Pyrolysis-catalytic steam reforming of waste plastics for enhanced hydrogen/syngas yield using sacrificial tire pyrolysis char catalyst

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ABSTRACT

Pyrolysis-catalytic steam reforming of waste plastics to produce hydrogen-rich syngas has been investigated using tire char as a sacrificial catalyst in a two-stage pyrolysis-catalytic steam reforming reactor system. The simultaneous steam reforming of the pyrolysis volatiles and 'sacrificial' steam gasification of tire char increased the overall yield of syngas and hydrogen in the gas products. Manipulating the catalyst temperature, steam input, char catalyst:plastic ratio influenced hydrogen yield. The presence of metals such as Zn, Fe, Ca and Mg in tire char, play a catalytic role in steam reforming reactions. The syngas production achieved when the catalyst temperature was 1000 °C and steam weight hourly space velocity was 8 g h^{-1} g^{-1} $_{catalyst}$ was 135 mmol H$_2$ g$_{plastic}^{-1}$ and 92 mmol CO g$_{plastic}^{-1}$. However, increasing the amount of char catalyst (4:1 char catalyst:plastic ratio) enabled hydrogen yields of 211 mmol g$_{plastic}^{-1}$ and total syngas yields of 360 mmol g$_{plastic}^{-1}$ to be achieved.

1. Introduction

Hydrogen is a zero-carbon-emission energy source at the end-use point, which is of great interest in the context of climate change and fossil fuel depletion [1]. There are many processes for hydrogen production, including from traditional fossil fuel and alternative energy sources such as coal, natural gas, biomass, plastics, etc. [2]. Biomass and plastics are considered more promising feedstocks for hydrogen production because they overcome the environmental impact of over-exploitation of non-renewable energy sources [3,4]. In addition, the enormous production and applications of plastics inevitably result in the growth in waste plastic accumulation, and much of the produced waste plastic stream cannot be treated appropriately. Every year, a quarter of all waste plastics end up in landfills, which occupy huge space, represent a waste of resource and has the potential to cause serious environmental problems [5]. Hydrogen production from waste plastics is a novel route to recycle plastics, which can effectively deal with the problems resulting from the management of waste plastics whilst generating a valuable energy source.

Combined pyrolysis-catalytic steam reforming is a thermochemical technology to convert waste plastics into a hydrogen-rich gas. The process typically uses a two-stage reaction system, where waste plastics are pyrolyzed in the first stage to produce pyrolytic volatiles which then pass into a second stage catalytic reactor, where steam reforming

reactions occur to generate hydrogen. The two-stage reactor has been used by many researchers [6–10] and has become a common reactor system for producing hydrogen from plastics because of its advantages such as separate temperature control between the two stages and producing effective and controllable reaction between pyrolysis volatiles and the steam reforming catalyst. Czernik and French [6] pyrolyzed polypropylene in a two-stage fluidized bed reactor with pyrolysis and catalytic steam reforming at 650 °C and 800 °C, respectively. They reported that polypropylene was completely transformed into volatiles that were subsequently reformed by steam producing a hydrogen yield of 170 mmol g$_{plastic}^{-1}$, accounting for 80% of the stoichiometric hydrogen potential. Erkiaga et al. [7] developed a continuous experimental reactor system that consisted of a conical spouted bed reactor for pyrolysis and a fixed bed reactor for catalysis. In the second stage fixed bed reactor, all the volatiles generated from pyrolysis of the plastics were converted into gas in the presence of the reforming catalysts. Various plastics were studied by Wu and Williams using laboratory prepared nickel-based catalysts [8–10]. The yield of hydrogen was improved by optimizing the process parameters, such as catalyst temperature and catalyst to plastic ratio.

In the catalytic stage of the pyrolysis-reforming system, catalysts obviously play an important role in promoting the conversion of volatiles derived from pyrolysis to gas. Metal-based catalysts, such as ruthenium, rhodium, iron and nickel, are widely used catalysts in the

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pyrolysis-catalytic steam reforming of waste plastics. Santamaria et al. [11] have reviewed the state-of-the art of metal catalysts for the steam reforming of the volatiles derived from pyrolysis of biomass and waste plastics. They reported that in addition to the type of reforming catalyst used, which would include type of metal, support material and use of promoters, several other operational parameters influence hydrogen yield; for example, the type of reactor, steam:plastic ratio, steam space velocity and catalyst design, including method of preparation, calcination temperature, metal loading etc. [11]. Some noble metals, such as ruthenium and rhodium, have been proved to have higher catalytic activity than nickel, but due to their high cost, would be expensive to use in practical commercial production [12]. Bimetallic and trimetallic catalysts have recently received considerable attention for improving catalyst activity for H_2 production from waste plastics [11,13]. Also, different metal-based catalysts were compared in relation to their catalytic activity and adaptability to produce hydrogen from the two-stage pyrolysis-catalytic steam reforming of polypropylene [9]. However, a problem with metal-based catalysts is that during reaction, carbonaceous deposits attach to the surface of the catalyst or block the pore structure, preventing hydrocarbons from interacting with the catalyst and resulting in catalyst deactivation.

In addition, many researchers [14–16] have used char as a catalyst because the char itself has hydrocarbon reforming activity; activities related to pore size, surface area and metal composition. El-Rub et al. [14] reported that the hydrocarbons would be adsorbed to the char active sites followed by steam reforming into CO and H_2. Yao et al. [15] investigated hydrogen production from biomass steam gasification with biochar using a two-stage fixed-bed reactor. The structure and composition of the catalyst indicated that the interaction of volatiles and biochar promoted the reforming of pyrolysis volatiles. Biochar has been shown to encourage hydrocarbon decomposition and water gas shift reaction during biomass steam reforming. Some metals such as Fe, K, Cu, and Ni have been introduced into char, for example, Min et al. [17] catalyzed hydrocarbon reforming using a Ni/char catalyst, and the results showed that Ni dispersed on the char showed higher activity in hydrocarbon reforming than char alone. Cu has been reported to promote syngas production and Fe and Cu are conducive to the formation of high-porosity carbon materials, improving the specific surface area and improving catalytic effectiveness [18].

When char has been used as a catalyst, carbonaceous coke deposits have also been formed that blocked the char pore structure, reducing the surface area [17]. However, the char and coke may be consumed by steam and pyrolysis components such as CO_2, creating new pore structures that inhibit catalyst deactivation [17,19]. Some studies [20–23] have investigated syngas production from char gasification. Char gasification involves a series of reactions, including steam gasification, Boudouard reaction and methanation, and the gas products are mainly composed of H_2, CO, CO_2 and CH_4 [22]. Yan et al. [20] conducted steam gasification experiments with biochar in a fixed bed reactor at temperatures between 600 and 850 °C and different steam input flow rates. The results showed that increasing the temperature and steam flow rate can improve the syngas yield. In addition, increasing temperature and steam flow rates produced increased H_2 yield [23]. Guizani et al. [24] found that both CO_2 and steam can promote pore development and increased surface area in chars during char gasification.

Most of the research into the use of pyrolysis chars as catalysts for hydrocarbon reforming have involved biochar and coal char, derived from biomass and coal pyrolysis respectively. The activity of the catalyst is not directly dependent on the specific surface area and pore volume, but also on the inorganic matter in the char support. The inorganic matter in char plays an important role in the catalytic performance, and the carbon in the char acts as catalyst and inorganic material support [25].

The char derived from the pyrolysis of waste tires is also a promising type of catalyst. The inherent properties of tire char and modified tire char have been reviewed in detail in relation to a wide range of higher

value-added applications, including gasification for the production of fuel gas, production of activated carbon, catalyst use and as catalyst support materials, and asphalt additives [26]. Importantly, tire char contains a high ash content and contains a range of transition metals, such as zinc, iron, cobalt and copper [26] which have been shown to be effective as active metals and catalyst promoters for the catalytic steam reforming of waste plastics [11]. Also, the particular characteristics of tire pyrolysis char with its inherent S-based active sites have advantageous catalytic properties. The catalytic performance of tire char enhanced by S-based active site has been shown to be useful for upgrading pyrolysis oil via cracking and deoxygenation [27]. Tire char with its particular high content of zinc and sulfur, mostly in the form of ZnS, have been shown to act as a strong Lewis acid that catalyses decarbonylation and steam reforming reactions of pyrolysis volatiles and also promotes the dissociation of steam [27]. Zhou et al. [28] investigated the upgrading performance of tire char on bio-oil and found that the inorganic components in tire char could preferentially crack heavy hydrocarbons. In the catalytic pyrolysis of scrap tires, tire char also showed a high selectivity of lightweight compounds, especially valuable single aromatics and syngas [29,30].

An additional advantage of using pyrolysis chars as steam reforming catalysts is not only their activity in relation to catalyst hydrocarbon reforming reactions but that the catalyst is also a reactant in the catalytic steam environment, which consequently results in complete gasification of the carbonaceous char. Tire char was first proposed by Al-Rahbi and Williams [31] as a sacrificial catalyst for hydrogen production and tar removal in a two-stage fixed-bed reactor during pyrolysis reforming of biomass. They found that acid-treated tire char as a catalyst produced less hydrogen and lower catalytic activity. The difference in hydrogen production between the untreated tire char and acid-treated tire char indicated that the metal in the char significantly improved water gas shift, hydrocarbon reforming and char steam gasification. Recent work reported by Tan et al. [27] investigated the production of hydrogen-rich syngas in steam reforming of lignite pyrolysis volatiles catalyzed by tire char. They reported that the lignite pyrolysis volatiles were more reactive than biomass pyrolysis volatiles in steam reforming under catalysis with tire char. Thereby, producing a different product slate because of the specific properties of tire pyrolysis char interacting with different species of pyrolysis volatiles. Therefore, it is interesting, and a novel aspect of the work reported here, to investigate the interaction of volatiles produced from waste plastics pyrolysis with waste tire char for the production of hydrogen-rich syngas and to understand the influence of process conditions on the final product slate. To the authors knowledge there are no detailed research reports on hydrogen-rich syngas production from waste plastics using tire char as a steam reforming catalyst.

