



Pyrolysis-plasma/catalytic reforming of post-consumer waste plastics for hydrogen production

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ABSTRACT

Different types of single waste plastics and a range of real-world mixed waste plastics from several different industrial and commercial sources have been processed in a pyrolysis-plasma/catalytic experimental reactor system for the production of hydrogen. The hydrocarbons produced from the pyrolysis stage were catalytically (Ni/MCM-41) steam reformed in a low temperature, non-thermal plasma/catalytic reactor. The polyolefin plastics, high density polyethylene, low density polyethylene and polypropylene produced the highest yield of hydrogen at 18.0, 17.3 and 16.3 mmol g⁻¹plastics respectively. The aromatic structured polystyrene produced a lower hydrogen yield of 11.9 mmol g⁻¹plastics and polyethylene terephthalate with an aromatic and oxygenated structure produced only 10.2 mmol g⁻¹plastics and a high yield of carbon oxide gases. The real-world mixed plastic waste produced yields of hydrogen in the range of 13.4–16.9 mmol g⁻¹plastics. The lowest hydrogen yield of 13.4 mmol g⁻¹plastics was produced from the mineral water bottle packaging waste due to the high content of polyethylene terephthalate in the plastic waste mixture.

1. Introduction

The consumption of plastic products in Europe is more than 53 million tonnes per year, of which; 33.5% is used in consumer packaging; 23.9% in building and construction; 9.7% in the automotive sector; 7.5% for electrical and electronic products; 4.9% in houseware, leisure and sports; and 4.4% in the agricultural industry with the remainder used in a wide variety of other sectors [1]. These plastics have a service lifetime of less than one year to more than 50 years before they become waste, for example, plastic packaging quickly becomes disposed to waste, whereas plastics used for automotive parts last more than 10 years before the automobile may be scrapped. Also, long term use of plastics in applications such as for house doors and windows and plastic piping for utilities can last for decades. Eventually, the plastics from different sectors become waste plastics, for example, around 29.5 million tonnes of post-consumer waste plastics are produced in Europe each year [1].

There is much concern and heightened publicity worldwide, around the issue of waste plastics and their impact on the environment. For example the majority of the 29.5 million tonnes of waste plastic collected in Europe in 2021, was either incinerated in waste to energy plants (12.4 Mt/y) or sent to waste landfill (6.9 Mt/y), with the

remaining 10.2 Mt/y recycled. The process options for the recycled waste plastics are dominated by mechanical recycling which produces a recycle material used to manufacture new, but low value, plastic products. An alternative process route for waste plastics is chemical recycling to produce high value commodities. The strategy to produce high value products from waste plastics to encourage more recycling through innovation and new processes has been identified as a beneficial option by the European Union [2].

Producing hydrogen from waste plastics via a chemical recycling process such as pyrolysis represents innovation and the production of a high value product. Hydrogen is a widely used commodity chemical used in oil refining, production of ammonia for manufacture of fertiliser, and also used as a feedstock to produce precursor chemicals for the production of plastics and pharmaceuticals. Future prospects for hydrogen, also predict expansion of demand in clean energy areas such as road transport and use in fuel cells as routes to the decarbonisation of the economy to mitigate the effects of climate change [3].

Commercially hydrogen is produced from fossil fuel natural gas (methane) by steam reforming of the methane in the presence of a catalyst, therefore, using waste plastics as a feedstock for hydrogen production would provide an alternative 'recycled waste' resource and would also represent a novel waste recycling option. Different process

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reactor systems have been reported for producing hydrogen from waste plastics based on the catalytic steam reforming process, involving pyrolysis of the plastics to produce volatile hydrocarbons which are subsequently catalytically steam reformed [4,5]. For example, different reactor designs and configurations for the two-stage pyrolysis-reforming process have included, (i) fixed bed - fixed bed [6,7], screw kiln - fixed bed [8], fluidised bed - fluidised bed [9] and spouted bed - fluidised [10]. Recently, the authors have investigated hydrogen production from waste plastics using a novel two-stage, fixed bed pyrolysis reactor coupled to a non-thermal plasma/catalytic steam reforming reactor [11, 12]. We reported that the presence of the non-thermal plasma catalysis reaction environment promoted steam reforming reactions of the pyrolysis hydrocarbons, with higher hydrogen yields produced as the plasma power was increased and also when the steam input was increased [11]. Another study [12] investigated the influence of different catalyst support materials and showed that higher hydrogen yields were found for catalyst support materials possessing low dielectric constant, high surface area and higher pore volumes, which in turn influenced plasma discharge, plasma-catalyst interaction and thereby, the extent of hydrocarbon reforming [12].

The non-thermal plasma/catalytic reaction environment has been investigated for use in a wide variety of process operations, including fuel and chemical production and use in air pollution control systems [13]. This interest is stimulated by the unique properties of the non-thermal plasma/catalysis reaction environment including its non-equilibrium characteristics, low energy costs and the ability to initiate physical and chemical reactions at low temperature ($<250\text{ }^{\circ}\text{C}$). A non-thermal plasma is generated as an electrical discharge between two electrodes with a large potential difference which induces an intense electrical field in the gas between the electrodes, thereby producing a high energy plasma. The plasma produced is a highly ionised gas consisting of high energy electrons, ions, radicals and excited species. The electron energy can reach 1 – 10 eV equivalent to temperatures of over 10,000 $^{\circ}\text{C}$ while the overall gas temperature remains low ($<250\text{ }^{\circ}\text{C}$) [14]. The non-thermal equilibrium character of the plasma enables kinetically and thermodynamically unfavourable reactions to occur at low temperatures. The existence of the catalyst in the plasma zone produces a synergistic effect to further enhance rates of reaction. The plasma can be generated on the surface and in the pores of the catalyst inducing strong plasma-catalyst interactions, thereby, enhancing reaction between the pyrolysis derived hydrocarbons and the catalyst [15, 16]. Therefore, pyrolysis of waste plastics with downstream non-thermal plasma/catalytic reforming promotes steam reforming of the hydrocarbons to produce hydrogen, but at the low temperatures of only $\sim 250\text{ }^{\circ}\text{C}$. Thereby, providing an alternative, low temperature, low energy process compared with conventional thermal catalytic hydrocarbon reforming which typically operates at temperatures of $\sim 800\text{ }^{\circ}\text{C}$.

The types of plastic used in the different sectors of the economy will influence the yield and composition of the products from the chemical recycling of waste plastics. Plastic packaging is mainly composed of polyethylene (PE) in the form of high density PE (HDPE) and low density PE (LDPE), polypropylene (PP), polyethylene terephthalate (PET) and lower quantities of polystyrene [17]. Building and construction plastics are mainly polyvinyl chloride (PVC) with smaller amounts of PE, expanded polystyrene and polyurethane. The plastics used in the automotive industry and household, leisure and sports sectors are predominantly PP with lower quantities of several other plastics and the agricultural plastics are mainly PE and PP. Municipal solid waste (MSW) consists of HDPE, LDPE, PP and PET with significantly lower amounts of PVC [18]. The processing of real-world waste plastics will consequently lead to differences in hydrogen yield from the pyrolysis-plasma/catalysis of waste plastics. Individual plastics have particular distinct polymer structures, for example, linear structure (e.g. polypropylene), linear-branched structure (e.g. low density polyethylene), or may contain an aromatic ring (e.g. polystyrene) or an aromatic structure with heteroatoms (e.g. polyethylene terephthalate).

Consequently, the pyrolysis products will be different, for example, the pyrolysis of polyethylene produces n-alkanes, alkenes and alkadienes with molecular range between $\text{C}_1 - \text{C}_{60}$, similarly pyrolysis of polypropylene also produces a series of alkenes and lower concentrations of a series of alkanes and alkadienes since they both have a polyalkene polymer structure [5]. Pyrolysis of polystyrene produces mainly aromatic styrene and other aromatic compounds, whereas polyethylene terephthalate pyrolysis yields mostly terephthalic acid and benzoic acid and gaseous CO and CO_2 due to the aromatic, oxygen-containing polymer structure of PET [5]. These evolved pyrolysis compounds will produce different products in the reactive plasma/catalytic steam reforming process. Therefore, it is important to understand how the individual plastics behave in the pyrolysis-non-thermal catalytic steam reforming process, particularly in relation to hydrogen yield.

