




# Three-stage pyrolysis–steam reforming–water gas shift processing of household, commercial and industrial waste plastics for hydrogen production

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## Abstract

Five common single plastics and nine different household, commercial and industrial waste plastics were processed using a three-stage (i) pyrolysis, (ii) catalytic steam reforming and (iii) water gas shift reaction system to produce hydrogen. Pyrolysis of plastics produces a range of different hydrocarbon species which are subsequently catalytically steam reformed to produce H<sub>2</sub> and CO and then undergo water gas shift reaction to produce further H<sub>2</sub>. The process mimics the commercial process for hydrogen production from natural gas. Processing of the single polyalkene plastics (high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP)) produced similar H<sub>2</sub> yields between 115 mmol and 120 mmol per gram plastic. Even though PS produced an aromatic product slate from the pyrolysis stage, further stages of reforming and water gas shift reaction produced a gas yield and composition similar to that of the polyalkene plastics (115 mmol H<sub>2</sub> per gram plastic). PET gave significantly lower H<sub>2</sub> yield (41 mmol per gram plastic) due to the formation of mainly CO, CO<sub>2</sub> and organic acids from the pyrolysis stage which were not conducive to further reforming and water gas shift reaction. A mixture of the single plastics typical of that found in municipal solid waste produced a H<sub>2</sub> yield of 102 mmol per gram plastic. Knowing the gas yields and composition from the single plastics enabled an estimation of the yields from a simulated waste plastic mixture and a ‘real-world’ waste plastic mixture to be determined. The different household, commercial and industrial waste plastic mixtures produced H<sub>2</sub> yields between 70 mmol and 107 mmol per gram plastic. The H<sub>2</sub> yield and gas composition from the single waste plastics gave an indication of the type of plastics in the mixed waste plastic samples.

**Keywords** Waste plastic · Hydrogen · Catalyst · Pyrolysis reforming · Water gas shift

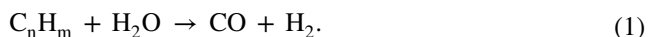
## Introduction

To combat the impacts of climate change there is growing momentum to move away from fossil fuels to alternative low carbon energy sources. Hydrogen is regarded as a clean energy carrier and may be used in automotive engines, gas turbines and fuel cells [1]. Hydrogen can be produced through a wide range of different routes, including hydrocarbon reforming, thermochemical and biological biomass processes and the electrolysis of water [2]. However, 99% of all commercial dedicated hydrogen production plants are based on fossil fuels,

with natural gas as the feedstock dominating production (76%), followed by coal (23%) [1]. The technology of choice for large-scale hydrogen production from natural gas (methane) is via steam methane reforming [1]. The natural gas, which typically contains  $\geq 95\%$  mol methane, may also contain low but significant concentrations of C<sub>2</sub>–C<sub>5</sub> hydrocarbons and trace levels of hydrogen sulphide [3]. The steam reforming processing of natural gas involves removal of sulphur by initial conversion of the sulphur to H<sub>2</sub>S by hydrogenation, followed by removal of the H<sub>2</sub>S in a ZnO fixed bed reactor. The natural gas is then catalytically steam reformed using super-heated steam and a nickel-based catalyst at high temperature (700–1000 °C) and pressure (0.3–2.5 MPa) in a tube reformer reactor. The natural gas hydrocarbons react with the steam to produce mainly hydrogen (~85%–94%) and carbon monoxide (~6%–15%) (Eq. 1), together known as syngas [4].

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The syngas undergoes further reaction to produce more hydrogen by reacting the carbon monoxide with steam via the water gas shift reaction and producing carbon dioxide and hydrogen.



The commercial process of hydrogen production typically uses a high-temperature (310–450 °C) water gas shift reactor followed by a low-temperature (200–250 °C) water gas shift reactor, the reactors are fixed bed and are operated in series. The hydrogen is purified using a pressure swing adsorption reactor.

The dominant use of fossil fuels for the production of hydrogen by catalytic steam reforming is accompanied by emissions of carbon dioxide, which are mainly emitted to the atmosphere. Estimations of 10, 12 and 19 ton of CO<sub>2</sub> for 1 ton production of H<sub>2</sub> from natural gas, oil and coal, respectively, have been reported [1]. Finding alternative feedstocks for the production of hydrogen is, therefore, an imperative and the subject of several recent reports [1, 2, 5]. One such feedstock that has received recent attention is the production of hydrogen from waste plastics [6–9]. Over 350 million tonnes of waste plastics are generated each year [10], representing a substantial potential feedstock for the production of hydrogen. Using waste plastics as the feedstock source for hydrogen would also represent a novel higher level hierarchical treatment option for waste plastics and go some way to mitigate the problems of waste plastics pollution in the environment [10, 11].

There have been several recent excellent reviews highlighting the potential of waste plastics as feedstocks for the production of hydrogen. For example, Dai et al. [8] reviewed the application of pyrolysis technology for recycling plastic waste to produce a range of products, such as fuels, naphtha, light olefins and hydrogen. They highlighted the potential of combined pyrolysis–catalysis reactor systems, as the process encourages higher catalytic activity and product selectivity, particularly in the case of hydrogen production. Foong et al. [12] reported on the application of advanced pyrolysis technologies for the production of gaseous fuel production with particular emphasis on hydrogen. They identified a range of novel pyrolysis technologies for their review, which comprised, catalytic pyrolysis, vacuum pyrolysis, microwave pyrolysis, solar pyrolysis, co-pyrolysis of different feedstocks and CO<sub>2</sub> pyrolysis. Key parameters that influence gas yield and composition, were reported to include feedstock properties and particle size, heating rate, reaction temperature, gas flow rate and reactor configuration. Lopez et al. [7] reviewed the processing of waste plastics via gasification

with the aim of producing syngas and hydrogen. They also identified pyrolysis of plastics coupled with downstream in-line catalytic steam reforming as a promising gasification technology development for the production of syngas with a high content of hydrogen, also notable was a zero content of tar in the product gases. Midilli et al. [6] reviewed the gasification technology option for the processing of waste plastics for the production of hydrogen. They concluded that although there are many challenges in the development of gasification technologies for hydrogen production, the potential for high yields of hydrogen to be produced from waste plastics has been recognised. Yang et al. [9] reported on the application of thermochemical catalytic processes (pyrolysis, gasification, hydrothermal and solvolysis) to produce fuels and chemicals, including hydrogen and other value-added materials. They reported on the range of catalyst developments investigated to improve the yield of the end-products. Noteworthy was their review of current demonstration scale and commercial scale facilities for the thermochemical recycling of waste plastics and the technical and operational challenges associated with scale-up and continuous operation of the technologies. Kumar et al. [13] presented a review of plastic treatment technologies aimed at the production of value-added petrochemicals such as crude-oil substitutes, aromatics, syngas and hydrogen via thermochemical technologies. They also considered the implications of commercial feasibility, and economic and environmental sustainability.

