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Effects of alkali- and alkaline-earth-metals on hydrogen generation during fluidized bed gasification of artificial waste

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Abstract−We evaluated the effects of Na, K, Ca, and the steam-to-biomass (S/B) ratio on gasification efficiency during syngas production. The results show that H_2 production was positively correlated with the S/B ratio. However, increases in the S/B ratio were limited because excessive steam decreased the reactor temperature and hampered the gasification process. Regarding the effects of alkali metals on syngas composition, we found that the addition of either Na or K increased the molar percentages of H_2 and CO, but decreased CH_4 and CO_2. The results also clearly show that the addition of Na or K improved the yield of syngas, the carbon conversion efficiency, and the cold gas efficiency. Improvements were especially pronounced with K. Furthermore, Ca had different interactions with Na and K during gasification. When Na and Ca existed simultaneously, H_2 production was enhanced.

Keywords: Gasification, Biomass, Alkali Metal, Alkaline Earth Metal, Fluidized Bed

INTRODUCTION

Among the several existing biomass energy conversion technologies, thermochemistry conversion methods are relatively mature. These methods include incineration, gasification, and pyrolysis technologies [1-3]. Gasification is a thermochemical conversion technology that converts biomass material into combustible gas through partial oxidation under high temperatures, and most of the products are gaseous. The synthetic gas mixture produced can be used as a raw material for power generation.

According to previous studies, fluidized gasifiers perform better than other types of gasifiers, largely because the available feed rate of the fluidized bed is greater than that of the fixed bed. In fluidized gasifiers, the heat and mass transfer can be provided by the fuel, high heating efficiency can be achieved, and there are few limitations on the types of feeding material. Hence, during the development of technology to use biomass energy for gas production, the fluidized bed gasifier is often the better choice [4,5].

Recently, discussions regarding the development of gasification technology have focused on whether gas production can achieve higher H_2 content and decreases in the formation of tar [6-8]. During the gasification process, tar formation poses a major problem because it can block the gasifier equipment and affect the production of syngas. A common method for the removal of tar is to add a catalyst or addition agent, which is both convenient and practical [6]. Many studies have found that added catalysts and additives increased H_2 production, heat value, carbon conversion, and the cold gas efficiency of the produced gas. Common catalysts or additives include CaO and Ni [9,10]. Hurley et al. [11] also demonstrated that when the biomass contained metals, such as Ni, Ru, Co, and Fe, the production of H_2 and CO was increased. Among these metals, the addition of Ni and Ru improved H_2 production the most. Wang et al. [12] showed that the addition of K_2CO_3 can increase H_2 production and stop the formation of tar. Therefore, the addition of catalysts and additives in a gasifier can have positive effects during biomass gasification.

During waste treatment, several types of metals such as heavy metals, alkali metals, and alkaline earth metals may be present in the waste material. Whereas Na, K, and Ca are generally found in municipal solid waste and agricultural waste. Using existing metals as catalysts for gasification, if possible, would not only enhance H_2 production but also reduce the need for additives. Hence, in this experiment, the effects of alkali metals, alkaline earth metals, and the steam-to-biomass (S/B) ratio on gasification were evaluated. The gas composition, gas yield, carbon conversion efficiency, and cold gas efficiency were determined. The experimental results provide valuable information that can be applied to the waste fluidized bed gasification process.

MATERIALS AND METHODS

1. Artificial Waste

To reduce the differences in the composition of the feeding waste, artificial waste was prepared in this study. Real waste could not be used because its composition is often very complex and bound to vary. The artificial waste was primarily composed of sawdust (6.77 g) and polypropylene (PP) (0.62 g). Additionally, 1.76 mL of an aqueous metal nitrate solution was added to the artificial waste material, and the mixture was covered with a polyethylene (PE) plastic bag (0.51 g). Each package of artificial feed material weighed 9.66 g. The main constituents of raw materials are listed in Table 1. The alkali metals were added in the form of two chemical compounds, $NaNO_3$ and KNO_3, and the alkaline earth metal was added in the form of $Ca(NO_3)_2$. The concentrations of Na, K, and Ca added were 0.7 wt% of the artificial waste. The specific experimental parameters evaluated included alkali metal elements (Na and K), alkaline

