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Catalytic conversion of biomass components and waste biomass for hydrogen/syngas production using biochar catalysts

Yukun Li, Paul T. Williams *

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

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ABSTRACT

Biochar produced from the pyrolysis of waste biomass (sawdust) was used as a catalyst in the two-stage, pyrolysis-catalytic steam reforming of biomass components and waste biomass in a two-stage fixed bed reactor. The thermal degradation characteristics of cellulose, hemicellulose and lignin as representative biomass components and waste biomass were determined by thermogravimetric analysis. In addition, potassium and calcium metal salts were added to a mixture of the three biomass components to investigate the effect of the alkali and alkaline earth metals on the process. The results showed that among the three main components, the pyrolysis-catalytic steam reforming of lignin produced the highest hydrogen and syngas yields in the presence of biochar catalyst. Mixing cellulose, hemicellulose and lignin produced a synergistic effect in the pyrolysis-catalytic steam reforming process, significantly promoting hydrogen release. Adding K and Ca metals to the biomass component mixture further increased the hydrogen and carbon monoxide yields. The product yield from pyrolysis-catalytic steam reforming of the waste biomass indicated that the process for real biomass is not a simple superposition of individual components, highlighting the complexity of real biomass systems. The proposed mechanism of pyrolysis catalytic steam reforming demonstrated the unique role of biochar, including its self-gasification, which significantly contributed to hydrogen and syngas production. This study not only underscores the synergistic effects in co-pyrolysis but also reveals the practical potential of biochar as a sacrificial catalyst for efficient hydrogen production.

1. Introduction

The continuous growth of global energy demand and the intensification of environmental pollution necessitate the urgent development of sustainable, low-carbon energy sources to address rising greenhouse gas emissions and energy security issues caused by excessive use of fossil energy [1]. In this context, biomass is considered an important energy source to replace fossil fuels due to its renewable, abundant and carbon-neutral characteristics [2,3]. Biomass thermochemical conversion technology is a crucial method for its efficient utilization, where biomass pyrolysis combined with steam reforming technology can convert biomass into clean and efficient gas products, especially hydrogen.

Hydrogen is regarded as a clean energy source with diverse applications, including fuel cells, industrial processes such as ammonia synthesis and oil refining [4]. It offers several advantages, such as high energy density, environmental sustainability, and versatility [5,6]. Hydrogen can be produced through various methods, such as natural gas reforming, water electrolysis, and biomass gasification. Among these, the two-stage pyrolysis-steam reforming process was chosen for its ability to utilize renewable biomass feedstock while simultaneously producing hydrogen-rich syngas and minimizing greenhouse gas emissions. Additionally, this approach allows for the efficient conversion of complex biomass volatiles into high-value products through catalytic reforming.

(i) Pyrolysis Characteristics of Biomass Components

Biomass primarily consists of cellulose, hemicellulose and lignin, each exhibiting significant differences in their pyrolysis behavior linked to their different chemical structures. Cellulose is a carbohydrate with a polysaccharide structure consisting of a linear polymer of $\beta(1 \rightarrow 4)$ linked D-glucose units and hemicelluloses are a group of polysaccharide carbohydrates but with a more complex linear and branched structure. Lignin has an even more complex structure, consisting of aromatic three-dimensional linkages in an alkyl-benzene structure [7]. It has been

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* Corresponding author.
E-mail address: p.t.williams@leeds.ac.uk (P.T. Williams).

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shown that interactions between these components can significantly affect product distribution during their co-pyrolysis, indicating the presence of a "synergistic effect" [8,9]. The differing gas and volatiles products evolved during the pyrolysis step will inevitably lead to variations in their reactions in the second step catalytic steam reforming process and consequently, the composition of the final gas product. Therefore, systematically studying the product distribution from pyrolysis-catalytic steam reforming of the main biopolymer components of biomass and their mixtures is of significance for revealing the complex reaction mechanisms involved in the catalytic reforming process.

(ii) Catalytic Reforming of Biomass Volatiles

In the process of catalytic reforming, the choice of catalyst is crucial for reaction efficiency and product selectivity. Nickel- and iron-based catalysts are widely used in the reforming of biomass pyrolysis hydrocarbons due to their high catalytic activity [10–13]. Akubo et al. [7] used 10 wt% Ni/Al_2O_3 as a catalyst in the pyrolysis-catalytic steam reforming of six agricultural biomass wastes using a two-stage fixed bed reactor. They demonstrated that the introduction of steam and catalyst in the pyrolysis-catalytic steam reforming process can significantly enhance gas and syngas yields, especially hydrogen. He et al. [13] investigated the catalytic properties of different Fe-modified Ni/Al_2O_3 catalysts in the steam reforming of biomass pyrolysis tar. The results showed that the addition of Fe significantly improved toluene conversion and hydrogen yield. However, a major disadvantage of these metal catalysts is their tendency to deactivate, shortening their life cycle. Coke deposition on the surface of the catalyst can encapsulate the active metal particles, preventing reactants from contacting the metal and thus leading to a decrease in the activity of the catalyst [14].

(iii) Char as catalysts in steam reforming process

As an alternative catalyst, char produced from pyrolysis of carbonaceous materials has been used in pyrolysis-catalytic steam reforming processes in relation to biomass. Common types of char include coal char, tire char and biochar [15–19]. In our previous work [16,17], we have employed tire char as catalysts for the steam reforming of plastic pyrolysis volatiles, demonstrating that it effectively increases the yields of hydrogen and syngas. The char catalyst is consumed or sacrificed in the process, acting as both a catalyst for the steam reforming process, but also the carbonaceous char is gasified by the added steam to produce hydrogen and carbon monoxide. Biochar is also widely used as a catalyst and catalyst support material due to its alkali metal content (such as potassium and calcium) and pore structure [18–23]. Feng et al. [20] investigated the role of biochar in the reforming of biomass model tar compound in a steam environment, showing that the tar reforming pathway includes homogeneous reforming and steam consumption. Sun et al. [21] showed that the catalytic properties of the biochar surface enhance the homogeneous reforming reactions of the model hydrocarbons, styrene and toluene, and promote the self-gasification of biochar, the water-gas shift reaction and the steam reforming of methane. Moreover, various char materials are used as catalyst support materials for metals for the catalytic gasification of biomass [2,24]. However, the catalytic activity of biochar is inherently lower than that of metal-based catalysts, and its consumption during the steam reforming process necessitates a continuous supply in practical industrial applications.

Table 1 summarizes key studies related to biomass pyrolysis and catalytic reforming, highlighting the novelty of this work. Catalysts play a critical role in improving the efficiency and selectivity of the reforming process. While nickel- and iron-based catalysts are widely used due to their high activity, their susceptibility to deactivation from coke deposition poses significant challenges. In contrast, biochar, a sustainable catalyst derived from the pyrolysis of biomass, has garnered attention for its catalytic properties. Its inherent alkali metal content (e.g., potassium and calcium) and porous structure facilitate reforming reactions while allowing simultaneous self-gasification to produce additional hydrogen and carbon monoxide. Despite these advantages, existing studies often focus on specific aspects, such as model tar compounds or specific biomass types, rather than providing a systematic analysis of the steam reforming behavior of key biomass components and their mixtures, especially in the two-stage reactor.

To address these gaps, this study investigated the pyrolysis-catalytic steam reforming of cellulose, hemicellulose, and lignin, both individually and as mixtures, in the presence of biochar. Additionally, the role of

Table 1
Studies on biomass pyrolysis and catalytic steam reforming.

