Hydrogen-Rich Gas Production from Steam Gasification of Biomass using CaO and a Fe-Cr Water-Gas Shift Catalyst

Qiang Tang,* Haibo Bian, Jingyu Ran, Yilin Zhu, Jiangong Yu, and Weilin Zhu

The technical feasibility of using calcium oxide (CaO) as a sorbent for CO_2 and Fe-Cr as a catalyst for the water-gas shift (WGS) reaction using syngas for the steam gasification of biomass was investigated. The effects of temperature, steam to biomass mass ratio, CaO to biomass molar ratio, and Fe-Cr WGS catalyst on gas composition were studied. Within a temperature range of 250 °C to 550 °C, the H_2 concentration increased from 1.2% to 17.1%, with a total increase of 16%. As the steam rate increased within the range of 0 kg/h to 0.12 kg/h, the maximum value of H_2 concentration increased from 12.1% to 17.13%, with a total increase of 5%. As the CaO to biomass molar ratio was increased from 0 to 2, the CO_2 concentration demonstrated a minimum value of 1.3%, and the H_2 concentration exhibited a maximum value of 53.1%. A catalyst to biomass mass ratio of 1 resulted in the minimum value of CO_2 concentration, which decreased from 7.9%, in the absence of CaO, to 1.6%. A CaO to biomass molar ratio of 1.5 resulted in the maximum value of H_2 concentration, which increased from 27.6%, in the absence of CaO, to 63%.

Keywords: Biomass; Steam; Gasification; H_2 production; CaO; Catalyst

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INTRODUCTION

Fossil fuel depletion has led to a serious energy crisis and is an impediment to sustainable development for human society. Constructing a clean and sustainable energy system, through the use of hydrogen as a replacement for fossil fuel energy systems, has been a serious challenge (Lin *et al*. 2002; Piekarczyk *et al*. 2013). Biomass is a promising source of hydrogen for clean and renewable energy. Biomass by steam gasification is an extensively used technology because of its superiority to other technologies of biomass processing, such as combustion and biochemical conversion, its improved conversion efficiency, and the flexibility of handling generated gaseous fuels (Meng *et al*. 2006; Madhukar *et al*. 2007; Han *et al*. 2013; Sreejith *et al*. 2014).

Theoretical and experimental research on biomass steam gasification has been studied by scholars over several decades. When steam is added into the biomass steam gasification process, researchers found that the H_2 in H_2O could be displaced to yield more H_2 by a water-gas shift (WGS) reaction (Aznar *et al*. 2006; Guan *et al*. 2007). However, the concentration of hydrogen is limited by chemical reaction equilibrium during the gasification process (Haryanto *et al*. 2007). In addition, large amounts of CO and CO_2, and limited amounts of CH_4 and tar, are generated at the same time during the biomass steam gasification process (Proll and Hofbauer 2008; Hu and Huang 2009; KarmaKar and Datta 2011; Amutio *et al*. 2012).

In this paper, abundant CaO sorbents were added to promptly capture CO_2 by CaO carbonation. Furthermore, Fe-Cr WGS catalyst were used to accelerate the rate of WGS reaction within a temperature range of 350 °C to 550 °C. The experimental temperature in this paper remains below 550 °C because of the catalytic activity of Fe-Cr WGS catalyst.

EXPERIMENTAL

Materials

Discarded pine sawdust in a wood processing plant in Chongqing was selected as the experimental material. The proximate and ultimate analyses of the used pine sawdust are shown in Table 1. After being dried at 110 °C for 2 h, the sawdust was sieved using size 60 mesh. The chemical formula of pine sawdust is identified as $CH_{1.8}O_{0.6}$ according to the ultimate analysis of pine sawdust.

