
DOI link
https://doi.org/10.1039/C7GC03662K

ePrints link
http://eprint.ncl.ac.uk/246794

Date deposited
26/03/2018

Embargo release date
13/03/2019

Copyright
This is the authors’ accepted manuscript of an article that has been published in its final definitive form by the Royal Society of Chemistry, 2018
This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
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 year). In the European Union (EU), and the UK, it is estimated that plastic waste contributes up to 10-13 % of municipal solid waste (MSW), of which 12.1 % (2.9 million tonnes) is HDPE. 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 consumption. 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 2014 or 31 % in the EU in the same year) 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). 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. They are photodegradable (i.e. are decomposed by the sunlight) into very small particles that can be transferred between ecosystems. Polyethylene is 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 by choking wildlife and distributing harmful organisms or toxic chemicals such as persistent organic pollutants (POPs). 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). 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 residue. 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 feedstock. PS and PET yield an aromatic yield while HDPE, LDPE and PP wax is formed by aliphatic hydrocarbons in the C11-C20 range. On top of that, temperature, heating rate, reaction time and the addi-
tion of catalysts also play an important role on product yields.\textsuperscript{19} Mastral et al.\textsuperscript{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 C\textsubscript{12-20} aliphatic hydrocarbons (67 wt%) followed by C\textsubscript{21-20} hydrocarbons (25 wt%), C\textsubscript{21-22} hydrocarbons (5 wt%) and around 3 wt% containing methane (0.03 wt%), C\textsubscript{2} (0.15 wt%), C\textsubscript{3} (0.57 wt%), and C\textsubscript{4} (2.27 wt%).\textsuperscript{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 use 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 C\textsubscript{2}-C\textsubscript{10} fraction to 44.55 wt% and the gas fraction to 24.44 wt% however only 0.62 wt% ethylene yield was obtained.\textsuperscript{22}

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.\textsuperscript{23,24} However, two major issues of zeolites are: i) 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 activity,\textsuperscript{25} and ii) their high cost ($30-$120 per ton for natural zeolites depending on particle size, the smaller the higher the price).\textsuperscript{26} López et al.\textsuperscript{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,\textsuperscript{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 catalyst have also been proposed for this application,\textsuperscript{29-31} including sulphated zirconia (SZ, SO\textsubscript{4}\textsuperscript{2-} – ZrO\textsubscript{2}) for polystyrene thermal cracking\textsuperscript{32} and for thermal decomposition of HDPE and coal mixtures.\textsuperscript{33} 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.\textsuperscript{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.\textsuperscript{24,31} The SZ will be prepared by a direct synthesis method as proposed by Eterigho et al.\textsuperscript{35} due to the enhancement in catalyst characteristics resulting in an increase in yield.\textsuperscript{36}

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 (10\textsuperscript{4}-10\textsuperscript{5} 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 electrons is not required in cold plasma. The exited 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-up.\textsuperscript{37} 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.\textsuperscript{38} and Deminsky et al.\textsuperscript{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 CO\textsubscript{2}) and and high value carbon products. Khani et al.\textsuperscript{40} reported the ability of cold plasma (DBD) to decompose n-hexadecane, lubricating oil (C\textsubscript{13}-C\textsubscript{42}) and heavy oil (C\textsubscript{6}-C\textsubscript{98}) into lighter fractions at temperatures up to 250 °C: up to 6.91 cm\textsuperscript{3}/min of ethylene was recovered from liquid n-hexadecane and a 56.8 % reduction on heavy hydrocarbons into C\textsubscript{4}-C\textsubscript{12} in the lubricating oil was achieved. Hao et al.\textsuperscript{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.\textsuperscript{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 Meichner et al.\textsuperscript{43}, Kogelschatz\textsuperscript{44} or Kogelschatz and Eliasson\textsuperscript{45} 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 plasma.\textsuperscript{46} Cold plasma may influence or add additional reaction pathways/kinetics 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) was 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 (CH₂=CH₂) 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 CO₂ 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 ± 0.54 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.*

