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1 **Autothermal CaO looping biomass gasification to increase process energy**
2 **efficiency and reduce ash sintering**

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8 **Abstract**

9 Biomass gasification is considered as a promising renewable energy technology
10 to address climate change caused by greenhouse gas emissions and produce portable
11 and clean energy products. However, biomass must be combusted in the traditional
12 gasification to maintain the process, while excessive gasification temperature will lead
13 to ash sintering, resulting in the shutdown of the equipment. Autothermal biomass
14 gasification is directly maintained by carbonation reaction, which can maximize the
15 production of combustible gas and reuse carbon dioxide in the flue gas. Lab-scale
16 results indicated that similar H₂ yield can be obtained via Auto-CaL-Gas technology at
17 lower operating temperatures. Moreover, H₂ concentration increased by 23.29% at 650°C
18 with CaO than at 750°C without CaO, and 14.11% at 550°C with CaO than at 650°C
19 without CaO, respectively, thus saving energy consumption and improving total energy
20 efficiency in the biomass gasification process.

21 Keywords: Biomass gasification; CaO; Auto-CaL-Gas; Biomass

1. Introduction

Climate change has caused many environmental problems ascribed to greenhouse gas emissions generated by human activities and energy consumption to meet the needs of daily life. Biomass energy, a renewable energy source, has attracted much attention in recent years because it is easy to store and transport and has a wide range of sources. Over the last two decades, biomass gasification has extensively studied for renewable energy production and contribute to solve climate change related problems[1-6].

However, biomass gasification still has several challenges to be solved. Firstly, the overall energy efficiency in biomass gasification needs to be improved[7]. Biomass gasification is divided into four stages: drying, pyrolysis, reduction and oxidation. Since the reaction in the gasification stage is mainly endothermic, conventional biomass gasification combusts part of the biomass by adding air to provide heat for gasification, resulting in reduced energy efficiency and poor syngas quality[8-13]. E. Shayan et al.[14] investigated and compared the performance of wood biomass and paper biomass in four gasification media (steam, oxygen, oxygen-enriched air and air) based on existing theoretical and experimental data in the literature. The results showed that conventional air gasification of wood biomass and paper biomass can get the syngas with the lowest cold gas efficiency and calorific value with the change of gasification temperature and moisture content , while steam gasification has the highest exergy efficiency, with a calorific value of gas production up to 11 MJ/Nm³.

Secondly, ash sintering is one of the main limitations of biomass gasification[15-18]. This is because the ash composition is complex and often deposited on the heat

transfer surface of various equipment, which not only increases the heat transfer resistance, but also reduces the stability of the system[17]. The deposition of derived from ash sintering is difficult to recover, causing a great negative effect on the thermochemical transformation of biomass. This effect not only reduces energy efficiency, but also shortens the life of the equipment[19]. Since the degree of ash sintering is directly affected by the operating temperature[20]. Gasification can be operated at lower temperatures to mitigate ash sintering. For instance, Li et al.[21] investigated ash fusion temperature using original and simulated biomass ashes and found that reactor operation at low furnace temperature can reduce the deterioration of ash sintering. The concept of adding simulated ash can be used to explore ash sintering. Simulated ash would not participate in the gasification reaction and can be used to study ash sintering during biomass gasification.

In order to improve energy efficiency and reduce ash sintering, CaO sorption enhanced biomass gasification was proposed by Curran et al[22]. Through the capture of CO₂, the equilibrium of gasification was proceeded to positive side, thus enhancing the gasification efficiency and the quality of syngas[23]. In a report from Acharya et al.[24], the concentration of hydrogen in the gas production approximately doubled to 54.43%, while the concentration of CO₂ decreased by 93.33% when CaO/ biomass =2 was applied compared to gasification without CaO. Han et al.[25] confirmed that the increase of CaO/C, H₂O/C and T is conducive to the generation of syngas composed of high concentration of H₂ and low concentration of CO₂ in a fluidized bed. Sun et al.[26] proposed a novel concept that utilizing exothermic carbonation reaction heat between

CaO-based materials and gas medium containing a high concentration of CO₂ to provide energy for biomass gasification, called auto-thermal CaO looping biomass gasification (Auto-CaL-Gas) technology. Meanwhile, flue gas could be introduced in this process to promote CO production. However, the significant increase in CO production may be related to the reactions between CO₂ and char, so whether this technology can promote syngas production remains to be further demonstrated. For this novel concept of autothermal biomass gasification, ash sintering which is one of the major limitations of biomass gasification needs to be researched.