Study	Feedstock	Catalysts	Method	Key findings
Zhao et al. [25]	Cellulose, hemicellulose and lignin		Pyrolysis	Cellulose produces light volatile compounds. Hemicellulose produces acids and ketones, while lignin generates tar and complex aromatic compounds.
Chen et al. [9]	Mixtures of cellulose, hemicellulose and lignin		Co-pyrolysis	Interactions between these components affect the product distribution, indicating the presence of a "synergistic effect".
Akubo et al. [7]	Agricultural biomass waste	Ni/Al_2O_3	Pyrolysis-catalytic steam reforming	The introduction of steam and catalysts enhances gas and syngas yield.
He et al. [13]	Biomass tar	$Fe/Ni/Al_2O_3$	Catalytic steam reforming	The addition of Fe improved toluene conversion and hydrogen yield.
Feng et al. [20]	Biomass tar	Biochar	Catalytic steam reforming	The activation process of the steam improves the lattice defects and functional groups of biochar, promoting the contact between hydrocarbons and biochar.
Sun et al. [21]	Styrene and toluene	Biochar	Catalytic steam reforming	The catalytic properties of the biochar surface enhance the homogeneous reforming reactions.
Yao et al. [18]	Biomass	Ni/Biochar	Pyrolysis-catalytic steam reforming	Ni supported on cotton derived biochar achieved a higher hydrogen yield of 46.04 mmol g^{-1}.
Present study	Cellulose, hemicellulose, lignin, mixtures, mixtures with K and Ca.	Biochar	Pyrolysis-catalytic steam reforming	The three components exhibited a synergistic effect during co-pyrolysis-catalytic steam reforming, which promoted the production of hydrogen, but inhibited the release of methane. The addition of K and Ca increased the syngas yield, especially carbon monoxide.

alkali metals such as potassium and calcium in influencing product distribution and reaction pathways is explored. By systematically comparing the product yields and reaction mechanisms of individual components and their mixtures, this study aims to reveal the synergistic effects and provide insights into optimizing biomass utilization for cleaner hydrogen production.

2. Materials and methods

2.1. Materials

The three biomass biopolymer components used in this experiment - cellulose, hemicellulose (Xylan) and lignin - were purchased from Sigma-Aldrich, UK Ltd. Waste biomass samples were obtained as waste wood processed pellets and shredded and sieved to produce a particle average size of 5 mm. To investigate the synergistic effects of the three components, a mixture was prepared with a cellulose: hemicellulose: lignin of 4:4:2, reflecting their typical proportions in lignocellulosic biomass as reported in the literature [26]. When exploring the role of metals in the pyrolysis process, $Ca(NO_3)_2{\cdot}4H_2O$ and KNO_3 were added to the mixture to ensure that the Ca and K contents in the mixture were 5 wt% respectively.

The catalyst used in the catalytic steam reforming stage was biochar derived from the pyrolysis of waste biomass using a one-stage pyrolysis reactor (40 mm dia., 200 mm high). The reactor was externally heated by a 1.5 kW electrical furnace. The biochar was produced under pyrolysis conditions of slow pyrolysis (20 °C min^{-1}) heating to a final temperature of 800 °C and held for 20 min. Table 2 presents the results of the ultimate and proximate analysis of the biomass components, waste biomass and biochar catalyst.

2.2. Two-stage pyrolysis-catalytic steam reforming of biomass

A two-stage fixed-bed experimental system was used to study the pyrolysis-catalytic steam reforming of biomass using biochar as the catalyst (Fig. 1). Before the experiment, 1 g each of feedstock and biochar catalyst was weighed and placed separately in the pyrolysis and catalytic reactors. Nitrogen gas at a flow rate of 100 ml min^{-1} was used as the carrier gas, and the outlet gas flow rate was monitored to ensure the system was leak-free. The catalytic stage was first heated to 900 °C, after which the feedstock in the pyrolysis reactor was heated to 600 °C. The generated pyrolysis volatiles were carried by nitrogen gas into the second stage (the catalytic stage). Simultaneously, steam provided by a steam generator at a flow rate of 8 ml h^{-1} was directly introduced into the catalytic stage. After a series of reactions, the pyrolysis products were collected in a 25 L gas sample bag after passing through a three-stage condenser. The collected gases were analyzed offline using gas chromatography (GC). To ensure the reliability of the experimental results, all tests were repeated to minimize errors. The results exhibited a very small standard deviation, with values for H_2, CO, CO_2 and CH_4 being 0.15 vol%, 0.07 vol%, 0.06 vol%, and 0.04 vol%, respectively, which confirm the high reliability and reproducibility of the experiments. All reported data are presented as average values for clarity and accuracy.

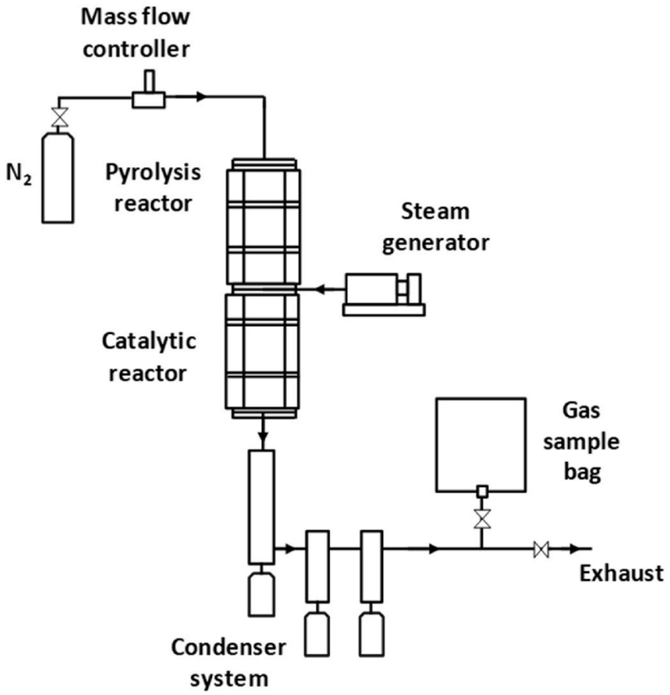

Fig. 1. Schematic diagram of the two-stage fixed bed pyrolysis-catalytic steam reforming experimental system.

2.3. Characterizations and products analysis

Biomass feedstocks and biochar catalysts were characterized by various techniques. The thermal decomposition characteristics and weight loss behavior of the biomass biopolymer components and waste biomass were studied by Mettler Toledo thermogravimetric analyzer (TGA). The metal contents of the waste biomass and biochar were analyzed through acid digestion followed by atomic absorption spectrometry using a Varian Fast Sequential Atomic Absorption Spectrometer (Varian AA240FS). The surface morphology and metal distribution of biochar were observed using high-resolution scanning electron microscopy (SEM, Hitachi SU8230) and Energy Dispersive X-ray Spectroscopy (EDXS, Oxford Instruments Aztec Energy system). The steam reactivity of biochar was evaluated by a thermogravimetric analyzer equipped for steam experiments (Netzsch STA 449, F3, Jupiter TGA).

Several indices were used to evaluate the pyrolysis-catalytic steam reforming process. The concentration of each gas product was determined by gas chromatography and used to calculate the higher heating value (HHV) of the total gas products, as shown in Eq. (1).

$$HHV\left(MJ\,Nm^{-3}\right) = H_2\% \times 12.75 + CO\% \times 12.64 + CH_4\% \times 39.82 + C_2H_4\% \times 63.40 \qquad \text{Eq. 1}$$

Carbon conversion refers to the proportion of carbon in the feedstock and catalyst converted into carbon-containing products, calculated by Eq. (2).

