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HIGH YIELD HYDROGEN FROM THERMAL PROCESSING OF WASTE PLASTICS

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ABSTRACT

The production of hydrogen from the pyrolysis-catalytic steam reforming of polyethylene, polystyrene and polyethylene terephthalate waste plastics was investigated using a two stage reactor. The highest yield of hydrogen (125 mmol $g^{-1}_{plastic}$) was obtained with polystyrene at a catalyst temperature of 900 ^{o}C and steam input weight hourly space velocity of 7.59 g h^{-1} $g^{-1}_{catalyst}$ with a 10 wt. % Ni/Al_2O_3 catalyst. Further investigation using polystyrene showed that the process parameters of high catalyst temperature (900 °C) and optimised steam input rate significantly increased the yield of hydrogen. Examination of several different catalysts (Ni/Al_2O_3, Fe/Al_2O_3, Cu/Al_2O_3, Co/Al_2O_3) showed that Ni/Al_2O_3, had by far the highest catalytic activity and selectivity towards the yield of hydrogen.

Key words: Waste; Plastics; Pyrolysis; Hydrogen; Catalysts

1. INTRODUCTION

Almost 62 million tonnes of new plastic materials were produced in the Europe Union in 2018 (PlasticsEurope, 2019). At the end of their service life, the plastics enter the waste stream, and in the EU more than 29 million tonnes of post-consumer plastic waste was generated in 2018 (PlasticsEurope, 2019). The current process routes for plastic waste management in the EU are 42.6% used for energy recovery (mainly through energy from waste incineration) and representing 12.4 million tonnes of waste plastics per year. Recycling of waste plastics stands at 32.5% (9.5 million tonnes) per year, however, of this tonnage, approximately 1.8 million tonnes is exported out of the EU. The export of waste plastics for recycling has shown a dramatic decrease recently, following the ban on plastic imports to China and Hong Kong in 2016. However, there has been some uptake of plastics imports by other countries, mainly by Malaysia, Indonesia, Vietnam, and Turkey (EUWID, 2019). There is still considerable disposal of waste plastics to landfilll across the EU, with 24.9% (7.2 million tonnes) per year sent to waste landfill.

There is also substantial concern related to waste plastics in the environment, associated with illegal dumping and littering, microplastics in the ocean environment, CO_2 emissions from incineration of waste plastics and landfilling which represents a waste of resource. In response, the European Commission has introduced 'A European Strategy for Plastics in a Circular Economy' for the sustainable management of waste plastics (EC, 2018). The strategy aims to encourage better design of plastic products, higher plastic waste recycling rates and more and improved quality plastic recyclate material to boost the market for recycled plastics. There was also encouragement for innovation and new process developments for recycling of waste plastics.

The overwhelming (~99%) process route for recycling waste plastics is through mechanical recycling, involving sorting, shredding, washing, drying and pelletising of the plastic to produce a recyclate material. The recyclate is used to produce new plastic products such as garden furniture, shoes, waste bins, automotive parts etc. However, there is growing interest in thermal recycling routes for waste plastics to produce higher value end-products. Pyrolysis is one such thermal recycling process, where the plastic is thermally degraded at moderate temperature (~500 °C) in the absence of oxygen to produce an oil and gas product for use as fuel or petrochemical feedstock (Schiers and Kaminsky, 2006; Al-Salem et al, 2010; Panda et al, 2010; Sharuddin et al, 2016; Al-Salem et al, 2019). The pyrolysis process has been further developed with the use of catalysts to produce a pyrolysis-catalytic process in a two-stage reactor system which produces significantly higher value products such as gasoline, hydrogen, aromatic chemicals and even carbon nanotubes (Czernik and French, 2006; Bazargan and McKay, 2012; Serrano et al, 2012; Miandad et al, 2016; Al-Salem et al, 2017; Williams, 2021). Separation of the pyrolysis step from the catalytic step in a two-reactor system has significant advantages over merely mixing the waste plastics directly with the catalyst (Serrano et al, 2012; Lopez et al, 2018). For example, the two reactors may be independently temperature controlled to optimise process control, any residues and dirt associated with the plastics remains in the pyrolysis reactor rather than contaminating the catalyst and the reacted catalyst may be more easily recovered, recycled and reused.

There has been recent interest in the production of hydrogen from waste plastics through a two-stage pyrolysis-catalysis process as a viable route to recycle waste plastics to a higher value product. Hydrogen is a high demand valuable commodity, with annual production of ~70 million tonnes per year. Hydrogen is mainly used in the production of ammonia for fertiliser, also for the upgrading of crude oil to premium grade fuels and for the production of cyclohexane and methanol as feedstocks for the chemical industry. In addition, with concerns related to climate change there is increasing interest in producing higher quantities of hydrogen for use as a non-polluting fuel in transport engines and fuel cells to support a future decarbonised economy (IEA, 2019; EC, 2019).

Hydrogen is currently produced almost exclusively from fossil fuels (~95%), the largest source being natural gas (methane). The key process step is the steam reforming of methane in the presence of nickel catalysts at temperatures of ~800 °C. The product gas largely consists of hydrogen and carbon monoxide and undergoes further processing to enhance the yield and purity of the hydrogen (EC, 2019). Producing hydrogen from waste plastics would offer an alternative feedstock and would also solve a major waste treatment problem. The concept is to produce a suite of hydrocarbon gases from the plastics which are then catalytically steam reformed in a process that mimics the industrial scale catalytic steam reforming of natural gas methane. The initial first stage of producing the hydrocarbon feedstock is to use pyrolysis, which involves the thermal degradation of the plastics at moderate temperatures (~500 °C) which produces a range of hydrocarbons including methane and other higher molecular weight hydrocarbon gases. The gases are passed directly (without the chance for any oil condensation) to a second stage catalytic reactor for catalytic steam reforming. Thereby, a two-stage process is established. The plastics found in municipal solid waste mainly consist of the thermoplastics, high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) (Delgado et al, 2007). These thermoplastic polymers are readily thermally degraded at temperatures of ~500 °C to produce hydrocarbon gases and vapours which form the feedstock gases for the process.

There have been several studies into the two-step pyrolysis-catalytic steam reforming process for the production of hydrogen from waste plastics using a range of different two-stage reactors, including fixed bed, screw kiln and fluidised bed reactors (Czernik and French, 2006; Wu and Williams, 2014; Namioka et al, 2011; Barbarias, 2016). The influence of various process parameters on the process has also been studied, for example, the influence of different types of waste plastic (Barbarias et al, 2018), different types of catalyst (Wu and Williams, 2009(a)) and catalyst temperature (He et al, 2009). To further develop the process of pyrolysis-catalytic steam reforming of waste plastics for hydrogen production, comprehensive process optimisation for different plastic types is required. There is also a need to understand how such processes can be optimised with different types of catalyst. In this study, different metal catalysts were used for the pyrolysis-catalytic steam reforming of different types of waste plastics under different process conditions were investigated with the aim of optimising the production of hydrogen.

