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Absorption-enhanced steam gasification of biomass for hydrogen production: Effect of calcium oxide addition on steam gasification of pyrolytic volatiles

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ABSTRACT

The effect mechanism of calcium oxide (CaO) addition on gasification of pyrolytic volatiles as a key sub-process in the absorption-enhanced steam gasification of biomass (AESGB) for H_2 production at different conditions was investigated using a two-stage fixed-bed pyrolysis–gasification system. The results indicate that CaO functions as a CO_2 absorbent and a catalyst in the volatiles gasification process. CaO triggers the chemical equilibrium shift to produce more H_2 and accelerates volatile cracking and gasification reactions to obtain high volatile conversion rates. Increasing the gasification temperature could improve the reaction rate of cracking and gasification of volatiles as well as the catalytic effect of CaO, which continuously increase H_2 yield. When the gasification temperature exceeds 700 °C, the sharp decrease in CO_2 absorption capability of CaO drastically increases the CO_2 concentration and yield, which significantly decrease H_2 concentration. The appropriate temperature for the absorption-enhanced gasification process should be selected between 600 °C and 700 °C in atmospheric pressure. Increasing the water injection rate (represented as the mass ratio of steam to biomass) could also improve H_2 yield. The type of biomasses is closely associated with H_2 yield, which is closely related to the volatile content of biomass materials.

Introduction

Hydrogen, as an ideal clean energy carrier, has important functions in future energy structure. Biomass, as the only C-containing renewable resources with CO_2 neutral emission and abundant amount, has been regarded as a promising renewable source for H_2 production [1]. Gasification, with the advantages of high efficiency, high conversion intensity and wide fuel adaptability, is one of the most intensively explored approaches for converting biomass to H_2 [2]. However, biomass, as the only hydrogen (H) source, produces considerably low H_2 yield because of its low content (generally less than 8%) [3–5]. Therefore, steam has been introduced into the

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biomass gasification process to produce extra H_2; a large number of H could be displaced from steam (H_2O) through the water–gas shift (WGS) reaction [6]. However, the H_2 yield from this conventional biomass steam gasification process is still limited by the chemical reaction equilibrium. A considerable amount of carbonaceous gases, e.g., CO, CO_2, and CH_4, and a specific amount of tar still exist in the product gas as the maximum experimental H_2 concentration is generally lower than 55 vol.% [7].

The absorption-enhanced steam gasification of biomass (AESGB) in the presence of calcium oxide (CaO) is a novel one-step technology for H_2 production. This method has recently gained increasing attention [8–16]. CaO, as a CO_2 absorbent, can effectively remove the CO_2 formed in the gasification process in situ. Thus, the limitations of chemical equilibrium of the reaction are altered, which results in the production of more H_2 [8,17]. Currently, several researchers have investigated this enhanced H_2 production process. The effect of various operation conditions, including molar ratio of CaO to C, temperature, mass ratio of steam to biomass, and so on, on the characteristics of H_2 production has been considered in thermodynamic analysis [13,18,19] and experimental studies [10,14,17,20,21]. A large increase in H_2 concentration and yield was obtained, which could be attributed to the reaction equilibrium shifts by the in situ CO_2 absorption of CaO. However, Udomsirichakorn et al. [22] found that CaO also functions as a catalyst during the AESGB process, which causes a higher H_2 production (256.81 mL g^{-1} biomass) and a 67% reduction in tar content within the temperature of 550 °C–700 °C. The actual process of AESGB for H_2 production is a very complex multi-phase reaction process that involves a large number of reactions [2]. The detailed mechanism of this gasification process in the presence of CaO cannot be attributed alone to chemical equilibrium shift stimulated by CO_2 absorption, that is, the catalytic effect of CaO [22,23], which is still rarely studied under this new process condition (600–700 °C, high amount of CaO addition) [24]. The detailed routes of equilibrium shift and catalytic mechanism remain ambiguous because of the complexity of the multi-phase reaction system. Thus, further studies should be performed to determine the mechanism of this gasification process.