Table 1. Proximate and Ultimate Analyses of Pine Sawdust (wt%)

Proximate analysis				Ultimate analysis				
M_{ad}	V_{ad}	FC_{ad}	A_{ad}	C_{ad}	H_{ad}	O_{ad}	S_{ad}	N_{ad}
6.58	77.85	14.93	0.64	46.67	6.98	38.53	0.36	0.24

Ad: as determined basis; M: Moisture; V: Volatile; FC: Fixed carbon; A: Ash

Pure CaO powder was used as a calcium-based sorbent with a calcination weight loss lower than 2%. Fe-Cr WGS catalyst is mainly composed of Fe_2O_3 (≥74%) and Cr_2O_3 (≥7.0%), and it has shown very good performance at intermediate temperatures of 350 °C to 550 °C. The non-volatile substance content of the catalyst reaches 99%. Pores within the catalyst body exhibit a cylindrical form which has 4 to 6 mm diameter and 3 to 5 mm length.

Methods

As shown in Fig.1, the fixed-bed gasifier was designed and constructed for this experiment.

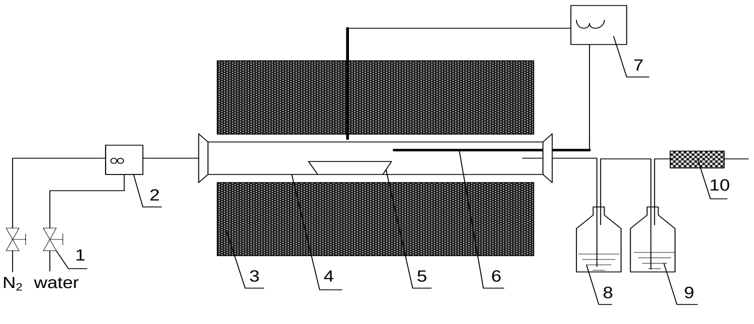

Fig. 1. A system diagram of the fixed-bed gasifier; 1- Control valve; 2-Steam generator; 3- Fixed-bed; 4- Quartz tube; 5-Trough; 6- Thermocouple; 7-Temperature control device; 8- Acetone; 9- Ice salt water; 10- Desiccant

The experimental system mainly includes the gas (steam and N_2) supplying unit, the fixed-bed reactor, and the syngas cleaning and collecting unit. Steam goes through the quartz tube placed in the furnace with nitrogen as a carrier gas and biomass steam gasification occurs in the quartz tube.

The quartz tube was preheated to 120 °C for 5 min, and then the trough with 10 g of biomass was put into the quartz tube. Steam, with nitrogen as a carrier gas, was bubbled into the quartz tube for 5 min to completely exclude the air in the quartz tube. Then the tube was heated in the furnace at a rate of 20 K/min. Product gas went through a tar absorption device, then a condensation and drying device, and into the collection device. The product gas was collected every 50 °C within the temperature range of 250 °C to 550 °C under different experimental conditions to study the change rules of the gas composition. Gasification temperature, steam to biomass mass ratio, CaO to biomass molar ratio, and the addition of catalyst were the main factors influencing the composition of product gas.

The product gas was collected for off-line analysis by means of the GC7900 (Techcomp Bio-Equipment Ltd., Shanghai, China) gas chromatograph, which was equipped with a TCD (thermal conductivity detector). High purity helium was used as a carrier gas.

RESULTS AND DISCUSSION

Influence of Gasification Temperature

The steam addition was 0.08 kg/h. The influence of temperature on product gas composition is shown in Fig. 2. The concentrations of H_2 and CH_4 increased with the rise in temperature. H_2 concentration increased from 1.2% to 17.1%, while CH_4 concentration increased from 1.4% to 21.2%. The concentrations of CO and CO_2 decreased with the rise in temperature. CO concentration decreased from 42.6% to 28.3%, and the CO_2 concentration decreased from 55.8% to 33.1%.