Table 2
Ultimate and proximate analysis of the biomass materials.

	Ultimate analysis					Proximate analysis			
	C	H	O	N	S	Moisture	Volatile	Fix carbon	Ash
Cellulose	42.67	5.60	51.2	0.53	0	2.02	88.50	5.79	3.69
Hemicellulose	40.88	5.82	52.81	0.49	0	4.44	77.54	13.75	4.27
Lignin	62.36	5.19	29.91	0.98	1.56	4.86	61.83	30.97	2.34
Waste biomass	47.34	4.88	44.42	0.14	0	6.51	78.42	12.43	2.64
Biochar catalyst	91.91	0.53	0.63	1.26	0	4.79	7.51	84.97	2.73

$$C_{conversion} = \frac{mass\ of\ C\ in\ each\ gas}{mass\ of\ C\ in\ feedstcok + mass\ of\ C\ in\ char\ catalyst} \quad \text{Eq. 2}$$

Synergy refers to the comparison between the experimental value from co-pyrolysis and theoretical value based on the additive values obtained from pyrolysis of the individual biopolymers based on the proportion of components. The theoretical value and Synergy were calculated by Eq. (3) and Eq. (4), respectively.

$$y_{theoretical} = \sum_{i=1} x_i \times y_i \quad \text{Eq. 3}$$

$$Synergy = \frac{y_{experimental} - y_{theoretical}}{y_{experimental}} \quad \text{Eq. 4}$$

Where x_i represents the proportion of biomass components and y_i is the individual gas yield from the corresponding biomass components.

3. Results and discussion

3.1. Characterization of feedstock and biochar

Fig. 2(a) and (b) show the thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) thermograms for cellulose, hemicellulose, lignin and waste biomass. As can be seen from Fig. 2, the decomposition temperature of cellulose is between 310 °C and 390 °C, and the maximum decomposition rate is observed at 2.59 wt% $°C^{-1}$ at 358 °C. This phenomenon is related to the highly ordered and stable crystalline structure of cellulose comprised of linear polysaccharide chains, which gives it moderate thermal stability and thus causes it to begin pyrolysis at higher temperatures (310 °C) than hemicellulose. In contrast, hemicellulose exhibits low thermal stability in the pyrolysis temperature range of 230–350 °C. This is attributed to the fact that hemicellulose is a branched polysaccharide with small molecular weights, disordered structure, and low chemical bond energy [27]. The DTG curve of hemicellulose shows two peaks at 265 °C and 297 °C, respectively, indicating that its decomposition process is relatively complex and might involve the gradual decomposition of different sugars. The pyrolysis behavior of lignin shows a wider pyrolysis temperature range from 200 to 600 °C. Lignin is a complex aromatic polymer with a high molecular weight, and its pyrolysis process occurs in multiple stages, including dehydration stage (below 200 °C), active pyrolysis stage (200–450 °C) and passive pyrolysis stage (above 450 °C) [28]. When the pyrolysis temperature increases to 900 °C, the residual char residues of cellulose, hemicellulose and lignin tend to stabilize at 7.70 wt%, 17.89 wt% and 40.52 wt%, respectively. This difference is related to their structure, as well as their volatile and fixed carbon content (as shown in Table 2). Similar thermal degradation behaviors of biomass components have been reported in the literature. For example, Collard et al. [29] reviewed the pyrolysis of biomass constituents and noted that cellulose decomposes within 300–390 °C, hemicellulose between 200 and 350 °C, and lignin over a wider range of 200–600 °C, consistent with our results.

The thermogravimetric mass loss of waste biomass during pyrolysis is related to the thermal decomposition of the biopolymers, cellulose, hemicellulose and lignin. Fig. 2(a) shows that the weight loss of waste biomass mainly occurs between 250 and 400 °C, with the maximum mass loss rate observed at 375 °C, which is 0.97 wt% $°C^{-1}$. The mass loss curve of waste biomass shows the multi-stage mass loss, reflecting the gradual decomposition of its components. Stefanidis et al. [8] also studied the pyrolysis of biomass components and waste biomass, pointing out that there was a synergy between biomass components and that the pyrolysis behavior of each component affected the pyrolysis of waste biomass.

The alkali metals (Na and K) and alkaline earth metals (Ca and Mg) in biochar have significant effects on the catalytic steam reforming of hydrocarbons. Scanning electron microscopy (SEM) analysis of the biochar catalyst was carried out and the results are shown in Fig. 3. Fig. 3(a) clearly shows the alkali and alkaline earth metal (AAEM) elements in biochar. The main components include Ca, K, Mg, Al, Fe, etc. Among them, the content of Ca is the highest, reaching 4.2 wt%, followed by K at 1 wt%. As observed in Fig. 3 (b), the surface of the biochar presents obvious ridges and grooves. Sun et al. [21] investigated the role of biochar in the pyrolysis of biomass by steam reforming and pointed out that the main metal components of biochar are Ca, Mg and K. In particular, Ca and Mg in biochar can combine with carboxylic acid and phenolic groups to form carboxylates and phenolic esters. With the extension of reaction time, these compounds become highly distributed on the surface of the char, which improves its catalytic reforming performance for tar [21]. The presence of K can reduce the activation energy of the reaction and significantly promote hydrogen production by inhibiting methane formation, especially at low to medium reaction temperatures [30]. The metal elements in biochar enhance their catalytic performance in the steam reforming process through various mechanisms, and the synergistic effect of these elements is a key factor in improving the hydrogen yield and reaction efficiency.

When using biochar as a catalyst, in addition to the catalytic role played by the AAEM species in biochar, the steam reactivity of biochar also plays a crucial role in product formation. Fig. 4 illustrates the steam

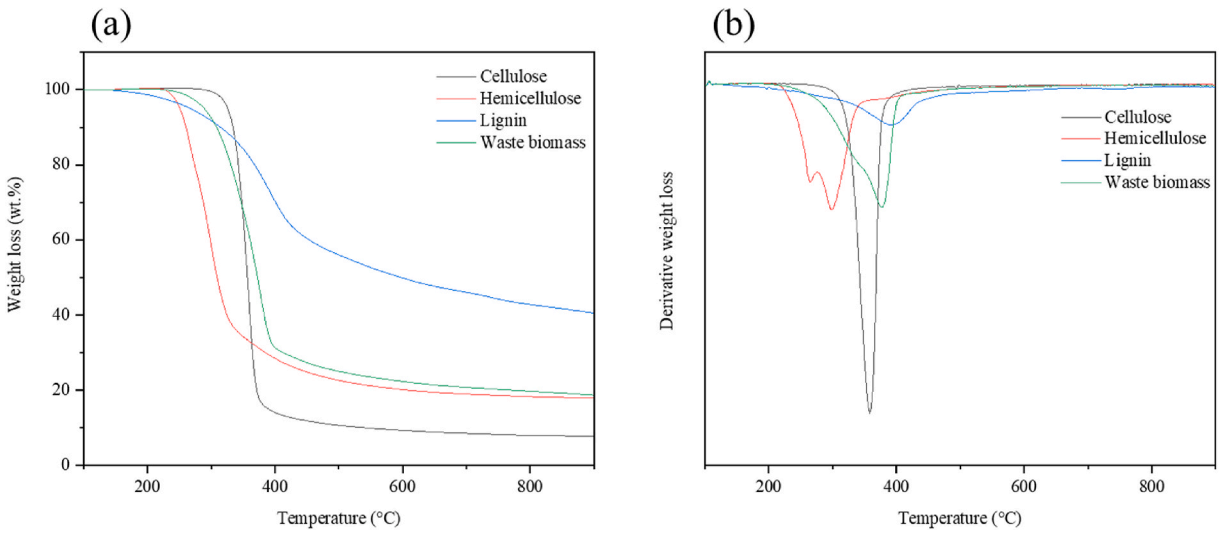

Fig. 2. (a) TGA analysis and (b) DTG analysis of feedstock.