<table>
<thead>
<tr>
<th>Waste HDPE (plastic bag)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate Analysis</td>
<td></td>
</tr>
<tr>
<td>Volatile matter/[wt.%]</td>
<td>77.70 ± 1.64</td>
</tr>
<tr>
<td>Ash/[wt.%]</td>
<td>10.36 ± 0.30</td>
</tr>
<tr>
<td>Fixed Carbon/[wt.%]</td>
<td>11.94 ± 1.67</td>
</tr>
<tr>
<td>Moisture/[wt.%]</td>
<td>0.10 ± 0.07</td>
</tr>
<tr>
<td>Ultimate Analysis</td>
<td></td>
</tr>
<tr>
<td>Carbon/[wt.%]</td>
<td>73.33 ± 0.38</td>
</tr>
<tr>
<td>Hydrogen/[wt.%]</td>
<td>13.28 ± 0.37</td>
</tr>
<tr>
<td>Nitrogen/[wt.%]</td>
<td>0.00 ± 0.30</td>
</tr>
<tr>
<td>Oxygen²/[wt.%]</td>
<td>13.40 ± 0.44</td>
</tr>
<tr>
<td>Calorimetry</td>
<td></td>
</tr>
<tr>
<td>High Calorific Value/[MJ/kg]</td>
<td>44.81 ± 0.36</td>
</tr>
<tr>
<td>TGA</td>
<td></td>
</tr>
<tr>
<td>Decomposition Temperature/[°C]</td>
<td>425-565</td>
</tr>
<tr>
<td>Activation Energy/[kJ/mol]</td>
<td>375.59 ± 39.69</td>
</tr>
<tr>
<td>Order of Reaction/[-]</td>
<td>1.70</td>
</tr>
<tr>
<td>DSC</td>
<td></td>
</tr>
<tr>
<td>Melting Temperature/[°C]</td>
<td>126.66 ± 0.25</td>
</tr>
</tbody>
</table>

### 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 cm³. 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](image_url)

### 2.3 Catalyst characterisation

A commercial zeolite HZSM-5 was obtained from Sigma-Aldrich (surface area = 211 m²/g and SiO₂/Al₂O₃ = 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 N₂ physisorption isotherms determined at 77 K using a Thermo Scientific Surfer and Brunauer-Šěmíttová-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 ± 15m²/g), which was higher than others reported at 108 m²/g (Etherigo et al.³⁵) or 119.3 m²/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 m²/g (no aging) to 104 m²/g (1 day aging at 150 °C)⁴⁹,⁵⁰. Used SZ presented a much lower surface area of just 10.83 m²/g suggesting that catalyst pores are covered with coke after reaction causing catalyst deactivation.

X-ray diffractograms (XRD) were obtained in a Panalytical XPert Pro Multipurpose Diffractometer (MPD) fitted with an X’elerator and a secondary monochromator (Cu-Kα 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: $\text{Zr(SO}_4\text{)}_2 \rightarrow \text{ZrO}_2 + \text{SO}_3$ and $\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2$. Results were similar to those showed by Eterigho et al.\textsuperscript{35,36} although the crystalline fraction of SZ was slightly higher in this case. The latter can also explains 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 bi-sulphate (VI) ($\text{Zr(SO}_4\text{)}_2$) 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.

Fresh and used SZ catalyst were scanned from 4000-6000cm$^{-1}$ 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$_2^-$ 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 $\delta_{O-H}$ bending frequency and the O-H stretch of the water molecules in the sulphate groups. These results agreed well with previous studies of SZ catalyst.$^{32}$ 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.