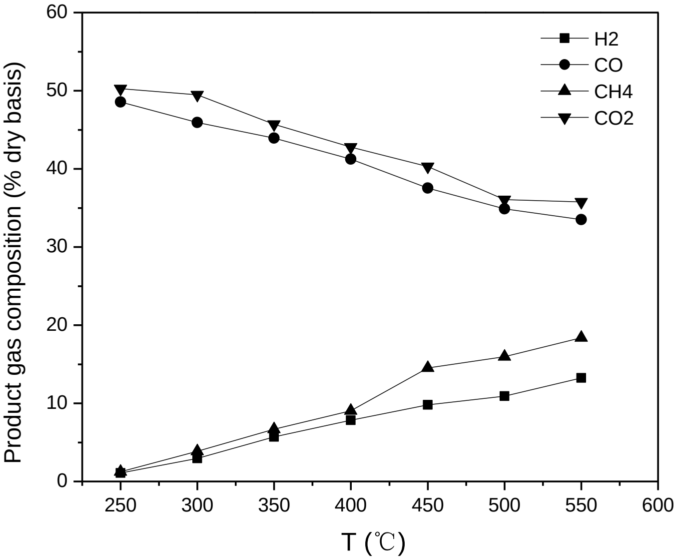

Fig. 2. Effect of temperature on product gas composition

The main reason for the observed decreases in CO and CO_2 concentrations is that the pyrolysis of biomass generated a large amount of volatiles within the temperature range of 250 °C to 550 °C. The reactions (1 through 7) were the major component reactions during the steam gasification process. Large amounts of CO and CO_2 were generated, because of the combination of C and O, which is from oxygen-containing functional groups with the pyrolysis at low temperatures. In addition, reactions (4) and (5), which yielded hydrogen, are endothermic reactions. Thus, the rise in temperature indicates a strong influence on reforming reactions, which contributes to hydrogen generation (Florin and Harris 2008; Efika *et al*. 2013). However, reactions (1), (2), (3), (6), and (7), which are exothermic reactions, were restricted to some extent with the rise of temperature.

$$C + O_2 \rightarrow CO_2 - 408.4\,kJ/mol \tag{1}$$

$$2C + O_2 \rightarrow 2CO - 246.4\,kJ/mol \tag{2}$$

$$2CO + O_2 \rightarrow 2CO_2 - 570.4\,kJ/mol \tag{3}$$

$$C + H_2O \rightarrow CO + H_2 + 131.7\,kJ/mol \tag{4}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 + 206\,kJ/mol \tag{5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 - 43.6\,kJ/mol \tag{6}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 75.24\,kJ/mol \tag{7}$$

Influence of Steam to Biomass Mass Ratio (S/B)

The influence of steam to biomass mass ratio on H_2 concentration is shown in Fig. 3. Both gasification temperature and the addition of steam contributed to the H_2 concentration.

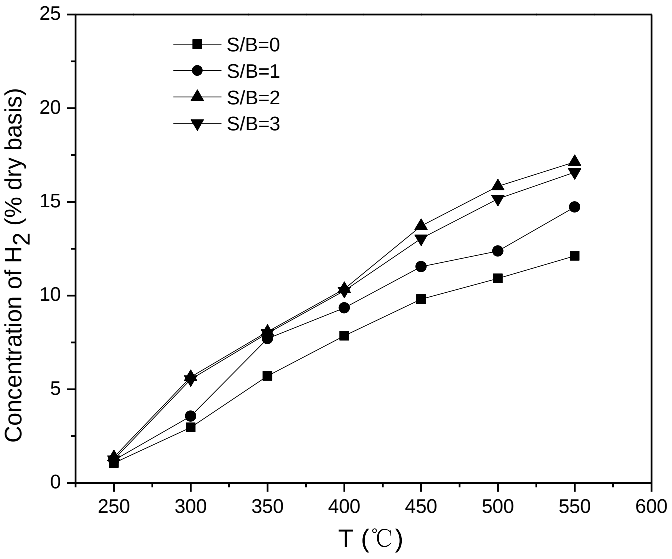

Fig. 3. Effect of S/B on the hydrogen concentration

Hydrogen concentration demonstrated a maximum value at 550 °C. The addition of steam enhanced reactions (4), (5), (6), and (7). Thus, the enhanced rate of these reactions is the major reason for the increase in hydrogen concentration. With the S/B increasing in the range of 0 to 2, the maximum content of H_2 increased from 12.1% to 17.1%. However, a minor decrease in hydrogen concentration was found with an increase with S/B increasing in the range of 2 to 3. A possible reason is excessive amounts of steam leading to a decline in the reacted region's temperature, and this results in reduction of the reaction rate of gasification reactions.