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Table 1. Ultimate analysis, proximate analysis, and heat value analysis of artificial waste

Species	Wood chips	PP	PE
LHV* (MJ/kg)	15.10	45.60	44.90
Moisture	0.74%	0.01%	0.01%
Volatile matter	81.6%	99.99%	99.99%
Fixed carbon	16.6%	<0.01%	<0.01%
Ash	1.07%	<0.01%	<0.01%
Carbon	43.12%	86.16%	85.71%
Hydrogen	5.80%	12.20%	13.04%
Nitrogen	5.01%	1.12%	0.86%
Oxygen	46.07%	0.52%	0.39%

* LHV : Lower heating value

earth metal (Ca), and S/B ratio. Table 2 lists the operating conditions for the experiments.

2. Fluidized Bed Gasifier

The reactor used in this study was a bubbling fluidized bed gasifier, as shown in Fig. 1. The main chamber was 1.2 m in height and 10 cm in diameter. The bed material was composed of silica sand that had a density of 2,600 kg/m^3 and an average particle size of 545 μm. The mass weight of the bed material was 2.2 kg. The height (H) of the sand bed was about 18 cm, which was approximately two times the diameter (D) of the furnace bed (H/D=2). Prior to the start of the experiment, the minimum fluidization velocity (U_{mf}) was determined from the plot of pressure drop versus gas velocity, using the method described in detail by Lin et al. [13]. This study used a value of 1.3 U_{mf} (0.10 m/s) to conduct these experiments. Additionally, this amount of air equaled an equivalence ratio (ER) of 0.3, which was also used to calculate the composition of the artificial waste.

Table 2. Operating conditions for the experiments

Run	Temperature (°C)	ER	S/B	$NaNO_3$ (wt%)	KNO_3 (wt%)	$Ca(NO_3)_2$ (wt%)
Run 1	800	0.3	1.0	-	-	-
Run 2	800	0.3	1.5	-	-	-
Run 3	800	0.3	2.0	-	-	-
Run 4	800	0.3	1.0	0.7		
Run 5	800	0.3	1.0	-	0.7	-
Run 6	800	0.3	1.5	0.7	-	-
Run 7	800	0.3	1.5	-	0.7	-
Run 8	800	0.3	1.0	0.7	-	0.7
Run 9	800	0.3	1.0	-	0.7	0.7

3. Operating Procedures

The experiment was started after the reaction temperature stabilized. Artificial wastes were inserted into the fluidized bed through the feed inlet at a feed rate of 1 package/20 s. During the experiment, we used a standard method to sample gas from the stacks (US EPA, Method 5 Train, M5). An active air-sampling pump (Model 224-44XR, SKC Gulf Coast Inc.) was used, and the gas was sampled at the collection bag. Collections were performed every 5 min, and the collection time was 48 s. The collection rate was 1 L/min. The gas produced by gasification was analyzed by gas chromato-