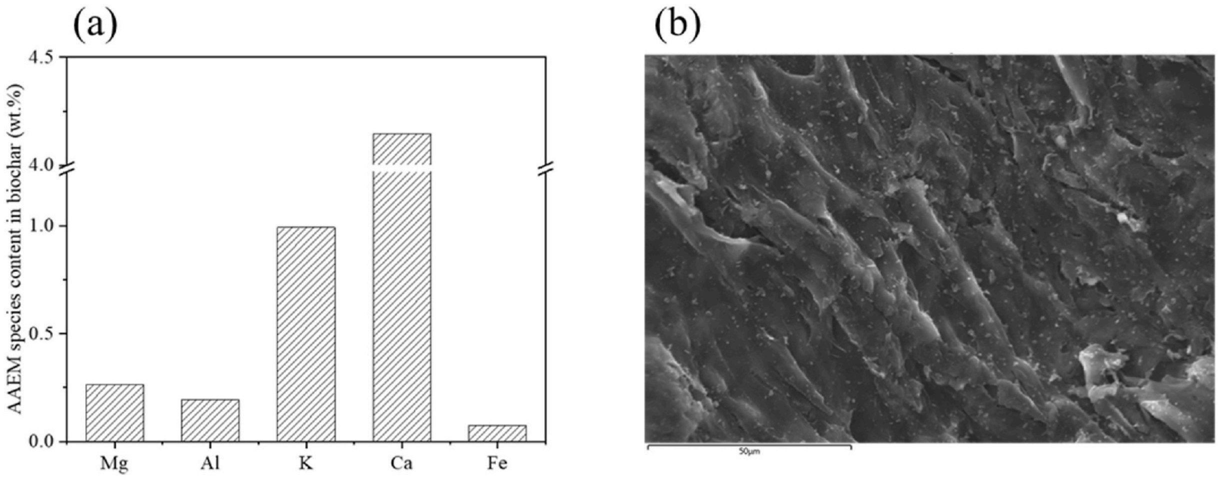

Fig. 3. (a) Metal contents in biochar, (b) SEM image of biochar.

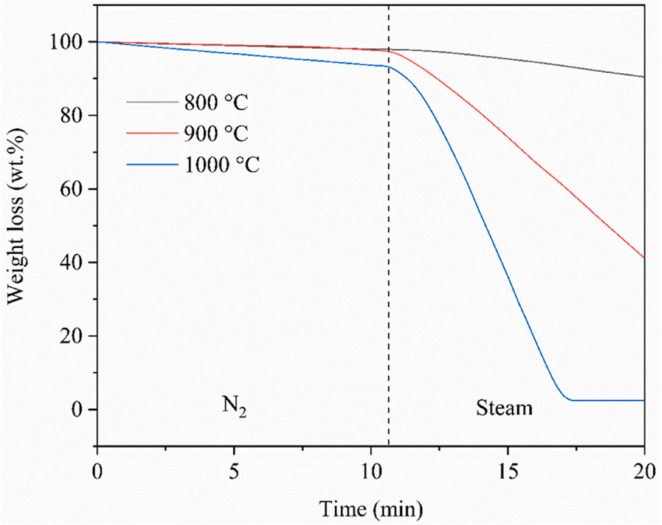

Fig. 4. Steam reactivity of biomass char at different temperatures.

reactivity of biochar at various temperatures. As shown, under a nitrogen atmosphere, the mass of biochar remains almost unchanged, indicating its good thermal stability. However, upon the introduction of steam, biochar experiences significant weight loss at all temperatures. This indicates that the biochar reacts with steam, leading to its consumption and the formation of gaseous products such as H_2 and CO. At the temperature of 1000 °C, the rate of weight loss of biochar was the highest, reaching 9.13 wt% min^{-1}, suggesting that high temperatures significantly enhance the steam reactivity of biochar and accelerate the reaction rate. At the temperature of 900 °C, biochar exhibits a moderate steam reaction rate of 5.66 wt% min^{-1}, while at 800 °C, it shows the lowest steam reactivity and minimal weight loss. The steam reaction of biochar is a typical endothermic process, and the reaction temperature plays an important role in gas production and carbon conversion. Yu et al. [31] investigated the effect of different reaction temperatures on the steam gasification of biochar. They demonstrated that high temperatures not only promote the char steam gasification, but also accelerate the Boudouard reaction, causing the remaining biochar to decrease significantly as the gasification temperature increases. In addition, it has been reported that the presence of AAEM in the raw material can further enhance the steam reactivity of char [32].

3.2. *Pyrolysis-catalytic steam reforming: gas yield and gas composition*

The pyrolysis-catalytic steam reforming of waste biomass, cellulose, hemicellulose and lignin and a mixture of the three biopolymers in a ratio of 4:4:2 was investigated. To further understand the influence of metal composition on pyrolysis, K and Ca metals were added to the mixture and also processed. Many studies [25,33,34] have reported that a large number of gas products are produced during the pyrolysis of biomass components, including hydrogen, carbon monoxide, hydrocarbons, and bio-oil volatiles. The unique chemical properties and structures of the three main components (cellulose, hemicellulose and lignin) lead to notable differences in the volatiles generated by their pyrolysis. For gaseous products, cellulose pyrolysis produces the highest amount of CO, hemicellulose yields the most CO_2, and lignin produces the most CH_4 [34]. In terms of bio-oil, cellulose-derived bio-oil is rich in sugars and furans, bio-oil from hemicellulose contains a high proportion of acids and ketones, and lignin-derived oil is mainly composed of phenolic compounds [25]. These volatiles then enter the catalytic steam reforming reactor, where they react with steam to produce gaseous products such as H_2 and CO. The gas compositions and yields observed in this study can be attributed to key reactions during the pyrolysis-catalytic steam reforming process. Primary pyrolysis reactions produce volatiles, char, and tar, while secondary cracking and reforming reactions (e.g., steam reforming, water-gas shift) catalyzed by biochar convert hydrocarbons and tar into H_2 and CO. For example, methane undergoes steam reforming ($CH_4+H_2O \rightarrow CO+3H_2$), contributing to the high hydrogen yield. Additionally, biochar gasification ($C + H_2O \rightarrow CO + H_2$) and the catalytic effects of K and Ca enhance the overall gas yield and syngas production.

Product yields and properties from pyrolysis-catalytic steam reforming of the three biomass components, their mixtures, mixtures with added metals, and waste biomass are shown in Table 3. It can be seen that among the three components, the gas yield from the pyrolysis-catalytic steam reforming of cellulose is the highest, reaching 330.59 wt %, while the lignin has the lowest yield at 296.89 wt%, which indicates that the decomposition of lignin tends to produce more solid residue. Wu et al. [35] studied the pyrolysis and steam gasification of biomass components under a metal catalyst, and reported a gas yield of 55.1 wt% and a solid yield of 48 wt% for lignin. In contrast, our experimental results show significantly higher gas yields when using biochar as a catalyst, highlighting its superior catalytic performance and ability to enhance gasification. The data in Table 3 are expressed in relation to the mass of input biomass feedstock only. The input from steam addition results in high gas yield, above 100 wt%, in relation to the mass of biomass feedstock.