Influence of CaO to Biomass Molar Ratio (CaO/C)

Pure CaO powder and 60-mesh pine sawdust were mixed evenly and divided into 5 groups according to the CaO/C (molar ratio) of 0, 1, 0.5, 1.5, and 2 before the experiment. The steam addition is 0.08 kg/h. The influence of the CaO to biomass molar ratio (CaO/C) of 1.5 is shown in Fig. 4. H_2 concentration increased from 28.1% to 53.1%. CH_4 concentration increased from 3.3% to 30.5%. The concentrations of CO and CO_2 showed significant declines with the rise in temperature of 1.5 for CaO/C. CO concentration decreased from 49.2% to 16.2%. At the same time, CO_2 concentration decreased from 30.3% to 1.3%. The major reason for the changes in CO_2 concentration and H_2 concentration is the addition of abundant sorbent, which enhanced reactions (8) and (9), yielding more H_2 in the product gas.

With CO_2 being absorbed, reduction of its partial pressure promotes a forward WGS reaction (6), which decreases the concentration of CO continuously and in turn yields more hydrogen. This in turn facilitates CO generation reactions, including reactions (4) and (5), which make the concentrations of CO and H_2 increase. At the same time, the WGS reaction increases the concentration of H_2 upon sorbent addition. In addition, the presence of CaO has some catalytic effect on the gasification reactions, but its activity is very complicated and further study is needed.

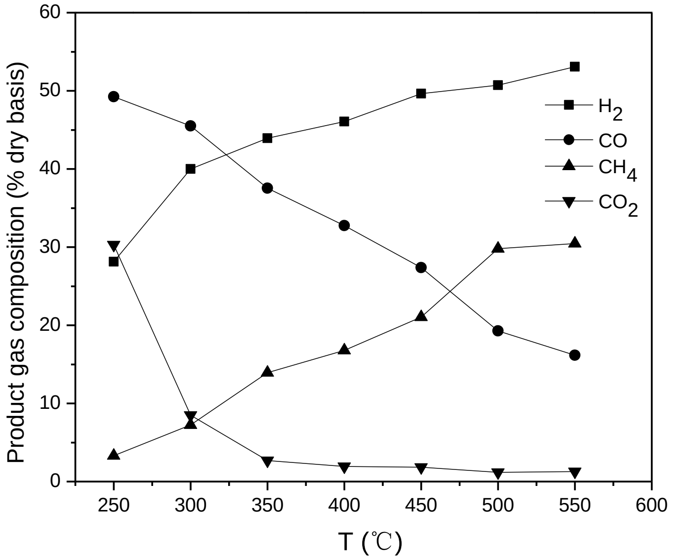

Fig. 4. Effect of CaO/C of 1.5 on the gas composition

$$CaO + CO_2 \rightarrow CaCO_3 - 178.3\ kJ/mol \quad (8)$$

$$C + 2H_2O + CaO \rightarrow CaCO_3 + 2H_2 - 88.2\ kJ/mol \quad (9)$$

The influence of CaO/C on CO_2 concentration is shown in Fig. 5. CO_2 concentration decreased with the rise in temperature. The optimum temperature range for the absorption of CaO to CO_2 was 350 °C to 550 °C. CO_2 concentration exhibited a minimum value of 1.3% at a temperature of 550 °C. CO_2 concentration decreased from 55.7% to 20.1%, with the value of CaO/C increasing from 0 to 2 at a temperature of 250 °C, and the absorption rate of CaO to CO_2 received a value of 64%. CO_2 concentration decreased from 33.1% to 1.3% at a temperature of 550 °C, and the absorption rate of CaO to CO_2 received a value of 96.1%. In fact, the increase of CaO to biomass molar ration greatly enhanced reactions (8) and (9), which substantially contributed to the reduction in CO_2 and enrichment of H_2. However, addition of more CaO (CaO/C>1.5) was proven to have less of an influence on CO_2 reduction, and CO_2 concentration ultimately stayed around 1%.