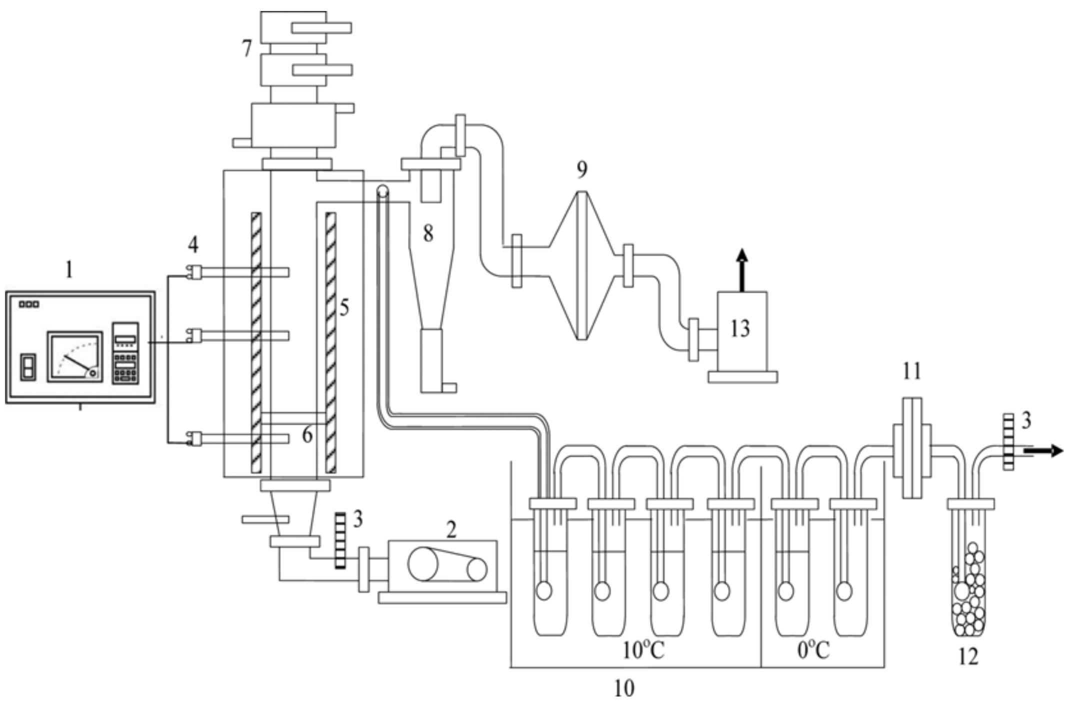

Fig. 1. Bubbling fluidized bed incinerator.

1. PID controller
2. Blower
3. Flow meter
4. Thermocouple
5. Electric resistance
6. Sand bed
7. Feeder
8. Cyclone
9. Carbon filter
10. Low temperature water tank
11. Particle filter
12. Silica gel
13. Induced fan

graph equipped with a thermal conductivity detector (TCD). The pipe column was composed of a Carboxen-1000 60/80 mesh. The main gases analyzed were N_2, H_2, CO, CO_2, and CH_4. The test data included the molar percentage composition, yield, and heat value of the produced gas. The carbon conversion efficiency and cold gas efficiency were also calculated in this study.

RESULTS AND DISCUSSION

1. Effects of Steam-to-biomass Ratio (S/B) on Gas Production

Fig. 2 illustrates the gas composition distribution at an S/B ratio of 2.0. From our experimental results, the gas composition was found to be stable after 15 min of operation. Fig. 3 shows the effects of the S/B ratio on gas composition. To simulate the effect of the S/B ratio on total gas production in the gasifier, water was added to the artificial wastes. The experimental results indicated that the H_2 molar percentage increased from 12.1% to 21.7% as the S/B ratio increased from 1 to 1.5. When the S/B ratio increased from 1.5 to 2, the H_2 molar percentage decreased from 21.7% to 21.2%. Luo et al. [14] demonstrated that the addition of steam in a gasifier can cause methane-steam reformation and a heat-absorbing reaction as follows:

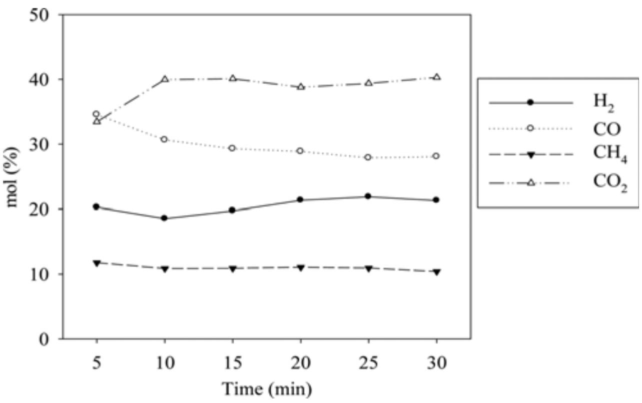

Fig. 2. The gas composition distribution (without nitrogen) at various operation times (temperature=800 ºC, ER=0.3, U/U_{mf}=1.3, and S/B=2.0).