Considering that pyrolysis is the first step of gasification, biomass materials that enter into the gasifier are first pyrolyzed into volatiles and solid residues (nascent char). Nascent volatiles and char immediately react with gasification agents (i.e., H_2O) to generate a high-grade product gas [25]. Therefore, the complex process of AESGB can be decoupled to several relatively simple processes in the presence of CaO, which include biomass pyrolysis, volatiles and char gasification, volatile–char interactions, and WGS reaction. The volatile content in biomass is generally higher than 70 wt.%; thus, volatiles gasification has an important function in the H_2 production process [26]. The present study focuses on the enhancing mechanism of CaO addition on the steam gasification of the pyrolytic volatiles of biomass. A two-stage fixed-bed pyrolysis–gasification system was used to generate nascent pyrolytic volatiles, which were subsequently gasified with steam in the presence of CaO. The effect mechanism of CaO addition at different operation conditions, including molar ratio of CaO to C (CaO/C), gasification temperature, water injection rate (representing the mass ratio of steam to biomass), and biomass feedstock, was analyzed.

Experimental

Materials

Five typical Chinese local biomasses, namely, corn stalk, cotton stalk, wheat straw, sawdust, and rice husk, with particle sizes ranging from 124 μm to 250 μm were used. Proximate and ultimate analysis of biomass materials were performed using a TGA2000 (Las Navas, Spanish) and a CHNS analyzer (EL-2, Vario Germany), respectively. The low heating value was analyzed using a bomb calorimeter (Parr 6300, Parr Instrument Company USA). The results are presented in Table 1. The five biomasses with different chemical compositions showed evident differences in volatile contents, which subsequently affect the pyrolytic volatiles gasification. The biomass samples were previously dried for 12 h at 105 °C before use.

CaO was obtained from the calcination of $CaCO_3$ (analytically pure, Sinopharm Chemical Reagent Co., Ltd.) in a muffle furnace at 850 °C in atmospheric pressure for 4 h.

Experimental setup and methods

The experiment was performed in a two-stage fixed-bed pyrolysis–gasification system, as shown in Fig. 1. In the first stage, the reaction tube, with an internal diameter of 45 mm and an effective heating length of 300 mm, and a hanging stainless basket loaded with the biomass materials were used for biomass pyrolysis. In the second stage, the reaction tube

Table 1 – Proximate and ultimate analysis of five biomass samples used in the experiment.

Biomass sample	Proximate analysis (wt.%, ad[c])				Ultimate analysis (wt.%, ad[c])					LHV[b] (MJ/kg)
	M	V	A	FC	C	H	N	S	O[a]	
Corn stalk	3.45	73.62	10.50	12.43	41.43	5.33	1.42	0.11	37.76	14.70
Cotton stalk	8.15	69.00	2.09	20.85	46.08	5.98	0.63	0.10	36.97	15.65
Wheat straw	5.03	67.36	9.50	18.15	39.69	5.49	0.53	0.18	39.58	13.91
Sawdust	4.30	78.48	1.67	15.56	48.25	5.93	0.07	0.18	39.60	16.65
Rice husk	4.29	59.90	16.19	19.62	39.47	5.26	0.34	0.07	34.38	13.70

[a] Calculated by difference.

[b] Low heating value.

[c] Air dry basis.

has an internal diameter of 26 mm and an effective heating length of 200 mm. CaO adsorbents were evenly distributed on a multi-orifice plate, which were used for absorption-enhanced gasification of pyrolytic volatiles. A stainless steel tube (0Cr25Ni20) with high temperature resistance was used for both stages.