2. MATERIALS AND METHODS

2.1. Materials

Three types of waste plastics were used in this study, representative of the main plastics found in municipal solid waste, polyethylene (in the form of high density polyethylene) (HDPE), polystyrene (PS) and polyethylene terephthalate (PET). All of the plastics were post-consumer real-world waste plastics and were obtained from Regain Polymers Castleford, UK. The waste plastic samples were characterized using proximate and ultimate analyses, and the results are shown in Table 1.

The characteristic data of the thermal decomposition of the various waste plastics were determined using thermogravimetric analysis (TGA) which indicates the temperatures of decomposition of the plastics. The results are shown in Table 2. The characteristic temperatures are; T_o, the onset temperature where the material starts to degrade; T_p is the peak temperature where the maximum degradation occurs; T_e is the end temperature where the degradation of the plastic ends. Total weight loss of the samples after the experiment represents the volatile content in the plastics, indicating that the waste plastics contained some solid filler or contamination dirt.

The main catalyst used in this study was Ni/Al_2O_3, and was used to investigate the pyrolysis-catalytic steam reforming of different plastics and for optimisation of process parameters, but other transition metal catalysts were also used for comparison (Fe/Al_2O_3, Co/Al_2O_3 and Cu/Al_2O_3). All the catalyst were prepared to give a 10 wt.% metal loading on the Al_2O_3 support. The catalysts were prepared using the wet impregnation method followed by calcination and reduction. In each case, a known amount of the metal nitrate hexahydrate was dissolved in deionised water and stirred using a magnetic stirrer for 30 minutes. A measured amount of Al_2O_3 support material was added to the slurry and stirred for a further 30 minutes. The mixture was then heated until a paste was formed which was oven dried overnight at 105 °C and then calcined at 950 °C for 3 hours. The catalyst was ground and sieved to obtain a particle size of 50 – 212 µm and then reduced in a tubular reactor under the reducing environment of H_2/N_2 (5% H_2 in 95% N_2) at 800 °C for 2h at a heating rate of 20 °C min^{-1}.

2.2. Experimental system

A schematic diagram of the two-stage, pyrolysis-catalytic steam reforming reactor system used for hydrogen production from waste plastics is shown in Figure 1. The 1st stage was the pyrolysis reactor containing the waste plastic (1.0 g) and the 2nd stage reactor which contained the catalyst (1.0 g). The reactors were constructed of stainless steel and were each 25 cm long x 2.2 cm diameter. Each reactor was separately heated using separate and controlled electrical furnaces using programmable temperature control. The pyrolysis temperature and catalyst temperature were independently monitored using thermocouples. The plastic sample was placed in a stainless steel crucible, suspended in the middle of the 1st stage pyrolysis reactor. The catalyst was placed on quartz wool which rested on a stainless steel mesh inside the 2nd stage reactor. Water, for the steam reforming process, was injected using a glass syringe controlled by a metered pump and entered the 2nd stage catalytic reactor for catalytic steam reforming. The amount of water that was reacted with the pyrolysis hydrocarbons was calculated by subtracting the amount of unreacted water collected in the condenser system from the total amount of water injected into the catalytic reactor obtained from weighing the input water syringe. Nitrogen, was used as the carrier gas with flow control using a mass-flow meter. At the outlet of the reactor system, air cooled and dry-ice cooled condensers trapped the condensable liquids. Non-condensable gases were collected in a 25L Tedlar^{TM} gas sample for later analysis using packed column gas chromatography.

The procedure for the experiments consisted of initial heating of the catalyst reactor to the desired temperature. Once the catalyst temperature in the 2nd stage had stabilised, the pyrolysis of the plastics commenced by heating the 1st stage pyrolysis reactor to a final temperature of 500 °C at a heating rate of 10 °C min^{-1} and held at 500 °C for 30 minutes. As the pyrolysis of the waste plastics proceeded, the evolved pyrolysis gases passed over the hot catalyst in the presence of steam for catalytic steam reforming to take place. At the end of the experiment, the residual solid from the pyrolysis reactor was collected along with the condensed liquids trapped in the condensation system and weighed to aid the determination of mass closure. The gases were analysed and quantified to enable the mass of gases to be determined which also enabled determination of the mass closure.

Initial experiments were undertaken, without the presence of the catalyst or steam input but using only the 1st stage pyrolysis reactor. These experiments were used to determine the concentration of gases and condensable oils derived from the waste plastics which would indicate the range of hydrocarbons passing into the 2nd stage catalytic reactor. The experimental conditions of heating rate and final temperature for the pyrolysis of the plastics were the same as those used for the main body of work on pyrolysis-catalytic steam reforming.

2.3. Gas analysis

The gases collected in the gas sample bag were immediately analysed off-line using three separate Varian CP-3380 packed-column gas chromatographs (GC). Hydrocarbons (C_1 – C_4) were analysed using a Varian gas chromatograph with flame ionisation detection (GC/FID), equipped with a 2m x 2mm column packed with 80 – 100 mesh HayeSep chromatography material and nitrogen carrier gas. A second Varian GC analysed permanent gases (H_2, O_2, N_2 and CO) with thermal conductivity detection

(GC/TCD), equipped with a 60 – 80 molecular sieve column and argon carrier gas. The third Varian GC/TCD analysed for CO_2 with a 80 – 100 mesh HayeSep column and argon carrier gas.

3. RESULTS AND DISCUSSION

3.1 Pyrolysis of different waste plastics

The initial experiments of pyrolysis of the waste plastics without the catalyst reactor stage or with steam input were undertaken and the results are shown in Table 3. Pyrolysis was undertaken, heating the reactor to the final temperature of 500 °C at a heating rate of 10 °C min^{-1} and held at 500 °C for 30 min. Table 3 shows the product yield and gas composition for the pyrolysis of high density polyethylene, polyethylene terephthalate and polystyrene. High density polyethylene produced an oil/wax liquid fraction at 87.0 wt.% of the plastic feedstock and 5.4 wt.% gas. The small fraction of solid residue was most probably due to the dirt and contamination of the post-consumer plastic waste. The composition of the oil/wax and gas produced from polyethylene is linked to the thermal degradation of the plastic polymer during the pyrolysis process. Figure 2 shows the repeating chemical unit for polyethylene, polystyrene and polyethylene terephthalate. Polyethylene is a polymer with ethylene as the repeating unit and thermally degrades by random scission to produce hydrocarbon fragments which then produce alkanes, alkenes and alkadienes end-products of a wide range of molecular weights from C_1 to C_{60} (Williams, 2006). Similar results were reported by Sogancioglu et al (2017) who investigated the pyrolysis of high density polyethylene at 500 °C.

Polyethylene terephthalate is a polymer based on a repeating structural unit containing aromatic and oxygenated hydrocarbon groups (Figure 2) and degrades through random scission of the polymer chain (Williams, 2006; Cit et al, 2010). The products from decarboxylation of the PET produces a gas consisting of mainly CO and CO_2 and a condensable oil/wax fraction which has been reported to consist of mainly terephthalic acid and benzoic acid (Williams, 2006; Cit et al, 2010). The PET also produced a significant quantity of residual char which has been attributed to secondary recombination of complex scission fragments resulting in polymerisation and increased quantities of char (Cit et al, 2010; Brems et al, 2011).

