction was hydrogen (0.4-1.7 wt%), methane (9.0-19.3 wt%) and C_2 - C_4 hydrocarbons (19.4-46.2 wt%). As shown in figure 8 the proportion of hydrogen was below 2 wt% and the gas comprised mainly of hydrocarbons from methane to C_4 with higher proportion of lighter hydrocarbons (C_1 and C_2) for all tested conditions.

Figure 8 showed cold plasma assisted pyrolysis of HDPE presented a considerable amount of C_2 and CH_4 followed by other hydrocarbons (C_3 - C_5). Compared to conventional pyrolysis where the proportion of C_2 is below 10 wt%¹² cold plasma doubled the proportions of C_2 up to 20 wt%. This increases the value of the gas stream as ethylene (CH_2 - CH_2) is a key chemical blocks used in chemical processes. About 80 % of the global production is used to polymerise either HDPE or LDPE to form plastic products^{69,70} with most ethylene manufactured from fossil fuels (mainly from steam reforming of naphtha obtained from crude oil^{69,70}). Being able to increase the proportion of monomer improves the profitability of plastic waste pyrolysis process with a low increase in the energy consumption (cold plasma consumption during experiments of 72-108 kJ for 90 J/mL and 180 J/mL respectively compared with the 684 kJ needed for the pyrolysis stage).

3.2.3 Wax composition

Unlike the gas fraction, the distribution of hydrocarbons in the wax fraction was not significantly modified by cold plasma pyrolysis: mostly C_{20+} followed by C_{12} - C_{19} and finally a small proportion of C_9 - C_{11} as shown in Figure 9. This behaviour suggested that as previously mentioned in section 3, cold plasma promotes the β -scission step, yielding lighter hydrocarbons i.e. the volatiles released (C_9 - C_{20+}) from the pyrolysis undergoes secondary cleav-

Fig. 7 Effect of temperature (500–700 °C), heating rate (30–75 °C/min) and SED (90–180 J/mL) on the gas, wax and solid residue yield of cold plasma assisted waste HDPE pyrolysis with no catalyst. Legend: Temperature (°C)/Heating rate (°C/min)/SED (J/mL)

Fig. 8 Effect of cold plasma SED (90–180 J/mL), temperature (500–700 °C) and heating rate (30–75 °C/min) on the gas composition. The total amount represents the corresponding gas yield (wt%). Legend: Temperature (°C)/Heating rate (°C/min)/SED (J/mL)

Fig. 9 Effect of temperature (500–700 °C), heating rate (30–75 °C/min) and cold plasma SED (90–180 J/mL) on the wax composition. The total amount represents the corresponding wax yield (wt%). Legend: Temperature (°C)/Heating rate (°C/min)/SED (J/mL)

age into C₁–C₄. Figure 10 shows the most probable reaction mechanism according to product yields and composition.

3.3 Effect of the catalyst in cold catalytic pyrolysis

Figure 11 shows the influence of catalysts: HZSM-5 (column 3) and SZ (columns 4–5) upon the product yields as well as the effect of cold plasma on the catalyst activity (columns 6–8). The addition of a small amount of acid catalyst (columns 4 and 5 in Figure 11) increased the gas yield over 45 wt% at low temperatures (i.e. 500 °C) compared with conventional pyrolysis and also with the effect of only the cold plasma (columns 1 and 2 in Figure 11). Since the energy requirements for cold plasma with the addition of a catalyst are lower than those of pyrolysis, decreasing the operating temperature to 500 °C with an increased in the monomer (C₂) recovered constitutes an improvement on the profitability of plastic waste pyrolysis and makes the process more competitive with current management methods i.e. incineration with energy

recovery and landfill disposal.

Packing catalyst into the cold plasma zone may reduce the discharge gap, reduce the breakdown voltage, enhance the average electron energy, and hence improve the reaction performance. On the other hand, the plasma can activate the catalyst, promote the reactions on the catalyst surface. Columns 5 to 8 in Figure 11 showed the effect of cold plasma on the catalyst. 10 wt% of SZ was added into the plasma section of the reactor and reused for three cycles without adding any fresh catalyst or altering the reactor. Further cycles could not be completed as coke deposition on the catalyst surface and discharge gap influencing the cold plasma performance in the reactor. It can be seen that the gas yield increased on the second cycle (second time it was used) but the gas yield was slightly reduced on the third one. This phenomena could be due to the promotion effect of cold plasma on catalysts (or synergistic effect) when they are added into the plasma zone⁷¹: i) catalyst can change the plasma discharge type from filament discharge to the combination of microdischarges