In this paper, several different single plastics, representative of those found in high concentrations in municipal solid waste (LDPE, HDPE, PP, PS and PET) were investigated using a two-stage pyrolysis, non-thermal plasma/catalyst reactor in regard to the production of hydrogen and other gases. Also, a mixture of these five plastics was prepared in the proportions found in MSW, to represent MSW waste plastic of known composition. In addition, 'real-world' mixed plastics from several different industrial and commercial sources were used in the reactor system to produce hydrogen. The waste plastic mixtures used were from the processing of, MSW, agricultural waste, mineral water bottles, household wastes (excluding PET) and from building construction sites.

2. Materials and methods

2.1. Waste plastics

The single waste plastics investigated were HDPE, PP and PS which were recycled waste plastics donated by Regain Polymers Castleford, UK and were in the form of 2–3 mm sized pellets. LDPE and PET were virgin plastics purchased from Sigma-Aldrich Ltd., UK, also in the form of 2 – 3 mm pellets. A blended mixture of the five plastic types was also prepared based on the composition reported by Delgado et al. [18] to simulate a mixture of the reported composition of real-world waste plastics typical of municipal solid waste, consisting of 42 wt% LDPE, 20 wt% HDPE, 16 wt% PS, 12 wt% PET and 10 wt% PP and designated as, MP_{SIM} .

In addition, various mixtures of real-world waste plastics found in municipal and industrial waste treatment plants were investigated. These wastes were real world post-consumer, commercial, municipal and industrial waste plastics which were collected and recycled. The samples consisted of (i) mixed plastics from household waste packaging (MP_{MSW}) (ii) mixed plastics from household waste (excluding PET) (MP_{HH}), (iii) mixed plastics from agricultural waste (MP_{AGRIC}), (iv) mixed plastics from mineral water bottle waste (MP_{MW}) (v) and mixed plastics from construction site waste (MP_{CONST}). All the mixed waste plastics were donated by the University of Pannonia, Hungary, except for the MP_{HH} sample which was obtained from a plastics recycling centre in Belgium.

The thermal decomposition profiles of the single and mixed plastics were determined using a thermogravimetric analyser (TGA), (Shimadzu TGA-50, UK, Ltd., UK). Initial sample preparation, particularly for the real-world plastic samples, required sub-sample preparation using coning and quartering to ensure a more homogeneous representative sample was used for TGA. Additionally, the plastics samples were ground to powder with a particle size of $< 0.5\text{ mm}$ using a cryogenic milling procedure under liquid nitrogen. Approximately 10 mg of the finely ground plastic powder was placed in the TGA and heated to $600\text{ }^{\circ}\text{C}$ at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. The plastic samples were also analysed for the CHONS element content using a CE Instruments Ltd., UK, Flash EA2000 instrument. The results for proximate analysis from the TGA data and elemental analysis of all the plastics are shown in Tables 1 and 2. Fig. 1 shows the thermodegradation TGA profiles of the single individual plastics. The peak degradation temperature for the

Table 1

Proximate and ultimate analyses of the individual waste plastics. (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

	PET	PS	HDPE	LDPE	PP
<u>Proximate analysis (wt.%)</u>					
Moisture content	0.06	1.72	0.14	0.01	5.68
Volatile matter content	85.64	98.25	97.84	99.95	95.00
Fixed carbon	13.10	nd	0.16	nd	nd
Ash	1.20	1.23	3.63	0.08	0.39
<u>Ultimate analysis (wt.%)</u>					
C	62.20	86.19	81.78	81.01	80.58
H	4.18	12.43	18.59	16.06	10.42
O	33.62	nd	nd	nd	8.89
N	nd	nd	0.54	0.94	0.95
S	nd	nd	nd	nd	nd

nd = not detected

decomposition of the plastics was, PS, 427 °C, PET, 446 °C, LDPE 480 °C, PP, 483 °C and for HDPE, 488 °C. Fig. 2 shows the thermodegradation TGA profiles of the mixed waste plastic samples. The peak degradation temperature for decomposition of the mixed waste samples was, MP_{MW}, 447 °C, MP_{HH}, 460 °C, MP_{SIM}, 465 °C, MP_{CONST}, 480 °C, MP_{AGRIC}, 492 °C and for MP_{MSW}, 492 °C.

2.2. Catalyst

The catalyst used throughout the experimental work was a 10 wt% Ni/MCM-41 catalyst, based on its advantages of efficiency and activity in the plasma catalytic reforming environment [12]. Details of the catalyst manufacturing process and methodology for catalyst characterisation have been described before [11], but are also briefly outlined here. The method used was wet-impregnation, using nickel nitrate hexahydrate as the nickel source and the MCM-41 support materials was obtained from Nankai University, China. The mixture of metal salt and support was dried, followed by calcination at a temperature of 750 °C followed by catalyst hydrogen reduction at 800 °C. The final particle size of the catalyst used in the experiments was 50 – 212 µm.

The prepared 10 wt% Ni/MCM-41 catalyst was analysed by N₂ adsorption-desorption on a Micrometrics Tristar 3000 analytical system to verify the surface area (Brunauer-Emmet-Teller (BET) method) and porosity (Barrett-Joyner-Hallender (BJH) method). X-ray diffraction (XRD) enabled the crystallinity of the catalyst to be identified and used a Bruker D8 diffractometer with Cu K α radiation and a 2 θ range of 10–80°. Temperature programmed reduction (TPR) enabled the determination of the reduction profile of the catalyst and was carried out with a Shimadzu TGA-50 instrument with hydrogen (5% H₂/95% N₂). The morphology of the catalysts was obtained by scanning electron microscopy (SEM) using a Hitachi SU8230 SEM. The three-dimensional internal structure and Ni-metal dispersion of the catalyst was also

Table 2

Proximate and ultimate analyses of the mixed waste plastics. (Nomenclature: MP_{SIM}: simulated mixed plastics, MP_{MSW}: mixed plastics from municipal solid waste, MP_{AGRIC}: mixed plastics from agricultural wastes, MP_{MW}: mixed plastics from mineral water waste, MP_{HH}: mixed plastics from household wastes (excluding PET), MP_{CONST}: mixed plastics from construction sites).

	MP _{SIM}	MP _{HH}	MP _{AGRIC}	MP _{MW}	MP _{MSW}	MP _{CONST}
<u>Proximate analysis (wt.%)</u>						
Moisture content	0.78	1.17	0.64	0.33	0.65	0.74
Volatile matter content	95.7	89.64	94.78	84.39	92.39	93.96
Fixed carbon	3.14	8.35	4.44	13.26	6.11	5.16
Ash	0.38	0.84	0.14	1.20	0.34	0.14
<u>Ultimate analysis (wt.%)</u>						
C	81.55	81.49	80.76	63.89	80.50	81.85
H	10.12	10.57	10.89	5.27	11.04	11.38
O	7.19	6.85	7.13	29.95	7.70	6.12
N	1.14	1.09	1.23	0.89	0.76	0.64
S	nd	nd	nd	nd	nd	nd

nd = not detected

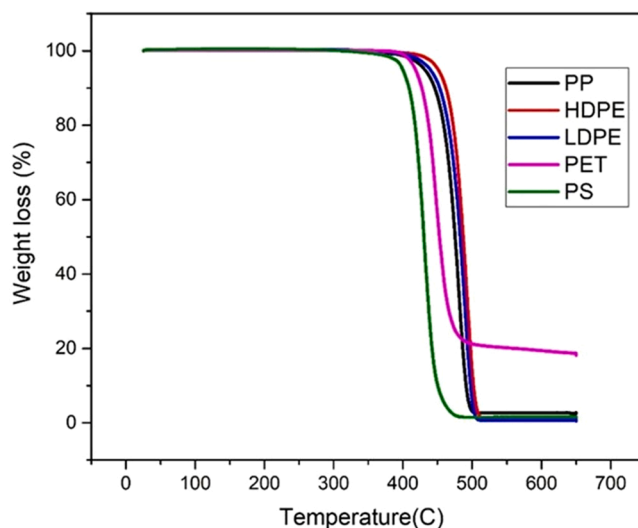


Fig. 1. Weight loss thermal degradation profile of the individual plastics. (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