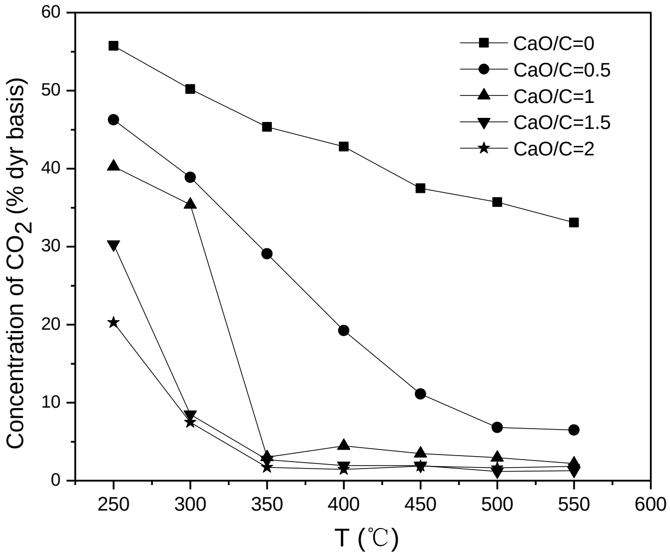

Fig. 5. Effect of CaO/C on carbon dioxide concentration

The influence of CaO/C on H_2 concentration is shown in Fig. 6. H_2 concentration increased with the rise in temperature and exhibited a maximum value at a temperature of 550 °C. H_2 concentration increased from 1.2% to 30.6%, with the value of CaO/C increasing from 0 to 2 at a temperature of 250 °C, and H_2 concentration increased from 17.1% to 53.1%, with the value of CaO/C increasing from 0 to 2 at a temperature of 550 °C. The dotted line in Fig. 6 represents the change of the H_2 concentration by assuming that CO_2 is absorbed completely by CaO without influence on other gasification reactions. Compared with the change in the H_2 concentration in the presence of CaO, Figure 6 shows how the addition of CaO breaks the balance of the reaction system by CO_2 sorption. This dynamic balance, CO_2 consumption by reaction (8), and the corresponding CO_2 generation by reactions (6) and (7) are the probable reasons for the subsided effect of sorbents of higher CaO/C values. However, addition of more CaO

(CaO/C>1.5) was shown to have less of an influence on H_2 enrichment, and H_2 concentration eventually stays around 53%. Thus, it may be concluded that the optimum value of the CaO/C for H_2 production is 1.5.