The pyrolysis of polystyrene produced a high yield of product liquid (97.0 wt.%) which was a viscous dark brown oil. Polystyrene is a polymer with an aromatic repeating structural unit (Figure 2) and thermal decomposes via firstly chain scission and then random scission (Williams, 2006). This results in the formation of high yields of styrene monomer (> 70 wt.% of the oil). Other hydrocarbons formed by the degradation process have been identified as styrene oligomers, benzene, toluene, ethylbenzene and methylbenzene (Williams, 2006).

Figure 3 shows the gas yield in mmol $g^{-1}_{plastic}$ from pyrolysis of the different plastics. From Table 3, the product gas yield was shown to be low from the pyrolysis of high density polyethylene and polystyrene and Figure 3 shows that the main gases produced were hydrogen and low molecular weight C_1 – C_4 hydrocarbons. For the pyrolysis of polyethylene terephthalate, the gas total yield gas yield produced was high at more than 50 wt.% (Table 3) and Figure 3 confirms that the main gases produced were CO and CO_2.

3.2. Pyrolysis-reforming of waste plastics

3.2.1. Pyrolysis-catalytic steam reforming of different plastics

The pyrolysis-catalytic steam reforming of the waste plastics was carried out using the two-stage pyrolysis-catalyst reactor with a fixed final pyrolysis temperature of 500 °C, catalyst temperature of 900 °C and a steam input rate weight hourly space velocity of 7.59 g h^{-1} $g^{-1}_{catalyst}$. The catalyst used was 10 wt.% Ni/Al_2O_3. The results shown in Table 4 show that the introduction of the catalytic steam reforming stage produced a significant increase in gas yield compared to the gas yields for pyrolysis alone. The results are calculated on the basis of input plastic and water (steam) and output product gas, liquid and char yield. However, some of the input water will contribute to steam reforming reactions generating high yields of gas. When the data is calculated on the basis of input mass of plastic, as shown in Table 4, in some cases, the gas yield produced will be well in excess of 100 wt.%. The data also allows the calculation of how much of the input water is reacted in the catalytic steam reforming process and thereby how much unreacted water is present in the condensation system. Table 4 shows that the gas yield in terms of the mass of input plastic generates a high yield of gas at 206.5 wt.% for polyethylene and 299.3 wt.% for polystyrene. This is reflected in the high amount of water which reacts with the hydrocarbon pyrolysis products derived from the first stage thermal degradation of the plastics during the catalytic steam reforming process (1.76 g g^{-1} for polyethylene and 2.72 g g^{-1} for polystyrene). The gas yield from the pyrolysis-catalytic steam reforming of polyethylene terephthalate was significantly lower at 88.2 wt.%, in terms of mass of plastic, compared to the other two plastics.

Figure 4 shows the product gas composition from the pyrolysis-catalytic steam reforming of the waste plastics with the 10 wt.% Ni/Al_2O_3 catalyst. Polystyrene produced the highest yield of hydrogen at 125.5 mmol $g^{-1}{}_{plastic}$ with carbon monoxide at 81.6 mmol $g^{-1}{}_{plastic}$. Polyethylene produced a lower yield of hydrogen at 94.5 mmol $g^{-1}{}_{plastic}$ and carbon monoxide yield at 53.0 mmol $g^{-1}{}_{plastic}$, compared to polystyrene. Polyethylene terephthalate produced the lowest hydrogen yield at 17.6 mmol $g^{-1}{}_{plastic}$ and carbon monoxide yield at 7.1 mmol $g^{-1}{}_{plastic}$. This shows that at this high catalyst temperature of 900 °C and in the presence of steam, the hydrocarbons derived from the pyrolysis of the plastics were catalytically steam reformed to produce mainly hydrogen and carbon monoxide.

The production of hydrogen on a commercial basis is via the catalytic steam reforming of methane (CH_4) in the presence of nickel catalysts at temperatures of ~800 °C to produce hydrogen and carbon monoxide (Eq. 1). Further steps in the commercial process involves, high temperature and low temperature catalytic water gas shift reaction with steam to convert the CO to CO_2, followed by CO_2 removal to produce hydrogen (Spath and Mann, 2001; IEA, 2019). The commercial process of catalytic steam reforming is mirrored by the catalytic steam reforming of the range of hydrocarbons (C_mH_n) (Eq.2) generated from the pyrolysis of the plastics;

$CH_4 + H_2O \rightarrow CO + H_2$ (Eq1.: Steam reforming of methane)

$C_mH_n + H_2O \rightarrow CO + H_2$ (Eq2.: Steam reforming of pyrolysis hydrocarbons)

For the pyrolysis of polyethylene, a wide range of alkane, alkene and alkadiene hydrocarbons are produced which, rather than being allowed to condense, pass to the second stage reactor where catalytic steam reforming reactions of these hydrocarbons takes place. This results in a high yield of gas consisting of mainly hydrogen and carbon monoxide as shown by Equation 2. The pyrolysis of polystyrene, produced a low yield of gas, but a high yield of condensable hydrocarbons consisting of mainly styrene and other single ring aromatic hydrocarbons (Williams, 2006). Table 4 shows a high gas yield is produced from the catalytic steam reforming of these aromatic hydrocarbons at 299.3 wt.% (in relation to mass of plastics) which consisted of mainly hydrogen and carbon monoxide as shown in Figure 4 and indicated by Equation 2. The steam reforming reaction is highly endothermic and therefore at the high reforming temperature (900°C), secondary reactions of the pyrolysis volatiles will occur resulting in more yield of C_1-C_4 hydrocarbons which are then reformed to produce syngas. Studies on gasification and steam reforming reactions have reported a reduction in tar content and increased syngas production at elevated temperatures (Erkiaga et al., 2013; Castillo et al., 2015). For polyethylene terephthalate, with a high oxygen content, the main gases produced from pyrolysis alone were CO and CO_2 and also a high liquid yield consisting of oxygenated organic compounds, including terephthalic acid and benzoic acid (Williams, 2006; Cit et al, 2010). The oxygen also promotes oxidation of the volatiles to form carbon dioxide, water and some carbon monoxide. For the gasification of different plastics, Kannan et al. (2013) reported the hydrogen/CO mole ratio decreased, while CO and CO_2 increased when polyethylene was mixed with polyethylene terephthalate compared to polyethylene alone. This was attributed to the dominance of oxidation reactions due to the presence of oxygen in the PET. Consequently, there were lower amounts of hydrocarbons available for the catalytic steam reforming reactions in the second stage catalytic reactor, thereby, producing a low hydrogen and carbon monoxide yield. Barbarias et al (2018) also reported significantly lower yields of hydrogen from the two-stage pyrolysis-catalytic steam reforming of polyethylene terephthalate compared to polyethylene, polypropylene and polystyrene.