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 $^\circ$C when the SED increased from 0 J/mL to 90 J/mL as shown in Figure 4. According to Bagri and Williams\textsuperscript{53} conventional pyrolysis of HDPE at at 500 $^\circ$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 $^\circ$C and 90 J/mL) approached more the amount of gas recovered through catalytic pyrolysis (77 wt% at 600 $^\circ$C and 5 wt% of HSZM-5) than that of conventional pyrolysis (15 wt% at 600 $^\circ$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 - 10eV\textsuperscript{54}) than the bond dissociation energies present in HDPE (C-H = 415kJ/mol and C-C = 331kJ/mol\textsuperscript{54}) 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 $\beta$-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 $^\circ$C). The addition of only 5 wt% HSZM-5 slightly decreased the pyrolysis temperature from 700 $^\circ$C (59 wt% of gas yield in conventional pyrolysis) to 600 $^\circ$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)\textsuperscript{55–57} and catalytic (carbocation mechanism pictured in Figure 6)\textsuperscript{57–59}. In the latter, the $\beta$-scission step is dominant and promotes the forma-
tion of smaller chains thereby enhancing the formation of lighter compounds, i.e. increases the gas yield \(^{58,59}\).

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 yield \(^{61}\). The weakest C-C bond in a linear hydrocarbon chain tends to be the 4\(^{th}\) carbon (bond dissociation energy of 282.4 kJ/mol compared to 335 kJ/mol for terminal C-C bond \(^{62}\)). 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 break 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 chain \(^{58}\). Then, the carbocation can either: i) accept a proton (H\(^+\)) from the Brønsted 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 \(\beta\)-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 elsewhere \(^{63}\) but it will not be
density and gas temperature in the discharge\textsuperscript{65,66}. This translates into a more reactive environment with more energetic electrons\textsuperscript{67} increasing the formation of carboxyl 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 occur\textsuperscript{68}. 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\textsubscript{2}-C\textsubscript{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\textsubscript{4} with higher proportion of lighter hydrocarbons (C\textsubscript{1} and C\textsubscript{2}) for all tested conditions.

Figure 8 showed cold plasma assisted pyrolysis of HDPE presented a considerable amount of C\textsubscript{2} and CH\textsubscript{4} followed by other hydrocarbons (C\textsubscript{3}-C\textsubscript{5}). Compared to conventional pyrolysis where the proportion of C\textsubscript{2} is below 10 wt\%\textsuperscript{12} cold plasma doubled the proportions of C\textsubscript{2} up to 20 wt%. This increases the value of the gas stream as ethylene (CH\textsubscript{2}=CH\textsubscript{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\textsuperscript{69,70} with most ethylene manufactured from fossil fuels (mainly from steam reforming of naphtha obtained from crude oil\textsuperscript{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\textsubscript{20+} followed by C\textsubscript{12}-C\textsubscript{19} and finally a small proportion of C\textsubscript{6}-C\textsubscript{11} as shown in Figure 9. This behaviour suggested that as previously mentioned in section 3, cold plasma promotes the \(\beta\)-scission step, yielding lighter hydrocarbons i.e. the volatiles released (C\textsubscript{9}-C\textsubscript{20+}) from the pyrolysis undergoes secondary cleav-

---

**Figure 6** Schematic representation to illustrate carbocation mechanism of HDPE over zeolites\textsuperscript{57,58}
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)

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 zone: 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. This two synergistic effects explained the increase in 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 pores  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 loosing 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 process  . 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 SO . Since catalytic experiments with SZ were performed below SO 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%).

**Acknowledgments**

HDPE waste were kindly provided by O’Brien Recycling Solutions (Wallsend, Newcastle upon Tyne, UK). CHN analysis and X-ray diffraction spectra were obtained at Advanced Chemical and Materials Analysis (ACMA) at Newcastle University and we would like to thank Richard Baron and Maggie White who respectively performed those analysis. X-ray photoelectron spectra were obtained at the National EPSRC XPS Users’ Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility. Laura S Diaz-Silvarrey designed and carried out the experiments and prepared the manuscript; Anh N. Phan and Kui Zhang revised manuscript.
**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


42. A. Harling, V. Demidyuk, S. Fischer and J. Whitehead, Applied Catalysis B: Environmental, 2008, 82, 180–189.