In this paper, tire pyrolysis char was used as a catalyst for pyrolysis-catalytic steam reforming of waste plastic whilst also acting as a feedstock for char-steam gasification to produce hydrogen-rich syngas. High density polyethylene (HDPE) was chosen as the representative plastic waste to investigate since it contributes as a major polymer found in post-consumer municipal solid waste plastic [5]. The influence of process parameters, including catalyst temperature, steam input, reaction time and catalyst:plastic ratio were investigated to optimize syngas production. The influence of temperature and steam input on ash content, metal composition and pore structure of the catalyst were also investigated.

2. Materials and methods

2.1. Feedstock

The plastic used in this work was high-density polyethylene (HDPE) and was produced from recycled end-of-life plastic waste and supplied in the form of 2 mm polymer pellets by Regain Polymers Limited, Castleford, UK. The ultimate analysis of the HDPE was determined by a FLASH EA2000 CHNS analyzer and oxygen was calculated by difference.

The results showed that the elemental content of HDPE consisted of 80.26 wt% carbon, 15.33 wt% hydrogen, 0.36 wt% nitrogen and 4.05 wt% oxygen and no sulfur was detected. Pure HDPE was expected to contain only carbon and hydrogen, but the plastic used in this study could be contaminated by other plastics in the recycling process or from additives used in the plastics manufacturing process. Proximate analysis characterised the properties of the plastic based on moisture, fixed carbon, ash, and volatile components. The high volatile fraction and low ash content of plastic waste are responsible for high hydrocarbon yields during pyrolysis [32]. The volatile, ash and fixed carbon fraction of HDPE were 93.64 wt%, 6.66 wt% and 0.16 wt%, respectively.

The catalyst used for the pyrolysis-catalytic steam reforming of the waste plastic was tire char produced from the pyrolysis of waste truck tire at a final pyrolysis temperature of 800 °C. The waste truck tire was prepared by removing the steel and shredding it into ~5 mm sized particles. The tire char was prepared using a one stage pyrolysis reactor constructed of stainless steel of dimensions, 40 mm diameter and a height of 200 mm and externally heated by a controlled 1.5 kW electrical furnace. The pyrolysis heating regime was heating from ambient temperature to a final pyrolysis temperature of 800 °C at a heating rate of 20 °C min^{-1} followed by holding at 800 °C for 20 min. The pyrolysis was undertaken several times to generate enough tire char for the experiments on pyrolysis-catalytic steam reforming of the waste plastic. The results of multiple tire pyrolysis experiments showed that the average yields of pyrolysis gas, oil and char were 7.70 wt%, 55.50 wt% and 36.50 wt%, respectively, with a small standard relative deviation, showing excellent repeatability.

2.2. Experimental reactor system and procedure

The pyrolysis-catalytic steam reforming experiments using waste plastics with the produced waste tire pyrolysis char was carried out in a two-stage fixed-bed pyrolysis reactor, and a schematic diagram of the experimental system is shown in Fig. 1. The reactor system comprised a steam injection system, carrier gas supply system, two-stage reactor (stainless steel), condenser system and gas collection and analysis system. The first stage reactor had an inner diameter of 40 mm and a height

Fig. 1. Schematic diagram of the two-stage pyrolysis-reforming reaction system.

of 200 mm, which was used for the pyrolysis of waste plastics, and was connected directly to the second stage separately heated catalytic reactor. The second stage reactor had an inner diameter of 22 mm and a height of 300 mm, and was used for catalytic reforming pyrolysis volatiles produced from the waste plastics. Quartz wool on a stainless steel mesh supported the tire char as a fixed bed of catalyst and was placed in the middle of the catalytic reactor. The products from the reactor were passed through three condensers: the first cooled by air, the other two cooled by dry ice, where the condensable products were collected as a liquid product, while the non-condensable gas was collected into a 25 L Tedlar^{TM} gas sample bag.

The waste plastics (1.0 g) and tire char catalyst (1.0 g) were weighed and placed in the pyrolysis reactor and catalytic reactor, respectively. The nitrogen flow rate was set as 100 ml min^{-1}. Before the experiment, nitrogen was continuously fed into the reactor to discharge the air in the reactor, and the outlet flowrate was monitored with a gas flowmeter to ensure a maintained stable flowrate. When the temperature of the catalytic reactor was stabilized at the desired temperature, the plastics in the first stage were heated and pyrolyzed; the heating rate was 20 °C min^{-1} to a final temperature of 600 °C, and maintained at this temperature for 20 min. The waste plastics pyrolyzed in the first-stage reactor produced volatiles which were passed directly into the second-stage reactor for catalytic steam reforming. The steam was also involved in steam-carbon (char) gasification reactions. The steam was generated from an automatic water injection pump to provide a steam atmosphere. Condensable product gases (unreacted water) were collected as a liquid in the condensation system. During the experiments, the catalytic temperature was varied from 800 °C to 1000 °C, the steam weight hourly space velocity was varied from 2 g h^{-1} g^{-1} catalyst to 10 g h^{-1} g^{-1} catalyst and the total gas collection time was 60 min.

2.3. Product analysis and characterization

The gaseous products collected in the gas sample bag were analyzed off-line by packed column gas chromatography (GC). The hydrocarbons (C_1-C_4) were analyzed using a Varian CP-3380 GC fitted with a 60–80 mesh column, a flame ionization detector and nitrogen carrier gas. Permanent gases (H_2, CO, O_2, N_2, CO_2) were analyzed by a second Varian 3380 GC with two separate columns with a thermal conductivity detector. H_2, O_2, CO and N_2 were analyzed on a 60–80 mesh molecular sieve column with an argon carrier gas, while CO_2 was analyzed on a HayeSep 80–100 mesh column with argon carrier gas. To ensure the accuracy of the experiments, pyrolysis gas from the experiments was injected and analysed in duplicate and sometimes triplicate. The mass of each gas was calculated by the molar percentage content of each gas and the molar percentage content of carrier gas. The liquid product reported was almost all comprised of condensed unreacted water, because most of the heavy, oil-range hydrocarbons produced by plastic pyrolysis were reformed into gas in the presence of steam. Only a small, negligible fraction of unconverted oil was observed (attached to the walls of the condenser). The mass of liquid was obtained by the mass of the condenser before and after the experiments. The product yield was the mass of product divided by the total mass of the input (the total mass of plastic, water, and char).

The waste tire used to prepare the tire char and the produced tire char were characterized using several different techniques. Metal contents analysis of samples was carried out using acid digestion followed by atomic absorption spectrometry. The samples were initially ashed and the ash was subsequently dissolved in a concentrated solution of nitric acid at 240 °C. The samples were prepared in duplicate. Analysis was performed using a Varian Fast Sequential Atomic Absorption Spectrophotometer (Varian AA240FS).

A high-resolution scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometry (EDXS) analysis was used to observe the morphologies and metal distribution of the tire char. The analysis used was a Hitachi SU8230 scanning electron microscope with
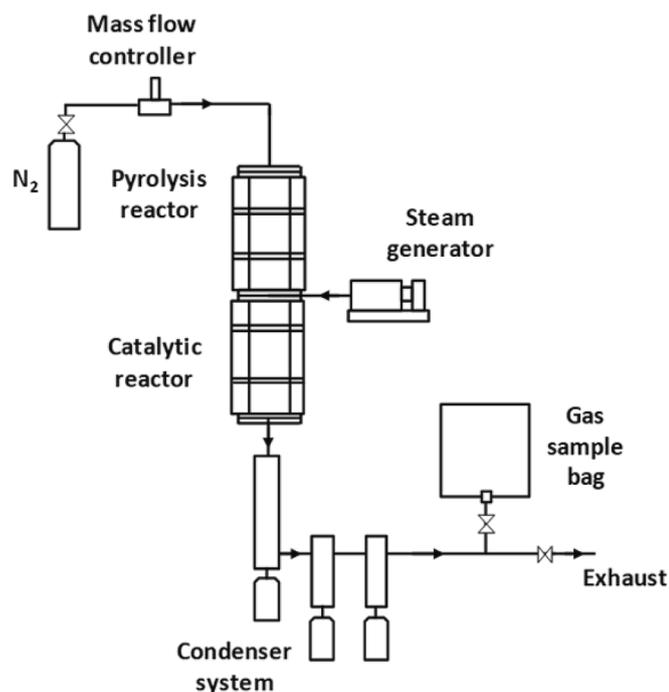
an Oxford Instruments Aztec Energy EDXS system. The used char catalysts were characterized using a Mettler Toledo thermogravimetric analyzer (TGA) to determine the ash content. A sample of recovered char was placed in the sample crucible of the TGA and heated to a temperature of 900 °C at a ramp rate of 25 °C min^{-1} in a N_2 atmosphere, followed by air (50 ml min^{-1}) and maintained at 900 °C for 15 min. The total specific surface area of samples was calculated from N_2 adsorption and desorption isotherms operating at 77 K based on the Brunauer-Emmet-Teller (BET) method using a Micrometrics Tristar 3000 instrument. The micropore and mesopore surface area were calculated from the N_2 adsorption isotherm via the t-plot method. The cumulative pore volume was determined from N_2 adsorption isotherms and calculated at a relative pressure P/P_0 of 0.99. The pore size distribution was obtained from the desorption isotherms via the Barrett-Joyner-Hallender (BJH) method.

3. Results and discussion

3.1. Characterization of the fresh tire char catalyst

The catalyst used in this study was tire char produced from tire pyrolysis in a N_2 atmosphere at a final pyrolysis temperature of 800 °C. Table 1 shows the ash composition and ultimate analysis of the tire char catalyst and also the waste tire rubber precursor. The waste tire rubber consists mainly of carbon (~80 wt%), hydrogen (~7 wt%) and significant concentrations of other elements (Zn, Fe, Ca, Si and S) derived from the fillers and additives used in tire manufacturing or deposited on the tire during use [33]. The pyrolysis process used to produce the tire char catalyst released volatile matter, thus increasing the ash and fixed carbon content of the product tire char, of which the ash content reached 14.72 wt%, which was consistent with other research [27,34]. The mass fraction of hydrogen in the tire char was significantly lower than that in the original tire because the hydrogen in the tire was converted to H_2, hydrocarbons and low concentrations of H_2S during pyrolysis [35]. The mass fraction of sulfur in tire char increased to 3.46 wt% compared with the original tire, which indicated that carbon consumption is faster than sulfur loss. The dominant sulfur species in the pyrolytic char have been reported as aliphatic sulfide and ZnS [36]. During the pyrolysis process, most of oxygen in the tire is retained in the tire char in the form of metal oxides, carbonates, silicates and oxygen-containing functional groups, so a decrease in hydrogen concentration leads to a relative increase in oxygen concentration.