The gas yield from the pyrolysis-catalytic steam reforming of the

Table 3
Product yields and properties from pyrolysis-catalytic steam reforming of the biomass feedstock using a biochar catalyst. Product yield is based on the mass of input biomass feedstock only.

	Cellulose	Hemicellulose	Lignin	Biopolymer Mixture	Biopolymer Mixture + K + Ca	Waste biomass
Gas yield based on only feedstock (wt. %)	330.59	314.03	296.89	315.46	321.99	329.36
Residue yield (wt. %)	17	15	37	23	20	19
H_2/CO molar ratio	3.12	3.52	3.63	3.54	3.20	3.53
HHV (MJ Nm^{-3})	9.76	10.20	10.71	10.19	10.41	10.20

mixture of the biopolymers was 315.46 wt%, and increased to 322 wt% when K and Ca metals were added, indicating that alkali metals have a certain catalytic effect on the formation of gas products. The residue yield of lignin was 37 wt%, which is related to its complex structure and high thermal resistance. The residue yield of the mixture with metals was 20 wt%, lower than that of the mixture without metal (23 wt%), suggesting that K and Ca can promote further decomposition of biomass and reduce the formation of solid residues. This phenomenon is consistent with the results of Lv et al. [36], who showed that biomass containing AAEM showed higher mass loss during pyrolysis and gasification than biomass without AAEM.

The H_2/CO molar ratio is an important parameter for assessing the quality of syngas in the catalytic steam reforming process and can be used as an indicator for its suitability in different applications. Among the gaseous products generated, lignin produces the highest H_2/CO molar ratio, reaching 3.63, while the molar ratio for hemicellulose, the biopolymer mixture and waste biomass are similar, at around 3.50. Other researchers have also reported syngas production via steam reforming of biomass under different conditions. For example, Akubo et al. [7] found that the pyrolysis of agricultural waste followed by steam reforming at 750 °C produced syngas with an H_2/CO molar ratio ranging between 2.73 and 3.92. Similarly, Chen et al. [37] demonstrated that the pyrolysis-steam gasification of wood sawdust at 800 °C resulted in syngas with an H_2/CO molar ratio of 1.01–1.63. In addition, the gas products from pyrolysis-catalytic steam reforming of lignin have the highest calorific value of 10.71 MJ Nm^{-3}, indicating that it releases the most energy during combustion. This is associated with higher hydrogen yield and abundant hydrocarbon generation. The HHV of the mixture increased after the addition of K and Ca metals, further indicating that alkali metals have a positive effect on the quality of the gas. This phenomenon was explained by Giudicianni et al. [38], who pointed out that the depolymerization and decomposition of the aromatic matrix determine the release of CH_4. Since lignin contains more aromatic structures, the gas produced during steam pyrolysis has a higher HHV.

Individual gas yields and gas compositions from pyrolysis-catalytic steam reforming of the three biomass components, their mixtures, the biopolymer mixture with added metals, and waste biomass are shown in Fig. 5. As shown in the figure, the hydrogen and syngas yield from the processing of lignin are the highest because lignin pyrolysis releases a significant amount of volatiles, such as phenolic compounds and aromatic hydrocarbons. These volatiles react with steam during the catalytic stage, leading to the generation of more gas. The high ratio of C/H in lignin further explains why the pyrolysis volatiles produced from lignin contained more syngas after steam reforming. The hydrogen yield from processing of lignin using biochar as a catalyst reached 110 mmol g^{-1}, which is much higher than the 18 mmol g^{-1} and 25 mmol g^{-1} reported in other studies [7,39]. This clearly demonstrates the dual role of biochar as a catalyst and reactant, significantly improving hydrogen production through catalytic reforming and self-gasification. With the addition of K and Ca, the hydrogen and syngas yield from the processing of the biopolymer mixture increases, suggesting that these alkali metal elements promote the biomass to produce more pyrolysis volatiles, thus enhancing the hydrogen yield after steam reforming. By studying the effects of various metal oxides on the pyrolysis of cellulose, lignin and poplar wood, Zhang et al. [40] pointed out that alkali metals can promote the pyrolysis of biomass to produce more volatile fractions. Fig. 5 (b) shows in detail the gas compositions of various components after the steam reforming reaction, mainly including H_2, CO, CO_2, CH_4 and C_2H_4. The concentration of H_2 and CO_2 in the gas products from pyrolysis-catalytic steam reforming of cellulose was 52.8 vol% and 28.2 vol%, respectively, which is related to the high oxygen content in cellulose. Although lignin is not easily completely converted into gas, the concentration of H_2 in its gas products is higher than that of other components. Akubo et al. [7] also noted that, in the presence of metal

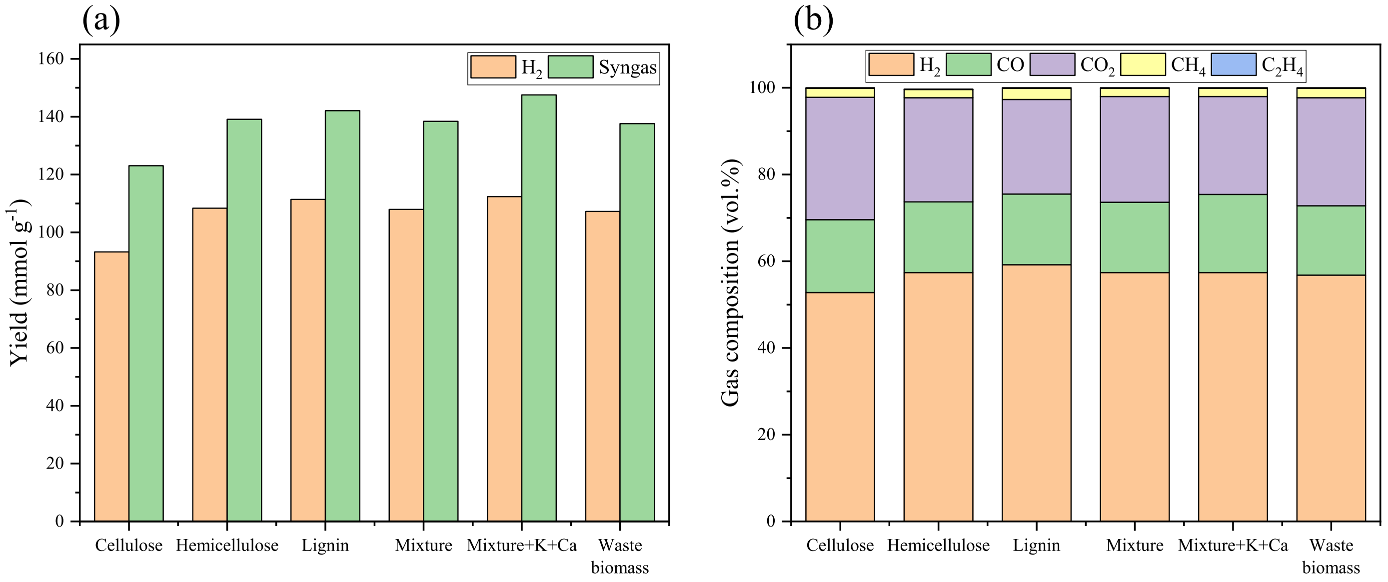

Fig. 5. Individual gas yield and gas composition from pyrolysis-catalytic steam reforming of biomass components, metal-impregnated components and waste biomass using a biochar catalyst.

catalysts, the concentration of H_2 in the gas produced from pyrolysis-catalytic steam reforming of lignin is higher than that from other components. This is because the aromatic rings and O-CH_3 chemical groups in the lignin structure contribute to CH_4 formation during pyrolysis, which is then carried into the second stage and converted to H_2.