Several research groups have developed reactor systems for hydrogen production from waste plastics that mimic the commercial catalytic steam reforming process [14–17]. Such systems involve a first stage pyrolysis of waste plastics to produce a suite of hydrocarbon volatiles that are directly passed to a second stage reactor for catalytic steam reforming. Czernik and French [17] were the first to also suggest that a further third stage water gas shift reactor could enable further production of hydrogen by steam reaction with the CO produced from steam reforming of plastics pyrolysis volatiles, again mimicking the commercial hydrogen production process.

In our previous report [18], we investigated the three-stage (i) pyrolysis, (ii) catalytic steam reforming and (iii) water gas shift processing of waste plastic to produce hydrogen from waste plastic. The plastic used was polypropylene (PP). In this work, we extend that work to investigate the three-stage process but use the main single plastics found in municipal solid waste (MSW), consisting of high-density polyethylene (HDPE), low-density polyethylene (LDPE), PP, polystyrene (PS) and polyethylene terephthalate (PET). We also investigated a mixture of single plastics representing the proportions found in MSW. In addition, we report on

the production of hydrogen using a three-stage process from ‘real-world’ mixed waste plastics from nine different household, commercial and industrial waste sectors.

## Materials and methods

### Materials

Several single and mixed waste plastics were investigated. The single plastics were HDPE and LDPE supplied by Beijing Ou Yuan Sheng Plastic Production Co., Ltd. (Beijing China). PP, PS and PET were supplied by Regain Polymers Ltd. (Castleford, UK). A simulated waste plastic (SWP) mixture of single plastics was processed, with a composition of 20% (in weight, the same in this Section) of HDPE, 42% of LDPE, 16% of PS, 10% of PP and 12% of PET which was

based on the typical proportions found in MSW [19]. For direct comparison with this known mixture of single plastics, a ‘real-world’ mixture of MSW-derived mixed waste plastics (real-world mixed plastics (RWMP)) was investigated.

The nine different ‘real-world’ mixed waste plastics were supplied from several different household, commercial and industrial waste sectors. The samples were provided by the University of Pannonia, Hungary, from different recycling plants and obtained by the authors from different UK waste recycling plants. The samples comprised: Plastics from electrical and electronic equipment (WEEE); Plastics from the agricultural sector (AGR); Plastic household detergent containers (DC); Plastics from computer monitors and televisions (CRT); Plastics from freezers and refrigerators (F); Automotive motor oil flasks (OF); Automotive vehicle plastic fuel tanks (FT); Food packaging waste plastics (FP) and Building and construction waste plastics (BC).

Elemental analysis of the plastics was carried out using a Thermo EA-2000 elemental analyser for the single waste plastics and the nine household, commercial, and industrial waste plastics, and the results are shown in Tables 1 and 2, respectively. Proximate analysis of the plastics was undertaken using a Schimadzu TGA-50 thermogravimetric analyser (TGA). The plastic sample (15 mg) was heated under nitrogen from 20 °C to 800 °C at 20 °C min<sup>-1</sup> and held at 800 °C for 10 min; the microbalance simultaneously recorded the mass loss of the plastic. From the thermal degradation profile, the mass of moisture, volatiles and char could be determined. The sample was heated to 915 °C, and air was added to promote the combustion of the carbonaceous char, thereby enabling the ash content to be recorded. The results for the plastic samples (‘as received’) are shown in Tables 3 and 4 for the single and mixed waste plastic samples, respectively.

The size of the plastic samples was ~2 mm for the single plastics and ~1 cm for the real-world, household, commercial and industrial mixed waste plastic samples. To ensure some form of homogeneity of the plastic samples, each was thoroughly mixed, and the ‘cone and quarter’ method was used to produce a representative sample. For TGA, the plastic samples were pulverised into ~500 nm sized particles in a cryogenic mill to ensure that a representative, homogeneous sample was used.

In addition, since the real-world mixed waste plastic samples came from various recycling centres, there would inevitably be some contamination due to incomplete separation of the different types of plastic, non-plastic contamination and dirt contamination or the presence of additives and fillers used in the plastics manufacturing process. Such contamination may influence the comparison of sample results between different recycling plants.

**Table 1** Elemental analysis of the single plastics (Unit: %, in weight)

Plastic	N	C	H	O	S
HDPE	0.94	80.58	18.48	nd	nd
LDPE	0.94	81.01	18.06	nd	nd
PP	0.03	84.45	13.81	0.91	nd
PS	0.86	86.19	12.43	0.52	nd
PET	0.55	62.03	11.40	26.02	nd
SWP	0.67	78.40	15.90	5.03	nd
RWMP	0.65	77.89	16.02	5.44	nd

*HDPE* high-density polyethylene, *LDPE* low-density polyethylene, *PP* polypropylene, *PS* polystyrene, *PET* polyethylene terephthalate, *SWP* simulated mixed waste plastics, *RWMP* real-world mixed plastics

**Table 2** Elemental analysis of the household, commercial and industrial waste plastics (Unit: %, in weight)

Plastic	N	C	H	O	S
WEEE	0.70	75.17	5.87	18.26	0.22
AGR	0.89	79.08	12.91	7.12	0.26
DC	1.33	77.43	15.06	5.93	0.25
CRT	4.82	85.10	7.80	2.29	0.26
F	1.15	71.95	6.86	20.05	0.22
OF	0.76	80.03	15.37	3.64	0.20
FT	0.12	83.88	12.80	3.03	0.17
FP	0.16	82.90	13.37	3.57	0.23
BC	0.14	80.91	12.22	6.74	0.22

*WEEE* Plastics from electrical and electronic equipment, *AGR* plastics from the agricultural sector, *DC* plastic household detergent containers, *CRT* plastics from computer monitors and televisions, *F* plastics from freezers and refrigerators, *OF* automotive motor oil flasks, *FT* automotive vehicle plastic fuel tanks, *FP* food packaging waste plastics, *BC* building and construction waste plastics

**Table 3** Proximate analysis of the single plastics (Unit: %, in weight)

Plastic	Ash	Volatile	Moisture	Fixed carbon
HDPE	0.38	99.27	0.72	nd
LDPE	0.08	99.95	0.01	nd
PP	0.79	98.70	0.51	0.01
PS	5.23	98.25	1.72	nd
PET	1.40	84.11	0.03	14.46
SWP	2.92	92.88	0.89	3.31
RWMP	2.54	93.65	1.03	2.92

**Table 4** Proximate analysis of the household, commercial and industrial waste plastics (Unit: %, in weight)

Plastic	Ash	Volatile	Moisture	Fixed carbon
WEEE	0.28	81.04	2.89	15.79
AGR	0.99	99.06	1.26	nd
DC	2.10	94.10	3.81	nd
CRT	3.71	93.02	1.40	1.02
F	0.80	81.99	20.10	nd
OF	0.89	99.10	1.03	nd
FT	0.66	99.23	0.55	nd
FP	1.74	99.15	0.90	nd
BC	0.81	99.17	0.49	nd

The three-stage processing of the plastics used a 10% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the 2nd stage reforming reactor and a 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the 3rd stage water gas shift reactor. The catalysts were prepared by a wet-impregnation method, the details of which are reported previously but are briefly outlined here [18]. The 10% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared from a nickel nitrate hexahydrate precursor and an alumina support to produce a slurry, which was then heated and dried before calcination, crushed and sized to produce 50–212 μm sized particles. The 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O using the same method. The 10% Ni/Al<sub>2</sub>O<sub>3</sub> and 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalysts were reduced at 800 °C for 2 h in the presence of hydrogen (5% H<sub>2</sub>, 95% N<sub>2</sub>).