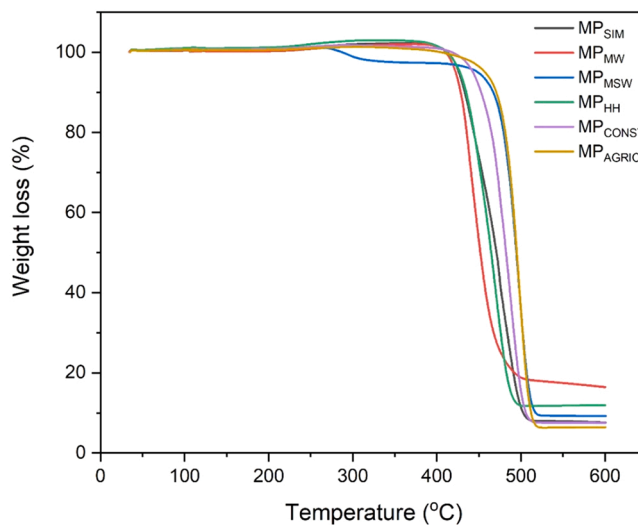


Fig. 2. Weight loss thermal degradation profile of the mixed plastics. (Nomenclature: MP_{SIM}: simulated mixed plastics, MP_{MSW}: mixed plastics from municipal solid waste, MP_{AGRIC}: mixed plastics from agricultural wastes, MP_{MW}: mixed plastics from mineral water waste, MP_{HH}: mixed plastics from household wastes (excluding PET), MP_{CONST}: mixed plastics from construction sites).

obtained using focused ion beam (FIB) with SEM and energy dispersive X-ray spectroscopy (EDXS). The system used was a FEI Helios G4 CX dual beam SEM. FIB is the process used for the sectioning/milling of the catalyst prior to SEM-EDXS analysis which mapped the presence of nickel in the catalyst. Temperature programmed oxidation of the used catalysts was undertaken using a Shimadzu TGA-50 thermogravimetric analyser with air as the carrier gas, to determine the types of carbon deposits on the catalyst surface.

2.3. Experimental reactor system

The two-stage experimental reactor system consisted of a 1st stage pyrolysis reactor and a 2nd stage non-thermal plasma reactor and was used to investigate the production of hydrogen. The 1st stage pyrolysis of the different plastics results in release of a range of hydrocarbons which are passed to the 2nd stage for steam reforming using plasma/catalysis. A schematic diagram of the reactor system is shown in Fig. 3. Details of the reactor system have been reported before [11,12]. The 1st pyrolysis reactor was made of stainless steel, (250 mm length x 20 mm diameter) heated by an external electric heater (1.5 kW). The plastics (1.0 g) were placed into a crucible located in the hot zone of the reactor. The 2nd stage was a Dielectric Barrier Discharge (DBD) non-thermal plasma reactor (Fig. 4) which was attached directly to the 1st stage pyrolysis reactor by a ceramic connector tube. Fig. 4 shows the flow of the pyrolysis gases and purge gas nitrogen gases through the reactor and catalyst. The plasma is generated in a plasma reactor by passing an electric current between the outer and inner electrode with a high potential difference generating an electric discharge in the gap between the electrodes, ionising the gas and generating a plasma. The gap between the electrodes contained the catalyst which was supported on quartz wool. The dimensions of the plasma reactor were a quartz tube (200 mm length x 22 mm diameter) around which was wrapped a copper mesh which served as the external electrode, inside the tube was a stainless

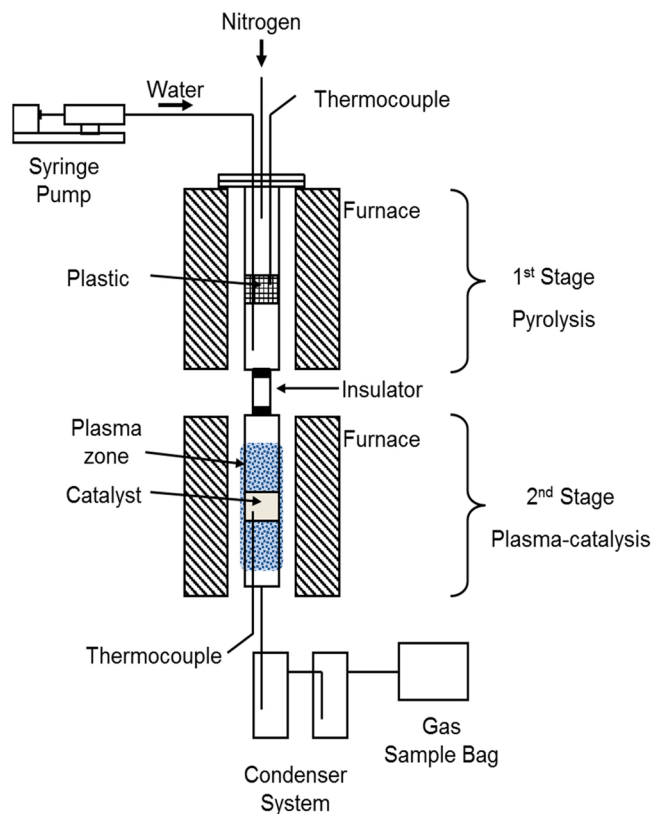


Fig. 3. A schematic diagram of the pyrolysis-non-thermal plasma reactor system.

steel rod which served as the inner electrode. The outer copper electrode was earthed and the inner electrode was supplied with high voltage alternating current power supply (AC, 0 – 240 V; 1500 Hz frequency). A constant discharge power was supplied to the non-thermal plasma reactor by adjusting the input voltage. The catalyst (1.0 g) was placed in the middle of the discharge region of the non-thermal plasma reactor. Although the non-thermal plasma reactions take place over a wide localised temperature range, the second stage plasma reactor was heated (250 °C) externally by an electric furnace to ensure a constant reactor temperature and to prevent steam or pyrolysis hydrocarbon condensation within the reactor. The temperature (250 °C) of the plasma reactor was determined from calibration of the temperature profile of the furnace with a thermocouple in the absence of plasma discharge. The thermocouple was subsequently removed for plasma/catalytic experiments to prevent interference with the plasma discharge. An oscilloscope (Tektronix MDO3024) monitored and recorded data throughout the experiments. Steam required for reforming was provided by metered water injection. The whole reactor system was purged with nitrogen which carried the product gases through air-cooled and solid CO₂ condensers and then into a 25 L gas sample bag for later off-line analysis.

The experimental methodology consisted of pre-heating the DBD plasma reactor to a constant temperature of 250 °C, then starting the pyrolysis of the plastics, heating from 20 °C to 500 °C. In the case of plasma reforming, steam was injected when the pyrolysis temperature reached 120 °C. The mass of residual char from the plastics pyrolysis and condensed liquids in the condensers was measured and mass of gas produced determined from the gas chromatographic data.

The collected product gases in the gas sample bag were analysed by packed column gas chromatography using three separate Varian UK Ltd, CP-3380 chromatographs; the first measured C₁ – C₄ hydrocarbons on a HaySep 80–100 mesh packed column and a flame ionisation detector (GC/FID) with N₂ carrier gas; the second measured permanent gases (H₂, O₂, N₂ and CO) with a 60 – 80 mesh molecular sieve column and a thermal conductivity detector (GC/TCD) with Ar carrier gas; the third measured CO₂ with 80 – 100 mesh HaySep column and GC/TCD with Ar carrier gas. The total mass of gas mass and individual gas mass yields were calculated from the individual gas concentrations, gas flow rate, known gas density and the Ideal gas law. The details of the gas analysis methodology have been reported before [11]. Repeat experiments were carried out and reported data is the average of the repeats.