3.3. Pyrolysis-catalytic steam reforming: carbon conversion

The pyrolysis volatiles produced in the first stage of biomass pyrolysis enter the second stage, where the biochar acts as both a catalyst and a reactant. In the presence of steam, the carbon in the biomass pyrolysis volatiles and in the biochar is converted into CO, CO_2, CH_4 and C_2H_4, and other gases, while generating a significant amount of H_2. Fig. 6 shows the carbon conversion in the entire pyrolysis-catalytic steam reforming process. Fig. 6(a) and (b) show the carbon conversion to CO and CO_2 for each feedstock. The carbon conversion to CO and CO_2 from cellulose and hemicellulose is higher than that from lignin. This is because the structures of cellulose and hemicellulose are simpler, and their generated volatiles are more easily converted into CO and CO_2 through steam reforming. In contrast, the aromatic structure of lignin leads to the generation of more complex volatile products after pyrolysis, resulting in more carbon remaining in the solid residue. The ultimate and proximate analysis of the three biopolymer components shows that the oxygen content of lignin is only 60 % of that of cellulose and hemicellulose, while the carbon conversion to CO and CO_2 during the pyrolysis-catalytic steam reforming process is higher than that of 60 % of cellulose and hemicellulose. This indicates that the pyrolysis volatiles of lignin react with more steam, consume the oxygen atoms from the steam, and produce more CO and CO_2. This also explains the high hydrogen yield from pyrolysis-catalytic steam reforming of lignin. The carbon conversion to CO from the mixtures is lower than that from the mixtures with added K and Ca, indicating that the addition of these metals promotes the conversion of carbon in the feedstock to CO but has only a minor effect on the conversion to CO_2. Notably, waste biomass, after the same treatment, exhibits a higher carbon conversion to CO_2.

Fig. 6(c) shows the carbon conversion to CH_4. It can be observed that the conversion to CH_4 from cellulose and hemicellulose is lower than that from lignin. This is because CH_4 is not readily produced during the pyrolysis of cellulose and hemicellulose, whereas lignin contains more O-CH_3 chemical groups, leading to the release of CH_4 during pyrolysis. After steam reforming, a small amount of CH_4 still remains in the gas product. The addition of K and Ca to the biopolymer mixture does not appear to significantly affect the formation of CH_4. The complex structure of waste biomass leads to the production of more CH_4 during pyrolysis. After steam reforming, C_2H_4 still exists in the pyrolysis volatiles, and the carbon conversion to C_2H_4 is shown in Fig. 6(d). Lignin has the lowest carbon conversion to C_2H_4, indicating that its aromatic structure is less conducive to generating short-chain olefin compounds after pyrolysis and steam reforming. In contrast, the long-chain hydrocarbons in cellulose and hemicellulose are more easily reformed into short-chain olefin compounds, such as ethylene. When processing waste biomass,

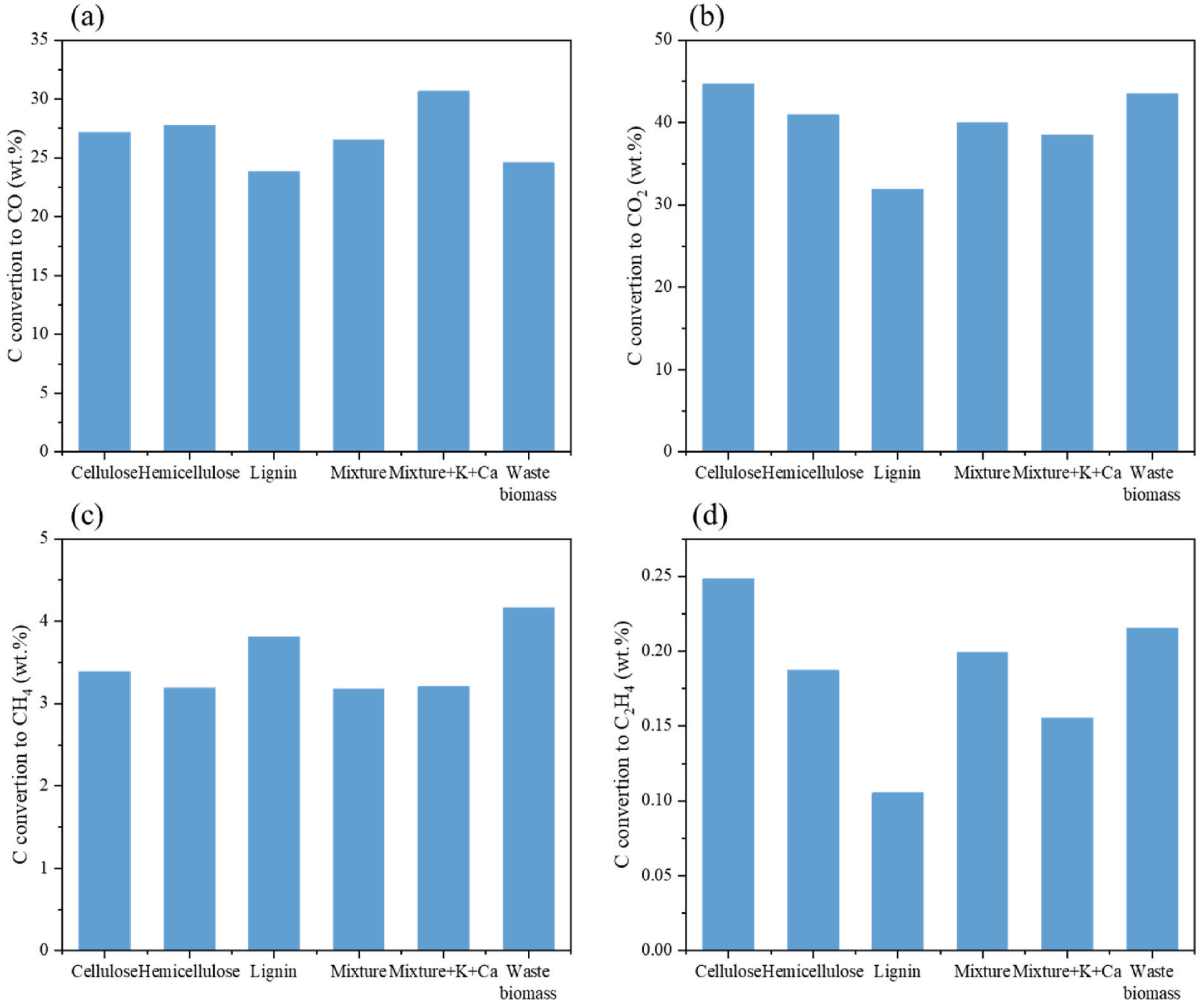

Fig. 6. Carbon conversion to (a) CO, (b) CO_2, (c) CH_4 and (d) C_2H_4.

the carbon conversion was 72.48 %. This is comparable to the 73.68 % reported by He et al. [13], who used an Fe-Ni catalyst for the steam reforming of biomass tar. The results highlight the effectiveness of biochar in achieving competitive conversion without conventional metal-based catalysts.