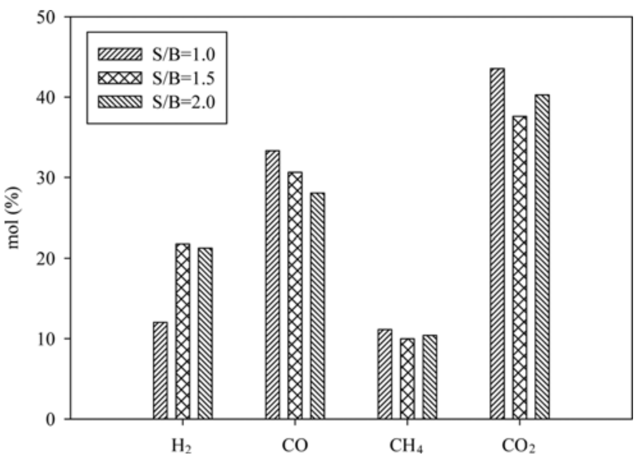

Fig. 3. The effect of the S/B ratio on the mole fraction of gas composition distribution (without nitrogen) (temperature=800 ºC, ER=0.3, and U/U_{mf}=1.3).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta GH = +206\ \text{kJ/mol} \qquad (1)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta GH = +165\ \text{kJ/mol} \qquad (2)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta GH = +247\ \text{kJ/mol} \qquad (3)$$

Where ΔGH represents the change in enthalpy.

Additionally, high temperatures can also promote tar reformation, tar cracking, and improve the yield of H_2 according to the following reactions:

$$Tar + n_1H_2O \rightarrow n_2CO_2 + n_3H_2 \qquad \Delta GH > 0 \qquad (4)$$

$$C_nH_m(Tar) + nCO_2 \leftrightarrow \left(\frac{m}{2}\right)H_2 + 2nCO \qquad \Delta GH > 0 \qquad (5)$$

$$C_nH_m(Tar) \leftrightarrow \left(\frac{m}{2}\right)H_2 + nC \qquad \Delta GH > 0 \qquad (6)$$

In addition to the above reactions, the water gas reaction and endothermic Boudouard reaction can also change the gas composition. This can occur via the following reaction equations:

$$C + H_2O \leftrightarrow H_2 + CO \qquad \Delta GH = +131\ \text{kJ/mol} \qquad (7)$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta GH = +175\ \text{kJ/mol} \qquad (8)$$

As can be seen from the above reactions, the proportion of H_2 in the produced gas increased and the proportion of CO_2 decreased because high temperatures are more likely to promote endothermic reactions.

However, when the S/B ratio increased to 2.0, H_2 production was not enhanced any further. Because water was added to the artificial waste, at a high S/B ratio, the water percentage of the artificial waste was excessively high and some amount of heat was likely absorbed, which decreased the temperature in the reactor. This would affect methane-steam reformation [15]. Indeed, Luo et al. [14] indicated that the addition of excessive water may reduce the temperature of the gasifier and affect gas composition. Thus, the S/B ratio can only be increased to a threshold value during gasification.

2. Effects of Different Alkali Metals on Gas Production

Fig. 4 illustrates the effects of the addition of Na and K on the

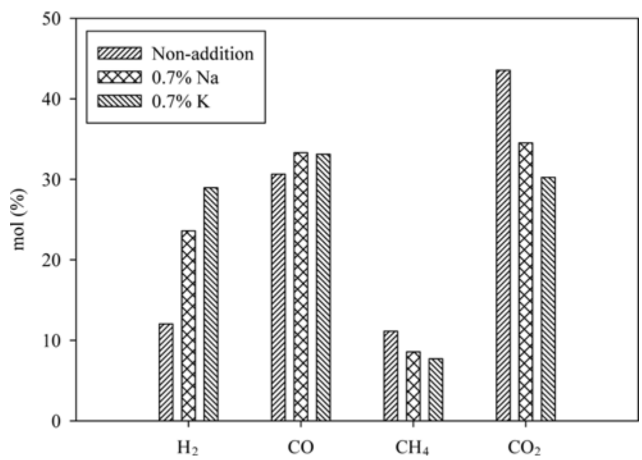

Fig. 4. The effect of the addition of different alkali metals on the mole fraction of gas composition distribution (without nitrogen) (temperature=800 ºC, ER=0.3, and U/U_{mf}=1.3, and S/B=1.0).

composition of produced gas. The S/B ratio during these experiments was 1. The produced gas consisted of H_2 (12.1%), CO (33.3%), CH_4 (11.12%), and CO_2 (43.53%) when no alkali metal was added to the artificial waste. The results showed that the molar percentage of H_2 increased greatly when the alkali metals were added into the gasification process. The molar percentage of H_2 increased to 23.6% when Na was added. The highest H_2 molar percentage of 29% was achieved when K was added. These results indicate that the addition of the alkali metals Na or K increased the production of H_2 and CO and decreased the production of CO_2 and CH_4. In terms of the percentage of produced H_2, the addition of K had a more pronounced effect on H_2 production than that of Na.