3. Results and discussion

3.1. Freshly prepared catalyst characterization

The 10 wt% Ni/MCM-41 catalyst used to investigate hydrogen production from the waste plastics using the two-stage pyrolysis-plasma/catalytic reforming reactor system was characterised. Fig. 5 shows the nitrogen adsorption-desorption isotherms (Fig. 5(a)) and calculations on this data enabled the surface area and pore size distribution of the freshly prepared Ni/MCM-41 catalyst to be determined (Fig. 5(b)). The adsorption-desorption isotherms with nitrogen determined at a temperature of 77 K were classified using the IUPAC system as Type IV with Type H3 hysteresis. This classifies the catalyst as having a mesoporous structure with interconnection of pores, and that the nitrogen is adsorbed through multilayer adsorption and capillary condensation. The pore size distribution (Fig. 5(b)) shows a peak of nitrogen adsorption in the size range of 2 – 50 nm confirming the mesoporous type porosity of the catalyst. Characterisation of the freshly prepared 10 wt% Ni/MCM-41 catalyst showed that the BET surface area was 417.0 m² g⁻¹, pore volume was 0.307 cm³ g⁻¹ and pore diameter was 3.6 nm.

Fig. 6(a) shows the XRD diffraction profile of the 10 wt% Ni/MCM-41 catalyst, showing that the main peaks (2 θ at 44.5° and 51.7°) are nickel metal, demonstrating that the prepared nickel catalyst was effectively reduced to produce the active metal. Also present was a peak (2 θ at 65.5°) representing nickel aluminate suggesting interaction

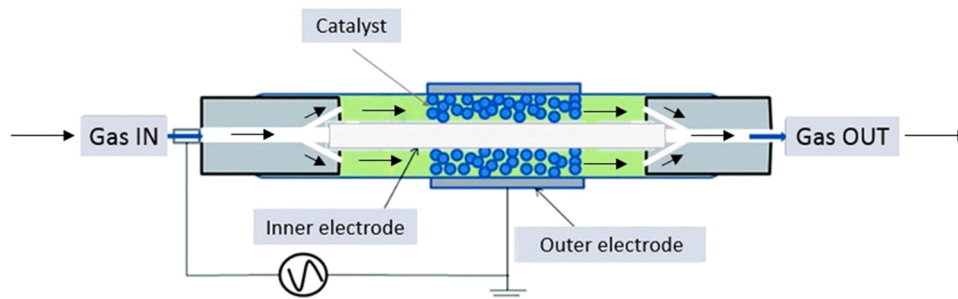


Fig. 4. Schematic diagram of the non-thermal plasma/catalysis reactor.

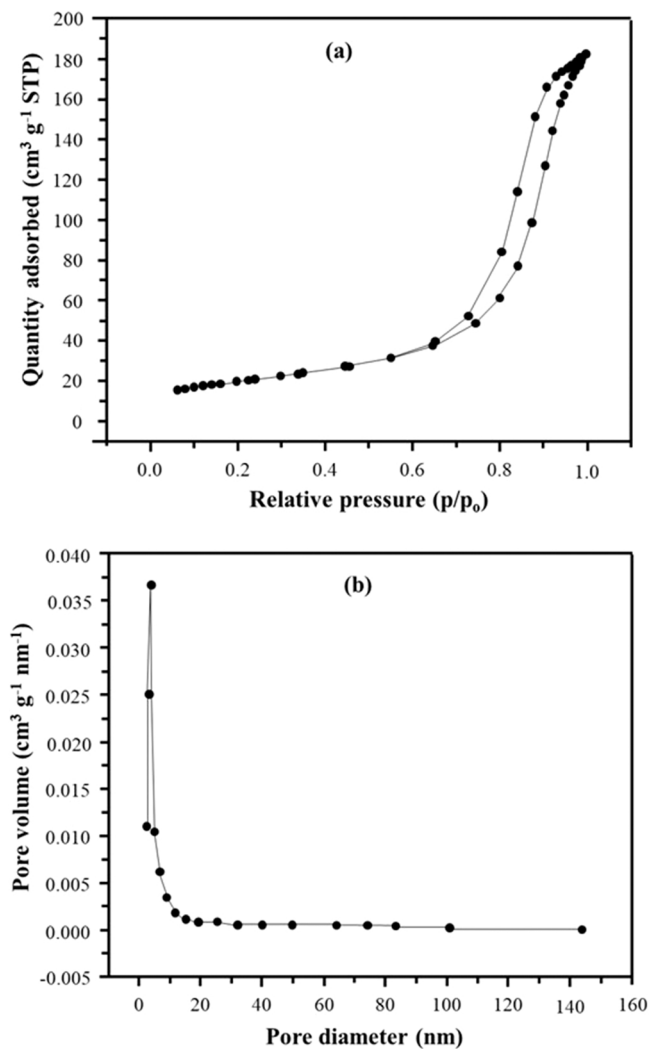


Fig. 5. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of the Ni/MCM-41 catalyst.

between the nickel and the MCM-41 support. Fig. 6(b) shows the H₂-TPR thermogram for the freshly prepared calcined 10 wt% Ni/MCM-41 catalyst and indicates the reduction of the NiO to Ni occurs at the high temperature range of ~700–800 °C, suggesting strong Ni-O interaction with the MCM-41 support material.

Fig. 7 shows the SEM image of the catalyst (Fig. 7(a)) and also the cross sectional FIB-SEM (Fig. 7(b)) and FIB-SEM-EDXS nickel mapping (Fig. 7(c)) on the MCM-41 support. The cross section (Fig. 7(b)) and nickel-mapping (Fig. 7(c)) shows that the nickel is well dispersed evenly throughout the catalyst cross section and into the internal pores of the

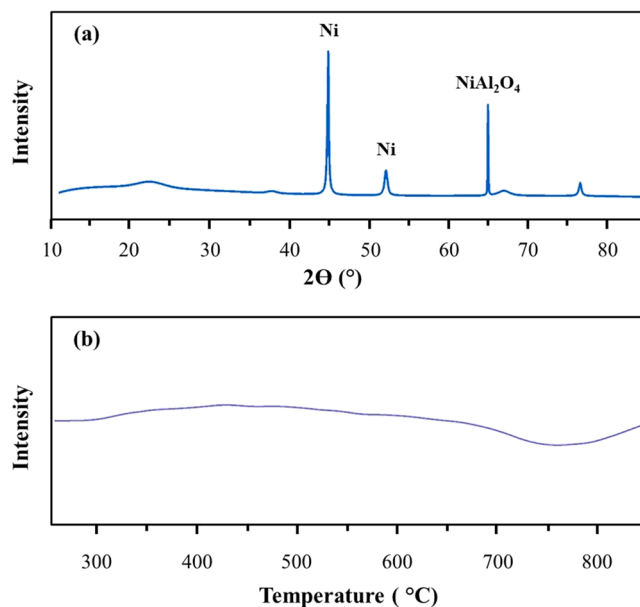


Fig. 6. X-ray diffraction (XRD) spectra (a) and hydrogen-temperature programmed reduction (H-TPR) thermogram of the Ni/MCM-41 catalyst.

catalyst, and again no large particles or particle agglomeration can be seen. The data indicating that the active metal interaction with the pyrolysis hydrocarbons produced from the plastics pyrolysis is facilitated by the effective dispersion of the nickel throughout the catalyst including into the porous structure.

3.2. Pyrolysis/non-thermal plasma catalysis of individual waste plastics

The pyrolysis with non-thermal plasma reactor system was used to examine the effect of plasma/catalytic cracking of pyrolysis volatiles without any input of steam in relation to the five individual plastics (HDPE, LDPE, PET, PS and PP) for hydrogen production. A plastic-catalyst ratio of 1:1 was used in each case in the absence of steam, the plasma electrical discharge was created with an input power of 80 W. The total gas yield and the hydrogen yield are shown in Table 3.