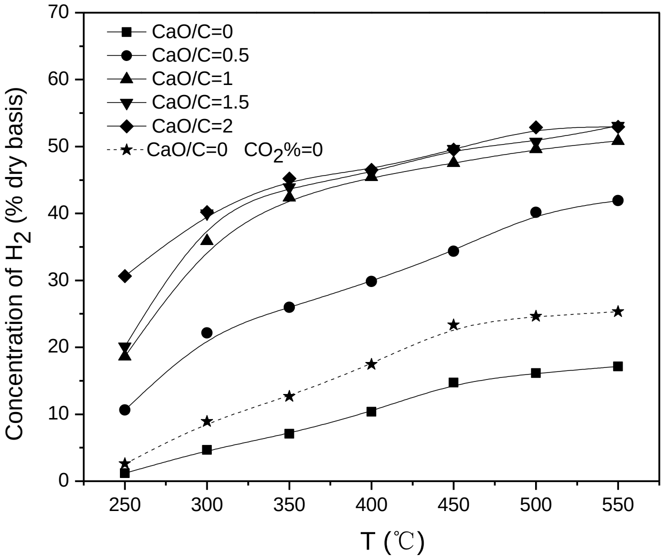

Fig. 6. Effect of CaO/C on hydrogen concentration

Influence of Fe-Cr Water-Gas Shift (WGS) Catalyst

Fe-Cr WGS catalyst was prepared for the experiment according to the catalyst to biomass mass ratio of 1, and placed behind the biomass so that the steam could pass through biomass and catalyst in turn.

The influence of Fe-Cr WGS catalyst in the absence of CaO is shown in Fig. 7a. With the rise in temperature, the H_2 concentration increased from 1.1% to 27.6%; CH_4 concentration increased from 1.4% to 20.6%; CO concentration decreased from 42.6% to 8%; and CO_2 concentration decreased from 55.8% to 41.9%. Compared with Fig. 2, the concentrations of H_2 and CO changed significantly in the presence of the catalyst. The maximum value for H_2 concentration increased from 17.1% to 27.6%, and the minimum value of CO concentration decreased from 27.3% to 8%. The major reason is that the addition of catalyst accelerated the reaction rate of reaction (6), which yields more hydrogen while reducing the CO concentration within the temperature range of 350 °C to 550 °C. The conversion rate of CO gets a value of 71.3%. However, the reaction rate of (6) is restricted greatly because of the high concentration of CO_2. Thus, the reduction of CO_2 concentration should be concerned in the presence of the catalyst, and this problem is discussed in the next section.

The influence of Fe-Cr WGS catalyst in the presence of CaO (Ca/C=1.5) is shown in Fig. 7b. With the rise in temperature, H_2 concentration increased from 20.9% to 63.9%; CH_4 concentration increased from 8% to 29.9%; and CO concentration decreased from 45.9% to 1.7%. The CO_2 concentration had a minimum value of 2.9% at a temperature of 350 °C, and then it gradually increased to 14.1% at a temperature of 400 °C and ultimately remained around 10%. The major reason for this was the addition of CaO enhancing reaction (8), which contributed greatly to the sorption of CO_2. The reduction of its partial pressure promoted forward reactions (6) and (7), which yielded more hydrogen within the temperature of 250 °C to 350 °C. With CO_2 being absorbed, the steam and CO concentrations increased, which led to the increment of the partial pressure of steam and CO, and this strengthened the catalyst to accelerate the reaction rate of reaction (6), while the steam and produced gas pass through the catalyst within the temperature range of 350 °C to 550 °C. Compared to Fig. 6, the conversion rate of CO had a maximum value of 96.4%. One possible reason is that the presence of sorbent contributed to the reduction of CO_2, and the lower concentration of CO_2 in the system had a strong influence on reaction (6) within the temperature range of 350 °C to 550 °C. Thus, it can be seen that partial pressure of all kinds of product gas should be considered as a key point during the steam gasification process.