Fig. 10 Proposed reaction pathway of cold plasma assisted high density polyethylene pyrolysis

and surface discharge inside the catalyst pores which creates a more oxidative atmosphere promoting the formation of lighter compounds; and ii) the cold plasma can vary the catalyst chemical composition, surface area and structure. These two synergistic effects explained the increase of gas yield on the second cycle of SZ. Coke deposition on SZ pores decreases the catalyst activity reducing the gas yield in the third cycle. However, as previously discussed in Section 1, zeolites can also suffer deactivation due to coke deposition in their pores²⁷ suggesting SZ catalyst can perform comparable to zeolites in terms of re-usability.

Figure 12 shows the re-usability study of SZ at 500 °C and 55 °C/min in the absence and presence of cold plasma (135 J/mL). The addition of SZ improved the gas yield compared to conventional pyrolysis as already mentioned above in section 3. The use of spent SZ in subsequent cycles in the absence of cold plasma showed a decrease in the gas yield from the second cycle forward, which therefore translates into lower ethylene yield, due to deactivation caused by coke deposition in the catalyst pores. Nonetheless, the performance was still better than conventional pyrolysis. When coupled with cold plasma, SZ showed a significant improvement compared to conventional pyrolysis as well (59 wt% gas yield on the first cycle compared to 6 wt%).

Figure 13 shows the re-usability study of HZSM-5 zeolite performed at 600 °C and 40 °C/min for four cycles as well as the one performed for SZ catalytic cold plasma assisted pyrolysis at 500 °C and 55 °C/min. Despite operation at two different pyrolysis temperatures, comparison in terms of performance with number of cycles without losing activity is still valid. However, product distribution cannot be compared as differences in product yield are not only influenced by the catalyst activity but also by the increase in temperature. The addition of HZSM-5 improved the gas yield compared to conventional pyrolysis as already mentioned above in section 3. The use of spent zeolite in subsequent cycles showed a decrease in the gas yield, which therefore translates into lower ethylene yield, due to deactivation caused by coke deposition in HZSM-5 pores. SZ catalyst coupled with cold plasma showed a significant improvement. The gas yield obtained (66 wt%) on the first cycle was higher than that of conventional pyrolysis at both 500 °C (6 wt%) and 600 °C (18 wt%). Although the performance of zeolites in terms of monomer recovery may appear better on the first cycle for both experiments (84 wt% gas yield at 600 °C and 5 wt% HZSM-5 as opposed to 66 wt% at 500

°C and 3 wt% SZ), further cycles showed that SZ achieved higher gas yields (77 wt% on the second cycle and 71 wt% on the third cycle) than HZSM-5 (64 wt% on the second cycle and 62 wt% on the third cycle) even at lower temperatures (500 °C for SZ and 600 °C for HZSM-5).

Although SZ suffers a certain degree of deactivation, its overall performance in terms of HDPE pyrolysis for monomer recovery should be considered. However, in industry, choosing a catalyst over another is not just a matter of better activity or selectivity but it is also of importance the potential regeneration, otherwise operational cost would be very high hindering the profitability of the process⁷². SZ deactivation is caused by coke deposition and it could be regenerated by combustion of that coke if and when regeneration is performed at temperatures below 550 °C to prevent thermal decomposition of SO₄. Since catalytic experiments with SZ were performed below SO₄ decomposition temperature, the release of no sulphur-based compounds was observed during this work; however, it is important to mention that if pyrolysis is performed at higher temperatures (>550 °C) this may occur subtracting value to SZ catalyst. Nevertheless, SZ appears as a suitable and more sustainable alternative than other catalysts used for similar purposes such as zeolites for HDPE catalytic cold plasma assisted pyrolysis for monomer recovery to valorised plastic waste.

