



Waste derived ash as catalysts for the pyrolysis-catalytic steam reforming of waste plastics for hydrogen-rich syngas production

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ABSTRACT

Ash derived from the oxidation of waste tire and processed municipal solid waste in the form of refuse-derived fuel have been investigated for their potential as catalysts in the pyrolysis catalytic steam reforming of high-density polyethylene to produce hydrogen-rich syngas. The surface morphology, element distribution, pore structure and metal composition of the ashes were characterized to explore the effects of these ash properties on the catalytic process. Further work using tire ash investigated the influence of the process parameters, catalytic temperature and catalyst plastic ratio in relation to the production of hydrogen and syngas. The results showed that tire ash had a higher specific surface area and pore volume than refuse-derived fuel ash, resulting in a slightly higher hydrogen yield compared to refuse derived fuel ash. An increase in the temperature of the catalytic steam reforming process with the tire ash catalyst significantly increased the hydrogen yield from 13.3 mmol g⁻¹plastic at 800 °C to 83.2 mmol g⁻¹plastic at 1000 °C. At higher catalyst:plastic ratios, the higher amounts of catalyst produced no discernable increase in hydrogen. A tentative reaction mechanism in relation to waste derived ash as catalysts for the steam reforming of plastics pyrolysis volatiles is provided.

1. Introduction

Plastics play a crucial role in modern society and are widely used in packaging, construction, automobiles, electronic equipment and various other industries. However, the widespread use and consumption of plastics have given rise to a corresponding increase in the scale and environmental impact of plastic waste. According to the European Trade Association, Plastics Europe, 29.5 million tonnes of post-consumer plastic waste were generated in Europe in 2020 [1]. This substantial volume of waste poses a serious challenge to the environment and sustainable development [2]. Consequently, there is an urgent and important need to address plastic waste and efficiently utilize plastic resources sustainably.

Converting plastic waste into valuable products, such as hydrogen, presents a sustainable and environmentally advantageous solution for managing plastic waste, while simultaneously promoting resource recycling and sustainable development. Pyrolysis, as an advanced thermochemical transformation technology, has received much attention for the processing of waste plastics for the production of syngas, and liquid fuels and chemicals [3–8]. To obtain hydrogen-rich syngas, post-processing of the pyrolysis hydrocarbon gases produced from

plastics via catalytic steam reforming using a commercial nickel-based catalyst (C11-NK) was reported in early work [5]. In the presence of a Ni-Mg-Al catalyst, mixed plastics were used in a pyrolysis-catalytic steam reforming process to convert the hydrocarbons in the pyrolysis gas/volatile products into hydrogen-rich syngas (H₂ and CO), where the hydrogen yield was reported to reach 151 mmol g⁻¹plastic [6]. Wang et al., [7] used an Fe-activated carbon catalyst for the pyrolysis-catalytic steam reforming of polypropylene and reported a hydrogen yield of 112.7 mmol g⁻¹plastic. Jiang et al. [8] used a molecular sieve KIT-6 Ni based catalyst for the production of hydrogen from different types of plastic in a two-stage pyrolysis-catalysis reaction system. Hydrogen yields from the plastics were attributed to the differences in pyrolysis volatiles produced related to the chemical structure of the individual plastic polymers. The adoption of a two-stage pyrolysis catalytic steam reforming technology offers several advantages: (a) individual temperature control for each stage, (b) more thorough integration of pyrolysis volatiles with the catalyst, (c) facilitation of catalyst recovery and reuse, and (d) suitability for mixed plastics and real-world plastics to prevent catalyst deactivation from dirt and plastic additives contamination [9].

The development of conventional catalysts (metals supported by porous materials) in the steam reforming of waste plastics has been

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comprehensively reviewed [10,11] and the most commonly reported catalysts are nickel based. For example, Yao et al. [12] investigated the production of hydrogen-rich syngas by catalytic steam reforming HDPE in a two-stage pyrolysis catalytic steam reforming reactor with Ni supported by different types of zeolites catalysts. Zhang et al. [13], reported on the effect of Fe addition to a Ni-based catalyst in relation to hydrogen yield and coke formation from pyrolysis catalytic steam reforming of waste plastics. Wu and Williams [14] developed a Mg-modified Ni-based catalyst and was shown to be effective for inhibition of coke formation.

Pyrolysis char has been used as a support material to produce char-nickel catalysts where the char texture and compositional characteristics promote the steam reforming of pyrolysis volatiles [15]. In our previous work [15,16], we further developed the use of waste derived pyrolysis chars as sacrificial catalysts. The particular characteristics of the waste derived chars was that the char catalyst contained metals with catalytic properties. Thereby the char was used as both catalyst for catalytic steam reforming but also acted as a reactant by undergoing in the steam gasification to improve hydrogen and syngas yield. It was found that the metal elements such as Zn, Fe, Ca and Mg contained in high concentration in the tire char increased the gas yield of the catalytic process, and the hydrogen yield reached $135 \text{ mmol g}_{\text{plastic}}^{-1}$ [15]. In our later work [16], and under the same experimental conditions, the use of biochar and refuse-derived fuel (RDF) char resulted in higher hydrogen yields than that of tire char, where yields of $198 \text{ mmol g}_{\text{plastic}}^{-1}$ and $155 \text{ mmol g}_{\text{plastic}}^{-1}$, respectively were achieved. In summary, the effect of char as a catalyst on gas yield was caused by char steam reaction and the catalytic performance of inorganic material in the char.

The range of fuels used in combustion systems for power generation has expanded from coal to other solid fuels, such as wastes and biomass, consequently, the combustion of such fuels is producing larger amounts of residual ash [17]. Given that ash contains a large number of catalytically active metals, the possibility of using ash as a catalyst for the catalytic steam reforming process has been proposed. For example, Al-Rahbi and Williams [18], used ash derived from coal, refuse-derived fuel and waste tires as catalysts for the pyrolysis-catalytic steam reforming of biomass. They demonstrated that the presence of ash increased the gas yield by 12–20 wt%, depending on the type of ash. Wang et al. [19], reported that coal ash contains SiO_2 , Al_2O_3 , Fe_2O_3 and a large amount of alkali and alkaline earth metals, which enhanced the steam reforming reaction in the catalytic steam reforming of bio-oil model compounds and improved the hydrogen yield and carbon conversion rate. Loy et al. [20], investigated coal bottom ash as a catalyst for the catalytic pyrolysis of rice husk for syngas production. The hydrogen concentration in the gas product increased by 8.4 vol% when waste coal ash was used as catalysts compared with non-catalytic pyrolysis [20].

Residual ash from several sources has been investigated for its use as a catalyst [18–20]. However, the existing literature has yet to explore the role of ash in the pyrolysis catalytic steam reforming of waste plastics. The composition and chemical structure of plastics exhibit distinct pyrolysis behaviors compared to, for example biomass, leading to the generation of different hydrocarbons and influencing the catalytic steam reforming process and product distribution. Therefore, it is important to investigate the role of ash in the catalytic steam reforming of pyrolysis volatile fractions derived from plastics. This study presents the use of two different sources of ash (tire ash and RDF ash) as catalysts for the catalytic steam reforming of high density polyethylene (HDPE) pyrolysis volatiles. The research explores the impact of different ashes in terms of gas yields and gas composition, with particular emphasis on the generation of hydrogen and syngas (H_2 and CO). Additionally, the work investigates the influence of process parameters such as different catalytic temperatures and catalyst-to-plastic ratios for the tire derived ash. Based on the composition of ash and its catalytic effects, a tentative mechanistic model for the catalytic steam reforming of pyrolyzed volatile fractions from waste plastics using ash as a catalyst is presented, offering initial insights into the complex reactions behind the catalytic steam reforming process.

2. Materials and methods

2.1. Feedstock and catalysts

High-density polyethylene (HDPE) was selected as the representative waste plastic for investigation, given its prevalence as the primary component in municipal solid waste plastics. The HDPE samples used in this study were obtained from Regain Polymers Limited, UK as post-consumer waste derived plastic. The plastic was supplied as oblate in shape, with an approximate diameter of 2–3 mm. Both ultimate analysis and proximate analysis were conducted using a Thermos EA-2000 CHNS analyzer and a Shimadzu TGA-50 thermogravimetric analyser (TGA) respectively.