During the experiment, the pyrolysis (first stage) temperature was fixed at 650 °C, whereas the gasification (second stage) temperature was varied from 450 °C to 900 °C. The accurately weighed CaO (CaO/C of 0–2) was preloaded onto the multi-orifice plate in the second stage. About 4 g of the dried biomass was placed in the hanging basket and kept away from the heating area. The two furnaces were heated to the set temperature with an N_2 flow rate of 200 mL min^{-1}. After the temperature in each reaction area (pyrolysis area in the first stage and CaO bed in the second stage) became stable, the injection pump was opened and water steam was introduced (accurately calibrated previously, varies from 0 g min^{-1} to 0.3 g min^{-1}) into the gasification area. After 10 min, as the steam fully filled the gasification area, the biomass basket was immediately placed in the pyrolysis area, and the absorption-enhanced biomass fast pyrolysis–gasification reaction started. The biomass samples were rapidly heated with pyrolytic volatiles evolving out instantly. The volatiles passed through the CaO bed and reacted with H_2O and CaO via volatiles gasification, WGS reaction, CaO carbonation, and so on to generate an H_2-rich product gas. The product gas was condensed, cleaned, dried, collected with a gas bag, and analyzed using a Micro-GC (Agilent 3000A) to determine the gas composition. Each pyrolysis–gasification process was conducted for 40 min to ensure the completion of the reaction. All experiments were performed in triplicate to confirm the reproducibility of the results.

After each experiment, the two-stage reaction tube was directly removed from the furnace for air quenching with continuous swiping of N_2 to ensure the cooling of solid sample in an inert atmosphere. The pyrolytic char and the used absorbent (CaO) were collected at room temperature. The solid residue (char) in the sample basket was weighed to determine the char yield. Gas yield was calculated using the N_2 balance because the gas volume of N_2 (carrier gas) is known (150 mL min g^{-1} × 40 min), and the N_2 concentration in the product gas was tested via GC.

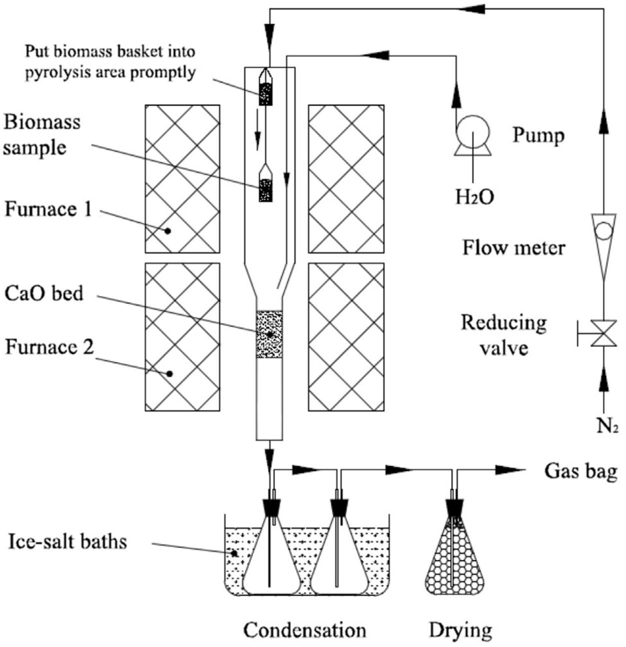


Fig. 1 – Schematic diagram of a two-stage fixed-bed pyrolysis–gasification system.

Table 2 – Experimental results of the corn stalk with different amounts of CaO addition.[a]

CaO/C	0	0.5	1	1.5	2
Char yield (wt.% dry biomass)	31.00	30.50	30.50	30.75	30.50
H_2 yield (mL g^{-1} dry biomass)	64.29	123.32	195.80	199.66	210.97
Composition of the gas product (vol.%)					
H_2	28.70	48.26	55.26	60.77	61.83
CO	31.96	24.01	20.44	14.36	12.08
CO_2	21.54	8.69	6.15	6.91	8.54
CH_4	15.09	15.16	14.80	14.33	13.93
C_{2+}	2.71	3.88	3.35	3.63	3.62

[a] The temperature of pyrolysis and gasification was 650 °C. The biomass weight in each experiment was 4 g, and water injection rate was 0.1 g min^{-1}.

The fresh and used CaO were characterized via X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V.) and scanning electron microscopy (SEM, Quanta 200, FEI) to confirm the possible reaction that occurred with CaO.