### Three-stage (i) pyrolysis, (ii) reformer, and (iii) water gas shift reactor system

The three-stage reactor system used for processing the plastics consisted of separate (i) pyrolysis, (ii) catalytic steam reforming and (iii) catalytic water gas shift reactors, as shown in Fig. 1 [18]. The process involved pyrolysis of the plastics under N<sub>2</sub>, which generated the pyrolysis volatiles that were passed with the N<sub>2</sub> carrier gas directly into the 2nd stage where catalytic steam reforming of the evolved hydrocarbons took place, generating H<sub>2</sub> and CO (Eq. 1). The product gases from reforming were carried to the 3rd stage,

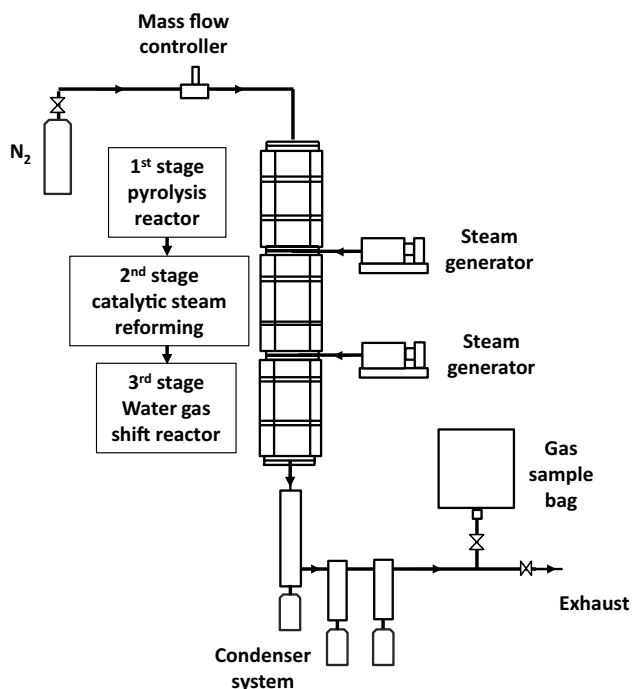
where the water gas shift reaction took place to generate further hydrogen (Eq. 2). Water and dry-ice cooled glass condensers in series condensed the liquid products, which consisted of unreacted water (condensed steam) and the final product gases were collected in a gas sample bag.

The three reactors were constructed of stainless steel, and each was separately heated and controlled using electrical furnaces. The size of the reactors was 30 cm×2.5 cm for (i) pyrolysis, 30 cm×2.5 cm for the (ii) catalytic steam reformer and 14.5 cm for (iii) water gas shift reactors. The mass of plastic used for pyrolysis was 1.0 g with a temperature programme of 20 °C to 500 °C at a heating rate of 20 °C min<sup>-1</sup> and held at 500 °C for 20 min. The 2nd stage reforming used 1.0 g of the 10% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at a temperature of 850 °C with 4 mL h<sup>-1</sup> steam input, and the 3rd stage water gas shift used 0.5 g of 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst at a temperature of 550 °C, also with 4 mL h<sup>-1</sup> steam input. The results are the average of at least two repeat experiments.

The experimental conditions were optimised, based on previously reported work examining a range of process parameters in relation to the 3rd stage (iii) water gas shift process using PP with a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the 2nd reforming stage and Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the 3rd stage [18]. The results are summarised in Fig. 2, where the influence of water gas shift Fe/Al<sub>2</sub>O<sub>3</sub> catalyst temperature, Fe loading on the catalyst, steam input flow rate and different types of catalyst support material are reported in relation to the yield of H<sub>2</sub> from PP plastic.

For Fig. 2, the water gas shift catalyst temperature experiments used a 4 mL h<sup>-1</sup> steam flow rate and 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst; Fe loading experiments (Fe/Al<sub>2</sub>O<sub>3</sub>) were carried out at 550 °C catalyst temperature and 4 mL h<sup>-1</sup> steam flow rate; Steam input experiments used 550 °C and 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst; Catalyst support experiments used 550 °C catalyst temperature and 4 mL h<sup>-1</sup> steam flow rate and 10% Fe loading.

For the work reported here and for the data presented in Fig. 2 for the water gas shift process conditions, the 2<sup>nd</sup> stage catalytic reforming reactor used a 10% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, since this has been shown in previously reported work to produce high yields of H<sub>2</sub> from waste plastics [20–22]. The optimised conditions used in this work for the 3rd stage water gas shift reactor conditions were, a 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst at a temperature of 550 °C, with a steam input rate of 4 mL h<sup>-1</sup>. From Fig. 2, although a higher loading of Fe produced a higher H<sub>2</sub> yield, an increase above 10% Fe was not deemed necessary for the gain in H<sub>2</sub> yield; Also, the support material of Al<sub>2</sub>O<sub>3</sub> produced the highest H<sub>2</sub> yield. The catalyst temperature of 550 °C was chosen as an effective temperature for H<sub>2</sub> production, without being excessive and the steam input rate of 4 mL h<sup>-1</sup> was used, since at higher steam inputs, catalyst flooding reduced H<sub>2</sub> yield.



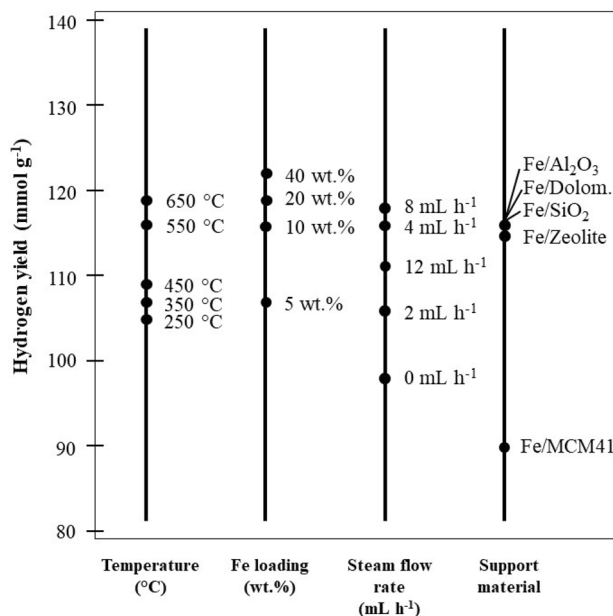
**Fig. 1** Schematic diagram of the three-stage pyrolysis–catalytic–water gas shift fixed bed reactor system

## Gas analysis

The product gases were analysed with three separate Varian CP 3380 gas chromatographs (Varian UK Ltd., Crawley, UK) (i)  $H_2$ ,  $N_2$ ,  $O_2$  and  $CO$  with a Hayesep 60–80 mesh column and thermal conductivity detector (TCD); (ii)  $CO_2$  with a Hayesep 80–100 mm mesh column and TCD and (iii)  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_8$  and  $C_4H_{10}$ , with a Hayesep 80–100 mm mesh column and flame ionisation detector. The mass of each gas was calculated from the volumetric gas concentrations compared to the concentration of standard gases, the physical properties of each gas, the gas flow rate and the Ideal Gas Law.