Since polystyrene produced a significantly higher yield of total gas and also higher hydrogen yield than polyethylene and polyethylene terephthalate, further work to understand the influence of process parameters and different types of catalyst on the yield of hydrogen was undertaken using polystyrene as the feedstock plastic.

3.2.2. Influence of catalyst temperature on the pyrolysis-catalytic steam reforming of polystyrene

Table 5 shows the product gas yield from the pyrolysis-catalytic steam reforming of polystyrene in relation to the temperature of the second stage 10 wt.% Ni/Al_2O_3 reforming catalyst maintained at a temperature of 700, 800 or 900 °C. The conditions of pyrolysis of the polystyrene were kept constant with a final temperature of 500 °C and the steam input weight hourly space velocity was 4.74 g h^{-1} $g^{-1}_{catalyst}$.

The influence of catalyst temperature on the gas yield from the pyrolysis-catalytic steam reforming of polystyrene shows that raising the temperature from 700 °C to 900 °C produces an increase in total gas yield from 156.7 wt.% to 226.9 wt.% (Table 5). This suggests that the higher catalyst temperature increased catalytic steam reforming of the hydrocarbons produced from the pyrolysis of polystyrene. The increase in the quantity of reacted water also confirms the increase in steam reforming of the pyrolysis hydrocarbons. In addition, the higher catalyst temperature is also likely to promote further thermal cracking of the higher molecular weight pyrolysis hydrocarbons to lower hydrocarbons in the second stage reactor.

The product gas from the pyrolysis-catalytic steam reforming of polystyrene was analysed in detail to determine the gas composition and the results in relation to catalytic reforming temperature are shown in Figure 5. The hydrogen yield clearly shows an increase in yield as the temperature of the catalyst was increased, rising from

72.8 mmol $g^{-1}_{plastic}$ at 700 °C to 103.8 mmol $g^{-1}_{plastic}$ at 900 °C. In addition, as part of the hydrocarbon reforming process carbon monoxide is also formed. Figure 4 also shows that not all of the pyrolysis hydrocarbons were steam reformed since there were small but significant quantities of methane and C_2 – C_4 hydrocarbons in the product gas.

Other researchers have also reported that increasing catalyst temperature promotes the steam reforming of hydrocarbon gases derived from the pyrolysis of plastics and thereby produces increased yields of hydrogen and carbon monoxide. For example, He et al (2009) used a two-stage pyrolysis-catalytic reactor to investigate hydrogen production from polyethylene and reported a marked increase in total gas yield, hydrogen and carbon monoxide with increasing catalyst reforming temperature. Barbarias et al (2016) investigated the influence of catalytic steam reforming temperature at 600, 650 and 700 °C in a continuous two-stage, pyrolysis- catalytic steam reforming reactor system for processing a range of different plastics. The first stage was a spouted bed reactor and the second catalytic stage used a fluidised bed reactor. They reported an increase in plastic conversion with increasing catalyst reforming temperature to produce enhanced yields of hydrogen and carbon monoxide. The influence of increased catalyst temperature from 600 to 900 °C for plastics produced from municipal solid waste has been reported for a two-stage pyrolysis-catalytic steam reforming reactor (Wu and Williams, 2010). The results showed that hydrogen yield doubled as the temperature was increased from 600 to 900 °C.

3.2.3 Effect of steam input on the production of hydrogen from waste polystyrene

Further work was undertaken to indentify the influence of the rate of steam input on hydrogen yield from waste polystyrene. Table 6 shows the product yeld in relation to steam inputs at, 4.74, 7.59 and 10.40 g h^{-1} $g^{-1}_{catalyst}$ weight hourly space velocity for the two-stage, pyrolysis-catalytic steam reforming of polystyrene.

Table 6 also shows that the gas yield in relation to the mass of plastic shows a marked increase in the total amount gas produced as the steam flow rate is increased, reaching a maximum of 299.3 wt.% at 7.59 g h^{-1} $g^{-1}_{catalyst}$ weight hourly space velocity. However, at the higher steam input of 10.40 g h^{-1} $g^{-1}_{catalyst}$ the total mass of gas produced was reduced. Figure 6 shows the composition of the individual gases produced from the polystyrene in terms of mmol gas $g^{-1}_{plastic}$. The individual main hydrogen and carbon monoxide gas yields reflect the total gas yield in that there is an increase then a decrease in yields as the steam flow rate is increased. Previous work on the pyrolysis-catalytic steam reforming of polypropylene has been shown to increase hydrogen yield due to the promotion of the steam reforming reaction (Wu and Williams, 2009(b)). However, at high steam inputs, the yield of hydrogen decreased, as also shown in this work (Figure 6). The initial increase is attributed to the increase in steam reforming of the pyrolysis hydrocarbons leading to enhanced hydrogen and carbon monoxide yields (Eq. 2) (Wu and Williams, 2009(b)). The decrease in yield of hydrogen and carbon monoxide at the higher steam flow rate is reportedly due to saturation of the catalyst. Therefore, there is an optimum steam:carbon ratio which maximises hydrogen yield.

The maximum yield of hydrogen was 125.5 mmol $g^{-1}_{plastic}$ and maximum yield of carbon monoxide was 81.6 mmol $g^{-1}_{plastic}$ obtained at 7.59 g h^{-1} $g^{-1}_{catalyst}$ weight hourly space velocity and catalyst temperature of 900 °C in the presence of the 10 wt.% Ni/Al_2O_3 catalyst.

3.2.4 Influence of metal catalyst type on the production of hydrogen from waste polystyrene

The effect of different types of metal-alumina catalysts for the two-stage pyrolysis-catalytic steam reforming of polystyrene in relation to the yield of hydrogen was investigated. Four different types of metal catalyst were used, Ni/Al_2O_3, Fe/Al_2O_3, Cu/Al_2O_3 and Co/Al_2O_3, each with 10 wt.% metal loading and produced at a catalyst calcination temperature of 950 °C. The experiments were carried out at a pyrolysis temperature regime of ambient to 900 °C, a catalyst reforming temperature of 900 °C and weight hourly space velocity of 7.59 g h^{-1} $g^{-1}_{catalyst}$. Table 7 shows that the Ni/Al_2O_3 catalyst gave the highest total gas yield of 299.3 wt.%, followed by Co/Al_2O_3, Fe/Al_2O_3 and then Cu/Al_2O_3. Hu and Lu (2010) investigated the catalytic steam reforming of acetic acid and also reported that Ni/Al_2O_3 and Co/Al_2O_3 havea high activity for acetic acid steam reforming while Fe/Al_2O_3 and Cu/Al_2O_3 have low activity. They attributed this to the different cracking activity of the metals toward C — C and C — H bonds. Ni and Co were active for cracking of both C — C and C — H bonds, while Fe was only active for the activation of C — C bonds and Cu was only active for the cracking of C — H bonds. The total gas yield for the different metal-alumina catalysts was linked to the amount of reacted water. For example, the amount of water consumed in the reaction using Ni/Al_2O_3 catalyst was significantly higher than the water consumed using the other three catalysts suggesting more steam reforming reactions.