The pore volume and pore size distribution of tire char is shown in Fig. 2. The dV/dD represents the pore volume per unit pore size. The higher the peak value of the dV/dD, the more abundant the corresponding pore size. As can be seen from Fig. 2, the pore size corresponding to the peak value of the differential pore volume was 4 nm and

Table 1
Ash composition and ultimate analysis of tire and tire char.

	Tire	Tire char catalyst
Ash content (wt.%)	4.62	14.72
Elemental analysis (wt.%)		
Carbon	78.35	79.02
Hydrogen	7.08	0.66
Oxygen	11.60	16.58
Nitrogen	0.44	0.29
Sulfur	2.54	3.46
Ash metals content (wt.%)		
Zinc	3.68	7.43
Silicon	1.16	2.20
Calcium	0.49	0.53
Magnesium	0.10	0.13
Potassium	0.11	0.12
Iron	0.34	0.44
Copper	0.03	0.04
Cobalt	0.06	0.12
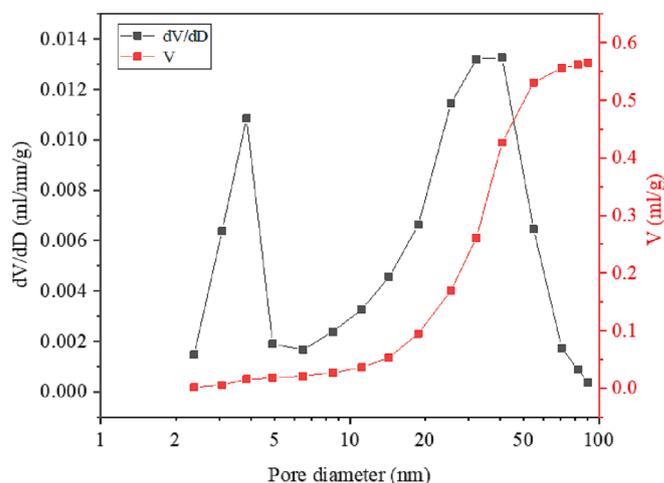
Fig. 2. Pore volume and pore size distribution of tire char.

30–40 nm, which indicated that the pore structure of tire char was mostly mesoporous. This was also confirmed by the specific surface area of tire char, which was 79 m^2 g^{-1}, of which the specific surface area of micropores was 9.25 m^2 g^{-1} and that of mesopores was 69.82 m^2 g^{-1}. The cumulative adsorption volume of the tire char is shown in the red curve in Fig. 2, and shows that the cumulative adsorption volume can reach 0.57 cm^2 g^{-1}. The 20–50 nm sized pores contributed most of the adsorption volume, and the average adsorption pore size was 22.75 nm.

The XRD spectra for the prepared tire char catalyst is shown in Fig. 3. The tire char catalyst contains two phases, ZnS and FeS in addition to SiO_2. Similar results were reported by Zhou et al. [28] for scrap tire char in relation to work investigating the upgrading of bio-oil. Other metals were not detected by XRD, indicating that they were in lower concentration or have amorphous structures. The diffraction peaks of ZnS and FeS for the fresh catalysts were sharp and narrow, which indicated that the phase has good crystallinity and a large grain size. According to the Scherrer equation, the average particle size of ZnS and FeS was calculated as 31 nm and 33 nm, respectively. Zhou et al. [28] also reported that Zn-bearing grains are nano-sized grains with a diameter of about 40 nm or lower.

Fig. 4 shows the SEM micrograph and elemental distribution (EDXS) of tire char and used tire char (catalyst temperature of 1000 °C). From

Fig. 3. X-Ray diffraction analysis of the tire char.
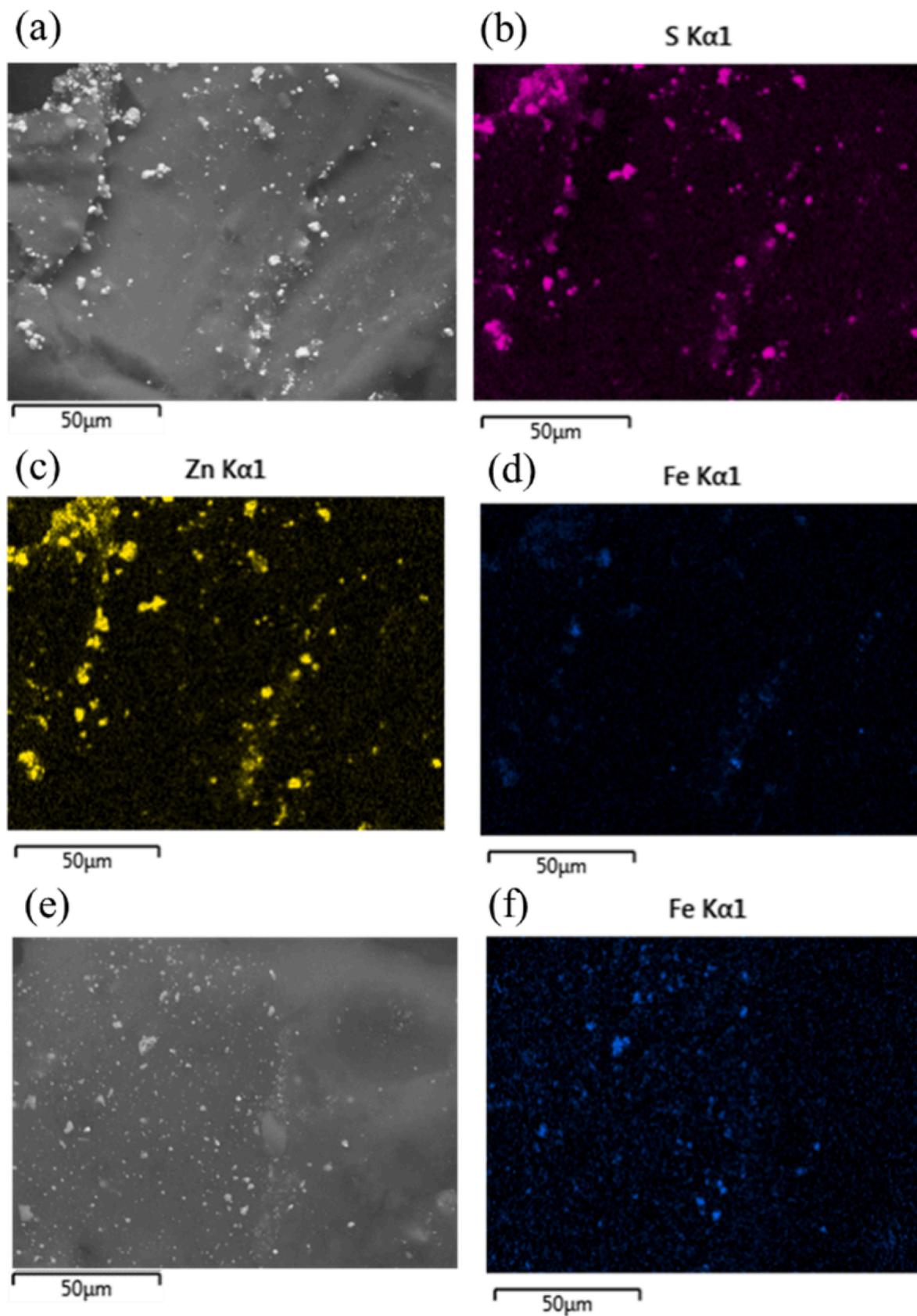
Fig. 4. SEM image and elemental mapping of tire char ((a)-(d)) and used tire char (1000 °C catalyst temperature) ((e) and (f)).

Fig. 4(a), it can be seen that most of the tire char surface is flat, but some raised particles exist on the surface. This is mainly because during the pyrolysis process, the devolatilization of tires caused some elements to combine and become exposed on the surface. The distribution of some elements (S, Zn and Fe) in the tire char is shown in Fig. 4(b), (c) and (d). As can be seen from Fig. 4(b) and 4(c), S and Zn are well dispersed on the surface of tire char. The S and Zn element added in the manufacture process of tire were not substantially released during the pyrolysis process and still existed in the tire char. Fig. 4(d) shows that the Fe content in the tire char is low and scattered sporadically on the tire char surface. Fig. 4(e) and (f) shows the surface morphology of the used tire char catalyst and the distribution of elements on its surface. It can be seen that there is no significant change to the tire char surface, however, no S and Zn could be detected by the EDXS analysis, indicating that the used tire char catalyst surface has no sulfur and Zn, or that the content is very low. This is because at temperatures of ~600 °C, the dissociative sublimation of ZnS occurs to produce Zn and Sx [37,38]. In addition, ZnS may react with steam to produce ZnO, H$_2$S, SO$_2$ and H$_2$ during steam gasification by the following equations [39,40]:

$$ZnS \rightarrow Zn + S_x \tag{1}$$

$$ZnS + H_2O \rightarrow ZnO + H_2S \tag{2}$$

$$ZnS + 3H_2O \rightarrow ZnO + SO_2 + 3H_2 \tag{3}$$

3.2. H$_2$ and syngas produced from HDPE with and without tire char catalyst

To compare the product distribution of hydrogen and syngas in the pyrolysis-catalytic steam reforming of HDPE at different temperatures and times with and without tire char catalysts, separate experiments were conducted using different experimental procedures. Several different gas syringes (each of 20 ml volume) were used to collect the product gas from the process at different times (corresponding to different pyrolysis temperatures), rather than using the gas sample bag to collect the total gas products. Each of the extracted 20 ml gas syringe samples was analyzed to obtain the gas composition, which can be used as an indicator of gas production in the presence and absence of the tire char catalyst. Fig. 5 shows a comparison of hydrogen and syngas production from the pyrolysis-catalytic steam reforming of HDPE with and without the tire char catalyst. For the 'with tire char' experiment, the catalyst temperature was 1000 °C and steam input was 8 ml h^{-1}. For the 'without tire char' experiment, the 2nd stage catalyst reactor was still maintained at 1000 °C and steam input was 8 ml^{-1}. Fig. 5(a) shows that

without tire char the hydrogen production mainly started at a pyrolysis temperature of 300 °C. With the rise of pyrolysis temperature, plastics were slowly pyrolyzed, and the release of pyrolytic volatiles was relatively stable. The steam reforming of these pyrolytic volatiles was carried out continually, so the hydrogen production did not change much between 300 and 500 °C. When the temperature continued to rise to 600 °C, the pyrolytic volatiles of plastics were released rapidly, and were reformed by steam to produce hydrogen and CO (Fig. 5(b)). With the advance of time, the plastic was almost completely pyrolyzed, so the production of hydrogen and CO showed a downward trend. Syngas production (Fig. 5(b)) showed a similar trend over time, but with addition of CO produced by the char gasification reactions. Akubo et al. [41] also found that in the process of pyrolysis catalytic steam reforming of biomass pyrolysis components, hydrogen production with catalyst at different times was significantly higher than that without a Ni-based catalyst under the same conditions. The difference in hydrogen content (shown in Fig. 5(a)) and the difference in syngas content (shown in Fig. 5(b)) with and without catalysts reflects the effect of the involvement of the tire char catalyst on the process.