3.4. Pyrolysis-catalytic steam reforming: Synergies between biomass components

The interaction between the different biopolymer components during the pyrolysis-catalytic steam reforming process of the mixture of cellulose, hemicellulose and lignin mixture (ratio of 4:4:2) was made by comparison between the results for the individual components. In addition, the influence of the addition of K and Ca metals on component interaction was also investigated. Fig. 7 shows the synergistic effect of biomass components on the yield of each gas in the pyrolysis-catalytic steam reforming process. In terms of hydrogen yield, the biopolymer mixture and mixtures with added K and Ca, all exhibit a positive synergistic effect. This indicates a significant synergistic effect between cellulose, hemicellulose and lignin during the pyrolysis process of mixtures, enhancing the efficiency of volatiles conversion into hydrogen during steam reforming. The biopolymer mixtures with added K and Ca show a higher hydrogen yield, suggesting that the addition of alkali metals further promotes hydrogen generation by facilitating the pyrolysis of the feedstock. Kan et al. [41] reported that the H_2 is mainly produced by the secondary decomposition and reforming of C=C and C-H groups of volatiles, and the addition of Ca facilitates this process. For the CO gas yield, there is no obvious synergistic effect in the processing of the biopolymer mixture. However, the CO yield significantly increases after the addition of K and Ca, demonstrating a positive synergistic effect. Regarding the CO_2 yield, the processing of the biopolymer mixture shows a positive synergistic effect, but the addition of K and Ca inhibits the generation of CO_2. This phenomenon can be explained by the catalytic effect of alkali metals: firstly, the presence of K and Ca effectively catalyzes the decomposition of organic oxides in the raw materials into CO instead of CO_2; secondly, Ca can react with steam to form $Ca(OH)_2$, which subsequently reacts with CO_2 to produce $CaCO_3$, thereby reducing the CO_2 concentration in the gas phase [42,43]. Additionally, these metals may enhance the secondary reaction (Boudouard reaction) between CO_2 and carbon in the feedstock, converting CO_2 into CO. In terms of CH_4 yield, the pyrolysis-catalytic steam reforming of the biopolymer mixture shows a negative synergistic effect. This is because the synergistic effect in the biopolymer mixture arises from changes in the pyrolysis atmosphere and gas-solid interaction induced by mechanical mixing. Studies have shown that when the three biopolymer components are mixed for pyrolysis, the volatiles released from cellulose inhibit the demethoxylation of lignin volatiles at temperatures below 600 °C, thereby suppressing methane formation [9]. In contrast, waste biomass has a more complex chemical structure, with intertwined components that may contain additional volatile organic and inorganic compounds. During the pyrolysis-catalytic steam reforming process, these compounds can crack and recombine, resulting in methane production.

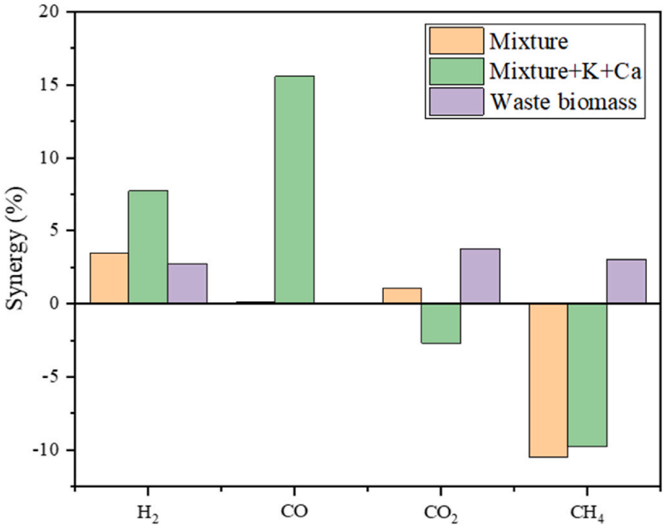

Fig. 7. Synergistic interaction of biomass components, the biopolymer mixture with added metals and waste biomass, on the yield of each gas in the pyrolysis-catalytic steam reforming process.

Liu et al. [44] studied the interactions among biomass components during pyrolysis by using a combination of thermogravimetry analysis and Fourier transform infrared spectroscopy. They observed significant differences between their experimental results and the calculated DTG curves, indicating strong interactions among the three biomass components. In addition, the presence of cellulose or hemicellulose promotes the pyrolysis of lignin to produce more phenolic volatile compounds during co-pyrolysis of biopolymer mixtures [45]. Hosoya et al. [46] also pointed out that the interactions of biomass components can affect the pyrolysis behavior, including the amounts of gas, oil and char products as well as the composition of products.

Fig. 7 also shows the synergistic effects in relation to waste biomass. This data was calculated based on the comparison of the product yields from the pyrolysis-catalytic steam reforming of the cellulose, hemicellulose and lignin mixture (ratio 4:4:2) and added metals with the product yield from waste biomass. The purpose was to demonstrate that the various components in real waste biomass also exhibit synergistic interactions. The yield of hydrogen from the waste biomass exhibited a positive synergistic effect, but was less than the mixture of the biopolymer mixture and the mixture with added K and Ca. There was no synergistic effect for CO production, but for the CO_2 yield, the processing of the waste biomass produced a significant positive synergistic effect compared with the biopolymer mixture. In terms of CH_4 yield, the processing of the waste biomass shows a positive synergy. The waste biomass is not just a simple combination of cellulose, hemicellulose and lignin, but these components are intertwined in complex ways to form materials with naturally porous structures and cell walls. This unique physical structure affects the heat and mass transfer behavior during pyrolysis. Additionally, the compositional variations and the presence of organic and inorganic compounds in waste biomass contribute to positive synergistic effects. The comparison between the biopolymer mixture and waste biomass highlights the additional effects of real-world complexity, including the interactions among intertwined components and the influence of minor organic and inorganic compounds. These differences further emphasize the importance of understanding synergistic interactions in both controlled model systems and actual waste biomass.

3.5. Pyrolysis-catalytic steam reforming: mechanism of catalytic conversion of biomass

During the pyrolysis-catalytic steam reforming reaction, biomass components undergo a series of changes, the evolution mechanisms of which are illustrated in Fig. 8. The exact molecular formula of lignin is complex and irregular, so it is represented by a simplified form $(C_9H_{10}O_2)n$. At low temperatures, cellulose first undergoes a dehydration reaction, where the bond between carbon and the hydroxyl group (Bond 1) is broken, releasing water and light volatile products [47]. The main pyrolysis reactions of cellulose occur between temperatures of 300 and 400 °C, where the β-1, 4-glucoside bond (Bond 2) in cellulose begins to break, generating glucose units. At high temperatures, bonds within the glucose unit break and recombine through ring opening, dehydration and cyclization reactions, leading to the formation of products like 5-hydroxymethylfurfural, furan etc. [48,49]. The pyrolysis of Xylan mainly occurs between 300 and 350 °C, with a mechanism similar to