Results and discussion

Effect of CaO/C on H_2 production

Table 2 shows the experimental results of corn stalk pyrolysis–gasification added with different amounts of CaO. The amount of CaO addition was determined and represented as the molar ratio of CaO to C, where C was determined via the ultimate analysis of the biomass samples, that is, the C

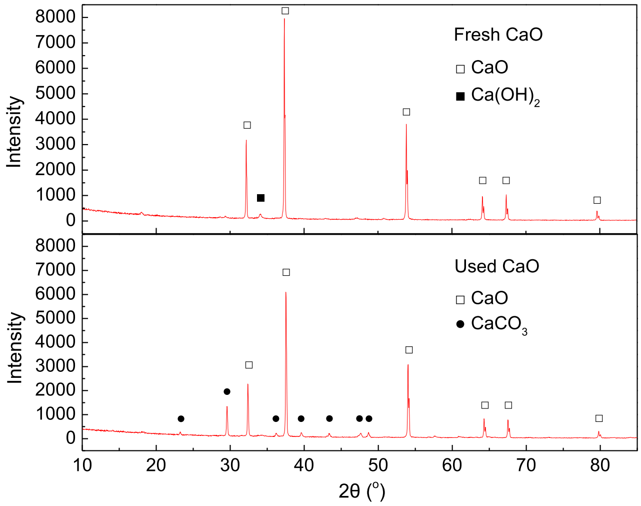


Fig. 2 – XRD patterns of fresh and used CaO during the absorption-enhanced pyrolysis–gasification of corn stalk.

contained in the biomass. As shown in Table 2, the char yield of corn stalk remained constant at the same pyrolysis temperature. This finding further confirmed the accuracy and reproducibility of the experimental results. The corn stalk pyrolysis–gasification without CaO addition produced a gas with low H_2 content of only 28.7 vol.%, whereas the total amounts of CO and CO_2 were greater than 53 vol.% and those of CH_4 and C_{2+} were 18 vol.%. Furthermore, the H_2 yield was only 64.29 mL g^{-1} dry biomass. This result could be attributed to the extremely low gasification temperature (650 °C) and the resulting limited steam gasification of pyrolytic volatiles [27].

When CaO was added, H_2 concentration and yield increased drastically with decreasing concentration of CO and CO_2. H_2 concentration and yield increased continuously with increasing CaO/C and the maximum values were 61.83 vol.% and 210.97 mL g^{-1} dry biomass at a CaO/C molar ratio of 2, respectively. However, CO_2 concentration decreased significantly, and the minimum concentration was 6.15 vol.% at a CaO/C molar ratio of 1. The detailed reactions in the absorption-enhanced pyrolysis–gasification process could be summarized as follows:

Biomass pyrolysis:

$$\text{Biomass} \xrightarrow{\text{Pyrolysis}} \overbrace{\underbrace{C_xH_yO_z}_{\text{Condensable volatiles}} + \underbrace{(H_2 + CO + CO_2 + CH_4 + \ldots)}_{\text{Noncondensable gas}}}^{\text{Pyrolytic volatiles}} + \underbrace{(C + \text{Ash})}_{\text{Char}} \tag{1}$$

Pyrolytic volatiles cracking:

$$C_xH_yO_z \rightarrow H_2 + CO + CO_2 + CH_4 + C_{2+}\ldots \tag{2}$$

Steam gasification of condensable volatiles:

$$C_xH_yO_z + H_2O \rightarrow CO + H_2 \tag{3}$$

Steam gasification of small molecular hydrocarbons:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4}$$

$$C_{2+} + H_2O \rightarrow CO + H_2 \tag{5}$$

WGS reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

CaO carbonation (CO_2 absorption):

$$CaO + CO_2 \rightarrow CaCO_3 \tag{7}$$

Hence, the increase in H_2 and decrease in CO and CO_2 could be attributed to the added CaO that reacted in situ with the produced CO_2 from the pyrolysis–gasification (reaction (7)); the chemical reaction equilibrium of WGS reaction (6) could then be shifted, which produced more H_2 [28]. Furthermore, the enhancing effect was strengthened with increasing amount of CaO (shown in Table 2).