The results showed that HDPE consisted of 80.26 wt% carbon, 15.33 wt% hydrogen, and a small amount of other impurities. The ash and volatile contents were 6.66 % and 93.64 %, respectively. The impurities and high ash content could be produced from additives used in the manufacture of the HDPE polymer or from other types of plastics or dirt carried over as contamination during the plastics recycling process.

The catalysts used for the catalytic steam reforming process were ash, derived from waste tires and municipal solid waste (MSW) in the form of refuse derived fuel (RDF). The process of RDF preparation from MSW, essentially involving the removal of non-combustible fractions such as glass and metals to produce a biomass/plastic mixed feedstock. The preparation of the ash from the tire and RDF involved initial preparation of a char followed by oxidation of that char to produce the ash samples for investigation. The tire and RDF were firstly pyrolysed under a flowing nitrogen purge gas atmosphere using a one stage stainless steel reactor heated by a 1.5 kW electrical furnace. Pyrolysis involved a slow pyrolysis heating regime from room temperature to a final temperature of $800 \text{ }^\circ\text{C}$ at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ followed by holding at $800 \text{ }^\circ\text{C}$ for 20 min. The tire ashes were prepared at from the tire-derived pyrolysis chars at different oxidation temperatures of $800 \text{ }^\circ\text{C}$, $900 \text{ }^\circ\text{C}$, and $1000 \text{ }^\circ\text{C}$ in a muffle furnace, and were designated as Tire ash 800, Tire ash 900, and Tire ash 1000, respectively. RDF ash was obtained from initial pyrolysis of the RDF to produce a char, followed by oxidation at a temperature of $800 \text{ }^\circ\text{C}$ in a muffle furnace. The reason why tire and RDF were first converted into char is that direct oxidation of tire and RDF generates large, potentially toxic, amounts of smoke. For the investigation of the influence of process parameters on the catalytic steam reforming process, the tire ash prepared at $800 \text{ }^\circ\text{C}$ was used as the catalyst. All the experiments in this study were conducted using 1.0 g HDPE and 1.0 g catalyst, except for the specific experiments that focused on investigating the influence of the catalyst to plastic ratio on the catalytic process.

2.2. Experimental reactor system and procedure

A schematic diagram of the experimental apparatus used for the pyrolysis-catalytic steam reforming of HDPE is shown in Fig. 1. The system comprised several key components, including a gas supply system, the two-stage reactor, a cooling system, a steam generator, and a gas collection and analysis system. The gas supply system ensured that the experimental process took place in an inert nitrogen atmosphere, eliminating any interference from the air. The steam generation system supplied steam to the second stage reactor where the reforming reactions took place in the presence of the ash catalysts. The two-stage reactor was constructed from stainless steel, and each stage was individually externally electrically heated (1.5 kW) and maintained at different temperatures. The cooling system was composed of three condensers, with the first being air-cooled, followed by two cooled by dry ice. These condensers effectively cool the gas products and condense any unreacted steam. The gas collection and analysis system collected the gas products in a 25 L Tedlar™ gas sample bag and subsequently analyzed them using several different gas chromatographs (GCs). HDPE (1.0 g) was placed in the pyrolysis reactor, while the ash catalyst (1.0 g)

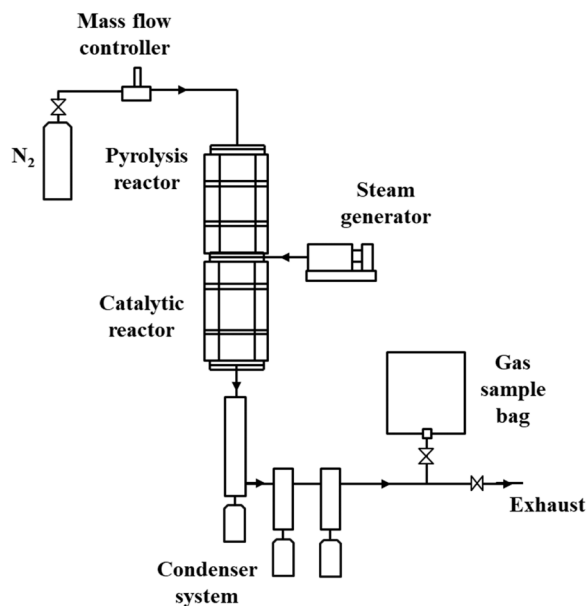


Fig. 1. Schematic diagram of the pyrolysis-catalytic steam reforming reactor.

was positioned in the catalytic reactor. The catalytic reactor was first heated to the desired temperature, after which the pyrolysis reactor was gradually heated from room temperature to 600 °C at a heating rate of 20 °C min⁻¹. Simultaneously, steam was injected into the second stage reactor. In the first stage, pyrolysis of plastic generated pyrolysis volatiles, which then directly entered the second stage. Here, a reforming reaction occurred in the presence of the ash catalysts and steam, forming gas products, which were collected in the gas sample bag after being cooled. The experimental conditions involved a steam weight hourly space velocity of 8 g h⁻¹ g⁻¹ cataly_{st} and the total gas collection time was 60 mins. To validate the experimental reactor system, many experiments were conducted at the same process conditions and demonstrated excellent experimental repeatability. For example, the standard deviation for the yield of gas, liquid and char was 1.34 wt%, 0.93 wt% and 0.02 wt% respectively and with a mass balance closure close to 100 wt% with a standard deviation of 1.191 wt%. Also, for the analysis of the product gases, H₂, CO, CO₂ and CH₄, the relative standard deviations were 0.149 vol%, 0.074 vol%, 0.055 % and 0.043 vol% respectively.

2.3. Products analysis and characterization

The pyrolysis gas products primarily consist of hydrocarbons (C₁ – C₄), permanent gases (H₂, CO, N₂), and CO₂. The contents of these gases were measured using different Varian CP-3380 GCs, and their yields were calculated based on Eq.1. The liquid product was almost exclusively composed of unreacted steam and only trace amounts of oil that had not been reformed by steam were observed. The total gas yield, yield of each gas, the ratio of experimental H₂ yield to theoretical H₂ yield (H₂ potential) and high heating value (HHV) were used to evaluate the efficiency of the pyrolysis-catalytic steam reforming process. The calculation formulae used are shown by Eq. 2- Eq.7.

$$\text{Gas yield}_{\text{total}}(\text{wt.}\%) = \frac{\sum m_{\text{each gas}}}{m_{\text{plastic}} + m_{\text{water}}} \quad (1)$$

$$\text{Liquid yield}_{\text{total}}(\text{wt.}\%) = \frac{\sum m_{\text{liquid}}}{m_{\text{plastic}} + m_{\text{water}}} \quad (2)$$

$$\text{Solid yield}_{\text{total}}(\text{wt.}\%) = \frac{\sum m_{\text{residue}}}{m_{\text{plastic}} + m_{\text{water}}} \quad (3)$$

$$\text{Mass balance} = \text{Gas yield}_{\text{total}} + \text{Liquid yield}_{\text{total}} + \text{Solid yield}_{\text{total}} \quad (4)$$

$$\text{Gas yield}_{\text{each gas}} \left(\frac{\text{g}}{\text{g}_{\text{plastic}}} \right) = \frac{V_{\text{each gas}}}{22.4} \times M_{\text{each gas}} / m_{\text{plastic}} \quad (5)$$

$$\text{H}_2 \text{ potential}(\%) = \frac{\text{Experimental H}_2 \text{ yield}}{\text{Theoretical H}_2 \text{ yield}} \quad (6)$$

$$\text{HHV}(\text{MJ Nm}^{-3}) = \text{H}_2\% \times 12.75 + \text{CO}\% \times 12.64 + \text{CH}_4\% \times 39.82 + \text{C}_2\text{H}_4\% \times 63.40 \quad (7)$$

Where $m_{\text{each gas}}$ represents the mass of each gas, m_{plastic} represents the mass of plastic, m_{water} represents the mass of water, m_{liquid} represents the mass of unreacted steam and trace amounts of oil, m_{residue} represents the mass of plastic residue, $M_{\text{each gas}}$ represents the molar mass of each gas, and $V_{\text{each gas}}$ represents the volume of each gas. The maximum theoretical hydrogen yield produced from the plastics was calculated based on the concept proposed by Czernik and French [5]. The calculation assumes that all the carbon and hydrogen in the raw feedstock materials were converted into carbon dioxide and hydrogen during the steam reforming process, including steam reforming and water gas shift reactions.