## Catalyst analysis

The water gas shift catalysts recovered after each experiment were analysed using temperature-programmed oxidation (TPO) to determine the mass of carbonaceous coke deposited on the catalysts in relation to the different and varied types of plastic used in the three-stage process. TPO was carried out with a Shimadzu TGA-50 instrument using a heating regime of ambient temperature to 800 °C heated at 20 °C  $min^{-1}$  in air at a flow rate of 50 mL  $min^{-1}$ . The weight loss of the sample due to carbon oxidation enabled the amount of carbon deposited to be determined.



**Fig. 2** Influence of the 3rd stage water gas shift process conditions with a  $Fe/Al_2O_3$  catalyst of catalyst temperature, Fe loading on the catalyst, steam input flow rate and different types of catalyst support material in relation to the yield of hydrogen from polypropylene (PP) plastic. wt.% means % in weight

## Results and discussion

### Three-stage processing of single plastics

The product yield and hydrogen yield obtained from the different plastics (HDPE, LDPE, PS, PET and PP) using the three-stage pyrolysis–catalytic steam reforming–water gas shift reactor system are presented in Table 5. The product yield consisted of gas and char with the residual mass balance comprised of liquid, which represented the unreacted and condensed steam (water). High gas yields were obtained for all of the single plastics at ~90% (in weight). The initial pyrolysis of plastics will produce a wide range of hydrocarbon volatiles, consisting of mainly aliphatic hydrocarbons from the polyalkene plastics (HDPE, LDPE, PP), mainly aromatic hydrocarbons from PS and mainly oxygenated compounds from PET thermal degradation. These volatiles are then catalytically reformed in the second stage reforming reactor and the product gases consisting of mainly  $H_2$  and  $CO$  then undergo a water gas shift reaction in the third stage reactor. There was no residual pyrolysis char produced from the HDPE, LDPE or PP plastics; however, PS and PET produced significant char residues, at 2.50% and 8.56% (in weight), respectively, as has been reported by others [23, 24]. For example, Marco et al. [24] suggested that the production of char from PET was induced by the existence of

the =O bonds of the ester groups in the polymer, as well as the presence of the doubly substituted aromatic nucleus in the PET structure. Krevelen and Nijenhuis [25], introduced the concept of the char-forming tendency of different plastic polymers during the pyrolysis process based on their chemical structure and reported that the tendency of char formation relevant to the plastic investigated here was polyalkenes <PS<PET.

Table 5 also shows the volumetric gas composition of the gases generated in the three-stage process from the single plastics investigated. The gas composition consisted of a high fraction of H<sub>2</sub> and CO (syngas) with the other main gases, consisting of CO<sub>2</sub>, CH<sub>4</sub> and hydrocarbons from C<sub>1</sub> to C<sub>4</sub> (C<sub>n</sub>H<sub>m</sub>). The volume composition of CO and CO<sub>2</sub> derived from PET makes a large contribution to the product composition, accounting for 26.2% and 10.0% (in volume), respectively. The higher quantities of carbon monoxide and carbon dioxide are attributable to the oxygenated polymer structure of PET.

The H<sub>2</sub>/CO ratios for the gases obtained from the three-stage processing of each of the different plastics are also shown in Table 5 (see also Fig. 3). The H<sub>2</sub>/CO ratio may be used to assess the process efficiency. It may be suggested that the higher the value obtained for the H<sub>2</sub>/CO ratio, the higher the amount of CO that has reacted with steam in the water gas shift reaction to form H<sub>2</sub>. When PP was utilised as the feedstock, the H<sub>2</sub>/CO ratio was the highest. It was found to be 3.33, which was higher than the H<sub>2</sub>/CO ratios of HDPE, LDPE, and PS, which were in the range of 2.61–2.89. This may be ascribed to a rise in the amount of CO that was reacted in the case of PP, as seen in Fig. 3b,

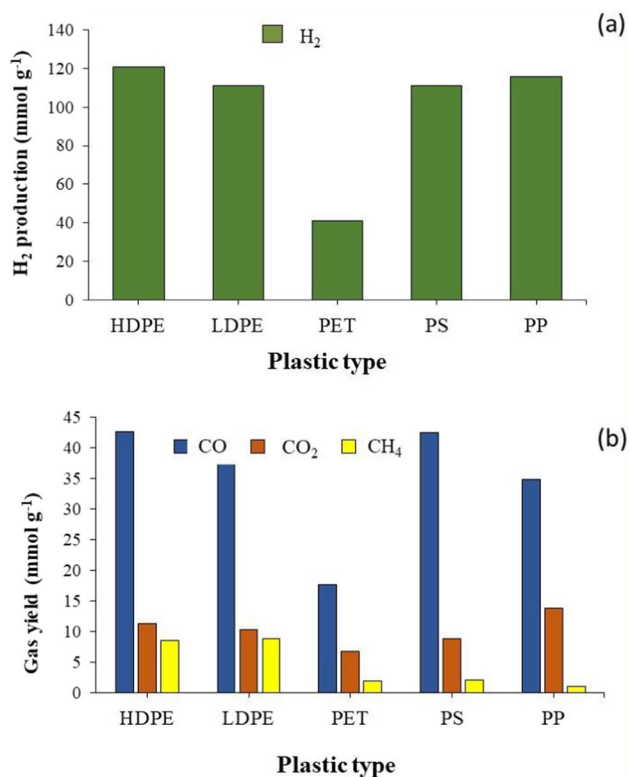
**Table 5** Product yield, gas volumetric composition and gas ratios from the three-stage pyrolysis-reforming-water gas shift processing of different types of single plastics

Item	HDPE	LDPE	PP	PS	PET
<i>Product yield (% in weight)</i>					
Gas	90.89	90.50	90.21	88.13	91.44
Char	0	0	0	2.50	8.56
<i>Gas composition (% in volume)</i>					
H <sub>2</sub>	65.50	65.40	69.90	67.50	60.90
CO	23.10	22.60	20.90	25.90	26.20
CO <sub>2</sub>	6.20	6.10	8.30	5.40	10.00
CH <sub>4</sub>	4.70	5.20	0.60	1.20	2.90
C <sub>n</sub> H <sub>m</sub>	0.60	0.70	0.80	0.10	0.10
<i>Gas ratios</i>					
H <sub>2</sub> /CO	2.84	2.89	3.33	2.61	2.33
H <sub>2</sub> /CO <sub>2</sub>	22.04	8.29	20.43	7.13	8.42
CO/CO <sub>2</sub>	9.64	2.61	8.76	2.11	2.52

where PP generated the least amount of CO following the water gas shift reaction stage. It should also be highlighted that PET has a significantly lower H<sub>2</sub>/CO ratio of 2.33, which can be attributed to the larger amount of CO generated during the pyrolysis and catalytic steam reforming stages of the process, which could not all be converted in the water gas shift reactor.