4 Conclusions

Both non-catalytic and catalytic cold plasma can be used for plastic waste pyrolysis to recover valuable products i.e. monomer in the gas stream (up to 24 wt% under the tested conditions). This achievement is not possible with conventional pyrolysis due to the low gas yield obtained (6 wt% at 500 °C) unless the operation temperature is over 700 °C (59 wt% gas yield and 27 wt% ethylene yield) which increases the operation costs and reduces the profitability of the process. Non-catalytic cold plasma proved to be able to double the gas yield as well as the amount of ethylene recovered operating at lower temperatures than those of conventional pyrolysis (63 wt% gas yield at 600 °C, 30 °C/min and 180 J/mol as opposed to 18 wt% at 600 °C, 40 °C/min no catalyst or cold plasma). The addition of an acid catalyst allowed to decrease the temperature even further maximising the gas yield (59 wt% gas yield at 500 °C and 10 wt% SZ). The ethylene yield recovered with SZ catalytic cold plasma HDPE pyrolysis (13 wt% on the first cycle increasing to 15 wt% on the second with subsequent decreased to about 13 wt% again on the third cycle) was lower than the one recovered under non-catalytic cold plasma at high temperature (16 wt% at 600 °C, 30 °C/min and 180 J/mol or 24 wt% at 700 °C, 75 °C/min and 180 J/mol). Although the ethylene yield recovered when SZ was added was 3 % below that at 600 °C, the energy requirements are considerably reduced when operating at low temperatures and therefore the addition of SZ can be seen as an improvement over the use of only cold plasma assisted pyrolysis of HDPE. SZ catalyst characterisation after every pyrolysis cycle to understand how cold plasma affects morphology would be beneficial and it will form part of future work.

Fig. 11 Effect of catalyst (H = HZSM-5 and S = SZ) on cold catalytic plasma pyrolysis at 500 °C and 55 °C/min. Legend: Temperature (°C)/SED (J/mL)/Catalyst weight (wt%)

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Fig. 12 Re-usability of catalyst (SZ) under catalytic pyrolysis (columns 2 to 5) and catalytic cold catalytic plasma assisted pyrolysis (columns 6 to 9) at 500 °C and 55 °C/min. Legend: Temperature (°C)/SED (J/mL)/Catalyst weight (wt%)

Fig. 13 Re-usability of catalyst (H = HZSM-5 and S = SZ) under catalytic pyrolysis at 600 °C and 40 °C/min (columns 3 to 6) and catalytic cold plasma assisted pyrolysis at 500 °C at 55 °C/min (columns 7 to 10) and comparison with conventional (columns 1 and 2). Legend: Temperature (°C)/SED (J/mL)/Catalyst weight (wt%)