The catalysts were characterized by various techniques to determine the surface morphology, metal content, metal distribution and metal form. The metals and alkali metals content of the ash samples was determined using acid digestion of the ash in nitric acid at 240 °C using an electrothermal plate digestion method. Then the content of elements in the produced solution was determined by a Varian Fast Sequential Atomic Absorption Spectrophotometer (AAS). The adsorption and desorption isotherms of the samples were obtained by an automatic N₂ adsorption analyzer (Micrometric Tristar 3000) operating at 77 K. Then the pore volume and specific surface area were calculated by the Brunauer-Emmet-Teller (BET) method while the specific surface area of micropores was determined through the t-plot method. Scanning electron microscopy (SEM, Hitachi SU8230) combined with energy dispersive X-ray spectrometry (EDXS) was used to observe the surface morphology of the sample and the distribution of surface elements. The phase compositions of the ash samples before and after use were determined using an X-ray powder diffractometer (XRD, Bruker D8) with a scanning speed of 0.05°/s. The used catalysts were also analysed by temperature-programmed oxidation (TPO) with a Shimadzu TGA 50 to determine the presence of any carbon deposits on the used catalysts.

3. Results and discussion

3.1. Characterization of the ash catalysts

The catalysts used in this study were characterized by AAS, BET, XRD and SEM-EDXS techniques to determine the metal content, metal form, metal distribution and pore structure of the waste derived ash catalysts. Table 1 shows the ash yield and also the metal content of the ash. Tire

Table 1

The metal content of different ash catalysts. Tire ash was produced at an oxidation temperatures of 800, 900 and 1000 °C and RDF ash produced at 800 °C oxidation temperature.

	Tire ash 800	Tire ash 900	Tire ash 1000	RDF ash
Ash yield (wt%)	17.33	17.08	16.33	48.44
Ash metal content (wt%)				
Na	1.15	0.51	0.07	3.13
Mg	2.09	2.21	2.33	2.17
Al	0.48	0.39	0.30	16.38
K	1.87	1.03	0.52	1.76
Ca	8.32	7.84	7.64	19.23
Fe	7.80	7.19	7.47	2.13
Si	31.83	32.03	32.52	39.22
Zn	43.25	44.76	46.86	1.32

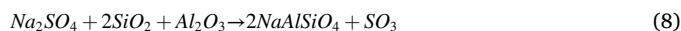
ash and RDF ash were derived from the oxidation of their produced pyrolysis chars under an air atmosphere. In this process, the volatile and fixed carbon in their char was completely converted into gas. The resulting ash yields were 17.33 wt% for tire char and 48.44 wt% for RDF char. The main elements in the tire ash were Zn and Si, where Zn is introduced in the tire manufacturing process to aid the rubber vulcanisation process and improve the physical properties of the rubber; Si (as SiO_2) is introduced as a substitute for carbon black to improve the wear resistance of the tire [21]. The Fe and Ca contents were around 7 %. Since the RDF ash originated from municipal solid waste, it exhibited a high ash content, rich in Si, Ca and Al elements. RDF ash has been reported to contain a large proportion of metal elements, with Si, Al and Ca accounting for over 70 wt% [22].

The pore structure of a catalyst significantly influences the diffusion of reactant molecules on the catalyst surface, reaction rate and selectivity. Therefore, surface area and porosity characteristics of the ash catalysts were determined and the results are shown in Fig. 2. The nitrogen adsorption and desorption isotherms of the different ash catalysts are shown in Fig. 2(a). The adsorption and desorption isotherms of RDF ash moderately increase when the relative pressure P/P_0 was < 0.8 , corresponding to the adsorption of micropores and mesopores. When the relative pressure was increased, the adsorption capacity approached a limit value. Simultaneously, capillary condensation occurred, causing the isotherm to rise faster with the appearance of hysteresis loops. This region corresponds to the adsorption in macropores. The adsorption and desorption isotherm of tire ash was clearly higher than that of the RDF ash catalyst. When the relative pressure P/P_0 was low, the adsorption capacity increased rapidly and the isotherm was convex. As the relative pressure continued to increase, the isotherm reached an inflection point, marking the formation of multilayer adsorption. Upon reaching saturated steam pressure, the adsorption capacity increased rapidly and reached an extreme value. According to the nitrogen adsorption and desorption isotherm of the two catalysts, it can be seen that the pore structure of tire ash was more abundant than that of the RDF ash. The adsorption capacity of different relative pressures also reflected the specific surface area of different pore sizes. Fig. 2(b) supported this observation, highlighting that the specific surface area of tire ash was higher, approximately $8.1 \text{ m}^2 \text{ g}^{-1}$, consistent with the nitrogen adsorption-desorption isotherm. The proportion of medium and large pores in tire ash was substantial, accounting for 76.8 %. Similar adsorption and desorption isotherms of the RDF ash also indicated that the specific surface areas was around $3 \text{ m}^2 \text{ g}^{-1}$. Pore volume is also one of the important parameters used to measure the pore structure of the catalyst, and the pore volume of the two catalysts also showed similar characteristics, among which the pore volume of tire ash reached

$2.8 \text{ cm}^3 \text{ g}^{-1}$.

The surface morphology and metal particle distribution of a catalyst are also important indices affecting catalyst activity. Fig. 3 shows the surface morphologies of the different catalysts and the distribution of surface elements determined by SEM-EDXS. Fig. 3(a) is the SEM image of tire ash, and it can be observed that the samples were mainly composed of large particles and nanoparticles with irregular shapes and different sizes. The particle size distribution spans from hundreds of nanometers to about $10 \mu\text{m}$. The bulk particles in the sample were scattered, and due to high temperature preparation of the sample, there is evident agglomeration among the particles. In addition, the presence of particles with diverse geometric sizes and morphologies contributed to the porous structure within the sample. Element mapping by EDXS indicated a uniform distribution of Zn elements in the tire ash with a high content, aligning with the results in Table 1. The concentration of Fe and Ca appeared to indicate agglomeration. Fig. 3(b) shows that the surface morphology of RDF ash was also composed of large particles and nanoparticles of different shapes and sizes, forming a multilevel, layered composite structure. The distribution of Ca, Al and Si also reflected the layered structure of the sample surface.

The ash catalysts used in the experiments was evaluated by XRD which can determine the form of metal present in the ash, and the corresponding diffraction pattern is shown in Fig. 4. Our previous study [15] found that Zn in tire char existed in the form of ZnS, while Zn in tire ash existed mainly in the form of ZnO and Zn_2SiO_4 . This is because ZnS reacts with O_2 to form ZnO during oxidation of the tire ash under air atmosphere. Also, at high temperature, synthesis of Zn_2SiO_4 by reaction of ZnO with SiO_2 may occur. The presence of Fe in tire ash was identified as Fe_3O_4 , with the corresponding XRD peak value at $2\theta = 35.2^\circ$. Compared with tire ash, the diffraction peaks of RDF ash were more numerous and weaker. Especially in the spectra when $2\theta > 40^\circ$, many insignificant XRD peaks were observed on the map, which were challenging to identify due to the abundance of low-concentration elements found in the RDF ash. The peaks in the diffraction pattern corresponded mainly to $\text{NaAlSi}_3\text{O}_8$, which may be the product of the more abundant elements in RDF oxidized under an oxygen atmosphere and high temperature conditions. In the study of the distribution and transfer of inorganic minerals in ash from RDF combustion, Yang et al. [23], reported that $\text{NaAlSi}_3\text{O}_8$ was produced by the following chemical reactions.