Figure 3a shows the yield of hydrogen produced by the three-stage processing of the single plastics. The largest hydrogen yield of 120 mmol per gram plastic was obtained with the HDPE feedstock, while the PET feedstock produced the lowest hydrogen yield of only 41 mmol per gram plastic. The thermal degradation of PET by pyrolysis produces mainly CO and CO<sub>2</sub> gases, and a liquid product consisting of mainly benzoic acid and other organic acid and a relatively high yield of char compared to the other plastics [26]. This is due to the oxygenated-aromatic structure of PET. Consequently, the pyrolysis of PET produces products that are not conducive to subsequent catalytic steam reforming, hence a low H<sub>2</sub> yield. HDPE, LDPE and PP all exhibit comparable pyrolysis behaviour owing to their similar polyalkene chemical structures. Most of the primary gaseous products produced by the pyrolysis of HDPE, LDPE and PP are alkanes and alkenes with short chain lengths [27]. For example, it has been reported that a random scission mechanism in the thermal breakdown of polyalkene polymers yields alkene hydrocarbon gases such as ethane, propane, and butane [27, 28]. It has been proposed that the production of alkanes and alkenes from the pyrolysis of LDPE and HDPE is more readily reformable in the steam reforming stage than the aromatic compounds produced during the pyrolysis of PS [29]. Barbarias et al. [29] reported that polyolefin plastics, PP and PE generated ~10% higher yields of H<sub>2</sub> compared to PS and almost twice that generated from PET. They suggested that the aromatic compounds produced from PS were less reactive in the catalytic reforming process than the linear hydrocarbons produced from PP and PE. Additionally, the oxygenated compounds produced from the pyrolysis of PET, i.e., benzoic acid and terephthalic acid, have an aromatic ring structure that is more refractory and less conducive to catalytic reforming [29]. However, the results for the three-stage process in this work (Fig. 3) suggest that the gas yield results for H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> are similar for the polyalkene plastics and PS feedstock. This suggests that the product gases from PS pyrolysis-reforming undergo further catalytic steam reforming and water gas shift reactions in the third stage water gas shift reactor.

Figure 3b shows the CO, CO<sub>2</sub>, and CH<sub>4</sub> gas yields generated by each of the single plastics from the three-stage process. The presence of significant yields of CO in the product



**Fig. 3** **a** Hydrogen and **b** other main gas yields ( $\text{mmol g}^{-1}$ ) from the three-stage pyrolysis–reforming–water gas shift processing of single plastics. *HDPE* high-density polyethylene, *LDPE* low-density polyethylene, *PP* polypropylene, *PS* polystyrene, *PET* polyethylene terephthalate

yield from the processing of the single plastics (Fig. 3b) also suggests that the effectiveness of the 3rd stage water gas shift reactor could be improved. This would enable further water gas reaction (Eq. 2) of the CO and consequent enhanced yield of  $\text{H}_2$ .

TPO was carried out on the reacted water gas shift  $\text{Fe}/\text{Al}_2\text{O}_3$  catalysts derived from the three-stage processing of the single plastic to determine the amount and type of carbon deposited on the catalyst surface. The TGA–TPO weight loss thermograms were used to calculate the amount of carbon deposited on the surface of the catalysts, and the results are shown in Table 6. The results show that the reacted 10% (in weight)  $\text{Fe}/\text{Al}_2\text{O}_3$  catalysts produced from the processing of the different single plastics had similar percentages of weight loss of less than 4% for all the plastics investigated. This suggests that the volatiles entering the third stage water gas shift reactor contained lower molecular weight chemical species more conducive to reaction and that the second stage catalytic steam reforming and cracking reactions reduced the chemical species such as aromatic compounds which tend to induce catalyst coking.

**Table 6** Formation of catalyst coke on the 10% (in weight)  $\text{Fe}/\text{Al}_2\text{O}_3$  third stage catalyst in relation to the three-stage pyrolysis–reforming–water gas shift processing of different single plastics (Unit: %, in weight)

Plastic	Water gas shift catalyst (10% $\text{Fe}/\text{Al}_2\text{O}_3$ ) carbon deposits
HDPE	3.27
LDPE	3.44
PET	2.87
PP	3.70
PS	3.10

### Three-stage processing of simulated and real-world mixed MSW plastics

The three-stage (i) pyrolysis, (ii) catalytic steam reforming and (iii) water gas shift reaction processing of SWP was compared with a real-world mixture of plastics obtained from the recycling of MSW in relation to the gas yield and  $\text{H}_2$  production. The simulated plastic mixture was prepared based on a typical representative MSW plastic mixture consisting of a blend of the single plastics HDPE, LDPE, PS, PET and PP (“Materials” Section). The RWMP was obtained from a MSW recycling centre containing a similar mix of plastics but with an exact unknown plastic composition. The results for product yield (gas and char) and volumetric gas composition are shown in Table 7. There was negligible production of any oil, and the balance of the mass was condensed unreacted water.

From Table 7, both the SWP and the RWMP have very similar gas yields at 89.05% and 88.47% and similar char yields of 4.93% and 5.30% (in weight), respectively. The volumetric gas compositions are also similar for the SWP and RWMP plastic mixtures. The  $\text{H}_2/\text{CO}$  ratios are similar between the two plastics, but the  $\text{H}_2/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  molar ratios are different, suggesting that the content of PET in the SWP mixture is higher than that in the RWMP, producing higher levels of  $\text{CO}_2$  and consequently influencing the gas ratios. In addition, the gas compositions from a three-stage reactor processing of the SWP and RWMP samples were similar to that produced from the processing of the single plastics, HDPE and LDPE, indicating that the high proportion of these two plastics, containing 42% of LDPE and 20% (in weight) of HDPE in the SWP, dominated product yields as well as gas composition.

Figure 4 shows that the yields of hydrogen were also similar for the two representative MSW plastic mixtures at 101 mmol per gram plastic for SWP and 104 mmol per gram plastic for the RWMP plastic sample. This suggests that the mixtures have a comparable plastic composition. A proximate and ultimate analysis confirmed that the SWP and RWMP samples also have similar contents of carbon,

hydrogen, nitrogen, oxygen and sulphur (Table 1). Barbarias et al. [29] investigated the two-stage pyrolysis-catalytic steam reforming of a mixture of HDPE (48%), PP (35%), PS (9%) and PET (8%, in weight) in relation to hydrogen production. They also reported the dominant contribution of the polyalkene plastics (HDPE and PP) in relation to the production of hydrogen and the reduced contribution of PS and PET. Wilk and Hofbauer [30] also reported that the presence of PET in a mixture of PET, PE and PS reduced the production of H<sub>2</sub> during steam/reforming/gasification of plastics.