Table 3 shows that the use of a second stage non-thermal plasma produced a significant gas yield from the pyrolysis/plasma cracking of the plastics. Our previous work [11] showed that compared to pyrolysis-catalysis of polyethylene at 250 °C, introduction of a plasma i. e. pyrolysis with non-thermal plasma produced a 55% increase in gas yield and that plasma/catalysis with a 10 wt% Ni/Al₂O₃ catalyst produced a 70% increase in gas yield. This is an indication that the introduction of the second stage non-thermal plasma has resulted in cracking of the pyrolysis vapours into gases. This is possible since the plasma interacts with the pyrolysis product gases producing a highly reactive environment of high energy electrons, excited chemical species, ions and

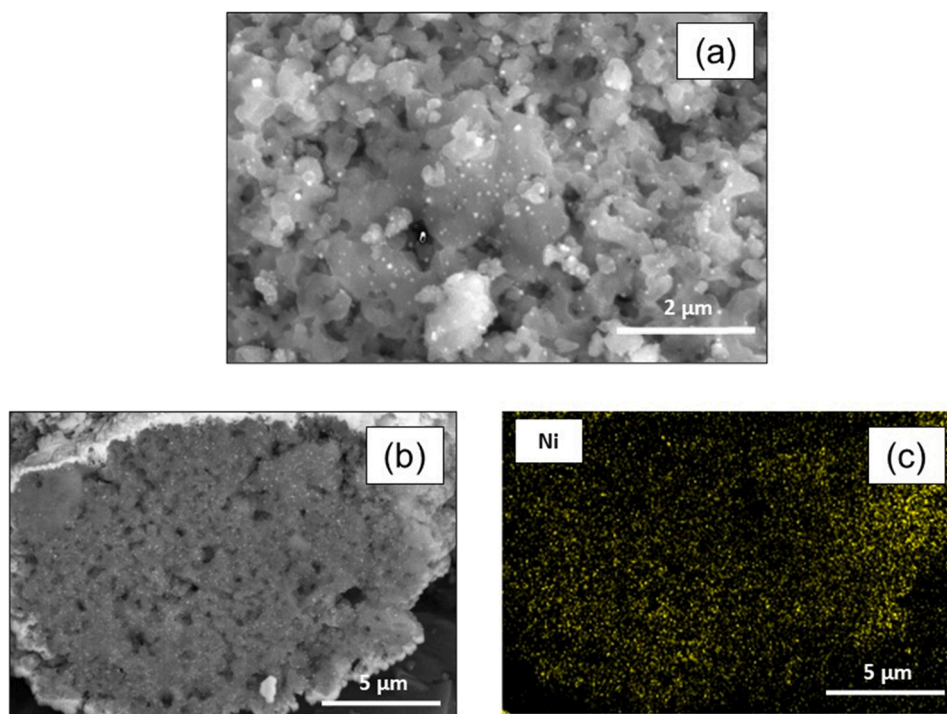


Fig. 7. (a) SEM image of the 10 wt% Ni/MCM-41 catalyst (b) cross sectional FIB-SEM and (c) FIB-SEM-EDXS nickel mapping of the 10 wt% of the Ni/MCM-41 catalyst.

Table 3

Products yield from the pyrolysis/non-thermal plasma catalytic cracking of individual waste plastics (plasma input power 80 W; no steam). (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

Product yield (wt.%)	Plastic type				
	LDPE	HDPE	PP	PS	PET
Gas	17.5	18.4	20.1	10.7	52.3
Liquid	82.0	76.0	79.0	87.6	23.3
Char	0.0	4.0	0.0	0.0	24.0
H ₂ yield (mmol g ⁻¹ plastic)	6.0	6.2	5.6	3.8	2.9
CO yield (mmol g ⁻¹ plastic)	0.0	0.0	0.0	0.0	4.6
Gas composition (Vol. %)					
H ₂	41.5	43.5	32.5	58.8	13.5
CO	0.0	0.0	0.0	0.0	38.8
CO ₂	0.0	0.0	0.0	0.0	34.7
CH ₄	10.7	10.8	10.4	10.6	5.9
C ₂ -C ₄	47.8	45.7	57.1	30.6	7.1

radicals. Within this highly reactive environment, high enough energy is produced to dissociate the C – C and C – H bonds of the hydrocarbon pyrolysis volatiles produced in the 1st stage even at the low experimental plasma reactor temperature of 250 °C [19].

PET which contains oxygen and aromatic containing groups produced the highest gas yield of 52.3 wt% with a char yield of 24.0 wt%. LDPE and HDPE produced similar gas yields at 17.5 wt% and 18.4 wt%, respectively, while the lowest gas yield was obtained with PS at 10.7 wt%. Polypropylene gave a gas yield at 20.1 wt% which is higher than the gas yield obtained from the other polyolefin plastics. The relatively lower bond dissociation energy of C – CH₃ compared with that of the C – H bond can result in more cracking of the PP to yield more gas than PE and PS. The similar gas yields from HDPE, LDPE and PP is due to the similarity in their structures which contains the group CH₂CH-X. These polymers degrade via random scission in the first stage to produce

similar products that are further cracked in the second stage plasma reactor.

The product volumetric gas composition produced from the process (Table 3), shows that the gas consisted of high volumetric concentrations of hydrogen, CH₄ and other light hydrocarbon gases (C₂ – C₄). The exception being the gas composition from polyethylene terephthalate where the gas was mainly CO₂, and CO produced from the thermal decomposition of the oxygenated species in the polymer structure.

Fig. 8 shows the gas yield in mmol g⁻¹plastic from the pyrolysis/plasma cracking (no steam) of the individual waste plastics in the presence of 10 wt% Ni/MCM-41 catalyst. The hydrogen yield from LDPE and HDPE was similar at 6.0 mmol g⁻¹plastic and 6.2 mmol g⁻¹plastic, respectively. The hydrogen yield from PP was 5.6 mmol g⁻¹plastic while PS and PET gave a hydrogen yield of 3.8 mmol g⁻¹plastic and 2.9 mmol g⁻¹plastic, respectively. CO and CO₂ were obtained from PET which were derived from the decomposition of the PET ester group. The introduction of the non-thermal plasma has altered the product selectivity. Further cracking of the pyrolysis volatiles was achieved with the plasma resulting in increased hydrogen yield and decreased yield of the lighter hydrocarbons. According to Diaz et al. [20], when the high energy electrons collide with the pyrolysis volatiles, there is a formation of highly reactive carbenium ions and radicals along the hydrocarbon chains that promote bond scission reaction mechanisms similar to those found in the thermal decomposition of hydrocarbons. The high surface area of the Ni/MCM-41 catalyst used in this work also provided large contact area and reactive sites for reactions to occur within the non-thermal plasma reactor [21,22].

Fig. 9 shows the temperature programmed analysis – derivative weight loss (DTG) thermograms of the used catalysts from the pyrolysis-plasma catalytic cracking (no steam) of pyrolysis volatiles from single plastics. The DTG thermograms show peaks of weight loss due to the oxidation of the carbon deposits on the surface of the catalysts at temperatures between ~250 °C to ~425 °C and higher temperatures of weight loss, ranging from ~450–600 °C. The DTG thermogram, for polystyrene processing, in particular, showing a major weight loss peak at the higher temperature. It has been reported that the carbon oxidation

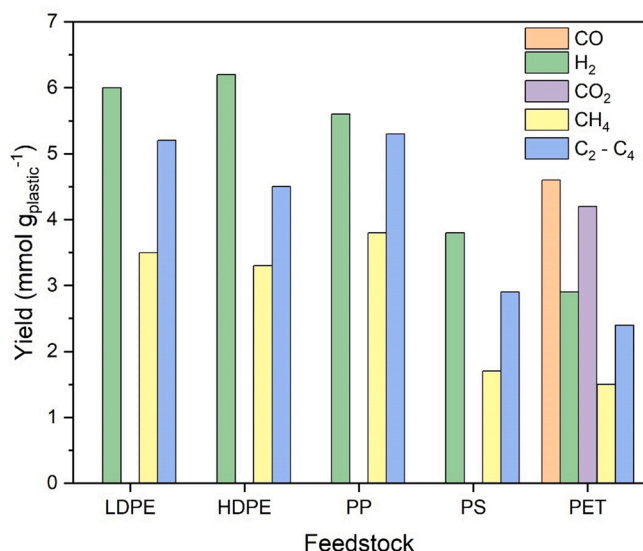


Fig. 8. Gas composition from the pyrolysis/non-thermal plasma catalytic cracking of individual waste plastics (input power 80 W; no steam). (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene.).