Figure 7 shows the gas composition produced from the different metal-alumina catalysts (mmol gas $g^{-1}_{plastics}$). The Ni/Al_2O_3 catalyst produced the highest yield of hydrogen and carbon monoxide followed by Co/Al_2O_3, whereas the Cu/Al_2O_3 and Fe/Al_2O_3 catalysts were similar. The highest yield and selectivity of hydrogen and carbon monoxide were obtained with the Ni/Al_2O_3 catalyst because nickel catalysts are more active for the cracking of both C — C and C — H. The nickel-alumina catalyst favours reactions such as steam reforming, water-gas reaction and reverse water-gas shift reaction that produce more hydrogen and carbon monoxide (Ananikov, 2015). It has also been suggested that desorption of products is more rapid on nickel-catalyst surfaces compared with other metal surfaces (Bond and Wells, 1965). It should also be noted that nickel-based catalysts are the most commonly used catalyst for the commercial production of hydrogen from natural gas.

This work has shown that high yields of total product gas and hydrogen (maximum 125.5 mmol $g^{-1}_{plastic}$) can be generated from the two-stage, pyrolysis-catalytic steam reforming of waste plastics. This novel process provides for the pyrolysis of the waste plastics which generates the hydrocarbons for catalytic steam reforming to produce hydrogen. The two-stage process enables a hydrocarbon feedstock to enter the catalytic steam reforming stage since any dirt/residues deposited on the waste plastics do not become pyrolysed and are retained in the pyrolysis reactor stage. The process therefore has great potential as a treatment option for waste plastics and generates a high value hydrogen-rich syngas product which could be further purified to produce hydrogen, commonly regarded as a ‘future fuel’.

The European Hydrogen Roadmap (EC,2019) sets out a route to a decarbonsied energy system for Europe by 2050. The report emphasises the advantage of hydrogen for aiding the decarbonisation of energy use in household heating, industry and transport sectors and also the expansion of the use of hydrogen as a feedstock for industry. There is a consequent requirement for expansion of hydrogen production with a prediction that hydrogen could provide up to 24% of total energy demand in Europe by 2020 (EC, 2019). Similarly, the International Energy Agency report on the Future of Hydrogen (IEA 2019) also reports on the potential for hydrogen to replace conventional fuels in a range of industrial, transport and power generating sectors and also predicts a major increase in the demand for hydrogen. In addition, the report highlights the issue of production of hydrogen from fossil fuels and the impact on climate change; with the startling statistic that current hydrogen production worldwide contributes an annual CO_2 emission of 830 Mt, more than the combined annual emissions of the United Kingdom and Indonesia. There is therefore a need for more sustainable sources and processes for hydrogen production. Plastics are mainly produced from fossil fuel petroleum, therefore, recycling of waste plastics to produce hydrogen represents a recycling of fossil fuel resources.

A route to scaling-up the process of pyrolysis-catalytic steam reforming of waste plastics may be envisaged since the first stage plastics pyrolysis is in various stages of commercial development. For example, Klean Industries (2021) operate a 15,000 tonnes/year plastics pyrolysis facility in Sapporo, Japan, that has been operating since 2000. The plant utilises a rotary kiln pyrolysis reactor to produce a pyrolysis oil. Further distillation of the oil produces a light oil that is used as a chemical feedstock for the production of new plastics, a medium fuel oil equivalent to diesel, and heavy oil that is used to generate electricity. Brightmark Energy (2021) are developing a 100,000 tonnes/year plastics pyrolysis plant at Ashley, Indiana, US, to produce a hydrocarbon oil for further processing into ultra-low sulphur diesel fuel, naphtha and wax. Other technology developers aiming to produce a pyrolysis oil from waste plastics include, for example, Plastics2Oil (2021), Agilyx (2021) and Beston (Henan) Machinery Company (2021) which are at various stages of development.

In addition, commercialisation of the pyrolysis-steam reforming (non-catalytic) process for the production of hydrogen is an emerging technology and is in early development with the establishment of the Protos project in Ellesmere Port, Cheshire, UK (PowerHouse Energy, 2021). The process involves pyrolysis of the waste plastic to produce a range of gases which are further heated to more than 850 °C in the presence of steam to reform the pyrolysis gases to produce hydrogen, and additionally carbon monoxide and methane. In the process, the hydrogen is separated and the off-gases combusted to produce electricity. The plant under development aims to process 35 tonnes/day of plastic waste and produce two tonnes of hydrogen, while generating 3.8MW of electricity.

The research presented here, adds to the body of knowledge required for the development and deployment of the technology of pyrolysis-catalytic steam reforming for the production of hydrogen. In particular, the influence of different plastics and different catalysts on the production of hydrogen has been presented. To take the process development further a full techno-economic assessment would be required.

4.0 CONCLUSIONS

Three different waste plastics (polyethylene, polyethylene terephthalate and polystyrene), which are among the majority of household waste plastics, were investigated for the production of hydrogen. A novel two-stage, experimental, pyrolysis-catalytic steam reforming reactor system was used for the investigation. The hydrocarbons produced from pyrolysis passed directly to the second stage reactor where catalytic steam reforming of the hydrocarbons produced mainly hydrogen and carbon monoxide. The highest gas yields were generated from polystyrene which produced 125.5 mmol H_2 $g^{-1}_{plastic}$ and 81.6 mmol CO $g^{-1}_{plastic}$. Polyethylene produced a lower yield of hydrogen at 94.5 mmol $g^{-1}_{plastic}$ and a carbon monoxide yield at 53.0 mmol H_2 $g^{-1}_{plastic}$. Polyethylene terephthalate produced significantly lower yields of hydrogen at 17.6 mmol $g^{-1}_{plastic}$ and carbon monoxide yield at 7.1 mmol $g^{-1}_{plastic}$. Low gas yields from polyethylene terephthalate were linked to the chemical structure of the plastic which produced a high solid residue from pyrolysis and also generated a low amount of hydrocarbons available for catalytic steam reforming. The combination of hydrogen and carbon monoxide represents syngas which is a valuable and readily used fuel and is produced in high yield from the waste plastic. For example, the pyrolysis-catalytic steam reforming of polystyrene produced a maximum syngas yield of 207.1 mmol syngas $g^{-1}_{plastic}$ (125.5 mmol H_2 $g^{-1}_{plastic}$ and 81.6 mmol CO $g^{-1}_{plastic}$).

Experiments with polystyrene investigated the effect of process parameters on the yield of hydrogen. Increasing the catalyst temperature from 700 °C to 900 °C showed a large increase in the total gas yield and also hydrogen yield. There was an optimum steam injection rate into the catalytic steam reforming reactor (7.59 g h^{-1} $g^{-1}_{catalyst}$ weight hourly space velocity). Low inputs of steam did not enable complete steam reforming of the hydrocarbon pyrolysis gases, but at high steam input, the catalyst became saturated and reduced the catalytic activity of the catalyst.