The used tire ash and RDF ash catalysts obtained from experimentation at the reforming temperature of 1000°C was also examined by XRD analysis (Fig. 4). By comparing the XRD patterns of tire ash and used tire ash, it was observed that the peak corresponding to ZnO in the

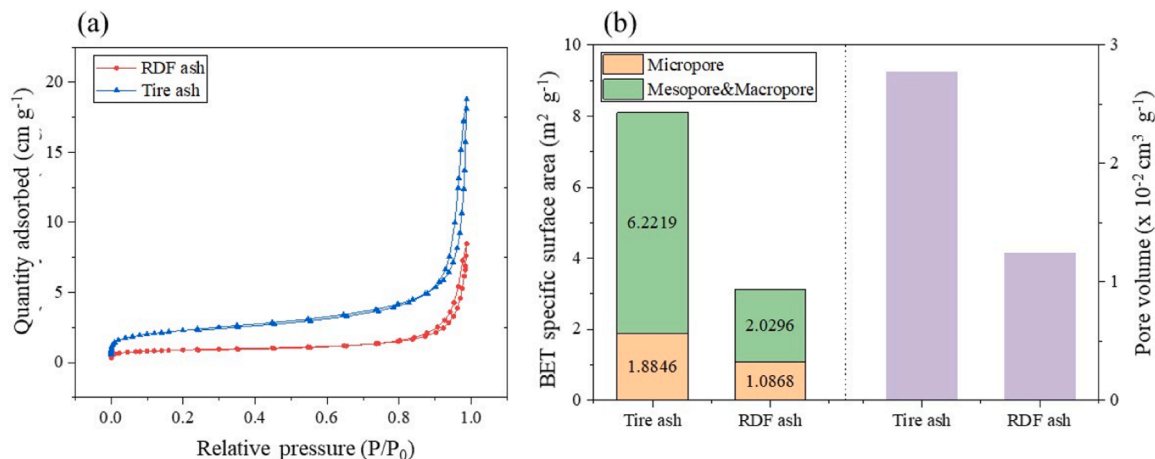


Fig. 2. (a) N_2 adsorption-desorption isotherms and (b) specific surface area and pore volume of ash catalysts (pore volumes shown in relation to micropores and mesopores/macropores).

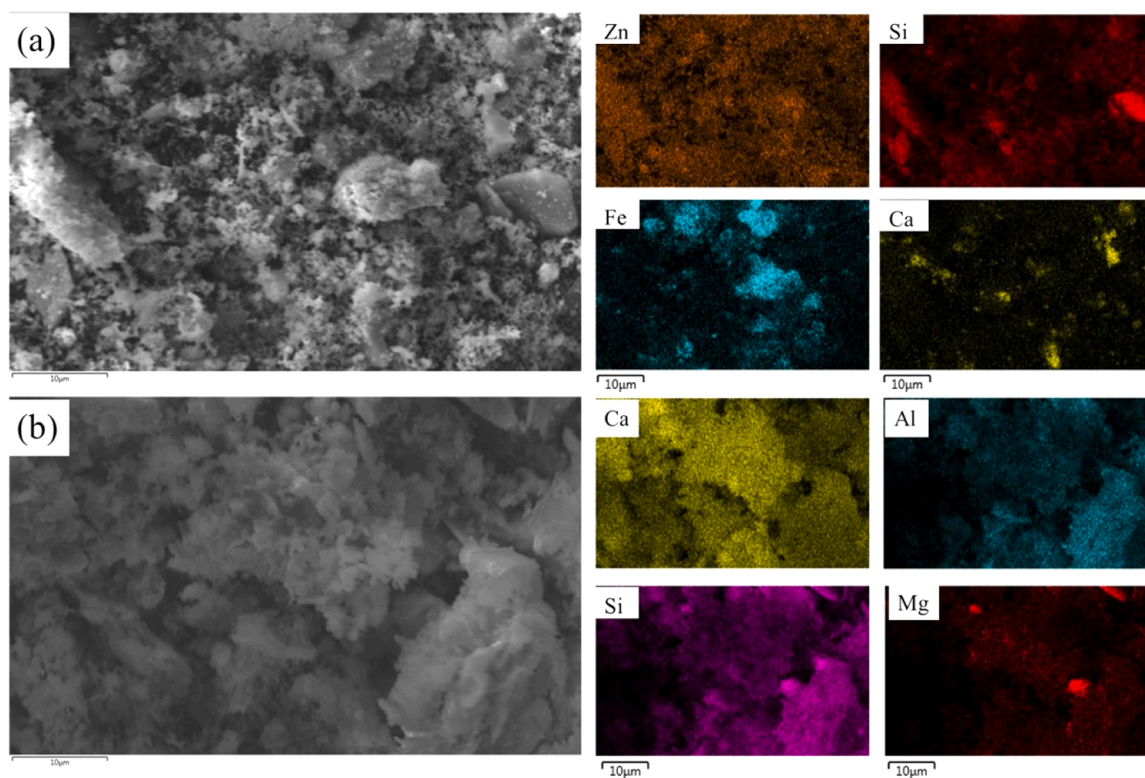


Fig. 3. SEM image and elemental mapping of (a) tire ash and (b) RDF ash.

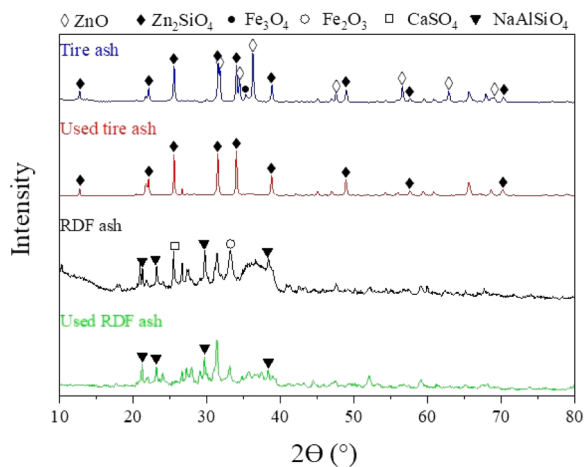


Fig. 4. X-ray diffraction analysis of ash catalysts and used ash catalysts.

used tire ash XRD spectra disappeared. This disappearance can be attributed to the reduction of metal oxides to metal elements by reducing gases such as H₂ and CO generated during the experiment. Additionally, the volatilisation of Zn to elemental forms at high temperatures further explains the decrease in Zn content after the reaction (see Section 3.4). The Fe₂O₃ observed in the used RDF ash was also reduced, with only NaAlSi₃O₈ being detected.

3.2. Influence of tire and RDF derived ash catalysts on the pyrolysis-catalytic steam reforming process

The influence of the two different types of ash catalysts on the products from the pyrolysis-catalytic steam reforming of HDPE were investigated. The total gas yield, gas calorific value and water consumption during the reaction are shown in Table 2. Fig. 5 shows the

Table 2

Total gas yield, HHV and reacted water in the presence of different ash catalysts.

	Tire ash 800	Tire ash 900	Tire ash 1000	RDF ash
Gas yield based on only plastics (wt %)	246.50	250.54	252.96	260.68
Water reacted (g)	1.96	2.05	1.99	1.68
HHV (MJ Nm ⁻³)	14.53	14.22	14.31	14.43

results for the catalytic steam reforming of the waste plastic (HDPE) in the presence of the tire-derived ash and RDF derived ash. Fig. 5 shows (a) product distribution, (b) gas yield, (c) hydrogen potential, and H₂/CO ratio and (d) gas volume composition in relation to the different ash catalysts. The results are for the tire ash produced from oxidation of tire char at furnace temperatures of 800, 900 and 1000 °C. In Table 2, the gas yield is based solely on plastic, providing an overview of total gas production in the different experiments. However, the gas yield in Fig. 5 (a) is based on both plastic and water input, providing a comprehensive mass balance for the entire process. As can be seen from Table 2, when tire ash was used as the catalyst, the total gas yield was about 250 wt%. In the presence of RDF ash, the gas yield was similar, at around 260 wt%. The reason why such a high gas yield can be achieved is because the steam introduced during the reaction was involved in the formation of non-condensable gas. It is of interest to present gas yields in terms of the yield from the plastics only, since the other inputs to the process are water (steam) and the waste derived ashes produced from a waste material, both of which could be deemed as low cost materials. When tire ash was used as the catalyst, about 2 g water was consumed in the catalytic process, while when RDF ash was used, 1.7 g water was consumed, which did not show obvious differences in the total gas yield but had an impact on the yield of each gas. As shown in Eq. (7), the high heating value of the gas is calculated from hydrogen, carbon monoxide and hydrocarbons. The heating value of the gas catalyzed by tire ash and RDF ash was between 14.2 and 14.6 MJ Nm⁻³.