The total hydrogen yield and syngas yield from pyrolysis-catalytic steam reforming of HDPE with and without catalyst are shown in the Table 2. The results show that at a catalyst temperature of 900 °C, the hydrogen yield increased by 18 mmol g$^{-1}_{plastic}$ when tire char was used as catalyst, compared to that without tire char catalyst, and at 1000 °C, the hydrogen yield increased by 63 mmol g$^{-1}_{plastic}$ when tire char was used as catalyst. Therefore, the presence of tire char improved the yield of hydrogen and syngas and the effect of tire char on the yield of hydrogen and syngas was more obvious with the increase of temperature. Yao et al. [15] also reported that char showed good catalytic performance towards H$_2$ production in the gasification of biomass with biochar as the catalyst in a fixed bed reactor.

Table 2
Total H$_2$ yield and syngas yield from HDPE with and without catalyst at different tire char catalyst temperatures..

	Without tire char catalyst		With tire char catalyst	
	H$_2$ (mmol g$^{-1}_{plastic}$)	Syngas (mmol g$^{-1}_{plastic}$)	H$_2$ (mmol g$^{-1}_{plastic}$)	Syngas (mmol g$^{-1}_{plastic}$)
900 °C	44	103	62	120
1000 °C	72	129	135	226
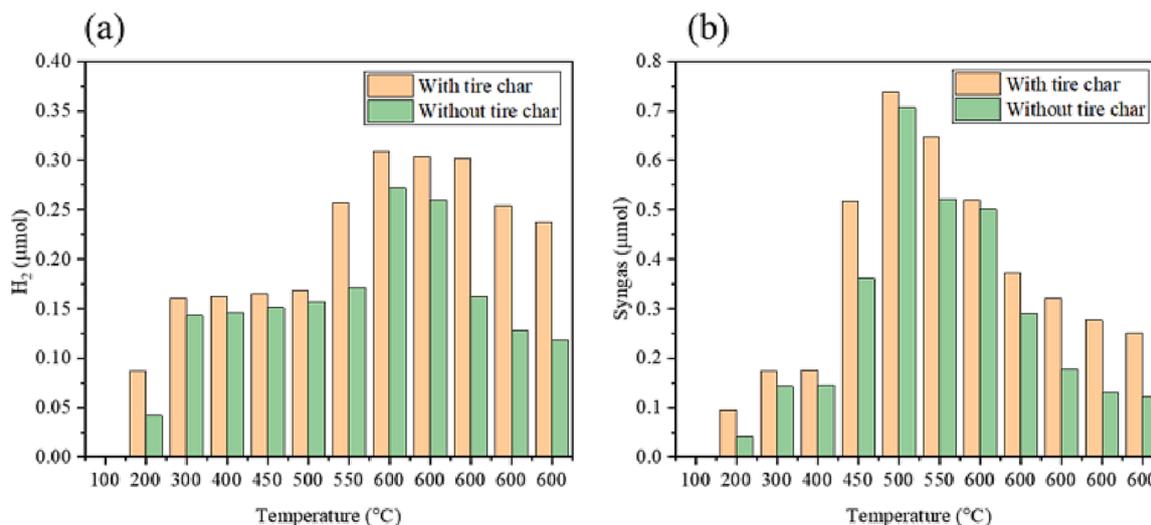
Fig. 5. H$_2$ and syngas (H$_2$ and CO) content in syringe at different pyrolysis temperature.

3.3. Influence of catalytic temperature on pyrolysis-reforming of plastic wastes

The influence of catalytic temperature on the composition of the final product gas was investigated at temperatures from 800 °C to 1000 °C at a fixed steam space velocity of 8 g h^{-1} g^{-1} $_{catalyst}$ and a reaction time of 60 min. The Influence of the temperature of the tire char catalyst in relation to (a) product yield, (b) H$_2$, CO and syngas yield, (c) volumetric gas composition and (d) residual char yield and ash content are shown in Fig. 6(a) – 6(d). The product yield data reported in Fig. 6 is based on the mass of input plastic sample, reacted water and reacted char. The product yield from pyrolysis-catalytic steam reforming of waste plastics at different catalytic temperatures are shown in Fig. 6(a). There was negligible char produced from the pyrolysis of the HDPE plastic, with complete conversion of the plastic to volatiles. The liquid shown in Fig. 6 (a) represents unreacted condensed water. Table 3 shows the data of gas yield reported in relation to the mass of plastic only and also shows the amount of reacted water. It can be seen from Table 3 that the amount of water consumed by the reaction of volatile species generated from each gram of waste plastic with tire char in the catalytic process increased from 0.80 g at 800 °C to 2.87 g at 1000 °C, and the corresponding gas yield, based on only the mass of plastic sample, increased from 256 wt% to 440 wt%, the gas being composed of mostly hydrogen and carbon monoxide (syngas). The product gas is produced from both the catalytic

Table 3
Influence of tire char catalyst temperature on the total gas yield based on the mass of plastic feedstock.

	Tire char catalyst temperature (°C)				
	800	**900**	**950**	**975**	**1000**
Gas yield based on the mass of plastic (wt. %)	256	294	413	420	440
Reacted water (g)	0.80	1.46	2.59	2.35	2.87

steam reforming of the hydrocarbon volatiles produced from both the pyrolysis of the plastic in the presence of the tire char catalyst but also from the steam gasification of the carbonaceous char catalyst material. That is, the tire char carbon is 'sacrificed' to increase the yield of hydrogen and syngas. The reaction of pyrolysis volatiles with steam via catalytic steam reforming is an endothermic reaction and was significantly promoted at high temperatures, increasing the total gas, hydrogen and carbon monoxide production. The remarkably high gas yield of 440 wt% is produced from the plastic pyrolysis and catalytic steam reforming of the pyrolysis volatiles and in-turn the input of reacted water and reaction of steam with the char via steam gasification to produce further gas yield. However, it is interesting to report that such high gas yields comprised of mostly hydrogen and carbon
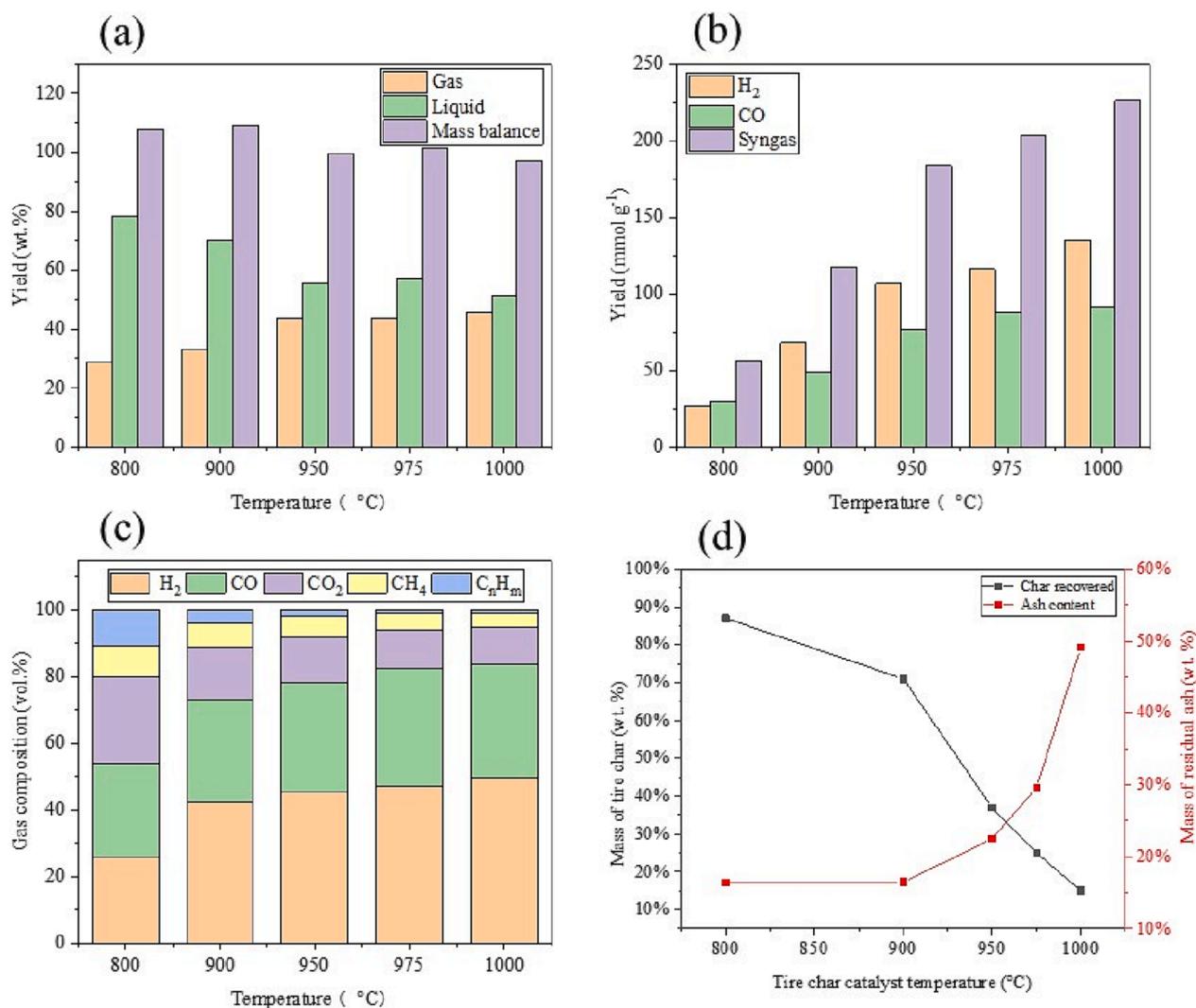
Fig. 6. Influence of tire char catalyst temperature on (a) product yield, (b) H$_2$, CO and syngas yield, (c) volumetric gas composition, (d) residual char yield and ash content. Yield based on the sample + water + reacted char.

monoxide can be achieved from waste plastics with input of low cost water and low cost waste derived char.