The concentrations of CH_4 and C_{2+} remained constant with different amounts of CaO added. This finding implied that the increase in H_2 concentration might be mainly due to the decreasing concentration of CO and CO_2 via WGS reaction. Adding CaO had no apparent enhancing effect on the steam gasification of small molecular hydrocarbons (CH_4 and C_{2+}, reactions (4) and (5), respectively). Hence, a high H_2 concentration and yield could be obtained by the addition of a catalyst, e.g., Ni-based [2,29] and Fe-based [30], to enhance the gasification of small hydrocarbons and H_2 formation.

The yields of CO were 71.59 and 61.35 mL g^{-1} dry biomass with CaO/C molar ratios of 0 and 1, respectively. The decrease in the yield of CO was much lower than the increase in H_2 yield (from 64.29 to 195.80 mL g^{-1} dry biomass), while the calculated yield of small molecular hydrocarbons still slightly increased. This finding indicated that the enhanced steam gasification of condensable volatiles (reaction (3)) had an important function in increasing the H_2 production with CaO addition. CaO functioned not only as catalyst but also as a CO_2 absorbent for the gasification process, even at a relatively low temperature (650 °C).

When the CaO/C molar ratio was greater than or equal to 1, H_2 concentration increased slightly but H_2 yield remained

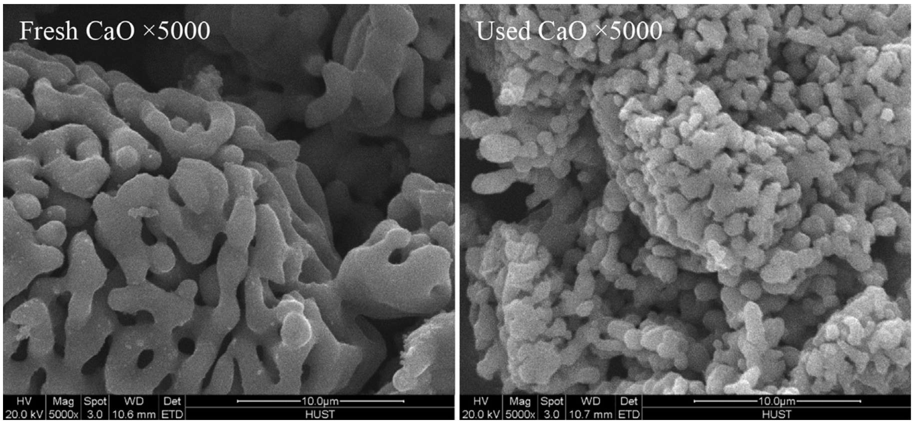
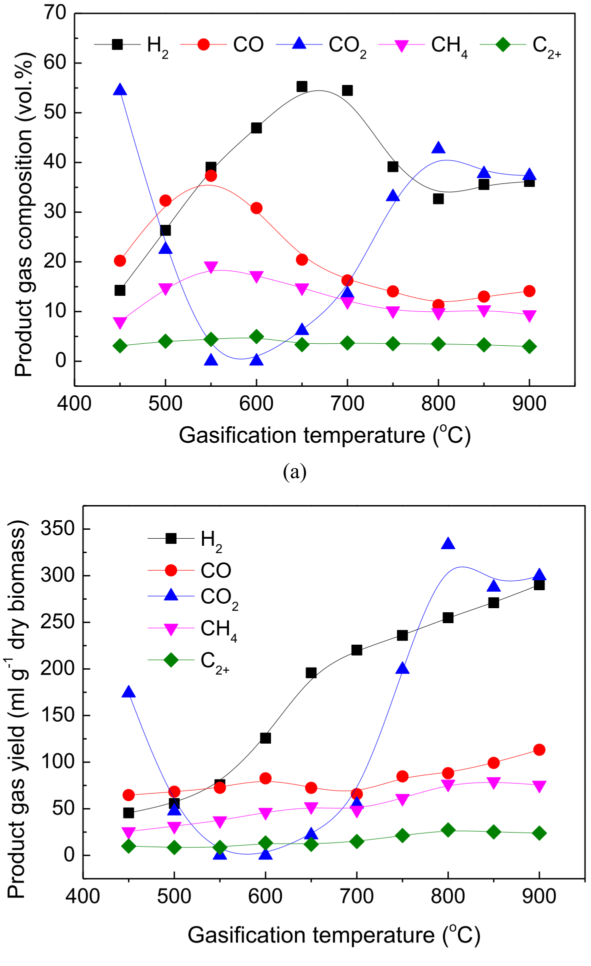


Fig. 3 – SEM images of fresh and used CaO during the absorption-enhanced pyrolysis–gasification of corn stalk.

constant, which indicated that the amount of CaO added might be sufficient. Thus, a CaO/C molar ratio of 1 was used in the subsequent work.