Different metal catalysts Ni/Al_2O_3, Fe/Al_2O_3, Cu/Al_2O_3 and Co/Al_2O_3, each with 10 wt.% metal loading were investigated to determine the optimum metal-alumina catalyst to maximise hydrogen production. Ni/Al_2O_3showed the highest catalytic activity which was related to the ability of nickel to crack both C-C and C-H bonds of the hydrocarbons derived from the polystyrene pyrolysis stage.

Overall, the two-stage process shows potential as an option for the management of waste plastics to produce a valuable end-product suitable for the development of the projected future hydrogen economy.

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TABLE CAPTIONS

Table 1. Proximate and ultimate analyses of the waste plastics

Table 2. Characteristic data of the thermal decomposition of the waste plastics

Table 3. Product yield from pyrolysis of the waste plastics

Table 4. Pyrolysis-reforming of different waste plastics (pyrolysis temperature 500 ^{o}C, catalytic reforming temperature 900^{o}C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).

Table 5. Effect of different catalyst temperatures on the pyrolysis-catalytic steam reforming of waste polystyrene (pyrolysis temperature 500^{o}C, steam weight hourly space velocity 4.74 g h^{-1} $g^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).

Table 6. Effect of steam weight hourly space velocity on the pyrolysis-reforming of waste polystyrene (pyrolysis temperature 500 °C, catalytic reforming temperature, 900 °C, catalyst, 10 wt.% Ni/Al_2O_3).

Table 7. Influence of different metal catalysts calcined at 950^{o}C on pyrolysis-reforming of polystyrene (pyrolysis temperature 500^{o}C, catalytic reforming temperature 900^{o}C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).

Table 1. Proximate and ultimate analyses of the waste plastics

	Polyethylene terephthalate (PET)	**Polystyrene (PS)**	**Polyethylene (HDPE)**
Proximate analysis (wt. %)			
Moisture content	0.0	1.72	0.14
Volatile matter	85.64	98.25	97.84
Fixed carbon	17.08	*nd*	0.16
Ash	2.58	5.23	3.63
Ultimate analysis (wt. %)			
C	62.20	90.66	81.78
H	4.18	10.65	10.59
O	33.62	*nd*	*nd*
N	*nd*	*nd*	0.54
S	*nd*	*nd*	*nd*
LCV (MJkg^{-1})	25.65	42.09	28.06

nd = not detected

Table 2. Characteristic data of the thermal decomposition of the waste plastics

Plastic Samples	**T_o (°C)**	**T_p(°C)**	**T_e(°C)**	**Weight loss (wt. %)**
Polystyrene	403.06	427.25	443.02	97.77
Polyethylene	466.50	487.82	497.69	93.71
Polyethylene terephthalate	420.79	445.52	460.68	82.53

Table 3. Product yield from pyrolysis of the waste plastics.

Product yield (wt.%)	**Waste Plastic Type**		
	Polyethylene (HDPE)	**Polyethylene terephthalate (PET)**	**Polystyrene (PS)**
Gas	5.4	50.4	1.5
Liquid	87.0	16.0	97.0
Solid	4.0	26.0	0.0

Table 4. Pyrolysis-reforming of different waste plastics (pyrolysis temperature 500 ^oC, catalytic reforming temperature 900 ^oC, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}{}_{catalyst}$, 10 wt.% Ni/Al_2O_3 catalyst).

	Waste Plastic Type		
	Polyethylene (HDPE)	**Polyethylene terephthalate (PET)**	**Polystyrene (PS)**
Gas yield (wt.%) (related to mass of plastic)	206.5	88.2	299.3
Reacted Water (g $g^{-1}{}_{plastic}$)	1.76	1.42	2.72

Table 5. Effect of different catalyst temperatures on the pyrolysis-catalytic steam reforming of waste polystyrene (pyrolysis temperature 500°C, steam weight hourly space velocity 4.74 g h^{-1} $g^{-1}_{catalyst}$, 10 wt.% Ni/Al_2O_3 catalyst).

	Catalyst temperature (°C)		
	700	**800**	**900**
Gas yield (wt.%) (related to mass of plastic)	156.7	196.4	226.9
Reacted Water (g $g^{-1}_{plastic}$)	1.26	1.29	1.69

Table 6. Effect of steam weight hourly space velocity on the pyrolysis-reforming of waste polystyrene (pyrolysis temperature 500 °C, catalytic reforming temperature, 900 °C, catalyst, 10 wt.% Ni/Al_2O_3).

	Steam weight hourly space velocity ($g\ h^{-1}\ g^{-1}_{catalyst}$)		
	4.74	**7.59**	**10.40**
Gas yield (wt.%) (related to mass of plastic)	226.9	299.3	242.6
Reacted Water ($g\ g^{-1}_{plastic}$)	1.69	2.72	2.22

Table 7. Influence of different metal catalysts calcined at 950°C on pyrolysis-reforming of polystyrene (pyrolysis temperature 500°C, catalytic reforming temperature 900°C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).

	Catalyst			
	Ni/Al_2O_3	**Fe/Al_2O_3**	**Cu/Al_2O_3**	**Co/Al_2O_3**
Gas yield (wt.%) (related to mass of plastic)	299.3	176.2	173.7	201.6
Reacted Water (g $g^{-1}_{plastic}$)	2.72	1.54	1.48	1.61

FIGURE CAPTIONS

Figure 1. Schematic diagram of the pyrolysis-reforming reactor

Figure 2. The chemical structure of the repeating unit for polyethylene, polystyrene and polyethylene terephthalate.

Figure 3. Gas composition (mmol gas $g^{-1}_{plastic}$) from pyrolysis of different waste plastics

Figure 4. Gas composition from pyrolysis-reforming of different waste plastics (pyrolysis temperature 500°C, catalyst reforming temperature 900 °C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).

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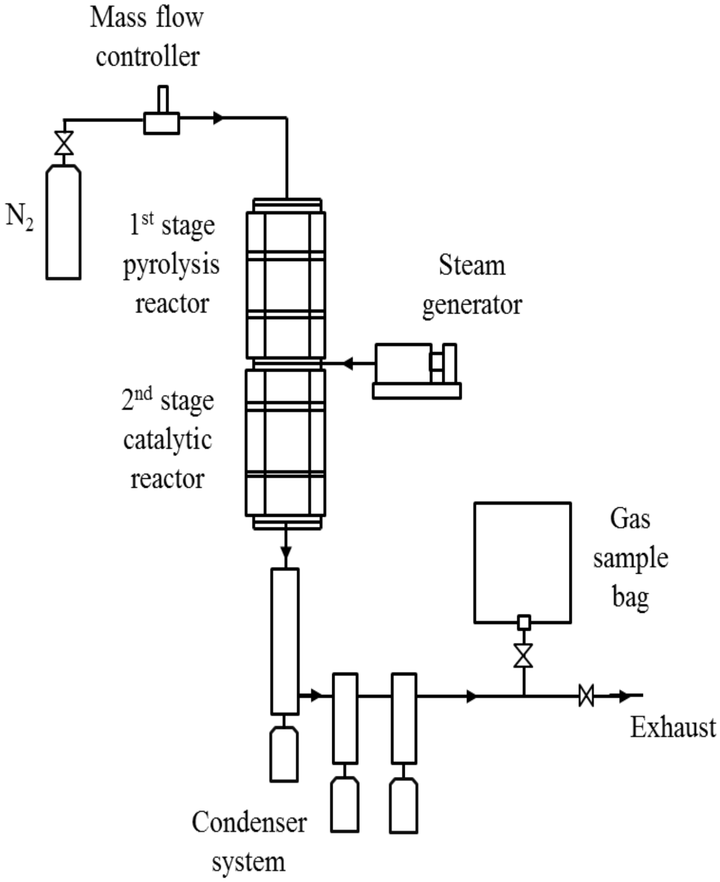
Figure 7. Gas composition from pyrolysis-reforming of waste polystyrene (pyrolysis temperature 500°C, catalytic reforming temperature 900°C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst calcination temperature 950°C, catalyst, 10 wt.% Ni/Al_2O_3).