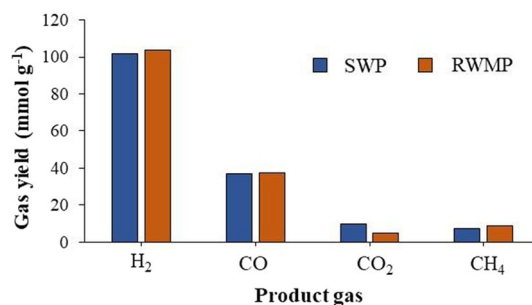
### Three-stage processing of household, commercial and industrial waste plastics

Nine different waste plastics from different waste treatment plants were used as feedstocks in the three-stage pyrolysis-catalytic steam reforming-water gas shift reaction process. Figure 5 shows the product yields obtained using the different household, commercial and industrial waste plastics. Product gases (Fig. 5a) accounted for more than 80% (in weight) of the product yield for all the waste plastic samples with liquid yield between 7%–12% (Fig. 5b). The agricultural plastic waste (AGR) generated the highest gas yield (90.10%), followed by the FP which produced 89.20%. Both the BC and FT produced similar gas yields of 87.18% and 87.43%, respectively. The pyrolysis char yields for these mixed waste samples (AGR, FP, BC and FT) were also the lowest at < 1% (in weight) (Fig. 5c).

Mixed waste plastics from the household, commercial and industrial sectors used in the work will contain many and varied types of plastic. Table 8 shows the most common plastics used in the sectors from which the real-world mixed plastic wastes originated. Table 8 shows that the AGR, FP, BC and FT mixed waste plastics will probably have a high

**Table 7** Product yield and gas composition from the three-stage pyrolysis-reforming-water gas shift processing of SWP and RWMP

Product yield	SWP	RWMP
<i>Product yield (% in weight)</i>		
Gas	89.05	88.47
Char	4.93	5.30
<i>Gas composition (% in volume)</i>		
H <sub>2</sub>	64.80	66.50
CO	23.50	24.10
CO <sub>2</sub>	6.20	3.20
CH <sub>4</sub>	4.60	5.70
C <sub>n</sub> H <sub>m</sub>	0.90	0.60
<i>Gas ratios</i>		
H <sub>2</sub> /CO	2.76	2.76
H <sub>2</sub> /CO <sub>2</sub>	10.45	20.78
CO/CO <sub>2</sub>	3.79	7.53



**Fig. 4** Gas yield (mmol g<sup>-1</sup>) from the three-stage pyrolysis-reforming-water gas shift processing of simulated waste plastics (SWP) and real-world mixed plastic (RWMP)

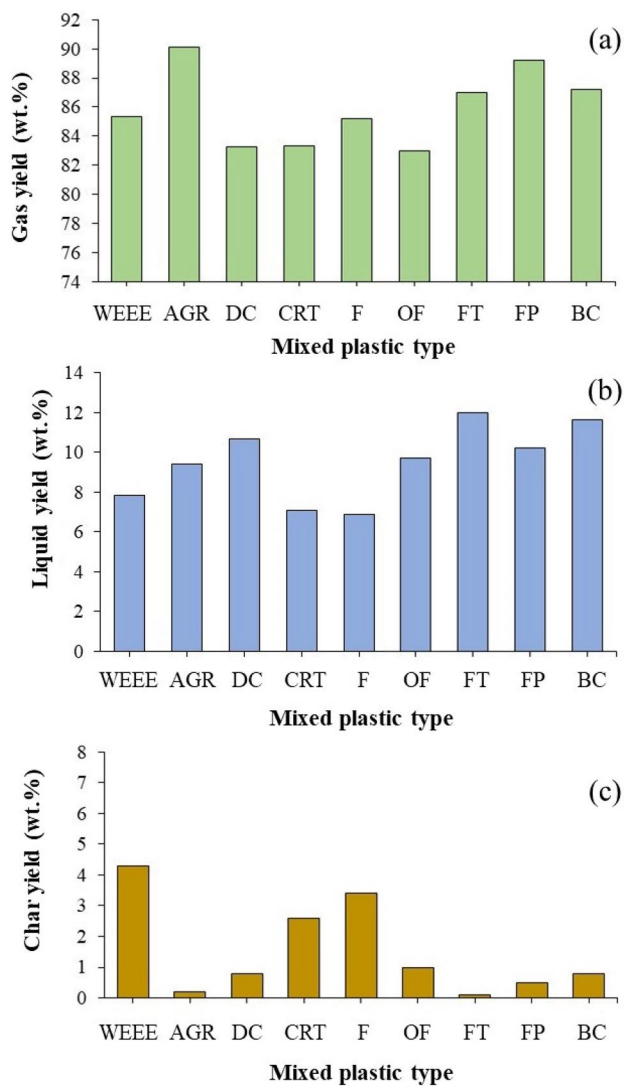
content of the polyalkene plastics (HDPE, LDPE and PP) which from the single plastic processing results (Table 5) generate a high gas yield (90%, in weight) and low char. In comparison, the other waste plastic samples generated between 80.23% and 85.34% (in weight) product gas.

There was a significant char yield produced from the 3-stage processing of WEEE, CRT and F. All three of these mixed plastic types will contain thermoset plastics, such as acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS). Thermoset plastics harden by curing and cannot be re-molded; whereas thermoplastics soften when heated and harden again when cooled. The pyrolysis of such thermoset plastics is reported to produce high yields of char [31, 32]. In separate experiments, virgin ABS and HIPS were processed in the three-stage reactor system and produced pyrolysis char yields of 4.3% and 2.3% (in weight), respectively. The total gas yields from the three-stage processing of ABS and HIPS were 82% and 85% (in weight), similar in range to that produced by the WEEE, CRT and F waste samples, containing a high proportion of these thermoset plastics (Table 8).

Figure 6 shows that carbon deposition on the 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst used in the 3rd stage water gas shift reactor for the processing of the different mixed plastic wastes using the three-stage reactor system. The highest catalyst carbon deposition was produced through processing the WEEE, DC, CRT, F and OF plastic wastes. These samples contained either, high fractions of either thermoset or thermoplastic type plastics, consequently, there did not appear to be a correlation between the type of plastic in the waste plastic mixtures and the likelihood of catalyst coking. In several cases, the mixed household, commercial and industrial wastes produced significantly higher catalyst coke formation than the single plastics (Table 6).

Figures 7 and 8 show the gas yields produced by the three-stage pyrolysis-catalytic steam reforming-water gas shift reaction process for the various types of mixed waste plastic samples. The predominant gases generated were H<sub>2</sub> and CO, with lower quantities of CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>-C<sub>4</sub> hydrocarbons.