The results obtained in this study regarding changes in gas composition may have been due to the promotion of oxygen conversion reactions in the presence of high concentrations of alkali metals. Sears et al. [16] and Mouijin et al. [17] found that alkali metals might be first oxidized in the presence of oxygen and would then react with CO_2 to produce CO and H_2. Therefore, Na_2O or K_2O may be the dominant species during gasification. Other studies have also reported the oxidation of alkali metals, followed by a circulating redox reaction with water. The equations that describe the metal-induced increase in the rate of reaction between H_2 and CO are as follows [18]:

$$H_2O+M_2O\bullet C=H_2+M_2O_2\bullet C \tag{9}$$

$$\alpha M_2O_2\bullet C+\alpha C=\alpha M_2O\bullet C+\alpha CO \tag{10}$$

$$(1-\alpha)M_2O_2\bullet C+(1-\alpha)CO=(1-\alpha)M_2O\bullet C+(1-\alpha)CO_2 \tag{11}$$

$$\text{Overall reaction } H_2O+\alpha C=H_2+(1-\alpha)CO_2+(2\alpha-1)CO \tag{12}$$

where M represents metal elements.

Mckee [19] studied these reactions further and used the equilibrium stability regions of the alkali metal catalysts to perform free energy calculations and uncover possible catalytic mechanisms. These mechanisms included a carbothermic reduction reaction, C-CO_2 reactions, and C-H_2O reactions.

Carbothermic reduction reaction

$$(Na, K)_2CO_3+2C=2(Na, K)+3CO \tag{13}$$

C-CO_2 reactions

$$2(Na, K)+2CO_2=(Na, K)_2O+CO \tag{14}$$

$$(Na, K)_2O+CO_2=(Na, K)_2CO_3 \tag{15}$$

C-H_2O reactions

$$2(Na, K)+2H_2O=2(Na, K)OH+H_2 \tag{16}$$

$$2(Na, K)OH+CO=(Na, K)_2CO_3+H_2 \tag{17}$$

According to the above equations, the molar percentage of H_2 will increase when alkali metals are added.

The data in Table 3 illustrate the effects of the addition of different alkali metals on gas yield. The gas yield was maintained within 1.86 Nm^3/kg without the addition of Na. After the addition of Na, the gas yield was 2.03 Nm^3/kg. The gas yield increased to 2.15 Nm^3/kg after the addition of K. The addition of K produced a higher gas yield than the addition of Na.

The data in Table 3 also show the effects of different alkali metals on carbon conversion, heat values, and cold gas efficiency. The results indicated that the carbon conversion was 87.6% without the addition of alkali metals. After the addition of alkali metals, the carbon conversion increased dramatically. The conversion efficiency was the highest (97.01%) when K was added. The total gas heat value was 2.79 MJ/Nm^3 when no alkali metals were added. After the addition of Na, the total gas heat value increased to 3.12 MJ/Nm^3. After the addition of K, the total gas heat value increased to 3.2 MJ/Nm^3. This indicates that the total gas heat value was the highest after the addition of K. The primary reason for the increase is that the addition of K can cause a reaction between water and tar, and more CO and H_2 can be produced. The cold gas efficiency increased from 34% to 42.3% after the addition of K. Overall, the alkali metal K had a greater effect on H_2 production, the production of other gases, carbon conversion, and cold gas efficiency than that of Na.