Therefore, the purpose of this paper is to illustrate that Auto-CaL-Gas technology is more energy efficient and can reduce ash sintering by comparing syngas production and observing the morphology changes of simulated silica ash obtained by autothermal biomass gasification and traditional biomass gasification.

2. Experimental

2.1 Materials

Lignin, a main component of the biomass, was purchased from Sigma-Aldrich Co., Ltd, (CAS number: 8086-05-1). Lignin used in this work is alkali lignin in brown powders. Calcium oxide and silica were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd without any further purification. 0.2g lignin and 0.05g silica were mixed with different proportions of calcium oxide and the samples were stirred to achieve good uniformity. The result of ultimate analysis of lignin is presented in Table 1.

Table 1 Ultimate analysis of lignin sample

Raw material	lignin
Unit	wt%, d
C	51
H	5
N	0.12
S	3.6
Others	40.28

2.2 Experimental Apparatus and Procedure

The experiment was conducted in a lab-scale fixed bed reaction system, as shown in Fig 1. The vertical fixed-bed reactor is a quartz tube with an inner diameter of 24 mm and a height of 520 mm. The quartz tube acts as a reactor externally heated by two adjacent mid-open electric heaters (each 200 mm high) using temperature controllers. The mixture of pre-mixed lignin, different proportions of calcium oxide and silicon oxide were evenly placed into the quartz tube and sandwiched by quartz wool (about 0.1g). The mixture of carbon dioxide and nitrogen passes through the reaction system from the upper end of the quartz tube. The total gas flow rate was 100ml/min, and the ratio of the inlet gas is controlled by changing each inlet gas flow rate. For each experiment, the reactor was heated at a rate of 30°C /min to the set temperature and held for 0.5h. The product gas was collected in a gas bag after passing through a condensation system containing an ice bath and a drying tube.

Different experimental conditions were obtained by changing gasification temperature, inlet gas ratio of CO₂, and mass ratio of calcium oxide to lignin. The experimental conditions are summarised in Table 2.

Figure 1. Schematic diagram of Auto-CaL-Gas technology reactor system. (1)Nitrogen cylinder
(2)CO₂ cylinder (3)Mass flowmeters (4) Quartz reaction tube (5)Heating furnace (6)Temperature
control (7)Reaction layer :Quartz wool+ sample+ quartz wool (8)Boiling flask-2-neck (9)Ice bath
(10)Drying tube (11)Off-line Gas chromatograph

Table 2 Experimental conditions of Auto-CaL-Gas technology

Case no.	lignin(g)	CaO(g)	Temp(°C)	Gas atmosphere
#1	0.2	0	550	15%CO ₂ +85%N ₂
#2	0.2	0.2	550	15%CO ₂ +85%N ₂
#3	0.2	0.6	550	15%CO ₂ +85%N ₂
#4	0.2	1	550	15%CO ₂ +85%N ₂
#5	0.2	0	650	15%CO ₂ +85%N ₂
#6	0.2	0.2	650	15%CO ₂ +85%N ₂
#7	0.2	0.6	650	15%CO ₂ +85%N ₂
#8	0.2	1	650	15%CO ₂ +85%N ₂
#9	0.2	0	750	15%CO ₂ +85%N ₂
#10	0.2	0.2	750	15%CO ₂ +85%N ₂
#11	0.2	0.6	750	15%CO ₂ +85%N ₂
#12	0.2	1	750	15%CO ₂ +85%N ₂
#13	0.2	1	650	30%CO ₂ +70%N ₂
#14	0.2	1	650	45%CO ₂ +55%N ₂

2.3 Product Characterization

Off-line analysis of gaseous products was performed by gas chromatography (Techcomp GC-7900) to quantify concentrations of the collected gas from gas bags, such as CO, CO₂, CH₄ and H₂. Syngas yield was obtained by external standard method [27].

SEM-EDX analysis was carried out by GeminiSEM 500 (Carl Zeiss Ltd., Shanghai, China). After the experiment, the residual solid particles were photographed by scanning electron microscope to observe the change of ash morphology and particle size distribution. The distribution of elements on the particle surface was detected by Energy dispersive x-ray spectrometry (EDX). The EDX spectrum recorded from a point on the sample surface only detected the concentration of each element at the selected point under the probe to ensure that the selected particle was the object of comparison [28].

3. Results

3.1 Influence of Temperature and CaO/Lignin Ratio on Syngas Production

Fig.2 shows CO and H₂ yield at different temperatures (550,650,750°C) and CaO/lignin ratios (0,1,3,5) using 15%CO₂ and 75%nitrogen. From the perspective of the overall trend, the yield of CO and H₂ significantly increases with the increase of CaO/lignin ratio and gasification temperature.