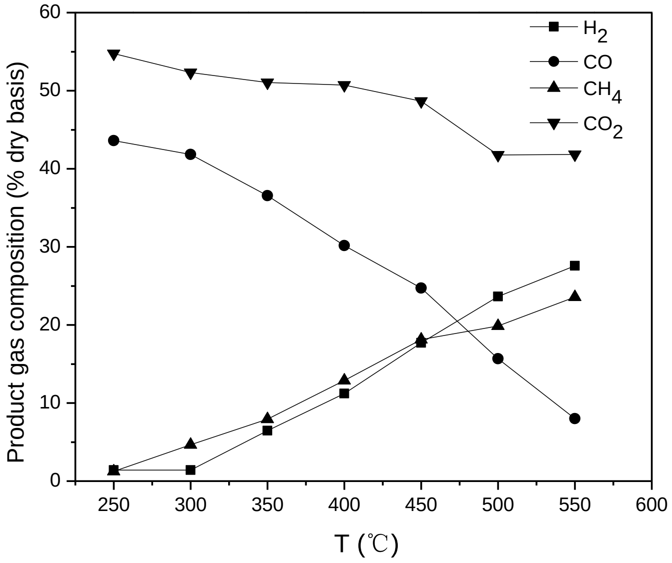

Fig. 7a. Effect of catalyst on gas composition in the absence of CaO

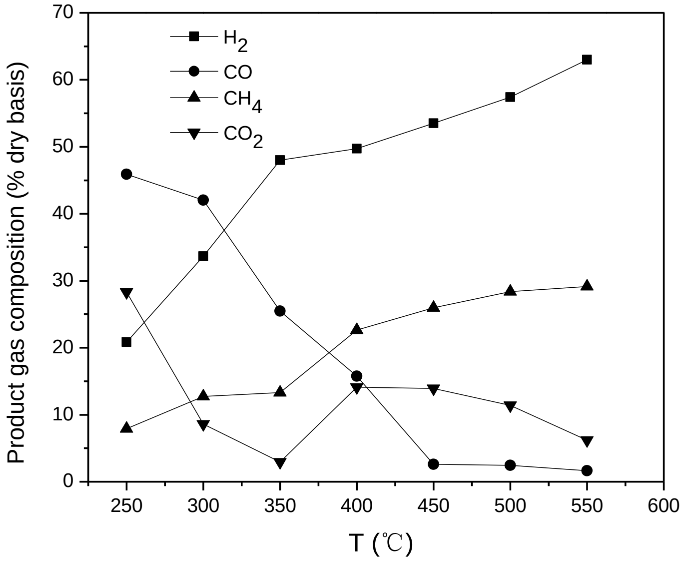

Fig. 7b. Effect of catalyst on gas composition in the presence of CaO

CONCLUSIONS

1. Hydrogen-rich gas production experiments *via* CaO sorption and Fe-Cr water-gas shift catalyst enhanced pine sawdust steam gasification were conducted in a fixed-bed gasifier. The influences of temperature, steam to biomass mass ratio, CaO to biomass molar ratio, and Fe-Cr water-gas shift catalyst on H_2 production were investigated for steam gasification.
2. The addition of steam contributes greatly to the increase of H_2 concentration. When the steam is increased in the range of 0 kg/h to 0.12 kg/h, the maximum value of H_2 concentration increases from 12.1% to 17.1%, with an increase of 5%. However, excessive amounts of steam leads to a decline in the gasification temperature, and this results in the reduction of gasification reaction rates. The optimum value of steam to biomass mass ratio is 2 for hydrogen production.
3. The presence of CaO has a significant influence on H_2 enrichment. The capture of CO_2 is achieved by the addition of CaO, and the presence of CaO has some catalytic effect on the gasification reactions. CO_2 concentration exhibited a minimum value of 1.3%, while H_2 concentration had a maximum value of 53.1%. The optimum value for the CaO to biomass molar ratio was 1.5 for hydrogen production.
4. The presence of a Fe-Cr water-gas shift catalyst accelerates the rate of the WGS reaction, which yields more hydrogen, while reducing the CO concentration within the temperature range of 350 °C to 550 °C. CO concentration decreases from 42.6% to 8%, and H_2 concentration increases from 1.1% to 27.6%. However, the reaction rate of the WGS reaction is restricted greatly by the high concentration of CO_2.
5. The presence of both the CaO and Fe-Cr water-gas shift catalyst has an obvious effect on hydrogen production. Through CO_2 sorption, the steam and CO concentrations increase, which leads to the increase of the partial pressure of steam and CO, in turn strengthening the catalyst to accelerate the reaction rate of the WGS reaction. Thus, the catalytic effect of the catalyst tends to be more obvious within the temperature range of 350 °C to 550 °C. CO concentration exhibited a minimum value of 1.6%, and H_2 concentration had a maximum value of 63%.

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