**Fig. 5** Product yield from the three-stage pyrolysis–reforming–water gas shift processing of different types of mixed plastics. *WEEE* Plastics from electrical and electronic equipment, *AGR* plastics from the agricultural sector, *DC* plastic household detergent containers, *CRT* plastics from computer monitors and televisions, *F* plastics from freezers and refrigerators, *OF* automotive motor oil flasks, *FT* automotive vehicle plastic fuel tanks, *FP* food packaging waste plastics, *BC* building and construction waste plastics. **a** gas yield; **b** liquid yield; **c** char yield. wt.% means % in weight

The highest yields of  $H_2$  production were found with the processing of AGR, OF, FT, FP and BC with a range between 102 mmol and 106 mmol  $H_2$  per gram plastic. These particular mixed waste plastics will be expected to contain a high fraction of polyalkene plastics (HDPE, LDPE, PP), as indicated in Table 8. Figure 3 shows that the  $H_2$  yield from such single polyalkene plastics also generated high  $H_2$  yields of ~115–120 mmol  $H_2$  per gram plastic from the three-stage process. The lower  $H_2$  yields from the different household, commercial and industrial waste plastics were associated

with those wastes containing higher fractions of thermoset plastics, such as WEEE, CRT and F.  $H_2$  yields from these WEEE, CRT and F plastic mixtures were 70, 85, and 80 mmol per gram plastic, respectively; the separate experiments where the virgin thermoset plastics ABS and HIPS were processed using the three-stage process produced similar  $H_2$  yields of 58 mmol per gram plastic and 80 mmol per gram plastic, respectively. Consequently, it may be suggested that the type of plastic, whether thermoset or thermoplastic, present in the mixed waste plastic can give an indication of the  $H_2$  yield produced from the three-stage process. Yao et al. [33] investigated the processing of real-world food packaging waste plastics comprised of drinks cups, lunch boxes and plastic bags, and wrapped them in a two-stage fixed bed pyrolysis–catalytic steam reforming process using a Ni–Fe monometallic and bimetallic alumina catalysts. The mixed plastic waste consisted of approximately 40% HDPE, 35% LDPE, 20% PP and 5% (in weight) PS. They reported  $H_2$  yields of 92.7 mmol per gram plastic obtained from the processing of the food packaging waste plastics, which gave a volumetric  $H_2$  content of 63% (in volume) in the product gas.

The syngas ( $H_2$  and CO) yields shown in Fig. 7 for the three-stage processing of the various types of plastic waste from different types of waste treatment facilities were in the following order: FT>BC>FP>OF>AGR>DC>CRT>F>WEEE.

Table 9 shows the volumetric gas composition and the  $H_2/CO$ ,  $H_2/CO_2$  and  $CO/CO_2$  gas ratios from the three-stage pyrolysis–reforming–water gas shift processing of the different types of household, commercial and industrial waste plastics. The product volumetric gas composition from the processing of all of the waste plastics contains high concentrations of  $H_2$  and CO (syngas) of more than 85% (in volume). Such a product gas is useful as a process fuel to provide the energy requirements for the process. The  $H_2/CO$  molar ratio for the different mixed waste plastics (Table 9) shows ratios between 2.27 from F and 3.03 from OF. The useful feedstock  $H_2/CO$  molar ratios for further processing to liquid fuels and chemicals are, however, typically lower, in the range of 1:1–2.2:1 [34].

More than 350 million tonnes of waste plastic are generated globally each year, and the range of household, commercial and industrial waste plastics investigated in this work make a major contribution to that total. The majority of plastics making up the waste stream arise from the packaging, building and construction, and transport sectors. Almost two-thirds of waste plastics arise from plastics with relatively short product life-spans. For example, plastic packaging has a typical product life span of only 0.5 years yet is the major contributing plastic to the waste stream. Whereas plastics from electrical and electronic equipment have a product lifespan of 8 years, transportation plastics an average of 13 years and building and construction plastics

**Table 8** The most common plastics used in the sectors from which the real-world mixed plastic wastes originated

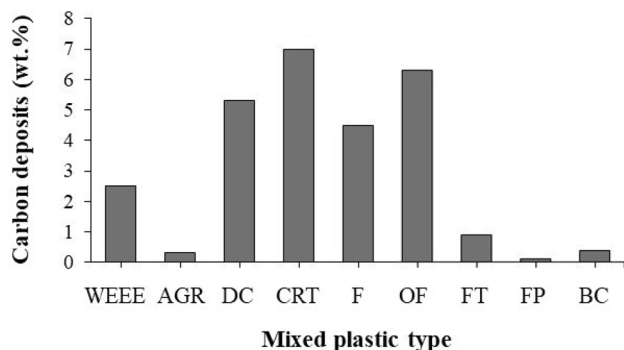
Mixed plastic	Types of plastic used in the sector
WEEE	A wide range of plastics including, polyethylene, PP, high impact PS, acrylonitrile butadiene styrene, PET, polyesters, polyamides, polycarbonates, phenolformaldehyde, nylon, polyurethane, polyvinyl chloride, brominated plastics
AGR	Polyethylene, polycarbonate, PP, polyvinyl chloride, ethylene–vinyl acetate, poly-methyl-methacrylate
DC	HDPE, PP, PET
CRT	Mainly acrylonitrile butadiene styrene, acrylonitrile butadiene styrene/polycarbonate blend, HIPS
F	Acrylonitrile butadiene styrene, PP, HIPS, polycarbonate, foamed polyurethane
OF	Mainly PP, HDPE
FT	Mainly PP, HDPE
FP	HDPE, LDPE, PET, polyvinyl chloride, PP, PS
BC	HDPE, LDPE, polyvinyl chloride, PS, PP, poly-methyl-methacrylate, polyester, phenolic resin, silicon resin

*HIPS* high impact polystyrene

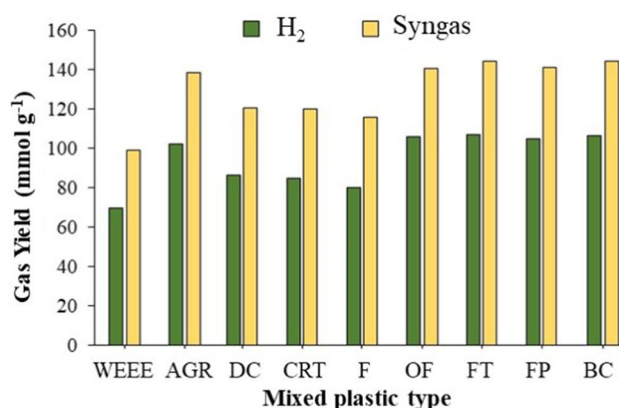
a lifespan of 35 years. However, such long product lifespan plastics will still eventually end up the plastic waste stream.