Fig. 6(b) shows that the yield of H_2 was significantly increased from 27 to 135 mmol $g_{plastic}^{-1}$, and the yield of CO increased from 29 to 92 mmol $g_{plastic}^{-1}$ when the tire char catalyst temperature was raised from 800 to 1000 °C. This was attributed to the positive effect of temperature on the reforming of hydrocarbons, methane reforming and Boudouard reaction due to the endothermic nature of these reactions. The relationship between increased H_2 yield and increased catalytic steam reforming temperature is well demonstrated in the literature [3,8,42,43]. Barbarias et al. [42] developed a continuous process consisting of the flash pyrolysis of HDPE in a conical spouted bed reactor followed by steam reforming in a fluidized bed reactor. Their results showed that H_2 yield increased from 170 mmol $g_{plastic}^{-1}$ at 600 °C to 187 mmol $g_{plastic}^{-1}$ at 700 °C, in which approximately 63% of H_2 was formed from steam and the remaining 37% from plastics. He et al. [43] also reported that a higher temperature resulted in a higher conversion of waste polyethylene into syngas with a significant increase in H_2 content. Fig. 6(b) also shows that as a consequence of higher yields of H_2 and CO, the syngas yield was increased at higher temperatures, rising from 56 mmol $g_{plastic}^{-1}$ at 800 °C to 227 mmol $g_{plastic}^{-1}$ at 1000 °C.

The volumetric gas composition of the gas derived from the pyrolysis of HDPE coupled with catalytic steam reforming and tire char gasification in relation to different catalytic temperatures is shown in Fig. 6(c). The gas products from waste plastics pyrolysis are mainly composed of H_2, CO, CO_2, CH_4 and C_nH_m, among which the total proportion of H_2 and CO i.e. syngas, ranged from 54 to 84 vol%. Fig. 6(c) shows that as the tire char catalyst temperature was increased from 800 °C to 1000 °C, the concentration of H_2 rose from 25.8 vol% to 49.9 vol%, while the concentration of C_nH_m decreased from 10.8 vol% to 0.7 vol%, and the concentration of CH_4 also showed a downward trend. Barbarias et al. [44] also reported that the steam reforming of CH_4 and $CnHm$ was almost complete at higher temperatures, but with only a small increase in the hydrogen concentration, when they reported on experiments of the continuous fast pyrolysis-steam reforming of HDPE. Several reactions may occur during the catalytic steam reforming stage in the presence of the tire char catalyst, as follows:

$$\text{Steam reforming} \quad C_nH_m + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2 \qquad (4)$$

$$\text{Methane steam reforming} \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (5)$$

$$\text{Water} - \text{gas shift} \quad CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (6)$$

$$\text{Water} - \text{gas (primary)} \quad C + H_2O \leftrightarrow CO + H_2 \qquad (7)$$

$$\text{Water} - \text{gas (secondary)} \quad C + 2H_2O \leftrightarrow CO_2 + 2H_2 \qquad (8)$$

$$\text{Boudouard} \quad C + CO_2 \leftrightarrow 2CO \qquad (9)$$
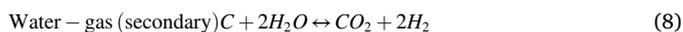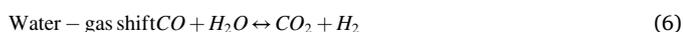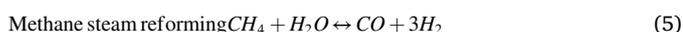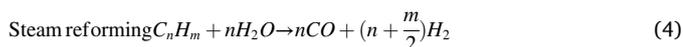
It has been suggested [45] that when the catalyst temperature is higher than 700 °C, the concentration of H_2 was mainly determined by Eq.4, Eq.5 and Eq.6. Since Eq.4 and Eq.5 are endothermic reactions, increasing the temperature promoted the reaction to move to the right, consuming a large amount of CH_4 and C_nH_m, thus increasing hydrogen production. It was concluded that temperature played an essential role in the decomposition of CH_4 and C_nH_m, which is consistent with research reported by Turn et al. [46]. Reaction of the steam with the tire char carbon via steam gasification also contributes to the yield of further hydrogen, CO and syngas (Eq. (7) and Eq. (8) In addition, CO_2 generated from the plastic reacted with carbon components contained in the plastic itself and fixed carbon components in tire char to generate more CO (Eq. (9)).

The mass of tire char recovered from pyrolysis-catalytic steam reforming of HDPE and the ash content of that residual char in relation to the different tire char catalyst temperatures investigated are shown in Fig. 6(d). The results show that 87 wt% of tire char was recovered at a catalytic temperature of 800 °C, while only 15 wt% of tire char remained after reaction at the catalyst temperature of 1000 °C. This is because the fixed carbon in the char (~85 wt%) reacted with steam to produce more gas. Char-steam gasification has been reported to be enhanced at high temperature [20], suggesting that more of the carbon in the tire char was involved in the gasification reactions and consequently less char was recovered. This also explained the increase in gas production as the temperature was increased.

The ash content of the residual tire char after the experiment was obtained by proximate analysis. The fixed carbon in the char was consumed, so the ash content of the remaining char was increased. The ash content of the un-used prepared tire char was 14.7 wt%, and when used as the catalytic steam reforming process at 800 °C the ash content in the residual tire char was 16.5 wt%, indicating that the metal composition in the tire char did not change significantly during reaction. However, at the higher catalyst temperature of 1000 °C, the ash content reached 50 wt% of the residual char, indicating that ~85 wt% of the carbonaceous char had been gasified by the input steam (Fig. 6(d)). It should also be noted that the zinc component of the tire char was volatilized at the high catalyst temperature of 1000 °C; the boiling point of pure zinc metal being 907 °C. Table 1 showed that the freshly prepared tire pyrolysis char had a Zn content of 7.43 wt%; analysis of the used char catalyst used at a temperature of 1000 °C produced a Zn content of only 0.96 wt%, suggesting significant loss of the zinc due to volatilization. Conesa et al. [47] investigated the pyrolysis and gasification of scrap tires in a pilot plant reactor and also reported that when the pyrolysis of temperature increased from 700 °C to 1000 °C, the Zn content of char decreased.

In addition to the catalytic steam reforming process, steam gasification of the carbonaceous tire char occurred, which consumed the carbon in the tire char and generated a large amount of gas, resulting in the enhancement of the pore structure of the tire char. Fig. 7(a) and 7(b) shows the pore volume and pore size distribution of tire char recovered from the experiments at the tire char catalyst temperatures of 900 and 1000 °C. The pore size distribution of the used tire char (900 °C) ranged from less than 5 nm to 100 nm with the main pore size being between 20 and 50 nm, and the cumulative adsorption pore volume was 0.61 ml g^{-1}. When the char catalytic temperature was increased to 1000 °C, the cumulative pore volume reached 0.84 ml g^{-1}. The carbon material obtained after steam activation was mainly mesoporous with limited microporosity.

Table 4 shows the pore structure data for the prepared tire pyrolysis char catalyst and the tire char after use at the catalyst temperatures of 900 °C and 1000 °C with a steam input flow rate of 8 ml h^{-1}. As observed in Table 4, the specific surface area of tire char increased from 79 m² g^{-1} for the prepared un-used tire char to 410 m² g^{-1}, for the tire char used at 900 °C. However, when the temperature was increased to 1000 °C, the surface area of the used tire char decreased to 381 m² g^{-1}. The higher temperature resulting in higher char-steam interaction and pore widening, pore wall destruction and consequent loss of surface area. The specific surface area of the micropores and mesopores of the tire char recovered at 900 °C is almost equal, however, when the temperature was increased to 1000 °C, the surface area of micropores was far less and almost all of the pores were mesopores.

3.4. Influence of steam input on pyrolysis-reforming of plastic wastes

Steam has been shown to be an important factor affecting hydrogen production in the pyrolysis-catalytic steam reforming of waste plastics because it promotes the steam reforming reaction and water gas shift reaction, resulting in the production of more gases, especially H_2 [46]. In addition, the steam/plastic ratio can improve process efficiency and facilitate hydrocarbon cracking [7]. In this work, the influence of different steam space velocities (from 2 to 10 g h^{-1} g^{-1} catalyst) was investigated with a maintained tire char catalyst temperature of 900 °C and reaction time of 60 mins. Fig. 8(a) – 8(d) shows the influence of
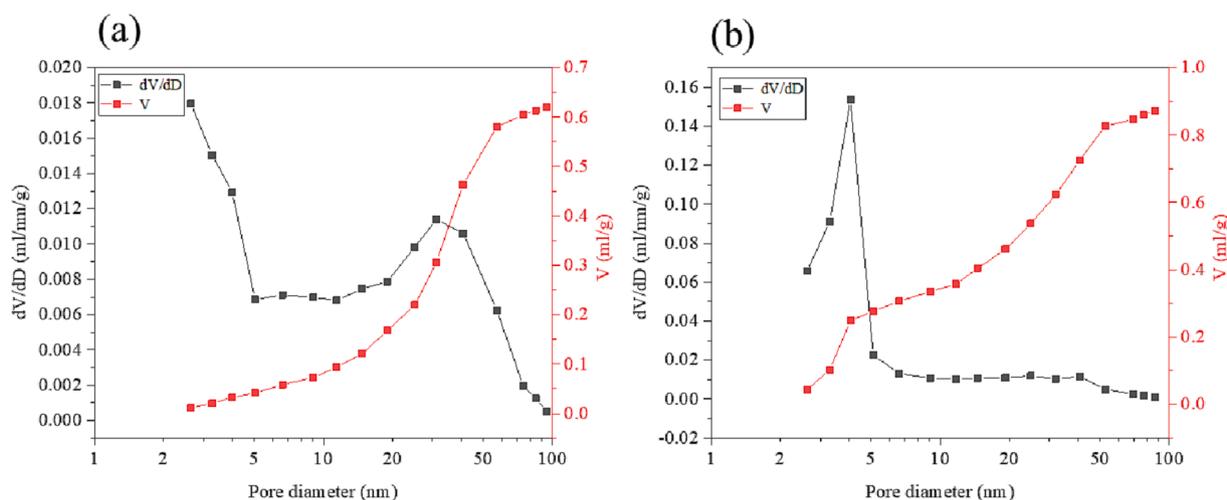
Fig. 7. Pore volume and pore size distribution of (a) used tire char at 900 °C and (b) used tire char at 1000 °C.