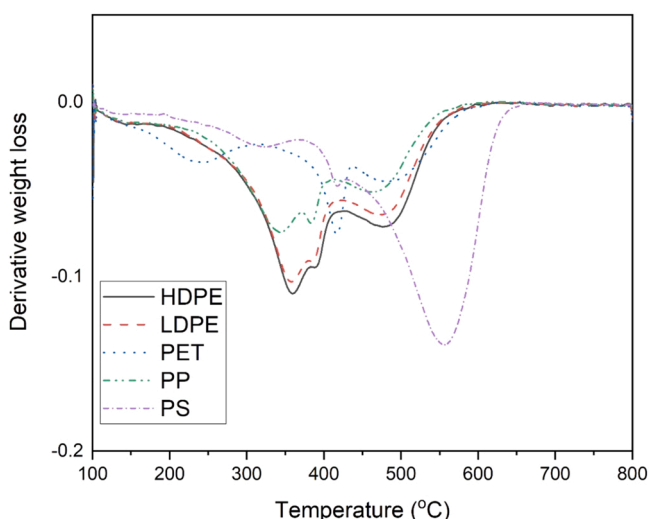


Fig. 9. Temperature programmed analysis – derivative weight loss (DTG) thermograms of the used catalysts for the pyrolysis-plasma catalytic cracking (no steam) of pyrolysis volatiles from single plastics. (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene.).

peak that occurs at low temperature is assigned to amorphous carbon which is more easily oxidised, while the higher carbon oxidation temperature is associated with more crystalline graphitic carbon which possesses high thermal stability [23,24]. The pyrolysis stage of the pyrolysis-catalytic cracking process will generate a suite of hydrocarbons, some of which will be high molecular weight, which will produce carbon deposits on the catalyst during the second stage catalysis. It has been shown that catalyst coking is minimised in a plasma environment partly due to the lowered catalyst temperature and increased surface oxidation in the plasma/catalyst environment [25].

3.3. Pyrolysis/non-thermal plasma catalytic reforming of individual waste plastics

This section describes the influence of adding steam to the second stage plasma/catalytic reactor with the aim of reforming the pyrolysis volatiles under plasma/catalytic conditions. The low temperature reforming of the pyrolysis hydrocarbon volatiles derived from the pyrolysis of the five different plastics was studied in the presence of the 10 wt% Ni/MCM-41 catalyst and a plasma power input of 80 W. Steam at 2 g hr⁻¹ was introduced into the system for the hydrocarbon reforming process. A plastic-catalyst ratio of 1:1 was used in each experiment. Table 4 shows the total product yield and the hydrogen and CO yields in mmol g_{plastic}⁻¹ from the individual waste plastics, also, shown are the volumetric gas compositions. In this study, the product yield calculations are reported based on the input of plastic and water (steam) and output of gas, liquid (pyrolysis oil + water) and char.

Table 4 shows that adding steam into the plasma/catalytic reaction environment promotes catalytic steam reforming and results in a markedly increased total yield of gas, increasing by ~100% compared to the results where no steam was introduced (Table 3). The increased yield of hydrogen and carbon monoxide suggests that the increase in total gas yield is due to the reforming of the hydrocarbons derived from the pyrolysis of the plastics. Table 4 also shows the volumetric gas composition, showing a decrease in C₁ – C₂ hydrocarbons, again indicative of hydrocarbon steam reforming of the pyrolysis volatiles. The highest gas yield from the pyrolysis/non-thermal plasma reforming of the plastics was obtained from the PET at 67.4 wt%. The total gas yield followed the trend: PET > PP > LDPE > HDPE > PS. The thermal pyrolysis/catalytic steam reforming of the individual waste plastics has been reported to produce high syngas yields at reforming temperatures of ~800 °C. In this study the non-thermal plasma was heated to only ~250 °C and the results presented here show that steam reforming has occurred at this low temperature. This is due the effects of the plasma, catalyst and plasma-catalyst interactions on the pyrolysis volatiles. The catalyst can provide new reaction pathways that lead to reduced reaction activation energies while the plasma can induce plasma chemical reactions. The plasma-catalyst interaction can result in synergy where both plasma and catalyst modify each other. For example, the addition of the catalyst into the plasma zone can modify the properties of plasma by promoting the electric field and altering the discharge type, while plasma can improve the adsorption of species at the catalyst surface as well as create hot spots on the surface and within the pores of the catalyst [26]. This plasma-catalyst synergy results in improved performance of the system and made the steam reforming process possible at the low temperature.

The gas yield of the product gases, in mmol g_{plastic}⁻¹, from the

Table 4

Products yield from the pyrolysis/non-thermal plasma catalytic reforming of individual waste plastics in the presence of 10 wt% Ni/MCM-41 catalyst (input power 80 W, steam WHSV 2 g h⁻¹ g_{catalyst}⁻¹). (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

Product yield (wt.%) (in relation to mass of plastic and steam)	Plastic type				
	LDPE	HDPE	PP	PS	PET
Gas	37.9	33.3	39.2	21.8	67.4
Liquid	61.9	62.7	60.8	77.5	8.6
Solid	0.0	4.0	0.0	0.0	24.0
H ₂ yield (mmol g ⁻¹ plastic)	17.3	18.0	16.3	11.9	10.2
CO yield (mmol g ⁻¹ plastic)	3.0	2.5	1.7	1.4	7.1
Gas composition (Vol. %)					
H ₂	61.3	65.9	53.1	67.8	24.3
CO	13.2	9.1	8.3	7.3	32.5
CO ₂	9.5	6.5	4.5	5.1	29.0
CH ₄	5.9	7.6	9.2	6.9	8.1
C ₂ -C ₄	10.1	10.8	24.9	12.9	6.1

pyrolysis/non-thermal plasma reforming of the individual waste plastics is shown in Fig. 10. The result of adding steam to the plasma reactor produces formation of H and OH radicals leading to the enhanced hydrogen yield from each of the individual plastics [27] compared to the experiments where steam was not introduced (Table 3). The OH radicals create additional reaction pathways for hydrocarbon conversion. In addition, the production of CO and the reduction of methane and C₂–C₄ hydrocarbon yields obtained from all the plastics and compared with the gas yields in the absence of steam (Fig. 8) showed that steam reforming reactions occurred with all the plastics. The production of CO₂ also indicated that the water gas shift reaction also took place to produce CO₂ and more hydrogen [28]. Pyrolysis-thermal catalytic steam reforming using nickel catalysts has been reported to have a high activity for hydrocarbon reduction as well as steam reforming of complex mixtures of hydrocarbons from different waste plastics while also promoting water gas shift reactions [23,29]. The interaction of the plasma and catalyst also resulted in a synergistic effect that leads to more decomposition and reforming of the pyrolysis volatiles. HDPE produced the highest hydrogen yield at 18.0 mmol g_{plastic}⁻¹, followed by LDPE at 17.3 mmol g_{plastic}⁻¹. The gas composition from HDPE and LDPE are similar due to their comparable polymer structure and compositions. The PS and PET gave lower hydrogen yields at 11.9 mmol g_{plastic}⁻¹ and 10.2 mmol g_{plastic}⁻¹ respectively. The lower hydrogen yield from PS and PET compared to the polyolefin plastics was due to the aromatic structure of the hydrocarbons obtained from their pyrolysis that are more difficult to crack compared to the alkenes and alkanes obtained from the polyolefin plastic polymer pyrolysis [5].