The crystal structure and microscopic morphology of the fresh and used CaO are shown in Figs. 2 and 3. As shown in Fig. 2, $CaCO_3$ crystals were found in the used CaO samples, which illustrated that the CaO carbonation reaction (in situ CO_2 removal, reaction (7)) did happen in the gasification process, which caused the absorption-enhancing effect on the gasification process via chemical equilibrium shift. A weak peak corresponding to $Ca(OH)_2$ was found in the spectrum of fresh CaO. This peak was possibly formed because of the absorbed moisture from the atmosphere during the sampling process.

Furthermore, from Fig. 3, it was observed that compared with the fresh CaO, the microscopic morphology of the used CaO changed with the generation of small particles and the blockage of pores or the reduction of their sizes, which could provide further evidence for this type of enhancing mechanism.



(a)

(b)

Fig. 4 – Effect of gasification temperature on the composition and yield of the gas product from the absorption-enhanced pyrolysis–gasification of corn stalk: (a) composition of the gas product; (b) yield of the gas product. Pyrolysis temperature was 650 °C, CaO/C was 1, and water injection rate was 0.1 g min^{-1}.

Effect of gasification temperature on H_2 production with CaO addition

Fig. 4(a) and (b) show the composition and yield of the product gas from the absorption-enhanced pyrolysis–gasification of corn stalk at different gasification temperatures. As shown in Fig. 4, the gasification temperature had a significant effect on the absorption-enhanced pyrolysis–gasification of corn stalk with CaO addition. When the gasification temperature was varied, the product gas composition and yield significantly changed. The reaction characteristics of the gasification process could be divided based on the changing trend of the composition and yield of the gas product into three temperature ranges, namely, 450 °C–600 °C, 600 °C–700 °C, and 700 °C–900 °C.

When the gasification temperature was from 450 °C to 600 °C, the concentration and yield of H_2 increased evidently, whereas the concentration and yield of CO_2 decreased drastically to 0 at 550 and 600 °C, which was similar to the result of Acharya et al. [31]. Increasing the temperature is unfavorable in terms of thermodynamic equilibrium because of the exothermic nature of CaO carbonation (CO_2 absorption) reaction (7) [6]. This result might indicate that CaO carbonation is controlled by the reaction kinetics in a low temperature range (450 °C–600 °C). The reaction rate of CaO carbonation increased with increasing gasification temperature, which resulted in a sharp decrease in CO_2 concentration and yield. This condition further enhanced the WGS reaction (6) to achieve a higher H_2 concentration and yield [6,32]. Furthermore, the cracking and steam gasification of pyrolytic volatiles (reactions (2) and (3)) were also intensified with increasing gasification temperature [33]. The yields of CO and small molecular hydrocarbons also increased, which was another reason for the changes in H_2 and CO_2, as well as in CO and CH_4.