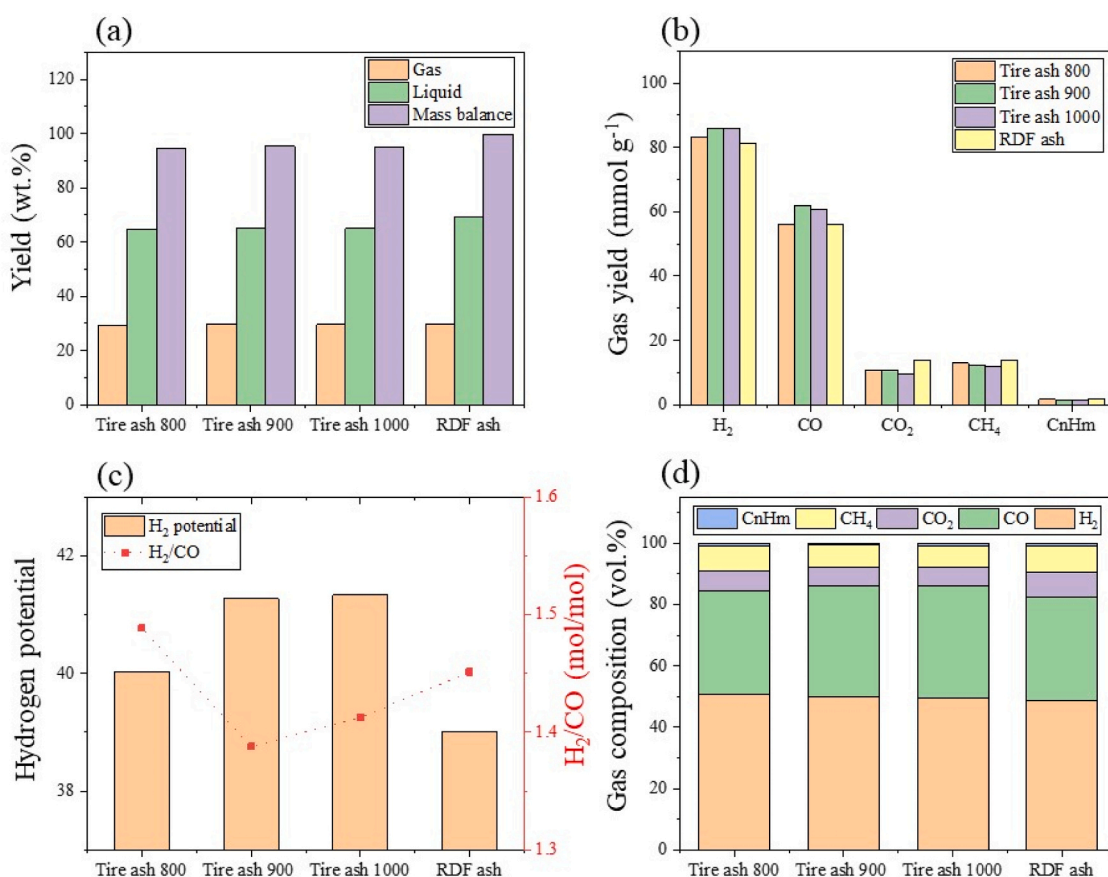


Fig. 5. Product distribution (a), individual gas yield (b), hydrogen potential and H₂/CO ratio (c) volumetric gas composition (d) for the catalytic steam reforming of waste plastic (HDPE) at a catalyst temperature of 1000 °C in the presence of different catalysts (tire ash produced from tire char at oxidation temperatures of 800 °C, 900 °C and 1000 °C and RDF ash prepared from RDF char at 800 °C).

The gas yield, liquid yield, and mass balance based on the plastic and water input are shown in Fig. 5(a), where the liquid represents the water after condensation of unreacted steam, because at 1000 °C, almost all the heavy hydrocarbons were reformed and no oil was formed. In the presence of the different catalysts, the gas yield was ~28 wt%, however, the effect of the different types of ash catalyst on the catalytic process was more obvious in the yield and composition of the individual gases. The yield of each product gas is shown in Fig. 5(b). When tire ash was used as the catalyst, the hydrogen yield ranged from 83 to 86 mmol g_{plastic}⁻¹, showing only a very small increase in hydrogen yield in relation to the different catalysts prepared from the pyrolysis char at different preparation temperatures of 800 to 1000 °C. As shown in Table 1, the metal types in the tire ash prepared at different oxidation temperatures were the same, but the metal content was slightly different. The tire ash prepared at an oxidation temperature of 800 °C contained a small amount of volatiles, while the ash prepared at a char oxidation temperature of 1000 °C was almost entirely inorganic, which also leads to slight differences in the hydrogen yield in the presence of the tire and RDF ash catalysts. Comparison of the RDF ash and tire ash catalyst produced at an oxidation temperature of 800 °C for the steam reforming process produced hydrogen yields which were similar at 81 mmol g_{plastic}⁻¹ and 83 mmol g_{plastic}⁻¹ respectively. This is mainly related to the physicochemical properties (metal composition and content, pore structure and surface morphology) of the catalysts. It can be seen from Table 1 that the elements in RDF ash were mainly Si, Al and Ca, and the elements in tire ash were mainly Zn, Si, Fe and Ca. These elements have been shown to catalyze the steam reforming of hydrocarbon volatiles, but the catalytic effect of different elements on the steam reforming of volatiles is different. The influence of different metals on the steam

reforming of polypropylene have been reported by Nahil et al. [24]. They pointed out that the presence of the metal can increase the hydrogen yield of the gas product; for example, at 800 °C, the hydrogen yield of processing polypropylene was increased from 26.9 to 45.9 mmol g_{plastic}⁻¹ when a Ni-Zn-Al catalyst was introduced. When Zn was replaced by Ca, the hydrogen yield was increased to 68.5 mmol g_{plastic}⁻¹. Zhang et al. [13] used a bimetallic nickel and iron catalyst, and reported that the hydrogen yield was 46.1 mmol g_{plastic}⁻¹, which was higher than that of monometallic nickel (30.5 mmol g_{plastic}⁻¹). The types of metal elements and their combinations in tire ash and RDF ash are complex, and the interaction between different metals may promote or inhibit the production of hydrogen. Wu and Williams [25] reported that when Mg was introduced into the Ni-Al catalyst, the hydrogen yield decreased slightly, but it had a better ability to inhibit coke generation.

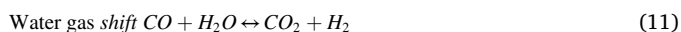
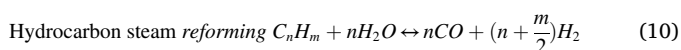
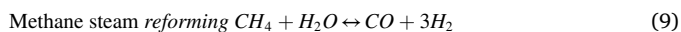
Although the production of total gas, H₂ and CO yield using the tire ash and RDF ash catalysts was quite similar for the ash produced at 800 °C oxidation temperature, their metal compositions were different and the specific surface area and pore volume of tire ash were larger than that obtained with RDF ash (Fig. 2). This may have a small influence on the catalytic performance of the ash catalysts. The influence of surface morphology on catalytic performance may be reflected in the exposure of the active metal sites, diffusion properties and contact area. Surface morphology affects the exposure of active sites, but in this study, due to the high content of metal, it can be seen from the EDXS elemental mapping, that almost all metal active sites were exposed, and volatile pyrolysis compounds derived from the waste plastic pyrolysis could fully contact with these active sites.

It can be seen from Fig. 3(a) and (b) that the surface morphology of

the tire ash and RDF ash catalysts was suitable for the diffusion of hydrocarbon and steam molecules into the catalyst interior. However, due to the differences in specific surface area and pore volume, the contact area between the reactant and the catalyst was different, which may influence the catalytic performance of the two catalysts. In addition, the metal distribution on the catalyst surface also affected the catalytic performance. The metal distribution on the catalyst surface was generally uniform and the pyrolysis volatiles were more easily diffused over the catalyst, while local areas of agglomeration also occurred thereby reducing activity. Yao et al. [26], reported three catalyst preparation methods, among which the sol-gel method significantly increased the dispersion of Ni on the catalyst surface and showed better catalytic performance in terms of hydrogen production. For example, the reported hydrogen yield of $60 \text{ mmol g}_{\text{plastic}}^{-1}$ from the steam forming of polyethylene used a catalyst prepared by the sol-gel method which contained much smaller and uniformly distributed nickel particles. This compared with $43 \text{ mmol g}_{\text{plastic}}^{-1}$ of hydrogen for the catalyst prepared by co-precipitation and $51 \text{ mmol g}_{\text{plastic}}^{-1}$ for the catalyst prepared by the impregnation method.