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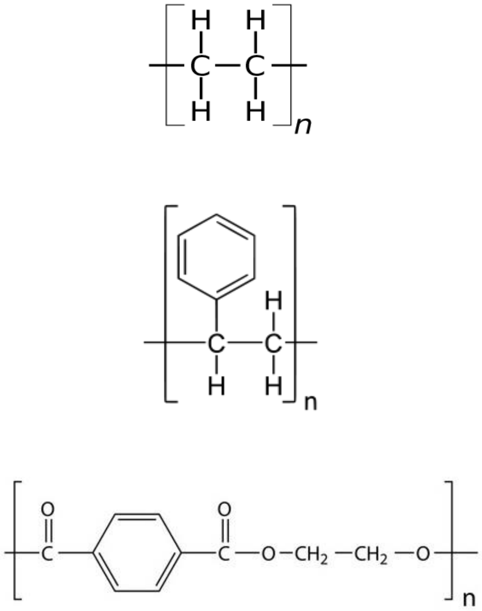

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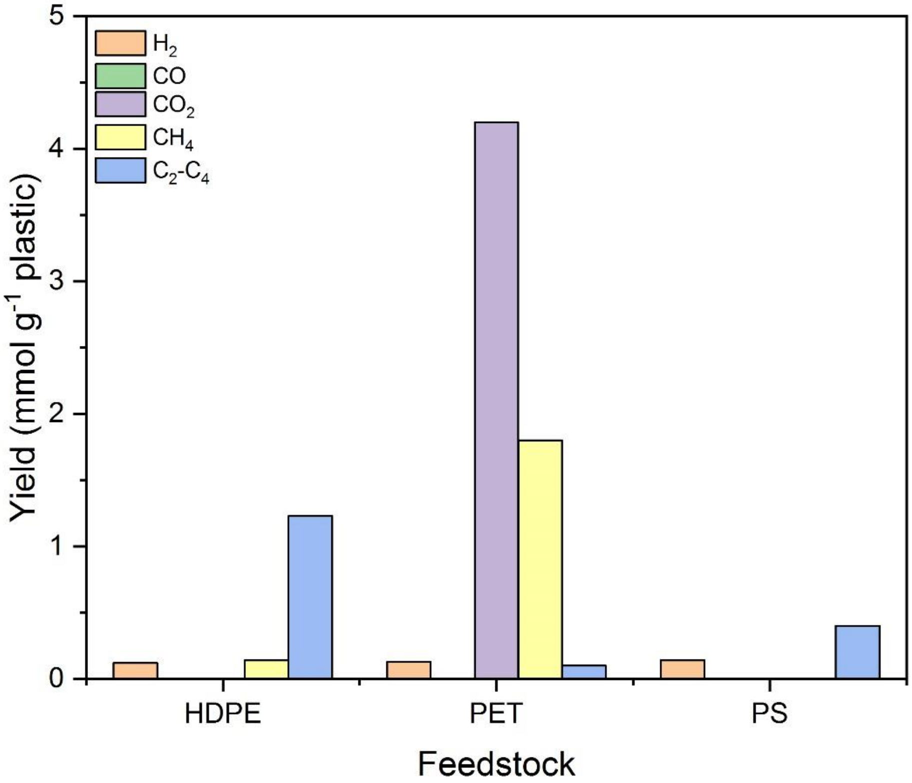


Figure 3. Gas composition (mmol gas $g^{-1}_{plastic}$) from pyrolysis of different waste plastics

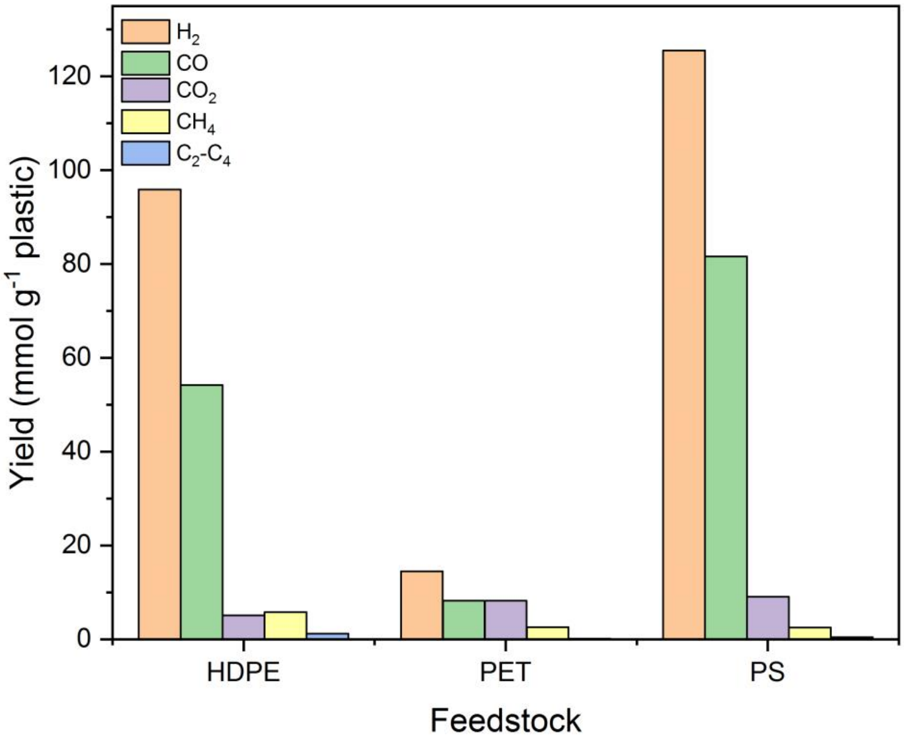
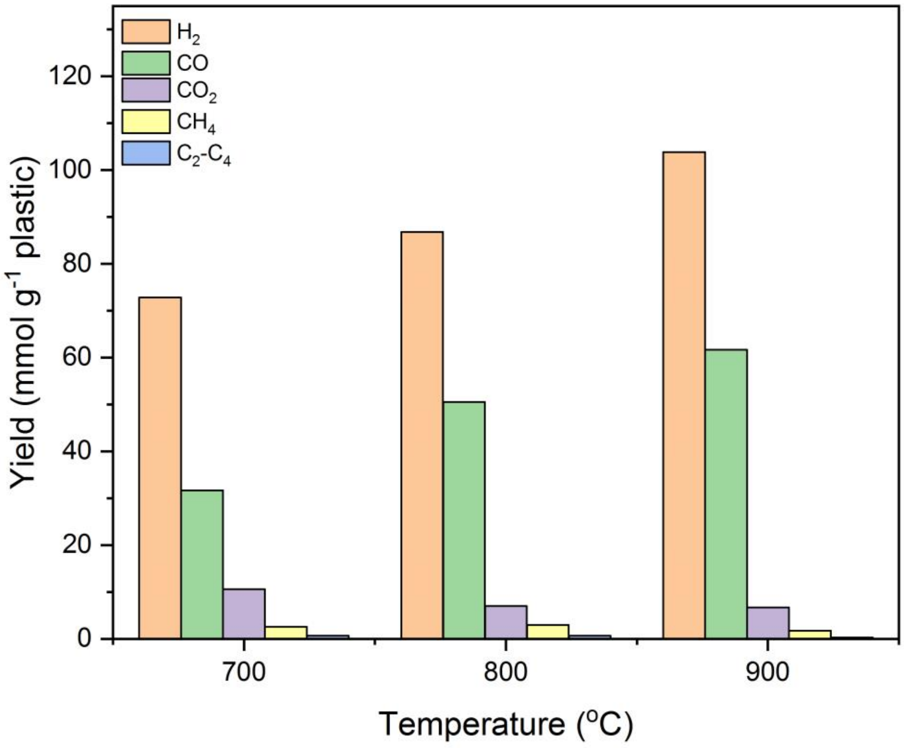