When the gasification temperature was increased to 700 °C, the H_2 concentration first increased and then slightly decreased at 700 °C, whereas the H_2 yield continued to increase significantly. Moreover, the concentration and yield of CO_2 increased evidently. These findings implied that increasing the temperature significantly affected the chemical equilibrium of CaO carbonation reaction within the temperature range of 600 °C–700 °C. The equilibrium partial pressure of CO_2 also gradually increased with increasing temperature [18,20]. The increased reaction rate of CaO carbonation caused by the increased temperature was lower than that of $CaCO_3$ calcination, which caused more CO_2 in the product gas. However, H_2 concentration and yield increased significantly (particularly between 600 °C and 650 °C). This increase might be due to the enhanced thermal cracking and steam gasification of the volatiles (reactions (2) and (3)) with increasing temperature. Thus, more permanent gaseous products, including generated H_2, and the increase in the yield of CO, CH_4, and C_{2+} could directly confirm this finding. Furthermore, increasing the temperature improved the catalytic effect of CaO on volatiles cracking and gasification (reactions (2) and (3), respectively), as well as WGS reaction (6). Moreover, although the absorption-enhancing extent of CaO addition on volatile gasification (reaction (3)) and/or WGS reaction (6) intensified with increasing temperature (600 °C–700 °C), the CO_2 concentration and yield in the product gas still increased. The enhanced reaction rate of CO_2 absorption (CaO carbonation) caused by the increase in temperature resulted in more captured CO_2 and a subsequent equilibrium shift of WGS reaction (6) and volatile gasification (reaction (3)). Thus, the original increase in the concentration and yield of CO through enhanced volatile cracking (reaction (2)) and gasification (reaction (3)) was compensated, as shown in Fig. 4.

When the gasification temperature was increased further to 900 °C, H_2 concentration decreased sharply and then slightly increased, whereas H_2 yield gradually increased. The concentration and yield of CO_2 showed a similar trend, which first drastically increased (700 °C–800 °C) and then gradually decreased (>800 °C). This finding was mainly due to the enhanced calcinations of $CaCO_3$, which was faster than the rate of CO_2 absorption on CaO [18]. Moreover, high temperature intensified the thermal cracking and gasification of volatiles (reactions (2) and (3)) as well as the catalytic effect of CaO, thus the H_2 yield increased.

The yield of CH_4 and C_{2+} continuously increased gradually in the whole temperature range (450 °C–900 °C). Although the thermal cracking of volatiles (reaction (2)) was the primary factor, this finding also implied that novel and more highly efficient catalysts should be involved to obtain higher H_2 yields.

Effect of water injection rate on H_2 production with CaO addition

Fig. 5 shows the composition and yield of the gas product from the absorption-enhanced pyrolysis–gasification of corn stalk at different water injection rates (0 g min^{-1} to 0.3 g min^{-1}, the total mass ratio of water (steam) to biomass could be calculated as 0–3 within the 40 min reaction time).

As shown in Fig. 5, H_2 had a minimum concentration of 47.45 vol.% and a minimum yield of 122.06 mL g^{-1} dry biomass without water injection. This finding suggested that external water injection should be introduced to increase H_2 production because pyrolytic water was apparently insufficient. When the water injection rate increased from 0 g min^{-1} to 0.1 g min^{-1}, the increase in H_2 concentration was relatively small but that of the H_2 yield was significant, that is, from 122.06 mL g^{-1} to 195.80 mL g^{-1} dry biomass. The increasing water injection rate led to the increase in the partial pressure of steam in the reaction system. This increase enhanced the gasification of volatiles (reaction (3)) and WGS reaction (6) and resulted in diminishing CO. When the water injection rate was greater than 0.1 g min^{-1}, the enhancing effect of the increased partial pressure of steam on volatile gasification and WGS decreased, but the concentration and yield of H_2 slightly increased. When the water injection rate was from 0.15 g min^{-1} to 0.2 g min^{-1}, H_2 concentration started to decrease, whereas CO_2 concentration increased evidently. This finding indicated that the adsorption of CO_2 on CaO (reaction (7)) was constrained in a high H_2O atmosphere. Hence, the selected water injection rate was 0.1 g min^{-1}, which was more suitable for this H_2 production process.

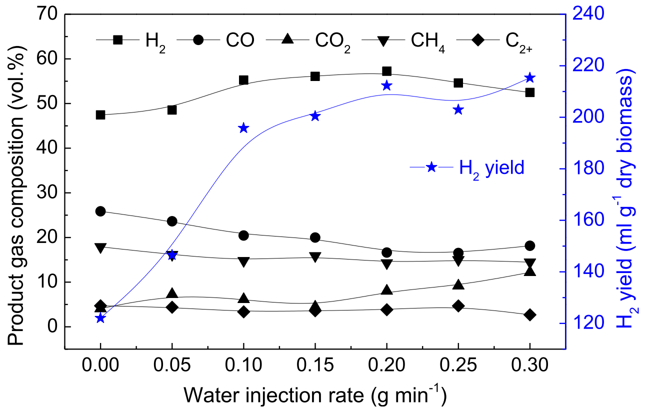


Fig. 5 – Effect of water injection rate on the composition and yield of the gas product from the absorption-enhanced pyrolysis–gasification of corn stalk. The temperature of pyrolysis and gasification was 650 °C, and CaO/C was 1.