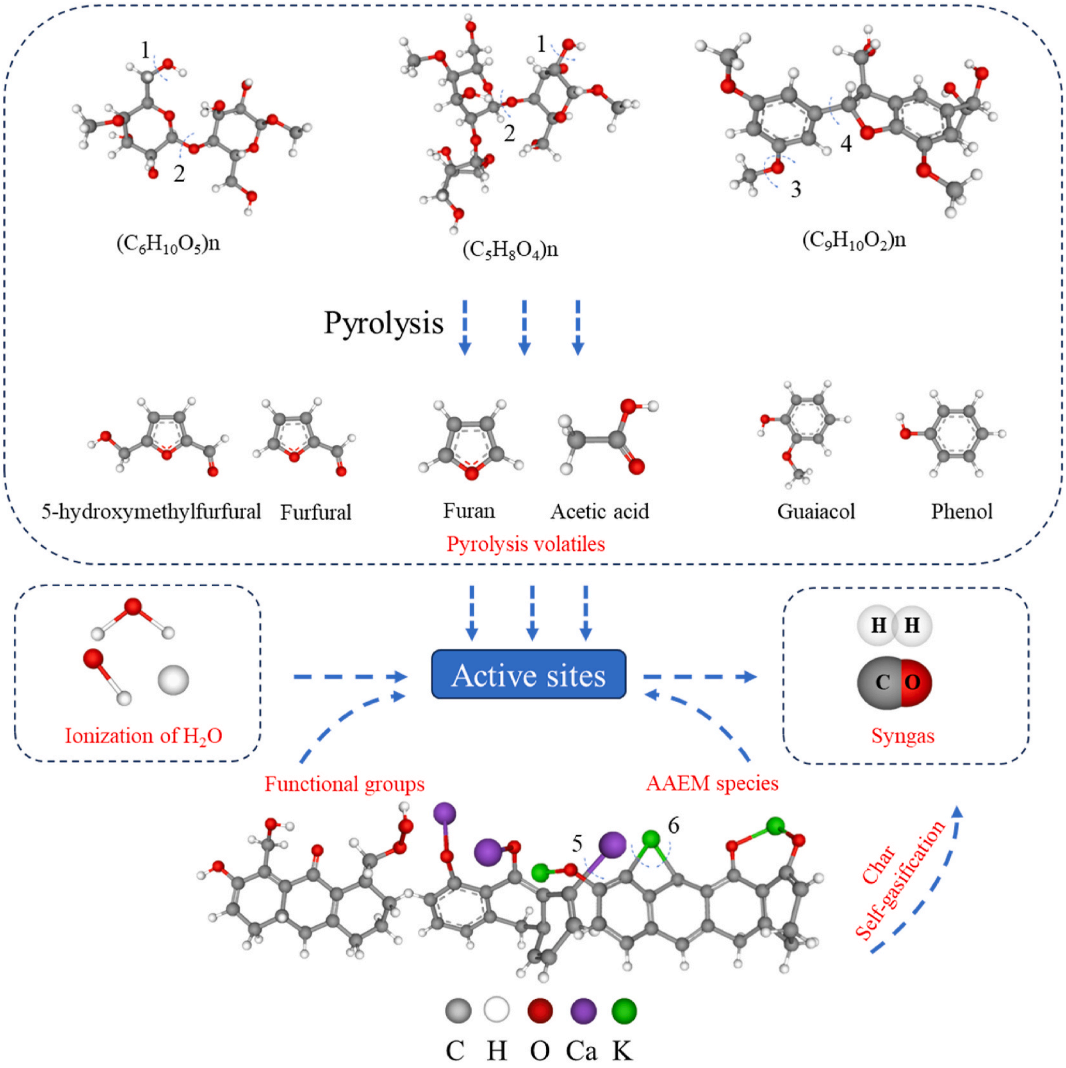

Fig. 8. Proposed pyrolysis-catalytic steam conversion of biomass for the production of hydrogen and syngas using biochar as a catalyst.

that of cellulose. The main products include acetic acid and furfural [50]. Lignin is a complex three-dimensional network structure formed by the polymerization of phenylpropane units, and its main pyrolysis reactions take place between 300 and 500 °C. In this temperature range, ether bonds (Bond 3) and C-C bonds (Bond 4) break, forming a series of aromatic compounds, including guaiacol and phenol [51]. When mixtures are pyrolyzed, hemicellulose decomposes first, producing volatiles that change the pyrolysis atmosphere for cellulose and lignin. In addition, heterogeneous reactions between these volatiles and the solid residues of mixtures lead to differences between the co-pyrolysis of the mixture and the separate pyrolysis of the three components. When metals such as K and Ca are added, Bonds 1–4 are more easily broken, and the raw material undergoes more complete pyrolysis.

The volatiles generated by pyrolysis in the pyrolysis reactor enter the second stage where a biochar catalyst is used. The surface of the biochar catalyst is rich in oxygen-containing functional groups as well as alkali and alkaline earth metals, which provides active sites for the catalytic steam reforming of the volatiles from the first stage. In the atmosphere of steam, ionization produces H and OH free radicals. These free radicals play an important role in converting AAEM from metallic to free radical forms. As shown in Fig. 8, bonds such as C-Ca (Bond 5) and C-K (Bond 6) are continuously broken and reformed. The bonding and breaking of carbon-AAEM increase the concentration of active sites in the biochar particles, providing more opportunities for hydrocarbon binding and cracking [20]. Additionally, the oxygen-containing functional groups on biochar can promote the steam reforming of hydrocarbon volatiles, as demonstrated by Yao et al. [18] and Shen et al. [15]. The K and Ca free radicals in biochar enter the gas phase, repeatedly forming and breaking bonds of pyrolysis volatiles, resulting in the transformation of pyrolysis volatiles. A series of bond-breaking and ring-opening reactions break down large hydrocarbons into lighter hydrocarbons and small gas molecules. On the biochar surface, hydrocarbons can combine with active sites and participate in further reforming reactions. Furthermore, biochar itself also participates in steam gasification to produce CO and H_2.

The findings presented in this manuscript offer valuable insights into the pyrolysis-catalytic steam reforming of biomass components and real biomass using biochar catalysts, providing a foundation for advancing hydrogen and syngas production technologies. However, this study also faces certain limitations. First, the experiments were conducted under controlled laboratory conditions, which may not fully show the complexities of real-world industrial settings. Second, while the addition of potassium and calcium demonstrated significant impacts, the specific contributions of individual metals in biomass have not been thoroughly investigated. Future studies could examine the effects of different concentrations of Ca and K and other metals, such as magnesium and sodium, to further enhance the understanding of their catalytic impacts. Moreover, scaling this approach for industrial applications requires optimizing reactor designs, and integrating these processes into broader clean energy systems. Additionally, investigating other types of biochar and their modifications with various metal loadings could further enhance the catalytic performance and adapt the process to different feedstocks. These efforts will help bridge the gap between laboratory studies and practical applications, advancing the sustainable utilization of biomass for clean energy production.

4. Conclusions

The three main biopolymer components of biomass (cellulose, hemicellulose and lignin), a mixture of these components, the biopolymer mixture with added metals, and waste biomass were first pyrolyzed at 600 °C in a pyrolysis reactor to produce pyrolysis volatiles. These volatiles were then directly reformed by steam at 900 °C in a second stage catalytic reactor in the presence of a biochar catalyst to produce hydrogen-rich syngas. The influence of alkali and alkaline earth metal addition and synergistic effects between the biopolymers were investigated. The main conclusions were.

(1) The differing compositions and structures of the three biomass components resulted in different pyrolysis volatiles, and thus different product distributions after catalytic steam reforming. The processing of lignin produced the highest hydrogen and syngas yields at 111.39 mmol g^{-1} and 142.08 mmol g^{-1}, respectively, followed by hemicellulose, with cellulose yielding the lowest amounts.

(2) The three components exhibited a synergistic effect during co-pyrolysis-catalytic steam reforming, which promoted the production of hydrogen, but inhibited the release of methane. The addition of K and Ca can significantly increase the syngas yield, especially carbon monoxide.

(3) Most of the carbon elements in the raw materials and catalysts were converted into gases, released as CO, CO_2, CH_4 and C_2H_4, with a small portion remaining in the solid residue.

(4) A mechanism was proposed whereby oxygen-containing functional groups on the surface of biochar, along with alkali and alkaline earth metals, provided active sites for pyrolysis volatiles. Bonds within steam and hydrocarbons were continuously broken and recombined at these active sites to produce hydrogen and carbon monoxide. In addition, the self-gasification of char enhanced the production of hydrogen and carbon monoxide.

CRediT authorship contribution statement

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

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Data availability

Data will be made available on request.

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