Table 4
Pore structure of tire char and used tire char.

	Surface area (m²/g)	Micropore surface area (m²/g)	Mesopore surface area (m²/g)	Average pore size (nm)	Cumulative pore volume (ml/g)
Tire char	79	9.25	69.82	22.75	0.57
Used char (900 °C)	410	205.70	204.40	6.11	0.61
Used char (1000 °C)	381	1.60	379.6	8.02	0.84

steam input on 8(a) product yield, 8(b) H_2, CO and syngas yield, 8(c) volumetric gas composition and 8(d) residual char yield and ash content. The reported product yield data (Fig. 8(a)) is calculated based on the input mass of plastic, the input of water and the amount of reacted tire char catalyst. In addition, Table 5 shows the effect of steam input on the gas yield calculated based on the mass of input plastic only also shown is the mass of reacted water. The results show that with the increase of steam space velocity from 2 g h^{-1} g^{-1} $_{catalyst}$ to 10 g h^{-1} g^{-1} $_{catalyst}$, the amount of water reacted increased from 0.75 g to 1.53 g (Table 5). There was a consequent marked increase in gas yield calculated in relation to the mass of plastic only, rising from 182 wt% at a steam input of 2 g h^{-1} g^{-1} $_{catalyst}$ to 299 wt% at 10 g h^{-1} g^{-1} $_{catalyst}$ steam input. However, when the steam space velocity rate was between 8 and 10 g h^{-1} g^{-1} $_{catalyst}$, the gas yield based on only plastic samples increased but did not change significantly. Clearly, increasing the steam input did not continuously improve the total gas yield, as similarly reported by Moghadam et al. [48] in an investigation of biomass steam gasification.

The yield of H_2, CO and syngas produced from the process in relation to steam input are shown in Fig. 8(b). There was an increase in hydrogen yield with increased steam input, rising from 32 mmol g$^{-1}_{plastic}$ at 2 g h^{-1} g^{-1} $_{catalyst}$ steam input to 70 mmol g$^{-1}_{plastic}$, at 10 g h^{-1} g^{-1} $_{catalyst}$ steam input, but the influence at higher steam inputs was less at the higher temperatures. This is because the higher steam input allowed the carbon in plastic and tire char to react with more H_2O, increasing the yield of H_2. Sattar et al. [49] investigated the effect of steam flowrate on pyrolysis gas during biochar gasification, and the results also showed that H_2 concentration increased with the increase of steam input. Eq.4, Eq.5 and Eq.6 moved to the right due to the increase of steam, and in addition, CO, CH_4 and C_nH_m were consumed to form more H_2. Li et al. [50] also found a similar trend in the catalytic steam gasification of palm oil in a fixed bed. However, at higher steam inputs, the catalyst active sites become saturated and reduce catalytic reforming reactions. Similarly, the CO yield increased from 34 mmol g$^{-1}_{plastic}$ to 48 mmol g$^{-1}_{plastic}$ between 2 and 6 g h^{-1} g^{-1} $_{catalyst}$ steam input but above this input, the change in CO yield was marginal. The data for H_2 and CO yield were also reflected in the yield of syngas in relation to steam input.

Fig. 8(c) shows the volumetric gas composition derived from the pyrolysis-catalytic steam reforming of waste plastics using the tire char catalyst at different steam space velocity. With the increase in steam space velocity from 2 g h^{-1} g^{-1} $_{catalyst}$ to 10 g h^{-1} g^{-1} $_{catalyst}$, the relative concentration of H_2 increased, rising from 35 vol% to 43.10 vol%, with CO showing a relative decrease in concentration.

The amount of tire char recovered after the pyrolysis-catalytic steam reforming of HDPE at a tire char catalyst temperature of 900 °C and the ash content of that char at different steam space velocities are shown in Fig. 8(d). The data show that the tire char recovered from the experiment at 2 ml h^{-1} was 94 wt%. As the steam input was increased, the amount of char recovered was less, for example at a steam space velocity of 8 g h^{-1} g^{-1} $_{catalyst}$, 71 wt% of char was recovered at the end of the experiment. The effect of steam input on char recovered and ash content was less than that compared to the results of the influence of catalyst temperature. The ash content of the residual char was 12.85 wt% at a steam space velocity of 2 g h^{-1} g^{-1} $_{catalyst}$, whereas ash content in the original tire char was 14.72 wt%. As the steam input was increased, the carbon in tire char reacted with more steam, reducing the amount of char carbon and thereby, increasing the ash content of the remaining char.

For comparison, when using a nickel-based catalyst in the pyrolysis-catalytic steam reforming of waste plastics, the mass of catalyst increased by between 3 wt% and 14 wt% after reactions under different conditions, which was attributed to deposition of carbonaceous coking deposits on the catalyst [8]. It has also been reported [51] that these carbonaceous deposits adhered to the surface of the catalyst and blocked the pore structure. However, in this when the tire char was used as catalyst, the carbon in the tire char reacted with steam to open the pore structure. When the steam space velocity was increased to 8 g h^{-1} g^{-1} $_{catalyst}$, more carbon in the char was consumed via steam gasification reactions, resulting in a developed pore structure, and a specific surface area that was four times that obtained at a steam space velocity of 4 g h^{-1} g^{-1} $_{catalyst}$, reaching 410 m² g^{-1}. With the increase in steam input, the development of micropore structure was promoted, the micropore surface area increased significantly, and the average pore size was
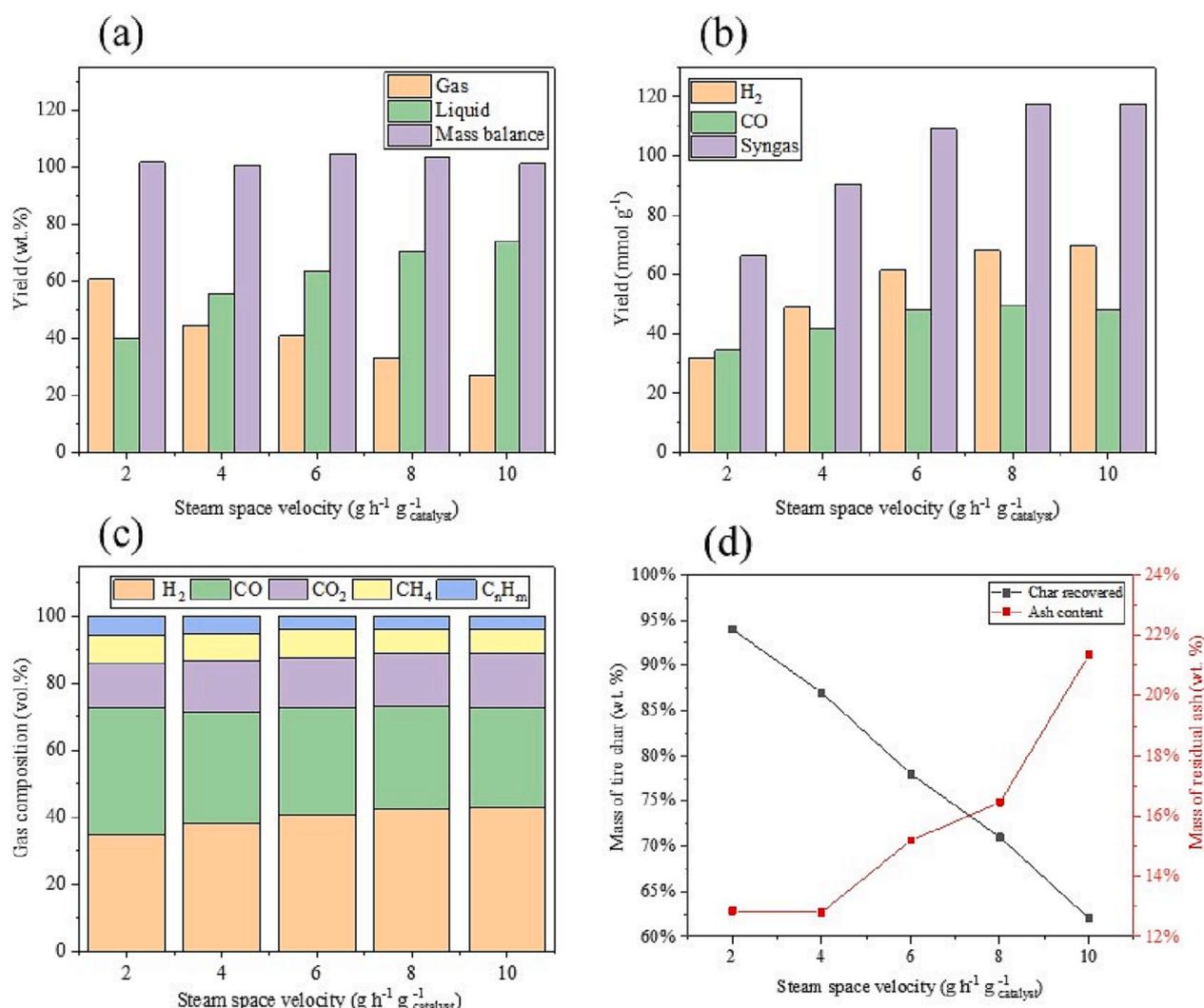
Fig. 8. Influence of steam input on (a) product yield, (b) H_2, CO and syngas yield, (c) volumetric gas composition, (d) residual char yield and ash content. Yield based on the sample + water + reacted char.

Table 5
Influence of steam input on the total gas yield based on the mass of plastic feedstock.