The five single plastics investigated in this work comprise the majority of plastics used in the various household, commercial and industrial sectors. For example, PP is the most used polymer at 16% of the total global plastic demand and is used in food packaging and the manufacture of automotive parts [10]. HDPE represents 12% of global plastic use for applications such as toys, bottles and pipes, and LDPE represents 12% of global plastic demand and is used for reusable plastic bags and food packaging film. Global demand for PS is 5% of the total with applications in food packaging, insulation and electronic equipment. The global demand for PET is 5% of the total and is mainly used in mineral water bottle manufacture [10].

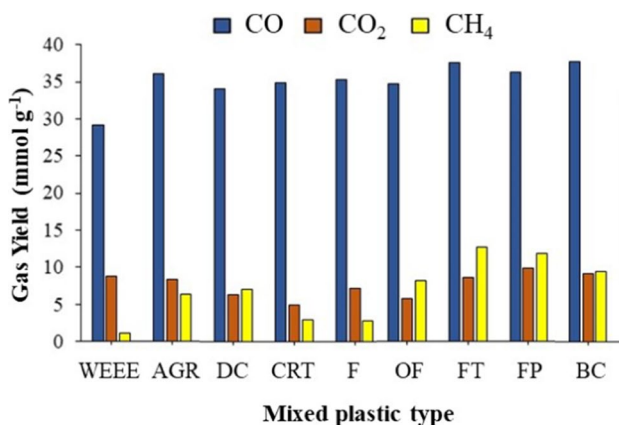
Undoubtedly, enormous amounts of waste plastics are being produced in a range of different household, commercial and industrial sectors. However, to further develop the three-stage (i) pyrolysis, (ii) reforming and (iii) water gas shift process to treat waste plastics to generate hydrogen,



**Fig. 6** Catalyst carbon deposition on the 3rd stage water gas shift 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst from the three-stage pyrolysis–reforming–water gas shift processing of different types of mixed waste plastics. wt.% means % in weight



**Fig. 7** Hydrogen and syngas yield (mmol g<sup>-1</sup>) from the three-stage pyrolysis–reforming–water gas shift processing of different types of mixed waste plastics



**Fig. 8** CO, CO<sub>2</sub> and CH<sub>4</sub> yield (mmol g<sup>-1</sup>) from the three-stage pyrolysis–reforming–water gas shift processing of different types of mixed waste plastics

**Table 9** Volumetric gas composition and gas ratios from the three-stage pyrolysis-reforming-water gas shift processing of different types of different types of mixed waste plastics

Item	WEEE	AGR	DC	CRT	F	OF	FT	FP	BC
<i>Gas Composition (% in volume)</i>									
H <sub>2</sub>	64.10	69.90	67.50	66.40	63.80	68.10	63.70	64.10	66.00
CO	26.80	20.90	25.90	27.30	28.10	22.50	22.40	22.20	23.30
CO <sub>2</sub>	8.00	8.30	5.40	3.90	5.70	3.80	5.10	6.00	5.40
CH <sub>4</sub>	1.00	0.60	1.20	2.30	2.30	5.30	7.60	7.30	4.10
C <sub>n</sub> H <sub>m</sub>	0.02	0.80	0.10	0.10	0.10	0.40	1.10	0.40	1.20
<i>Gas ratios</i>									
H <sub>2</sub> /CO	2.39	2.83	2.53	2.43	2.27	3.03	2.84	2.76	2.81
H <sub>2</sub> /CO <sub>2</sub>	18.78	8.42	8.72	9.11	9.87	8.72	9.11	9.87	6.72
CO/CO <sub>2</sub>	8.69	2.52	2.67	2.82	2.89	2.67	2.82	2.89	1.70

there are a number of challenges to be overcome. Technical challenges include the development of the process from batch to a continuous process. The commercial processing of natural gas to hydrogen is continuously involving high-temperature and high-pressure tube reactors for the catalytic steam reforming stage and fixed bed reactors for the water gas shift stage. Consequently, the pyrolysis stage should be a continuous system such as fluidized bed [17] or spouted fluidized bed pyrolysis reactors [16]. For example, Barbarias et al. [29] processed different plastics in a two-stage spouted bed pyrolysis reactor followed by reforming of the pyrolysis volatiles in a fluidized bed catalytic steam reformer. The H<sub>2</sub> yields reported from their continuous two-stage process were much higher than those reported in this work, for example, 34.8 g H<sub>2</sub> per 100 g plastic (173 mmol H<sub>2</sub> per gram plastic) was produced from the processing of PP [29]. The high yield of H<sub>2</sub> reflecting the more effective reaction environment of their continuous fluidized bed reactors compared to the three consecutive fixed bed reactors used in this work. In addition, a full lifecycle analysis and techno-economic assessment of the whole system, should be modelled for example, as performed by Chari et al. [35] for lifecycle analysis and Al-Qadri et al. [36] for techno-economic analysis for similar thermal waste plastic processing systems.

## Conclusions

This work investigated the three-stage (i) pyrolysis, (ii) reforming and (iii) water gas shift processing of different single plastics and a wide range of household, commercial and industrial mixed waste plastics with the aim of producing hydrogen. Of the single plastics investigated, HDPE produced the highest yield of hydrogen at 120 mmol per gram plastic, followed by high yields of H<sub>2</sub> from LDPE, PP and PS at between ~115 mmol and 118 mmol per gram plastic. The hydrogen yield from PET was significantly lower than that

produced from the other single plastics, since the derived pyrolysis products, CO, CO<sub>2</sub> benzoic acid and other organic acids are not readily catalytically reformed.

Comparison of the hydrogen and syngas yields produced from the three-stage process from a simulated mixture of the five single plastics and a real-world mix of plastics derived from MSW was performed. The total gas yields were very similar at 88.5%–89.1% (in weight) and also the hydrogen yields at 101 mmol H<sub>2</sub> per gram plastic for simulated mixture of plastics and 104 mmol H<sub>2</sub> per gram plastic for the real-world mixed plastic sample. Analysis of the H<sub>2</sub>/CO, H<sub>2</sub>/CO<sub>2</sub> and CO/CO<sub>2</sub> molar ratios suggested that the amount of PET in the simulated mix of plastics was higher than that of the real-world plastic mix.

Nine different household, commercial and industrial mixed waste plastic samples were also investigated in relation to hydrogen and syngas yield. All nine waste plastics produced total gas yields of over 80% (in weight), consisting of mainly H<sub>2</sub> and CO, with lower quantities of CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>–C<sub>4</sub> hydrocarbons. The plastic mixtures containing thermoset type plastics generated high char yields. The mixed plastics that contained more polyalkene plastics produced the highest hydrogen yields from the three-stage (i) pyrolysis, (ii) reforming and (iii) water gas shift processes of between 102 mmol and 106 mmol H<sub>2</sub> per gram plastic.

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**Data availability** Data will be made available on request.

## Declarations

**Conflict of interest** The corresponding author, Professor Paul T. Williams is an editorial board member of *Waste Disposal and Sustainable Energy*.

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