Fig. 11 Shows the temperature programmed analysis – derivative weight loss (DTG) thermograms of the used catalysts for the pyrolysis-plasma catalytic reforming (with steam) for the single plastics (80 W power input). The DTG weight loss peaks representing oxidation of the carbon deposits on the catalyst during the TPO analysis. The lower temperature (~250 °C to ~425 °C) carbon oxidation peaks representing oxidation of amorphous carbon and the higher temperature (~450–600 °C) carbon oxidation peaks representing oxidation of the more stable graphitic type carbon. Compared to the plasma cracking DTG thermograms shown in Fig. 9, the DTG thermograms for the plasma catalytic reforming shown in Fig. 11, suggest lower amount of amorphous carbon is present, with a shift to more graphitic carbon deposition on the catalysts. Previous work has shown that the presence of steam

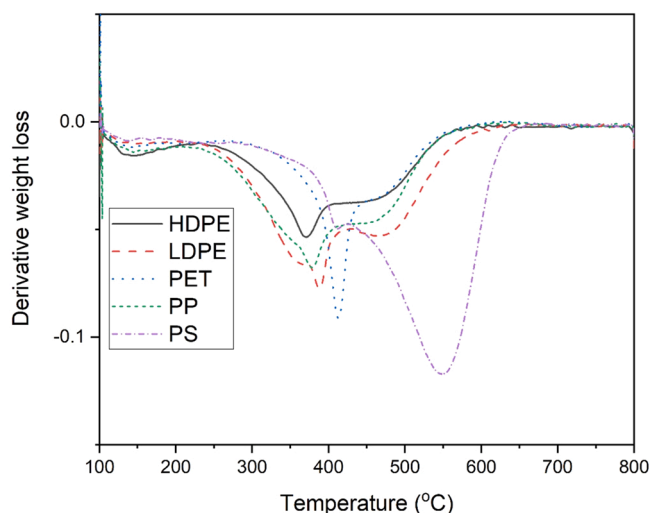


Fig. 11. Temperature programmed analysis – derivative weight loss (DTG) thermograms of the used catalysts for the pyrolysis-plasma catalytic reforming (with steam) of pyrolysis volatiles from single plastics. (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

during the catalytic reforming process, serves to oxidise the less stable amorphous carbon [30].

3.4. Pyrolysis/non-thermal plasma catalytic reforming of mixed waste plastics

Hydrogen production from the pyrolysis with non-thermal plasma/catalytic steam reforming of the different mixed real-world industrial and commercial waste plastics was investigated. The plastics included a simulated mixture of plastics (MP_{SIM}) prepared using the individual single plastics. In addition, mixed plastic waste from different industrial and commercial sectors were investigated, which included (i) household waste packaging (MP_{MSW}) (ii) household waste (excluding PET) (MP_{HH}), (iii) agricultural waste (MP_{AGRIC}), (iv) plastic mineral water bottle waste (MP_{MW}) (v) building construction site waste (MP_{CONSTR}). In each case, pyrolysis-plasma/catalysis was undertaken at the following conditions, pyrolysis temperature, 500 °C, plastic-steam ratio 1:1, steam flow rate, 2 g hr⁻¹, plasma input power of 80 W, 10 wt% Ni/MCM-41 catalyst. The results for product yield in relation to mass of plastic, syngas yield (H₂ and CO) and gas volumetric composition for each mixed plastic are shown in Table 5.

The mineral water bottle mixed plastic packaging waste gave the highest gas yield at 62.4 wt%. The simulated mixture of single plastics and mixed plastics from municipal solid waste, mixed plastics from agriculture, and mixed plastics from household packaging (excluding PET) produced similar gas yields of around 32–34 wt%. The lowest gas yield (27.3 wt%) was produced with the mixed waste plastic from construction sites.

Fig. 12 shows the gas yield (mmol g_{plastic}⁻¹) from the processing of the mixed waste plastics. Hydrogen is the main gas obtained from all the plastics with various yields of carbon dioxide, carbon monoxide, methane and C₂–C₄ hydrocarbons. This suggests that the pyrolysis hydrocarbons derived from the mixed plastics have been reformed at low temperature in the DBD reactor. The highest hydrogen yield (16.9 mmol g_{plastic}⁻¹) was obtained from the simulated mixed plastics followed by mixed plastics from agriculture (16.8 mmol g_{plastic}⁻¹). The high fraction content of the polyolefin plastics in the simulated waste plastic resulted in a gas composition similar to that of the polyethylene. The agricultural waste plastics used in this study was comprised of mainly polyethylene and polypropylene and this could be the reason for the high hydrogen yield from pyrolysis reforming of the MP_{AGRIC}. The

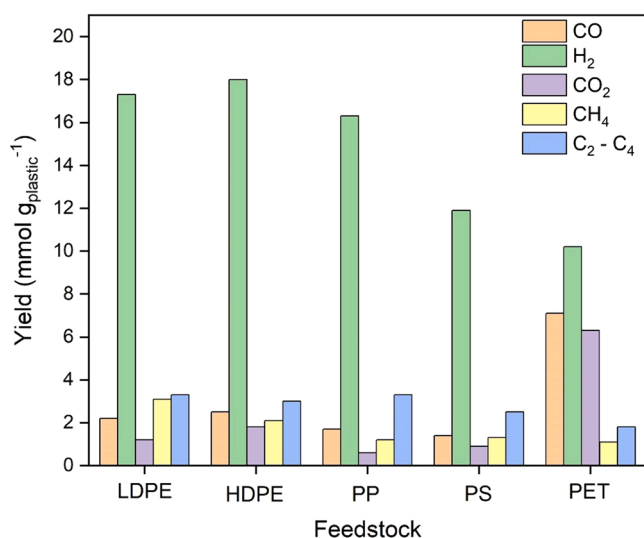


Fig. 10. Gas composition from the pyrolysis/non-thermal plasma catalytic reforming of individual waste plastics in the presence of 10 wt% Ni/MCM-41 (input power 80 W, steam WHSV 2 g h⁻¹ g_{catalyst}⁻¹). (Nomenclature: PP: polypropylene, HDPE: high density polyethylene, LDPE: low density polyethylene, PET: Polyethylene terephthalate, PS: polystyrene).

Table 5

Products yield from the pyrolysis/non-thermal plasma reforming of real-world waste plastics in the presence of 10 wt% Ni/MCM-41 catalyst (input power 80 W, steam WHSV $2 \text{ g h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$). (Nomenclature: MP_{SIM}: simulated mixed plastics, MP_{MSW}: mixed plastics from municipal solid waste, MP_{AGRIC}: mixed plastics from agricultural wastes, MP_{MW}: mixed plastics from mineral water waste, MP_{HH}: mixed plastics from household wastes (excluding PET), MP_{CONST}: mixed plastics from construction sites).

Product yield (wt %) (in relation to mass of plastic and steam)	Plastic type					
	MP _{SIM}	MP _{MSW}	MP _{AGRIC}	MP _{MW}	MP _{HH}	MP _{CONST}
Gas	36.1	34.2	34.6	62.4	32.7	27.3
Liquid	61.9	63.8	62.4	48.4	65.3	69.7
Solid	2.0	2.0	3.0	17.0	2.0	3.0
H ₂ yield (mmol g _{plastic} ⁻¹)	16.9	15.4	16.8	13.4	16.0	15.4
CO yield (mmol g _{plastic} ⁻¹)	1.4	1.6	1.4	6.7	1.1	2.6
CO ₂ yield (mmol g _{plastic} ⁻¹)	59.7	58.6	54.4	52.5	49.4	51.7
Gas composition (vol%)	8.9	7.8	9.4	8.0	11.0	10.2
H ₂	12.5	23.3	20.7	3.8	27.4	17.5
CO						
CO ₂						
CH ₄						
C ₂ – C ₄						