	Steam weight hourly space velocity (g h^{-1} g^{-1} $_{catalyst}$)				
	2	**4**	**6**	**8**	**10**
Gas yield based on the plastic sample (wt. %)	182	260	285	295	299
Reacted water (g)	0.75	1.10	1.37	1.46	1.53

reduced from 17.20 nm to 6.11 nm.

3.5. Influence of char catalyst:plastic ratio

The tire char produced from the waste tire was examined for hydrogen production from pyrolysis-catalytic steam reforming of HDPE at a catalyst:plastic ratio of 0.5:1, 1:1, 1:2 and 1:4. The tire char was generated at a final pyrolysis temperature of 800 °C, the catalytic temperature was kept constant at 1000 °C, and the steam space velocity was 8 g h^{-1} g^{-1} $_{catalyst}$. Fig. 9(a)–9(d) show the influence of catalyst:plastic ratio on 9(a) product yield, 9(b) H_2, CO and syngas yield, 9(c) volumetric gas composition and 9(d) residual char yield and ash content. As before the yields are calculated based on the input of the plastic, water

(steam) and reacted char. Table 6 shows the data for gas yield in terms of the mass of plastic as the only input, also shown is the mass of reacted water.

The product yield in relation to the char catalyst:plastic ratio is shown in Fig. 9(a), and shows that as the catalyst:plastic ratio was increased from 0.5:1 to 4:1, the gas yield increased from 41 wt% to 68 wt %. In terms of the total gas yield based only on the input of plastic waste to the process is considered (Table 6), very high amounts of gas are observed, with total gas yield rising from 364 wt% at a plastic: catalyst: plastic ratio of 0.5:1 to 666 wt% gas at a ratio of 4:1. This clearly reflects the interaction of steam and char, since the mass of reacted water increases from 2.22 to 4.37 as the ratio of char catalyst was increased. It has been reported [8] that a slight increase in gas yield was observed as the catalyst ratio was increased, for the two-stage pyrolysis-catalysis of waste plastics with a Ni-based alumina catalyst, while in this study, the gas yield showed a significant increase. This is because most of the gas came from the steam gasification of the tire char, which can be observed by catalytic steam reforming the tire char and water consumed in the process (Table 6).

Fig. 9(b) and 9(c) shows that the main gases associated with the large amount of gas generated was hydrogen and carbon monoxide i.e. syngas. The yield of H_2 increased with the increase in catalyst, rising from 109 mmol g$^{-1}_{plastic}$ at a catalyst:plastic ratio of 0.5:1 to 211 mmol g$^{-1}_{plastic}$ at a ratio of 4:1. Similarly, the CO increased from 72 mmol g^{-1} to 149
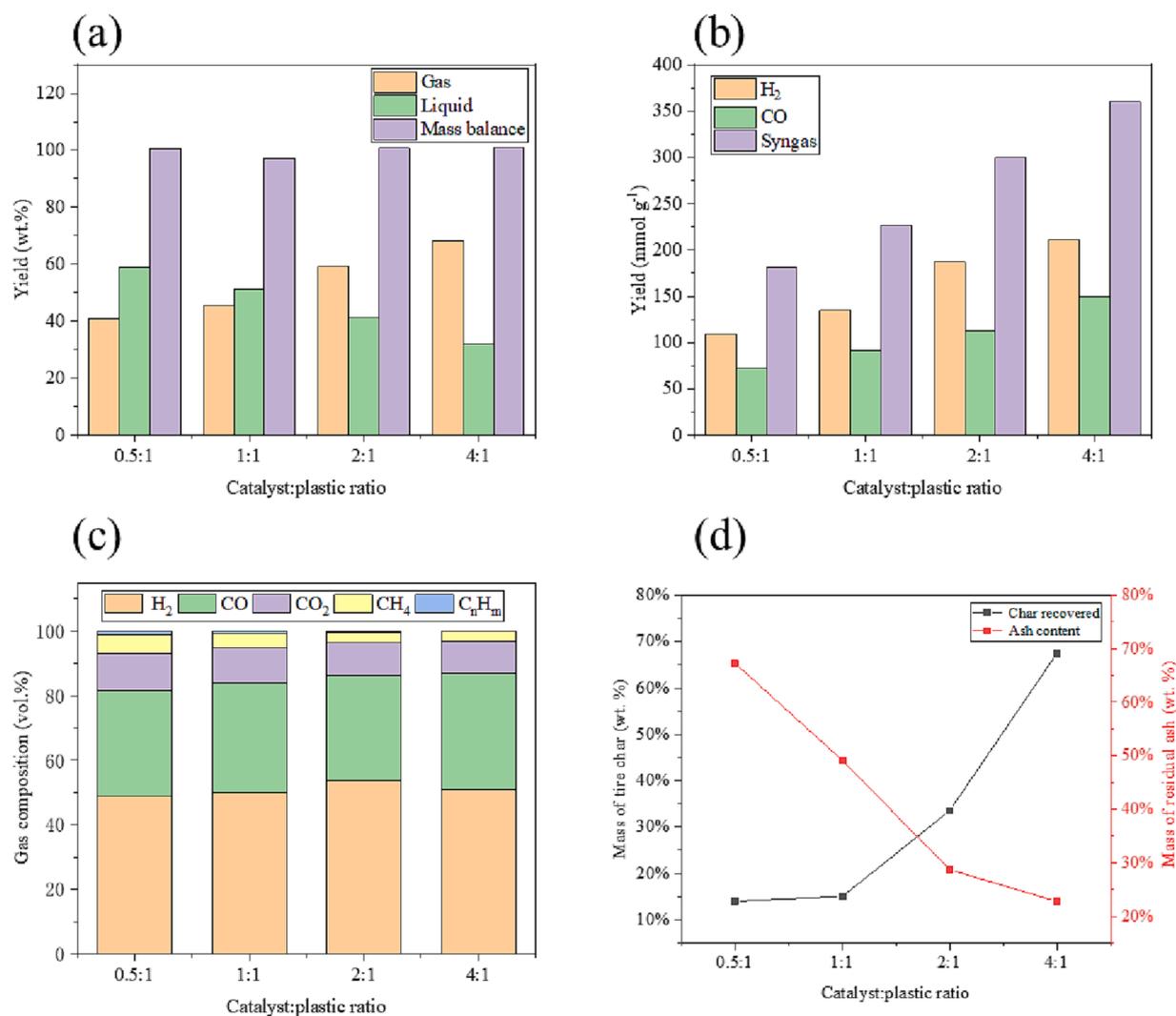
Fig. 9. Influence of catalyst:plastic ratio on (a) product yield, (b) H_2, CO and syngas yield, (c) volumetric gas composition, (d) residual char yield and ash content. Yield based on the sample + water + reacted char.

Table 6
Influence of catalyst:plastic ratio on the total gas yield based on the mass of plastic feedstock.

	Catalyst:plastic ratio			
	0.5:1	1:1	2:1	4:1
Gas yield based on the plastic sample (wt. %)	364	440	533	666
Reacted water (g)	2.22	2.87	3.00	4.37

mmol $g_{plastic}^{-1}$ at a ratio of 4:1. The consequent syngas yield at the char catalyst:plastic ratio of 4:1 was 360 mmol $g_{plastic}^{-1}$. Due to the metal content in tire char, the increase of catalyst ratio suggests that more metal active components were introduced, thus promoting the reforming reaction of plastic pyrolysis volatiles. On the other hand, the gaseous products from the steam gasification of tire char are mainly H_2 and CO, with little CH_4 being formed. The steam can react with more of the fixed carbon in the tire char, resulting in higher H_2 and CO production. However, as reported in other work [8], when nickel-based catalysts were used, the increase in gas product yield was mainly due to the improved steam reforming of hydrocarbons. In addition, the increase in gas yield was less, for example, the increase in hydrogen yield was only about 10 wt% [8]. From the results of Section 3.6 (below), where char was steam gasified in the absence of plastics pyrolysis, the H_2 yield from

char gasification alone was around 70 mmol $g_{plastic}^{-1}$. Therefore, when the catalyst:plastic ratio was increased from 1:1 to 4:1, the H_2 yield was increased by only 76 mmol $g_{plastic}^{-1}$, with increasing catalyst:plastic ratio producing more residual, char, indicating that the carbon char reaction with the steam was restricted.

The influence of changing the catalyst:plastic ratio on the product volumetric gas composition (Fig. 9(c)) for the catalytic pyrolysis steam reforming of HDPE with the tire char catalyst was marginal. When the ratio of catalyst:plastic was increased from 0.5:1 to 2:1, the H_2 concentration increased from 49.1 vol% to 53.8 vol%, but, when the ratio of catalyst:plastic was further increased to 4:1, the H_2 concentration decreased to 50.9 vol%. When the ratio of catalyst:plastic was increased from 2:1 to 4:1, the yield of H_2 increased, but the concentration of H_2 decreased by 2.90% due to the increased content of CO in the pyrolysis gas. The CO_2 reaction with the carbon in the tire char was dominant, resulting in the consumption of a large amount of CO_2. With the increase of catalyst:plastic ratio, the concentrations of CO_2, CH_4 and C_nH_m showed a decreasing trend. This is related to steam reforming (Eq.4), methane steam reforming (Eq.5) and the Boudouard reaction (Eq.9), which promoted the production of CO and H_2. The hydrocarbons mainly reacted with steam for reforming. Under constant steam input, the concentration of C_nH_m and CH_4 decreased, indicating that the increase of catalyst proportion had an obvious promoting effect on the reforming reactions of hydrocarbons.