Fig. 5(c) shows the hydrogen potential calculated based on the experimental hydrogen yield and theoretical maximum hydrogen yield, which can show the hydrogen production ability of different catalysts for steam reforming of the HDPE pyrolysis volatiles. Also shown is the molar ratio of H_2/CO which is an important criterion to evaluate the quality of syngas, which determines the various end-uses of the syngas. When RDF ash (prepared at an oxidation temperature of 800°C) was used as catalyst, the hydrogen potential was 39 wt%, compared with the tire ash 800 catalyst where the experimental hydrogen yield was similar to RDF ash at 40 wt% of the maximum hydrogen yield. When tire ash prepared at a higher oxidation temperature was used, the experimental hydrogen yield slightly increased to 41.3 wt% of the theoretical hydrogen yield. This is because the ash prepared at high temperatures had a high content of inorganic material and did not contain volatiles.

For the whole catalytic process, the production and consumption of hydrogen and CO mainly involve the following reactions (Eq.9 – Eq.11) [27,28]:



According to Eq.9, Eq.10 and Eq.11, theoretically, the H_2/CO molar ratio should exceed 2. When nickel-based catalysts were used, the H_2/CO molar ratio in the gas products from steam reforming of plastics was between 2 and 3. Zhou et al. [29], impregnated 10 wt% Fe to a nickel-based catalyst and carried out steam reforming of plastics at low temperature (500°C), and reported that the H_2/CO ratio was greatly improved, reaching 13. However, the H_2/CO molar ratio of the gas product in this experiment was below 2, mainly due to the methanation of H_2 and CO during the catalytic process (the reverse reaction of Eq.9). The presence of inorganic substances in ash promoted methanation reactions at high temperatures. Mei et al. [28] also pointed out that some elements in the inorganic ash content are exogenous promoters used to modify methanation catalysts. When tire ash and RDF ash were used as catalysts, the H_2/CO molar ratio produced from catalytic steam reforming of the HDPE pyrolysis volatiles was between 1.4–1.5. A H_2/CO molar ratio between 1 and 2 make the gas products suitable for methanol synthesis and for a H_2/CO molar ratio of about 1 oxo-synthesis is the most suitable application for utilization of the produced gas [30].

The volumetric gas composition produced from the pyrolysis-catalytic steam reforming of HDPE with the different ash catalysts is shown in Fig. 5(d). It can be seen that when tire ash and RDF ash were used as catalysts, the hydrogen volumetric gas concentration was about 50 vol%. For hydrocarbons, the concentration of CH_4 in the gas products

of tire ash and RDF ash as catalysts were about 8 vol%, and the concentration of CnHm was about 1 vol%.

Fig. 6 shows the temperature programmed oxidation (TPO) analysis of the used tire ash and used RDF ash obtained after the catalytic steam reforming of waste plastic (HDPE) at a catalytic reforming temperature of 1000°C . The TPO analysis of the used ash samples involves oxidation under a flowing air atmosphere where oxidation of any carbonaceous coke deposits formed on the catalyst during the reforming process are oxidized, resulting in a loss of mass, identified by the thermogravimetric analyser. With the increase in TPO oxidation temperature, the mass of ash of used tire and RDF ash showed no weight loss and only a very slight increase at higher temperature. This indicated that there was no carbon deposition on the catalyst during the catalytic steam reforming of the plastics pyrolysis volatiles. The H_2 and CO produced during the steam reforming process reduced the oxides in the ash, and during the TPO process, the reduced material was oxidized, resulting in a slight increase in the mass of the used catalyst.

3.3. Influence of process parameters on the pyrolysis-catalytic steam reforming process using tire ash catalyst

Tire derived ash prepared at a tire char oxidation temperature of 800°C was used as the catalyst to study the influence of different process parameters on the pyrolysis-catalytic steam reforming of HDPE. With a constant steam input of $8 \text{ g h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$, three different catalytic temperatures and plastic: catalyst ratios were investigated. The total gas yield, water reacted, and HHV for the different process parameters are shown in Table 3. When the temperature of the ash catalyst was increased from 800 to 900°C in the catalytic steam reforming process, there was a slight increase in the gas yield, which increased by about 10 wt% to 174 wt% (based on the mass of input plastic only). Further increasing the catalytic reforming temperature resulted in a significant rise in gas yield. This increase can be attributed to an augmented participation in the steam reforming reaction, consequently, the amount of water in the catalytic process was also increased. In the reported experiments related to the catalytic steam reforming of polypropylene, a minimal change in gas yield was also reported for the pyrolysis-catalytic steam reforming of polypropylene when the catalyst temperature was increased from 800 and 900°C [31]. Table 2 shows that at a catalytic reforming temperature of 800°C , the heating value of the product syngas was the highest, at 22.79 MJ Nm^{-3} , primarily influenced by the content of gases with higher heating values (such as CH_4 and CnHm). As the temperature of the catalyst increased, these hydrocarbons were thermally and catalytically degraded into light molecular weight gases with a decreasing heating value. Kantarelis et al. [30] investigated the effect of temperature on gas product properties for the high-temperature

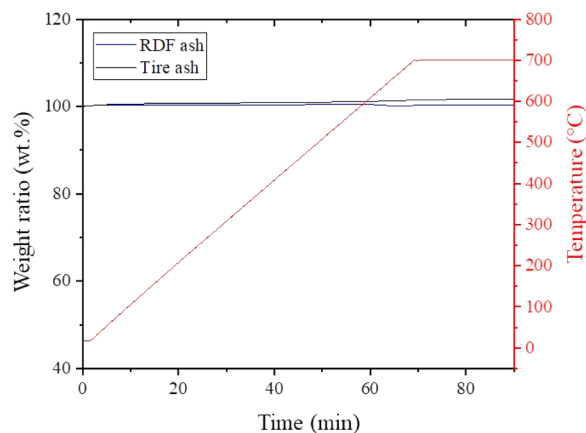


Fig. 6. Temperature programmed oxidation (TPO) analysis of used ash catalysts.

Table 3

The total gas yield, HHV and reacted water in the presence of tire ash catalysts at different process parameters from the catalytic steam reforming of waste plastic (HDPE).

	Catalytic steam reforming temperature (°C)				
	800	900	1000	1000	1000
Catalyst:Plastic ratio (g g_{plastic}^{-1})	1.0	1.0	1.0	0.2	0.5
Gas yield based on only plastics (wt%)	163.47	174.30	246.50	242.73	245.51
Water reacted (g)	0.62	0.93	1.96	1.61	1.86
HHV (MJ Nm ⁻³)	22.79	17.31	14.52	14.17	14.33

steam gasification of plastic wastes, and their results showed that the HHV of the product gas decreased from 39.42 to 13.47 MJ Nm⁻³ when the process temperature was increased from 700 °C to 1050 °C for the same reaction time. Table 2 also shows that by comparing the properties of gas products under three different catalyst ratios, it can be seen that the total gas yield and heating value increased slightly with the increase of catalyst ratios, maintaining at about 245 wt% and 14.3 MJ Nm⁻³, respectively. Compared with a catalyst ratio of 0.2 and 1 g g_{plastic}^{-1} , more steam was involved in a series of reactions during the catalytic process, which affected the distribution of individual gases.

Fig. 7 presents the results for the catalytic steam reforming of the waste plastic (HDPE) in relation to the process parameters of catalyst temperature (800–1000 °C) and catalyst:plastic ratio (1:1, 1:0.2 and 1:0.5) undertaken at a catalyst temperature of 1000 °C. The tire ash catalyst was prepared from tire char at an oxidation temperature of 800 °C. The product distribution, individual gas yield, hydrogen

potential and H₂/CO ratio, and volumetric gas composition from the pyrolysis catalytic steam reforming of the waste plastic are shown in Fig. 7(a)–(d) respectively. It can be seen from Fig. 7(a) that catalytic steam reforming temperature in the presence of the tire ash catalyst had a significant influence on the distribution of pyrolysis catalytic products. When the catalytic temperature of the tire ash catalyst was increased from 800 °C to 1000 °C, there was an increase in gas yield, accompanied by a decrease in liquid yield. Under different catalyst ratios, the gas yield based on plastic and water input remained relatively constant at around 28.3 wt%. Compared with the catalyst ratio of 0.5 and 1 g g_{plastic}^{-1} , the liquid yield was higher when the catalyst ratio was 0.2 g g_{plastic}^{-1} , because the amount of catalyst added affected the reaction between hydrocarbons and steam during the experiment. A lower catalyst ratio resulted in less steam participation in the reforming reaction, leading to the condensation of unreacted steam condensing into liquid water which is collected in the condensers of the reactor system. This is consistent with the change in the amount of water in the reaction process described in relation to Table 3. Fig. 7(b) shows the individual gas yields for the different process parameters investigated. When the catalytic reforming temperature was 800 °C, the hydrogen yield was 13.27 mmol g_{plastic}^{-1} , but when the catalyst temperature was further increased to 1000 °C, the hydrogen yield was greatly increased, reaching 83.20 mmol g_{plastic}^{-1} . This indicated that the steam reforming of hydrocarbons (Eq. 9) was relatively weak at low temperatures, hindering their conversion to gases and resulting in lower gas yields with higher condensed liquid (unreacted gas) yields. For catalyst ratios of 0.5 and 1 g g_{plastic}^{-1} , the hydrogen yield was similar at around 83 mmol g_{plastic}^{-1} , while at a catalyst ratio of 0.2 g g_{plastic}^{-1} , the hydrogen yield was slightly lower at 77.4 mmol g_{plastic}^{-1} .