Table 3. The effect of alkali metals on the behavior of gas production

			Non-addition	Na	K
Gas yield	(Nm^3/kg)		1.86	2.03	2.15
Carbon conversion	(%)		87.60	92.61	97.01
Heat value	(MJ/Nm^3)	H_2	0.03	0.1	0.11
		CH_4	0.97	0.79	0.89
		CO	1.79	2.23	2.20
		Total	2.79	3.12	3.20
Cold gas efficiency	(%)		34.00	38.60	42.30

3. Effects of the Addition of an Alkaline Earth Metal on Gas Production

Fig. 5 shows the effects of the addition of Ca on the composition of gas produced by a bubbling fluidized bed gasifier. After the addition of Na and Ca, H_2 increased to 36.5% and CO_2 decreased to 30%. However, after the addition of K and Ca, the H_2 decreased to 21.0%. We estimate that this change of relative gas composition was caused by alkaline earth oxides after the addition of an alka-

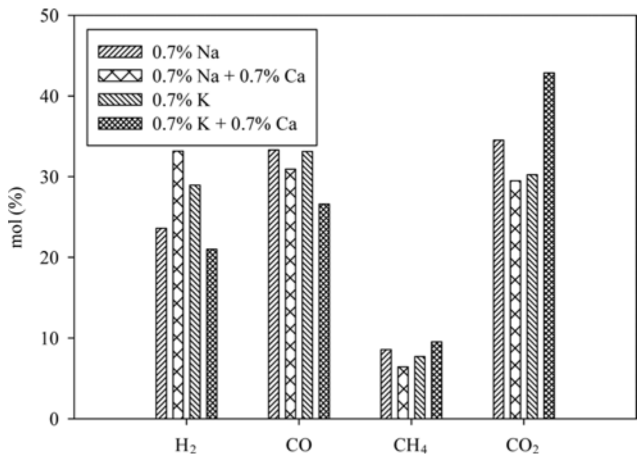

Fig. 5. Comparison of the addition of an alkali metal and an alkaline earth metal on the mole fraction of gas composition distribution (without nitrogen) (temperature=800 °C, ER=0.3, and U/U_{mf}=1.3, and S/B=1.0).

line earth metal.

Florin and Harris [20] noted that Ca ions may easily form CaO in a high-temperature environment, and that CaO can capture CO_2 in the gasifier to produce $CaCO_3$ and reduce the CO_2 content (Eq. (18)). Additionally, the reactions shown below in Eqs. (19), (20), and (21) proceed towards the right. These phenomena likely were responsible for reducing the generation of CO and CH_4 (which have high calorific values) and producing H_2 (which has a low calorific value). Based on what is known about H_2 conversion, the addition of CaO could increase the H_2 yield while depleting CO and CH_4.

$$CaO+CO_2 \rightarrow CaCO_3 \qquad \Delta GH=-170.5\text{ kJ/mol} \qquad (18)$$

$$C+2H_2O \rightarrow CO_2+2H_2 \qquad \Delta GH=+100\text{ kJ/mol} \qquad (19)$$

$$CH_4+2H_2O \rightarrow CO_2+4H_2 \qquad \Delta GH=+165\text{ kJ/mol} \qquad (20)$$

$$CO+H_2O \rightarrow CO_2+H_2 \qquad \Delta GH=-41\text{ kJ/mol} \qquad (21)$$

After the addition of Ca, the gas yield increased from 2.01 Nm^3/kg to 2.12 Nm^3/kg. The total cold gas efficiency had a downward trend after the addition of Ca. Therefore, coexistence of Na and Ca can be expected to increase the gasification efficiency and enhance H_2 production.

CONCLUSIONS

We considered the effects of Na, K, and Ca additions on the gasification efficiency of artificial wastes in a fluidized bed gasifier. The experimental parameters investigated included the addition of alkali metals (Na and K), the addition of an alkaline earth element (Ca), and variations in the S/B ratio. The experimental results indicated that a steam conversion reaction occurred when the S/B ratio was 1.5. Also, the H_2 composition of gas increased. The increase in the S/B ratio was limited because excessive steam affected the temperature in the reactor and worsened the gasification process. Regarding the effects of the addition of Na and K on gas production, we found that the addition of either Na or K increased the amount of H_2 and CO produced and decreased the amount of CH_4 and CO_2 produced. The gas yield, carbon conversion, total gas heat value, and cold gas efficiency increased after the addition of alkali metals. Hydrogen production, gas yield, carbon conversion, and cold gas efficiency improved more after the addition of K than after the addition of Na. However, the added Ca had a different interaction with Na and K during gasification. When Na and Ca existed simultaneously, the gasification efficiency increased, which thereby enhanced H_2 production.

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