Figure 4. Gas composition from pyrolysis-reforming of different waste plastics (pyrolysis temperature 500°C, catalyst reforming temperature 900 °C, steam weight hourly space velocity 7.59 g h^{-1} g$^{-1}_{catalyst}$, catalyst, 10 wt.% Ni/Al_2O_3).



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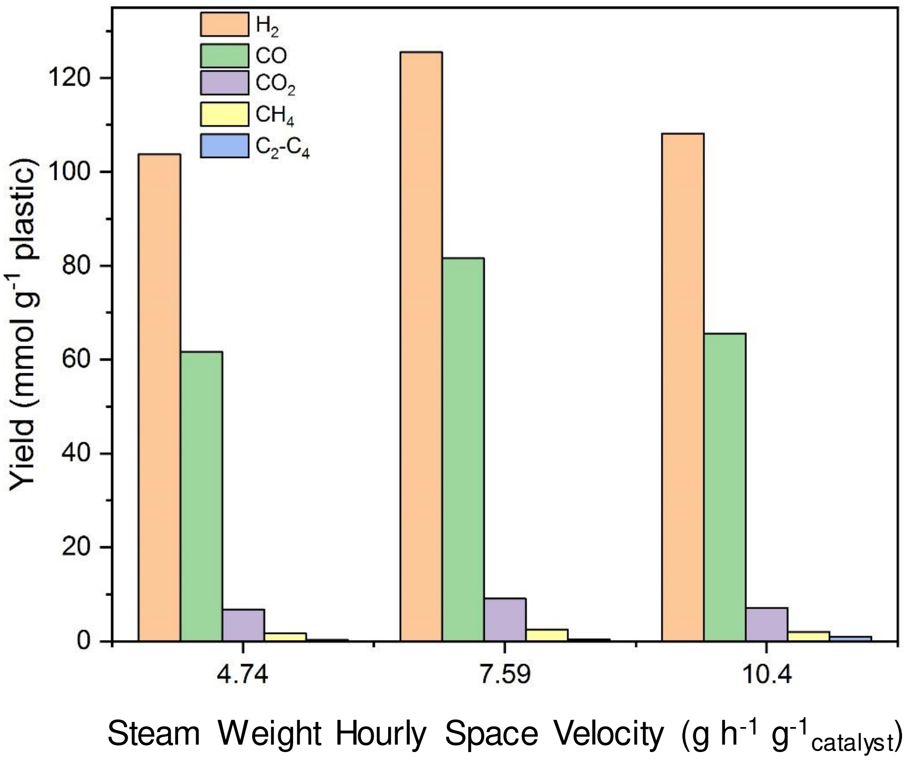

Figure 6. Gas composition from pyrolysis-reforming of waste polystyrene (pyrolysis temperature 500°C, catalytic reforming temperature 900°C, catalyst, 10 wt.% Ni/Al_2O_3).

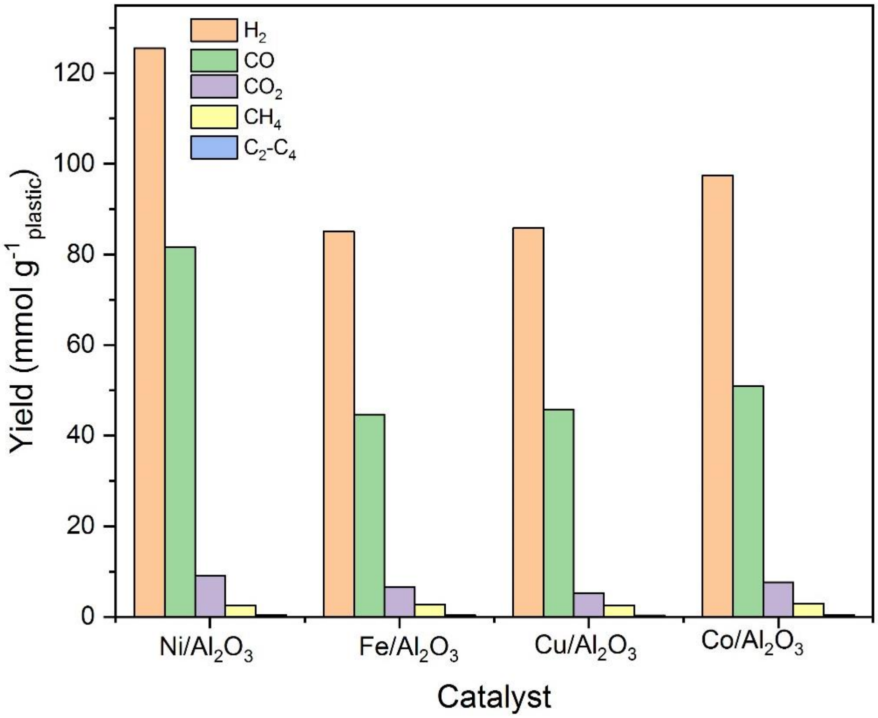

Figure 7. Gas composition from pyrolysis-reforming of waste polystyrene (pyrolysis temperature 500°C, catalytic reforming temperature 900°C, steam weight hourly space velocity 7.59 g h^{-1} $g^{-1}_{catalyst}$, catalyst calcination temperature 950°C, catalyst, 10 wt.% Ni/Al_2O_3).