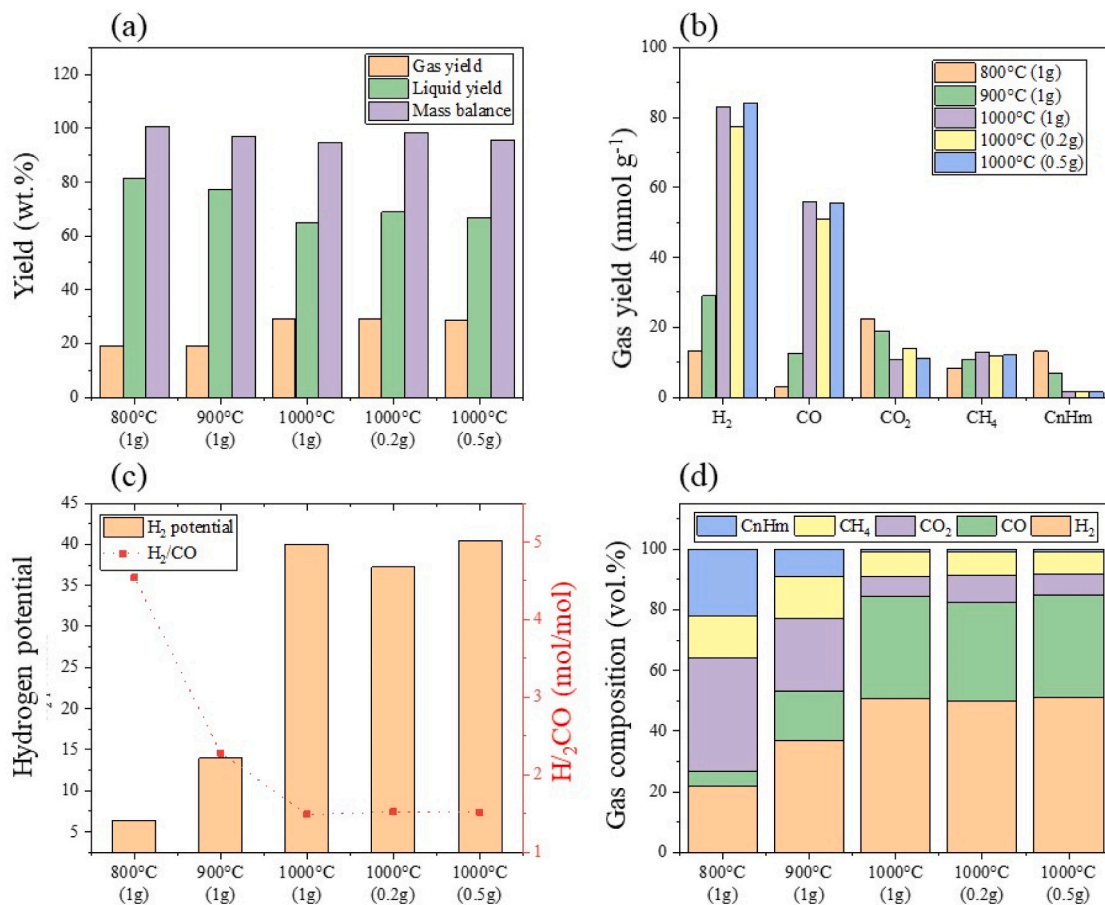


Fig. 7. Product distribution (a), individual gas yield (b), hydrogen potential and H₂/CO ratio, and volumetric gas composition from pyrolysis catalytic steam reforming of waste plastic (HDPE) under different process parameters (catalyst temperature (800 – 1000 °C) and catalyst:plastic ratio (1:1, 1:0.2 and 1:0.5 at 1000 °C)).

This suggested that a certain amount of catalyst promoted the generation of hydrogen, however, beyond a certain point, increasing the amount of catalyst does not consistently increase hydrogen yield, signifying a tendency towards saturation in the catalytic process.

At different process parameters, the hydrogen potential and H₂/CO molar ratio of gas products from the processing of the HDPE waste plastic are shown in Fig. 7(c). The data show that the hydrogen potential increased sharply with the increase of catalyst temperature. For instance, at 800 °C, the hydrogen yields only constituted 6.38 wt% of the theoretical hydrogen yield, but when the catalyst temperature was increased to 1000 °C, the hydrogen potential reached 40 wt%. In addition, the influence of different catalyst: plastic ratios showed that when the catalyst ratio was 0.2 g g_{plastic}⁻¹, the hydrogen potential was the lowest, at 37.23 wt%. At 800 °C, the conversion of hydrocarbons to hydrogen and CO is minimal, with the resultant CO reacting with steam to form CO₂. As the temperature continued to rise, the water gas shift reaction (Eq.11) was inhibited. Therefore, the H₂/CO molar ratio decreased with increasing temperature. The molar ratio of H₂/CO in the gas products generated under different catalyst ratios tended to be stable at about 1.5.

The catalyst temperature had a significant impact on the volumetric composition of the gas products from the pyrolysis-catalytic steam reforming of waste HDPE (Fig. 5(d)). For example, at a catalytic steam reforming temperature of 800 °C, the hydrogen concentration in the gas product was 22 vol%, while when the temperature was increased to 1000 °C, the hydrogen concentration reached 50 vol%. The increase in volumetric hydrogen concentration was achieved at the expense of consuming CH₄ and C₂₊ as well as heavy hydrocarbons in the pyrolysis product. In the process of pyrolysis-catalytic steam reforming of different plastics, Cortazar et al. [32] also pointed out that the increase in temperature leads to higher conversion of CH₄, thus increasing the product H₂ concentration. In contrast, the impact of catalyst: plastic ratio on gas composition appears relatively weak. The hydrogen concentration in the gas product was maintained at 50 vol% and the concentration of syngas was around 85 vol%, which also explained why the heating values of gas products obtained at the three catalyst: plastic ratios were similar. Wu and Williams [33] also reported that in a study of Ni/CeO₂/Al₂O₃ as a catalyst for the steam reforming of polypropylene, it was observed that the concentration of CO in the gas products increased with higher catalyst temperature, while the concentration of CO₂ exhibited a decreasing trend [33]. Their study also reported that within a catalyst: plastic ratio in range of 0.25 to 1, there was no significant change in the concentration of each gas, aligning with the work reported here.

In this study, the maximum hydrogen yield was 83 mmol g_{plastic}⁻¹, which was obtained at a temperature of 1000 °C with tire ash as the catalyst. In our previous work [15], we examined the pyrolysis-thermal steam gasification (without catalysts) at the same reforming temperature of 1000 °C. The hydrogen yield was 72 mmol g_{plastic}⁻¹ which showed the catalytic effect of ash on the steam reforming process, producing an increase in hydrogen yield of 12.16 %.

Some researchers have used catalysts with better catalytic performance, such as nickel-based catalysts, which can lower the reforming temperature, for experiments carried out on the catalytic steam reforming of waste plastics at temperatures between 700 and 900 °C. For example, Yao et al. [12] compared the hydrogen yield from pyrolysis catalytic steam reforming of HDPE with and without a catalyst at 850 °C, noting a 20 % increase in hydrogen yield with the Ni/ZSM5 catalyst. Al-Fatesh et al. [11] reported that the hydrogen yield from pyrolysis-catalytic steam reforming of waste plastics ranged from 66 to 135 mmol g_{plastic}⁻¹, depending on process parameters and catalyst type. Plasma technology was also used to generate hydrogen from HDPE, with Ma et al. [34], achieving a high-yield H₂ production (102.52 mmol g_{plastic}⁻¹) in plasma-catalysis mode at a temperature of 500 °C. In summary, while ash may not significantly enhance the hydrogen yield in comparison to conventional nickel-based catalysts,

waste derived ashes still demonstrate a certain level of catalytic activity.