3.6. The influence of reaction time

To study the influence of reaction time of the catalyst char 'on-stream' in relation to the gas yield and gas composition, 1 h, 2 h and 4 h reaction times were investigated at the catalyst temperature of 1000 °C. The previous reported sections used a reaction time of char 'on-stream' of 60 min (1 h). As discussed above, the formation of H_2 is mainly generated firstly from the pyrolysis volatiles produced by pyrolysis of the HDPE which reacts with steam via the catalytic steam reforming process and also from the fixed carbon in the tire char reacting with steam via gasification reactions. To determine the influence of the different routes to hydrogen production, experiments of tire char with steam were carried out but with the absence of any HDPE pyrolysis, to determine the hydrogen generation from the tire char only. Fig. 10 shows the (a) H_2 yield and (b) CO yields from steam gasification of char in addition to showing the pyrolysis-catalytic steam reforming of HDPE using the tire char. The H_2 yield produced from the sacrificial gasification of tire char after 1 h reaction time on-stream, was 70 mmol $g_{plastic}^{-1}$, accounting for 52% of the total H_2 obtained from pyrolysis-catalytic steam reforming of HDPE using tire char. Further experiments at 2 h and 4 h reaction time showed that steam gasification of the tire char produced 89 mmol $g_{plastic}^{-1}$ of H_2 and 120 mmol $g_{plastic}^{-1}$ of H_2, respectively, accounting for 50% and 64% of the total H_2 production. When the reaction time was increased from 1 h to 2 h, the total hydrogen yield increased by 44 mmol $g_{plastic}^{-1}$, but, the total hydrogen yield only increased by 10% when the reaction time was further increased to 4 h. This indicated that the effect of time on the steam reforming reaction became less because as the time was increased, the amount of volatiles produced by the plastic and tire char gradually decreased in the reactor, so the production of hydrogen became reduced. Al-Rahbi and Williams [31] produced hydrogen from biomass gasification using tire char as a catalyst, and reported that reaction time significantly impacted the amount of tire char recovered after reaction, and the increase in gas yield became slower with the increase of reaction time.

As for the CO yield (Fig. 10(b)), it can be seen that when the reaction time was increased from 1 h to 2 h, the total CO yield increased by 15 mmol $g_{plastic}^{-1}$, reaching 107 mmol $g_{plastic}^{-1}$, but the total CO yield did not change significantly when the reaction time was further increased to 4 h. This is consistent with the variation of CO yield and concentration with reaction time reported for the pyrolysis-catalytic steam reforming of biomass using tire char as catalyst; when the reaction time was 2 h, both the yield and concentration of CO reached the maximum [31]. This is because as the reaction time is increased, the rate of CO generation is

consistent with the rate of CO consumption. The CO yield remained constant, but the total gas yield increased. For tire char steam gasification only, the CO yield showed a trend of rising first and then decreasing because the carbon in the char reacted with steam to generate H_2 and CO. As the reaction time continued to increase, the carbon in char decreased, so the production rate of CO was less than the consumption rate of CO in water gas conversion. The CO yield from char accounted for 37%, 42% and 37% of the total CO yield at 1 h, 2 h and 4 h, respectively. The maximum yield of hydrogen for the pyrolysis-catalytic steam reforming of the plastics with tire char was achieved at the reaction time of 4 h and was 189 mmol $g_{plastic}^{-1}$, and the carbon monoxide yield was 106 mmol $g_{plastic}^{-1}$, representing a total syngas production of 295 mmol $g_{plastic}^{-1}$.

The tire char recovered after reaction and its content of ash in relation to reaction time are shown in Fig. 11(a) for the tire char gasification alone (no HDPE pyrolysis) and in Fig. 11(b) for the HDPE pyrolysis-catalytic steam reforming. Fig. 11(a) shows that the tire char recovered from steam gasification of the char (no plastics pyrolysis) and the ash content of the char at different reaction time shows that when the reaction time was 2 h and 4 h, the remaining tire char was only 10 wt% and ash content of the residual char reached 99 wt%, indicating that the fixed carbon components in the tire char were almost totally converted into gas. Similarly, for the pyrolysis of HDPE coupled with the catalytic steam reforming (Fig. 11(b)), the tire char recovered and ash content showed a similar trend to that with tire char only (Fig. 11(a)).

This work has shown that the production of hydrogen and syngas from the pyrolysis-catalytic steam reforming of waste plastics can be enhanced by using a tire derived pyrolysis char as the catalyst. In that, the tire char acts as both a steam reforming catalyst but also takes part in the reaction by steam gasification of the carbonaceous char to produce more hydrogen and carbon monoxide. This paper focused on the study of product distribution and catalyst properties of tire char used as catalyst in pyrolysis-catalytic steam reforming of waste plastics under different process parameters. High temperature (1000 °C) catalytic steam reforming, with high steam input (weight hourly space velocity; 8 g h^{-1} g^{-1} catalyst) and increased char catalyst:plastic ratio (4:1) resulted in maximized hydrogen and syngas yield. Tire char, as a low-cost material, has shown excellent performance in pyrolysis-catalytic steam reforming of plastic to produce syngas, which is suggested to be related to the transition metals within the char. However, in this paper, we did not conduct any in-depth research on which metal plays a greater role in the catalytic process. In the future, the extent to which different metals such as iron, copper, and zinc contribute to the catalytic process needs to
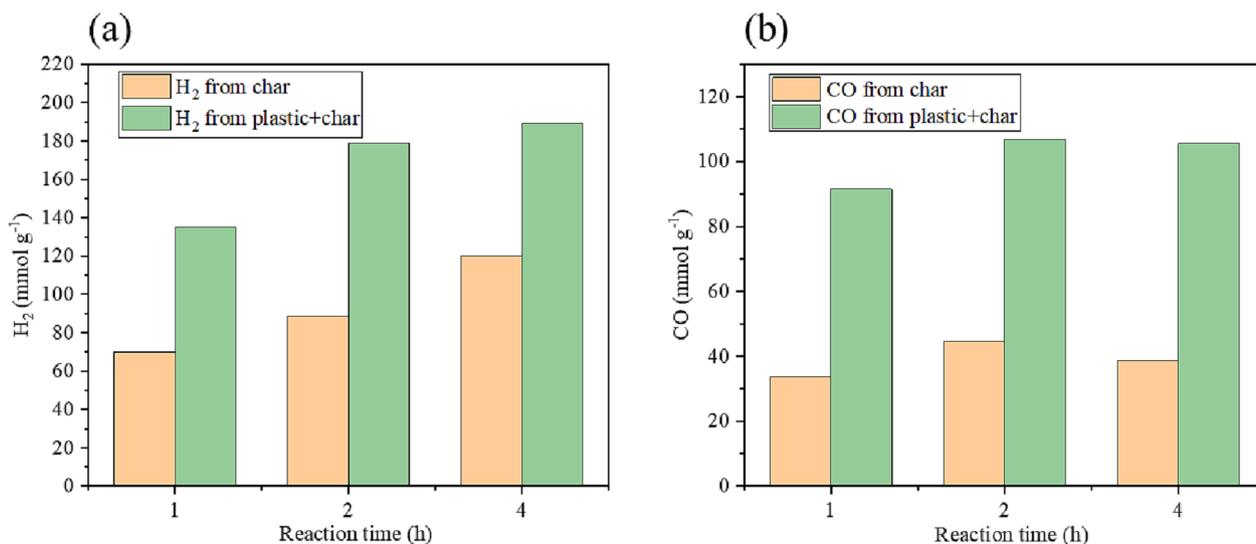
Fig. 10. H_2 and CO yields at different reaction time.
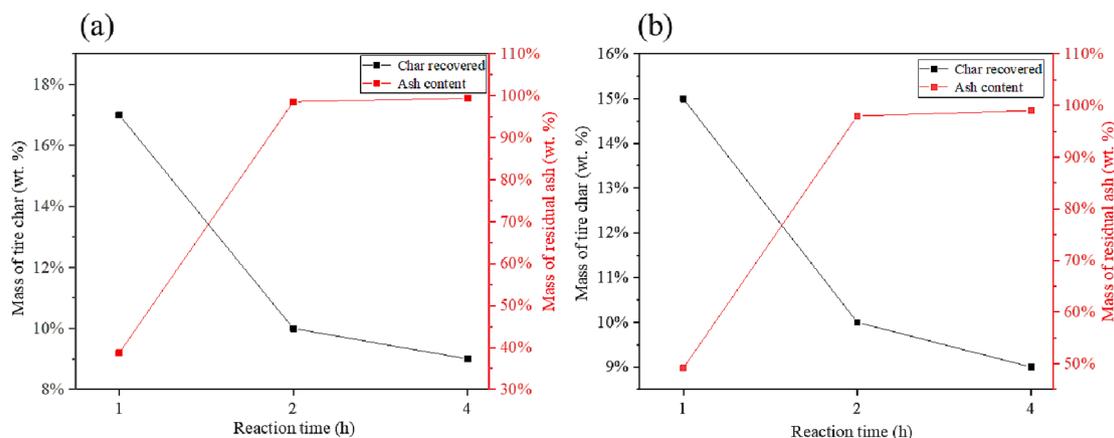
Fig. 11. Tire char and ash content of tire char recovered from (a) steam gasification of tire char alone (no HDPE pyrolysis) (b) pyrolysis-catalytic steam reforming of HDPE with tire char catalyst in relation to different reaction times.

be further studied to determine the active phase in the tire char that really plays a role. In addition, it should be noted that by the nature of the sacrificial catalyst, the tire char is consumed by steam gasification during the batch process used in these experiments. Also, the plastic feedstock is also processed as a batch system. Consequently, to further develop the process, continuous feeding of the waste plastics to the system is required and regular replenishment of the tire char catalyst is also required.

4. Conclusions

In this paper, tire char from the pyrolysis of waste tires has been shown to be effective in increasing hydrogen and syngas yield in the pyrolysis-catalytic steam reforming of waste HDPE. The tire char acts as a catalyst to promote catalytic steam reforming reactions, but also participates in steam-carbonaceous char gasification reactions. The tire char is consequently consumed or 'sacrificed' during the process with the aim of maximizing hydrogen and syngas yield.

(1) When the char catalyst temperature was increased to 1000 °C, the gas yield based on the mass of plastics increased dramatically producing 440 wt% of gas and 135 mmol H_2 $g_{plastic}^{-1}$.

(2) Steam promoted the steam reforming reaction and steam-carbon gasification reactions, producing more gases, especially hydrogen. However, as the steam input was further increased, hydrogen production changed only slightly, indicating a catalyst saturation point in the steam reforming process.

(3) Increasing the catalyst temperature and steam space velocity decreased the amount of tire char recovered after reaction with a consequential increase in the ash content of the residual char.

(4) The influence of increasing the amount of char catalyst in relation to the amount of plastics, produced an increase in hydrogen yield, for example, at a catalyst plastic ratio of 4:1 the H_2 yield was 211 mmol $g_{plastic}^{-1}$.

(5) The sacrificial tire char contributed significantly to the overall yield of hydrogen, with ~50% derived from the steam gasification of the tire chars.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgements

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