Effect of biomass types on H_2 production with CaO addition

Fig. 6 shows the composition and yield of the gas product from the absorption-enhanced pyrolysis–gasification of the five typical Chinese biomasses, namely, corn stalk, cotton stalk, wheat straw, sawdust, and rice husk. As shown in Fig. 6, high H_2 concentration and yield with relatively lower CO and CO_2 in the product gas were obtained for the five biomass samples. CO_2 concentration was lower than 10 vol.% in all samples, which indicated that CaO addition showed significant CO_2 absorption capability among different biomasses. The maximum H_2 concentration was obtained from corn stalk (55.26 vol.%), whereas the minimum was from sawdust (47.59 vol.%). Moreover, CO and CH_4 yields also differed among the five experimental biomasses. This difference is mainly caused by the different chemical compositions of the biomass materials, which are shown in Table 1. Furthermore, the ash content or alkali and alkaline earth metallic (AAEM) species in each biomass, as shown previously [14], might also

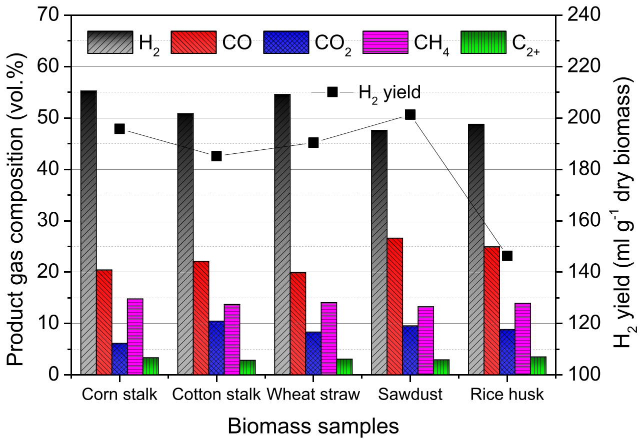


Fig. 6 – Effect of CaO addition on the composition and yield of the gas product from the absorption-enhanced pyrolysis–gasification of different types of biomass. The temperature of pyrolysis and gasification was 650 °C, CaO/C was 1, and water injection rate was 0.1 g min^{-1}.

significantly affected the H_2 production process. However, CaO addition still resulted in relatively uniform H_2 production properties and similar H_2 concentration among the different biomasses. The differences in the yields of H_2 might be attributed to the different biomass volatiles, as shown in Table 1. The trend in H_2 yield was as follows: sawdust (201.30 mL g^{-1} dry biomass) > corn stalk (195.80 mL g^{-1} dry biomass) > wheat straw (190.38 mL g^{-1} dry biomass) > cotton stalk (185.17 mL g^{-1} dry biomass) > rice husk (146.34 mL g^{-1} dry biomass).

Conclusions

The enhancing effect of CaO addition on biomass pyrolytic volatiles gasification for H_2 production was investigated in a two-stage pyrolysis–gasification system at different conditions. The addition of CaO evidently enhanced the volatiles gasification. CaO, as a CO_2 absorbent and a catalyst, stimulated the chemical equilibrium shift to produce more H_2 and accelerated the volatiles cracking and gasification reactions. Gasification temperature directly affected the CO_2 absorption capability, catalytic effect of CaO, and reactivity of volatiles cracking and gasification. The optimum gasification temperature for the absorption-enhanced gasification process was between 600 °C and 700 °C in atmospheric pressure. Increasing the water injection rate (S/B) to a suitable value was beneficial to improve H_2 yield. Biomass type shows a close relationship with H_2 yield, which was also closely related to the volatile content of biomass materials.

Acknowledgments

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