3.4. Proposed reaction scheme

The pyrolysis catalytic steam reforming of HDPE process is divided into two stages: (1) the pyrolysis stage where decomposition of HDPE into a large number of hydrocarbons (CH₄, C₂H₄, C₃H₈, etc.) and higher molecular weight hydrocarbons occurs; (2) the steam reforming stage facilitates the derived pyrolysis hydrocarbons to react with the steam introduced in the reaction process in the presence of the ash catalyst to produce H₂, CO, and CO₂. The reaction process is illustrated in Fig. 8, and the reactions involved in this process are presented based on Eq.9, Eq.10 and Eq.11. Many studies [32,35,36] have also invoked these reactions for the production of hydrogen from waste plastics via the catalytic steam reforming process. While the mechanism of metal catalytic steam reforming of waste plastics has been illustrated, the corresponding mechanism of ash catalytic steam reforming of waste plastics still needs to be clarified. Therefore, we propose a tentative mechanistic model for hydrogen production from plastics via a pyrolysis-catalytic steam reforming process using ash catalysts (taking tire ash as an example). The conceptual model is depicted in Fig. 8, providing a preliminary insight into complicated reactions underlying the catalytic steam reforming process.

In general, the metal surface is the main active site for the dehydrogenation or C – C dissociation of hydrocarbons. The crystalline structures of metal oxides found in tire ash include Fe₃O₄ and MgO, which can also help water activation and promote water-gas shift reactions [37]. Magnesium oxide, in particular, is known for its capability in the heterolytic cleavage of water [38]. The broken C – H and H – O bonds rearrange and combine to form H₂ and CO. Throughout the catalytic process, certain metal oxides are reduced to metal elements by the generated H₂ and CO to form a stronger active site. Additionally, the abundant presence of amorphous SiO₂ in tire ash acts as an intermediate reducing agent to reduce metal oxides and CO₂ and also acted to adsorb metal ions and high molecular weight hydrocarbons [39]. The inclusion of CaO in the ash has been demonstrated to support the dry reforming of hydrocarbons, with the resulting CO₂ being adsorbed at the CaO active site [20].

Fig. 8 summarizes the possible mechanism of hydrocarbon steam reforming during the pyrolysis catalytic process. The hydrocarbons produced from the pyrolysis of plastics are adsorbed on the catalyst, interacting with the metal oxide or metal. In the case of heat input, the hydrocarbons dehydrogenate to produce H radicals and C₁ – C₂ radicals, such as CH ≡ CH, C ≡ C and ·CH₂. Steam was easily dissociated into H and OH free radicals under the catalysis of metals and metal oxides. The primary source of hydrogen lies in the combination of these hydrogen free radicals. Xuan et al. [40], pointed out that the hydrogen generated by the combination of H free radicals generated by hydrocarbon dehydrogenation accounted for 15.46 % of the total hydrogen yield. Combining H free radicals generated by hydrocarbon dehydrogenation and hydrogen free radicals generated by hydrolysis separation was the main path of hydrogen production, accounting for 67 % of the hydrogen yield. CO is produced by combining OH radicals from water with C radicals. Under the influence of the catalyst, CO further undergoes dissociation to form carbon. At high temperatures, this carbon is engaged in the water-gas shift reaction, contributing to hydrogen production. This also explains the high hydrogen yield produced at a catalyst temperature of 1000 °C and the absence of carbon deposits detected on the used ash catalyst.

The role of the metals in tire ash is important to the catalytic process, and Fig. 9 provides the changes in the metal content before and after the reaction. At a catalytic reforming temperature of 800 °C, there was an increase in the metal concentration in the tire ash. This can be attributed to the reduction of some metal oxides during the catalytic process. When the temperature of the catalyst was raised to 1000 °C, the reaction involved in the catalytic process became more intense, but some of the

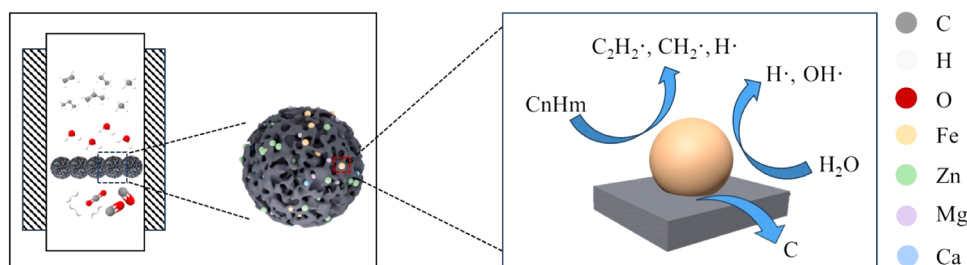


Fig. 8. Proposed reaction scheme of catalytic pyrolysis using tire ash catalyst.

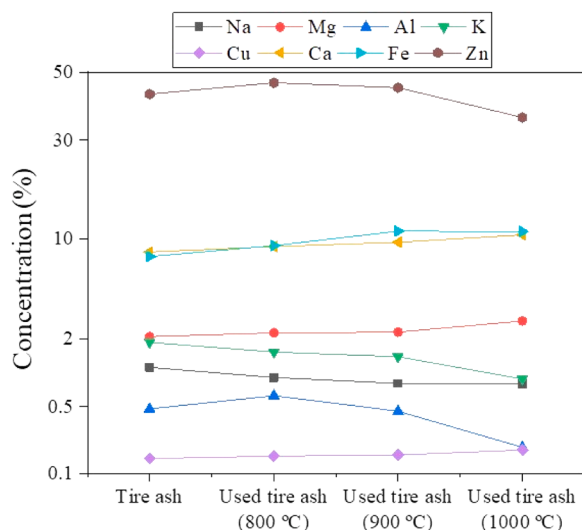


Fig. 9. Metal concentration in tire ash before and after reaction (tire ash prepared from tire char oxidation at 800 °C).

reduced metal elements were vaporised at this temperature, particularly Zn. Despite this, the concentration of key catalytic metals such as Fe, Ca, and Mg increased relatively, and these metals possessed high boiling points. Consequently, the used ash catalyst exhibited potential for reuse and is well suited for higher temperatures.

4. Conclusions

In this paper, ashes were derived from waste tires and refuse derived fuel (RDF) by pyrolysis and oxidized to produce ash catalysts, which were used for pyrolysis-catalytic steam reforming of waste HDPE plastic. The physicochemical properties of the ash were characterized in detail using SEM-EDX, BET surface area and porosity and AAS techniques. The effect of process parameters on gas yield was investigated, and a catalytic mechanism of ash was proposed.

- (1) Compared with RDF ash, tire ash had a higher specific surface area and pore volume, which indicated that the macromolecular hydrocarbons had a larger contact area with the catalyst, resulting in a higher hydrogen yield of $83 \text{ mmol g}_{\text{plastic}}^{-1}$ for the tire ash catalyst.
- (2) The increase in temperature of the catalyst promoted the steam reforming of hydrocarbons and significantly increased the hydrogen yield. Using tire ash as a catalyst, as the temperature was increased from 800 to 1000 °C, a more than 6 times increase in the hydrogen yield was achieved, reaching $83.2 \text{ mmol g}_{\text{plastic}}^{-1}$.
- (3) Increasing the catalyst: plastic ratio also enhanced the hydrogen yield. However, when the plastic: catalyst ratio was $0.5 \text{ g g}_{\text{plastic}}^{-1}$, the catalytic process tended to reach a stable hydrogen

production, and further increasing the amount of catalyst no longer significantly improved the hydrogen yield.

- (4) A reaction mechanism was proposed where under the influence of the catalysts, hydrocarbons and steam undergo chain-scission and chemical bond breaking, generating many free radicals. These free radicals recombine to form H_2 and CO . The used catalyst exhibited minimal change in metal content, and no carbon deposition was detected on the catalyst surface at high temperatures, indicating the potential for catalyst recycling.
- (5) The utilization of two readily available and low-cost materials in the form of waste tires and refuse derived fuel as feedstocks to produce ash catalysts for hydrogen production from waste plastics offers a positive contribution to sustainable resource utilization.

CRediT authorship contribution statement

Li Yukun: Writing – original draft, Methodology, Investigation, Formal analysis. **Williams Paul:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

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

Data Availability

Data will be made available on request.

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