References

- 1 J. (Trucost) Raynaud, *Valuing Plastics: The Business Case for Measuring, Managing and Disclosing Plastic Use in the Consumer Goods Industry*, Unep techreport, 2014.
- 2 Eurostat, *Municipal waste*, http://ec.europa.eu/eurostat/cache/metadata/en/env_wasmun_esms.htm, 2016, Online.
- 3 Eurostat, *Municipal waste landfilled, incinerated, recycled and composted in the EU-27, 1995 to 2014*, http://ec.europa.eu/eurostat/statistics-explained/index.php/File:Municipal_waste_landfilled,_incinerated,_recycled_and_composted_in_the_EU-27,_1995_to_2014.png#file, 2016, Online.
- 4 Plastic Europe, *Plastic - The Facts 2014-2015*, <http://www.plasticseurope.org/Document/plastics-the-facts-2014.aspx?Page=DOCUMENT&FolID=2>, 2016, Online.
- 5 J. Hopewell, R. Dvorak and E. Kosior, *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 2009, **364**, 2115–2126.
- 6 N. Themelis and C. Mussche, *2014 Energy and economic value of municipal solid waste (MSW), including non-recycled plastics (NRP), currently landfilled in the fifty States*, Earth engineering center - columbia university technical report, 2014.
- 7 G. Lopez, M. Artetxe, M. Amutio, J. Bilbao and M. Olazar, *Renewable and Sustainable Energy Reviews*, 2017, **73**, 346–368.
- 8 I. Kyrikou and D. Briassoulis, *Journal of Polymers and the Environment*, 2007, **15**, 125–150.
- 9 R. Verma, K. Vinoda, M. Papireddy and A. Gowda, *Procedia Environmental Sciences*, 2016, **35**, 701–708.
- 10 D. Barnes, F. Galgani, R. Thompson and M. Barlaz, *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 2009, **364**, 1985–1998.
- 11 L. Diaz-Silvarrey and A. Phan, *International Journal of Hydrogen Energy*, 2016, **41**, 16352–16364.
- 12 P. Williams and E. Williams, *Energy & Fuels*, 1997, **13**, 188–196.
- 13 E. Williams and P. Williams, *Journal of Analytical and Applied Pyrolysis*, 1997, **40**, 347–363.
- 14 F. Pinto, P. Costa, I. Gulyurtlu and I. Cabrita, *Journal of Analytical and Applied Pyrolysis*, 1999, **51**, 39–55.
- 15 Y. Sakata, M. Uddin, K. Koizumi and K. Murata, *Polymer Degradation and Stability*, 1996, **53**, 111–117.
- 16 Miskolczi, N. and Barthaa, L. and Deaka, G. and Jover, B., *Polymer Degradation and Stability*, 2004, **86**, 357–366.
- 17 T. Bhaskar, M. Uddin, K. Murai, J. Kaneko, K. Hamano, T. Kusaba, A. Muto and Y. Sakata, *Journal of Analytical and Applied Pyrolysis*, 2003, **70**, 579–587.
- 18 A. Adrados, I. De Marco, B. Caballero, A. López, M. Laresgoiti and A. Torres, *Waste Management*, 2012, **32**, 826–832.
- 19 K. Lee, *Material Recycling-Trends and Perspectives*, InTech, 2012, pp. 175–192.
- 20 F. Mastral, E. Esperanza, P. Garcia and M. Juste, *Journal of Analytical and Applied Pyrolysis*, 2002, **63**, 1–15.
- 21 G. Elordi, M. Olazar, G. Lopez, M. Artetxe and J. Bilbao, *Industrial & Engineering Chemistry Research*, 2011, **50**, 6650–6659.
- 22 G. Elordi, M. Olazar, R. Aguado, G. Lopez, M. Arabiourrutia and J. Bilbao, *Journal of Analytical and Applied Pyrolysis*, 2007, **79**, 450–455.
- 23 N. Rahimi and R. Karimzadeh, *Applied Catalysis A: General*, 2011, **398**, 1–17.
- 24 A. S. Burange, M. B. Gawande, F. L. Lam, R. V. Jayaram and R. Luque, *Green Chemistry*, 2015, **17**, 146–156.
- 25 D. Serrano, J. Aguado and J. Escola, *ACS Catalysis*, 2012, **2**, 1924–1941.
- 26 R. Virta, *Zeolites*, U.S. geological survey - minerals information technical report, 1997.
- 27 A. López, I. De Marco, B. Caballero, A. Adrados and M. Laresgoiti, *Waste Management*, 2011, **31**, 1852–1858.
- 28 D. Serrano, J. Aguado, J. Rodríguez and A. Peral, *Journal of analytical and applied pyrolysis*, 2007, **79**, 456–464.
- 29 D. Serrano, J. Aguado and J. Escola, *Applied Catalysis B: Environmental*, 2000, **25**, 181–189.
- 30 J. Aguado, D. Serrano, G. San Miguel, J. Escola and J. Rodríguez, *Journal of Analytical and Applied Pyrolysis*, 2007, **78**, 153–161.
- 31 J. Aguado, D. Serrano and J. Escola, *Industrial & Engineering Chemistry Research*, 2008, **47**, 7982–7992.
- 32 G. Yadav and J. Nair, *Microporous and mesoporous materials*, 1999, **33**, 1–48.
- 33 K. Liu and H. Meuzelaar, *Fuel processing technology*, 1996, **49**, 1–15.
- 34 B. Reddy, P. Sreekanth and P. Lakshmanan, *Journal of molecular catalysis A: chemical*, 2005, **237**, 93–100.
- 35 E. Eterigho, J. Lee and A. Harvey, *Bioresource technology*, 2011, **102**, 6313–6316.
- 36 E. Eterigho, *phdthesis*, Newcastle University, 2012.
- 37 B. Sarmiento, J. Brey, I. Viera, A. González-Elipe, J. Cotrino and V. Rico, *Journal of Power sources*, 2007, **169**, 140–143.
- 38 S. Ahmed, A. Aitani, F. Rahman, A. Al-Dawood and F. Al-Muhaish, *Applied Catalysis A: General*, 2009, **359**, 1–24.
- 39 M. Deminsky, V. Jivotov, B. Potapkin and V. Rusanov, *Pure and applied chemistry*, 2002, **74**, 413–418.
- 40 M. Khani, A. Khosravi, E. Dezhbangooy, B. Hosseini and B. Shokri, *IEEE Transactions on Plasma Science*, 2014, **42**, 2213–2220.
- 41 H. Hao, B. Wu, J. Yang, Q. Guo, Y. Yang and Y. Li, *Fuel*, 2015, **149**, 162–173.
- 42 A. Harling, V. Demidyuk, S. Fischer and J. Whitehead, *Applied Catalysis B: Environmental*, 2008, **82**, 180–189.
- 43 J. Meichsner, M. Schmidt, R. Schneider and H. Wagner, *Non-thermal plasma chemistry and physics*, CRC Press, 2012.
- 44 U. Kogelschatz, *Plasma chemistry and plasma processing*, 2003, **23**, 1–46.
- 45 U. Kogelschatz, B. Eliasson and W. Egli, *Le Journal de Physique IV*, 1997, **7**, C4–47.