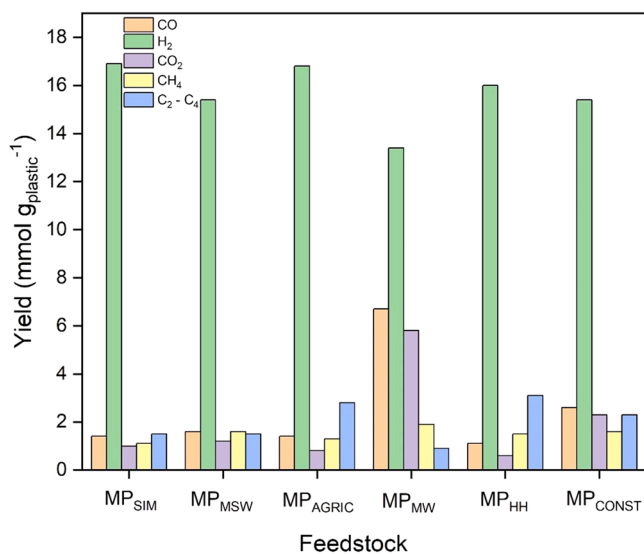


Fig. 12. Gas composition from the pyrolysis/non-thermal plasma reforming of real world waste plastics in the presence of 10 wt% Ni/MCM-41 (input power 80 W, steam WHSV $2 \text{ g h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$). Nomenclature: MP_{SIM}: simulated mixed plastics, MP_{MSW}: mixed plastics from municipal solid waste, MP_{AGRIC}: mixed plastics from agricultural wastes, MP_{MW}: mixed plastics from mineral water waste, MP_{HH}: mixed plastics from household wastes (excluding PET), MP_{CONST}: mixed plastics from construction sites.

mixed plastics from household wastes (excluding PET), (MP_{HH}) gave a higher hydrogen yield and lower CO and CO₂ yield compared to the mixed plastics from municipal solid waste (MP_{MSW}) reflecting the effect of PET content in the MSW. The mixed plastics from household wastes (excluding PET) (MP_{HH}) and the mixed plastics from construction sites (MP_{CONST}) gave similar hydrogen yields at 16.0 and 15.4 mmol g_{plastic}⁻¹ respectively, while the lowest hydrogen yield (13.4 mmol g_{plastic}⁻¹) was obtained with the mixed plastics from mineral water packaging waste (MP_{MW}). On the other hand, the highest CO and CO₂ yield was obtained with the mixed plastics from mineral water packaging waste (MP_{MW}) at 6.7 and 5.8 mmol g_{plastic}⁻¹, respectively. The mineral water packaging

consisted mainly of polyethylene terephthalate with a high oxygen content. The mixed plastics from construction sites (MP_{CONST}) which was composed of polystyrene, polyurethane, polyethylene, and polypropylene produced a gas composed of 15.4 mmol g_{plastic}⁻¹ with CO and CO₂ yield of 2.6 and 2.3 mmol g_{plastic}⁻¹, respectively.

Fig. 13 shows the temperature programmed analysis – derivative weight loss (DTG) thermograms of the used catalysts for the pyrolysis-plasma catalytic reforming (with steam) of pyrolysis volatiles from mixed waste plastics. The thermograms show several overlapping peaks for each of the different waste plastics mixtures, showing the presence of a complex mixture of amorphous and crystalline graphitic carbon deposited on the catalysts which oxidise at low temperature and high temperature respectively. The thermograms reflect the mixtures and interaction of the different individual plastics (**Fig. 11**) making-up the composition of the different plastic mixtures.

The work reported here has shown that moderate (~16–18 mmol g_{plastic}⁻¹), but significant yields of hydrogen can be obtained from different common single plastics and also from commercial and industrial mixed waste plastic mixtures. It is established that waste plastics represent a major environmental problem if they are not managed appropriately. It has been reported that worldwide, more than 350 million tonnes of waste plastics are generated each year [31]. Significant tonnages of waste plastic are associated with specific commercial and industrial sectors, for example, 142 Mt/y from waste packaging, 34 Mt/y from the automotive sector and 16 Mt/y from the building/construction industry [31]. Such large tonnages of plastics could be exploited as a source of hydrogen instead of being regarded as a waste problem.

4. Conclusions

The two-stage pyrolysis with non-thermal plasma/catalytic steam reforming has been investigated in relation to single plastics and waste plastic mixtures. Initial experiments conducted using pyrolysis-plasma catalysis without any steam, showed that secondary cracking of pyrolysis volatiles from the individual plastics showed that the composition and structure of the plastic polymer affected the product yield and distribution. It is suggested that the cracking proceeded via electron impact reactions that were able to break the C – C and C – H bonds in the plastics

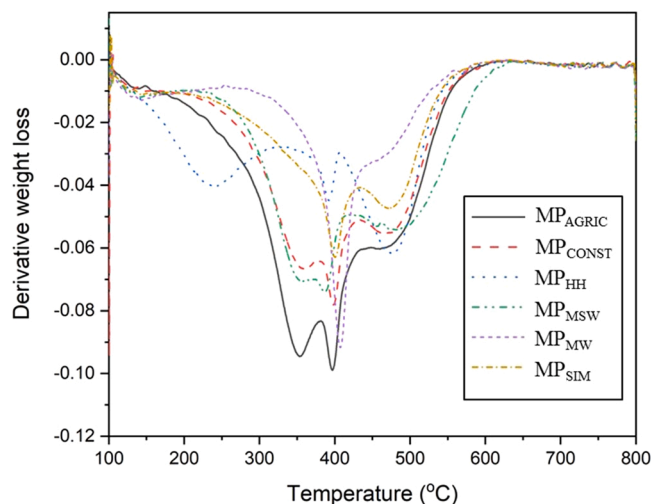


Fig. 13. Temperature programmed oxidation – derivative weight loss (DTG) of the used catalysts for the pyrolysis-plasma catalytic reforming (with steam) of pyrolysis volatiles from mixed waste plastics. (Nomenclature: MP_{SIM}: simulated mixed plastics, MP_{MSW}: mixed plastics from municipal solid waste, MP_{AGRIC}: mixed plastics from agricultural wastes, MP_{MW}: mixed plastics from mineral water waste, MP_{HH}: mixed plastics from household wastes (excluding PET), MP_{CONST}: mixed plastics from construction sites).

at low temperature. Polypropylene produced the highest amount of gas compared to the other polyolefin plastics due to the bond dissociation energy of the C – CH₃ bond being lower as compared to C – H bonds. On the other hand, polystyrene which contains aromatic groups gave the lowest gas yield.

The introduction of steam into the system for reforming of the pyrolysis derived hydrocarbons showed that steam reforming occurred at the low experimental temperature with the production of hydrogen and carbon monoxide from all the individual waste plastics. The yield of hydrogen was increased compared to the plasma cracking (absence of steam) of the plastics. Water gas shift reactions may also have occurred with all the plastics as evidenced by the production of CO₂. HDPE produced the highest amount of hydrogen at 18 mmol g_{plastic}⁻¹ with LDPE and PP producing similar yields due to similarity in their structure and composition. On the other hand, the PET and PS which contain aromatic groups in their structures, produced the lowest amount of hydrogen and for PET, higher amount of CO and CO₂.

Hydrogen production from pyrolysis/non-thermal plasma reforming of simulated mixed waste plastics and mixed plastics from several different post-consumer and industrial sources was also achieved at 250 °C. Among the mixed plastic wastes investigated, the simulated mixed plastics, produced from mixing of the single plastics, produced the highest amount of hydrogen at 16.9 mmol g_{plastic}⁻¹ followed closely by mixed waste plastics from agriculture. Mixed plastics from municipal solid waste, mixed plastics from household packaging (excluding PET), and mixed plastics from construction all produced hydrogen in the range of 15 – 16 mmol g_{plastic}⁻¹. The lowest hydrogen yield and the highest yield of carbon oxides was obtained with the mineral water packaging waste which was mainly composed of PET. The composition of the mixed plastics played a significant role in the yield and composition of the final products and also hydrogen yield.

CRedit authorship contribution statement

Idris Aminu: Investigation, Writing – original draft preparation. **Mohamad A. Nahil:** Methodology. **Paul T. Williams:** Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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