- 46 K. Zhang, G. Zhang, X. Liu, A. Phan and K. Luo, *Industrial & Engineering Chemistry Research*, 2017, **56**, 3204–3216.
- 47 C. C. Chien, C. C. Chien, L. Chen and F. Chang, *Waste Management*, 1993, **13**, 221–235.
- 48 N. Tangchupong, W. Khaodee, B. Jongsomjit, N. Laosiripojana, P. Prasertthadam and S. Assabumrungrat, *Fuel Processing Technology*, 2010, **91**, 121–126.
- 49 W. Stichert and F. Schüth, *Journal of Catalysis*, 1998, **174**, 242–245.
- 50 L. Hamouda, A. Ghorbel and F. Figueras, *Studies in Surface Science and Catalysis*, 2000, **130**, 971–976.
- 51 C. Strydom and G. Pretorius, *Thermochimica acta*, 1993, **223**, 223–232.
- 52 T. Witoon, T. Permsirivanich, N. Kanjanasontorn, C. Akkraphataworn, A. Seubsai, K. Faungnawakij, C. Warakulwit, M. Chareonpanich and J. Limtrakul, *Catalysis Science & Technology*, 2015, **5**, 2347–2357.
- 53 R. Bagri and P. T. Williams, *Journal of Analytical and Applied Pyrolysis*, 2002, **63**, 29–41.
- 54 Y. Fan, W. Zhao, S. Shao, Y. Cai, Y. Chen and L. Jin, *Energy*, 2018, **142**, 462–472.
- 55 J. Ceamanos, J. Mastral, A. Millera and M. Aldea, *Journal of Analytical and Applied Pyrolysis*, 2002, **65**, 93–110.
- 56 N. Gascoin, A. Navarro-Rodriguez, P. Gillard and A. Mangeot, *Polymer degradation and stability*, 2012, **97**, 1466–1474.
- 57 K. Sobeih, M. Baron and J. Gonzalez-Rodriguez, *Journal of Chromatography A*, 2008, **1186**, 51–66.
- 58 J. Weitkamp and L. Puppe, *Catalysis and zeolites: fundamentals and applications*, Springer Science & Business Media, 2013.
- 59 E. Vogt and B. Weckhuysen, *Chemical Society Reviews*, 2015, **44**, 7342–7370.
- 60 CDS Solutions, *Degradation Mechanism - Random Scission*, This journal is © The Royal Society of Chemistry [year] <http://www.rsc.org/contents/uploads/2015/02/Degradation-mechanisms-random-scission.pdf>, 2017, Online.
- 61 B. C.L. and H. M.M., in *Thermal Decomposition of Polymers*, SFPE Handbook of Fire Protection Engineering, 2015, ch. Chapter 7, pp. 1–110.
- 62 J. Dean, *Lange's handbook of chemistry*, 1999, 36.
- 63 R. Bruckner, *Advanced organic chemistry: reaction mechanisms*, Elsevier, 2001.
- 64 P. Kong, L. Nelson and B. Detering, *Non-thermal plasma systems and methods for natural gas and heavy hydrocarbon co-conversion*, 2005, US Patent 6,896,854.
- 65 X. Tu and J. Whitehead, *Applied Catalysis B: Environmental*, 2012, **125**, 439–448.
- 66 D. Petrović, T. Martens, J. Van Dijk, W. Brok and A. Bogaerts, *Journal of Physics D: Applied Physics*, 2009, **42**, 205206.
- 67 H. Song, J. Choi, S. Yue, H. Lee and B. Na, *Catalysis Today*, 2004, **89**, 27–33.
- 68 T. Wampler and E. Levy, *Analyst*, 1986, **111**, 1065–1067.
- 69 Intratec, *Ethylene Production via Steam Cracking of Naphtha - Cost Analysis. Ethylene E72A*, Intratec techreport, 2016.
- 70 H. Wittcoff, B. Reuben and J. Plotkin, *Industrial Organic Chemicals, Third Edition*, 2013, 139–209.
- 71 J. Van Durme, J. Dewulf, C. Leys and H. Van Langenhove, *Applied Catalysis B: Environmental*, 2008, **78**, 324–333.
- 72 H. Wittcoff, B. Reuben and J. Plotkin, *Industrial Organic Chemicals, Third Edition*, 2013, 637–679.