As can be seen in Fig. 2(a), the yield of CO does not increase significantly at lower temperature (550°C) when the ratio of CaO/lignin increases. However, the yield of CO at 650°C firstly enhances slightly from 1.12 mmol/glignin without CaO to 1.79

mmol/g lignin when CaO/lignin ratio is 3 and then sharply reaches 4.48 mmol/g lignin at CaO/lignin=5, which exhibited a 4-fold increment. This interesting result is consistent with the more than 3-fold CO production improvement obtained by Sun et al [26]. By increasing CaO/lignin ratio from 0 to 5, the yield of CO at 750°C enhanced approximately 3-fold. It is worth mentioning that the yield of CO as the temperature increases to 750 °C is much higher than that obtained at the other two temperatures. This is because the Boudouard reaction (Eq 2) is an endothermic reaction. The reaction equilibrium moves positively when the temperature exceeds 700°C, promoting the formation of CO. The relationship between CO yield and CaO/lignin ratio is well consistent with the results reported from Ahsanullah et al. [29], where CO production was improved with the enhancement of CaO/biomass ratio. Moreover, cellulose showed a better performance than lignin for CO production. The generation of CO is mainly from the cracking of carbonyl (C=O) and carboxyl (C=O) groups in biomass. Therefore, CaO carbonation heat provides energy for the cleavage of functional groups during autothermal CaO looping biomass gasification and thus promotes the production of CO.

Fig.2(b) indicates that the yield of H₂ enhances effectively with the increase of CaO/lignin ratio and gasification temperature. As the CaO/ lignin ratio increases from 0 to 5, the yield of H₂ increases the most at 650°C, indicating the activity of CaO is more effective at this temperature. The positive effects of temperature and CaO/biomass ratio on hydrogen generation have been well studied in previous studies [24, 25, 29-32]. The reasons could be interpreted as follows: 1) Char and tar are more readily

converted to gas at higher temperatures[31] , so hydrogen production increases with the increment of temperature.2)Removing CO₂ by CaO can promote water gas shift reaction(Eq 3) due to the decline of partial pressure into forward direction resulting in a higher yield of hydrogen.3)CaO carbonation reaction(Eq1) releases heat when capturing carbon dioxide, raising the ambient temperature, leading to increased tar cracking and char conversion.4)CaO could play a catalyst role in tar decomposition[33]. It is worth mentioning that, H₂ yields obtained at case #3 and case #5 were 1.91 (mmol/g lignin) and 1.70 (mmol/g lignin), respectively, and H₂ yields obtained at case #7 and #9 were 4.64 (mmol/g lignin) and 4.39 (mmol/g lignin), respectively. This indicates that similar H₂ yield can be obtained via Auto-CaL-Gas technology at relative lower operating temperatures, thus saving energy consumption and improving total energy efficiency in the biomass gasification process. The results show that autothermal CaO looping biomass gasification is a promising technology.

Fig.3 demonstrates the composition of syngas with different temperatures and CaO/lignin ratios. In general, as the amount of CaO added increases, the gas composition of CO₂ decreases accordingly. In particularly, CO₂ composition declines significantly from 87.6% to 48.8% at 650°C when CaO/lignin ratio is up to 5 (Fig.2(b)). Zhou et al.[11] also found the reduction of CO₂ composition which was due to CaO sorption slowed down with the increase of temperature up to 700°C, indicating that the activity of CaO is more efficient for CO₂ sorption at 650°C.

As can be seen from Fig.3(a), the composition of H₂ in syngas increases from 2.2% (without CaO) to 29.6% (CaO/lignin =5) at 550 °C, while the content of CO and CH₄

only changes slightly. It is indicated that with the addition of CaO, lignin tends to produce H₂ more than CO which is consistent with previous studies from Ahsanullah et al[29]. In Fig.2(b), the composition of H₂ and CO both increases gradually with the increase of CaO/lignin ratio. In the trend of CO composition changes is different from that in previous literatures[25, 30]. Therefore, it is suggested that the lack of steam prohibited water gas shift reaction converting CO into H₂ in the gasification process. Meanwhile, CO₂ is continuously fed into the reaction system to react with CaO releasing heat to facilitate biomass decomposition and other related gasification reactions. Char generated by biomass pyrolysis also reacts with CO₂ to produce CO due to Boudouard reaction (Eq 3)[11, 34]. According to Fig.3(c), the larger proportion of CO in syngas is due to the fact that the Boudouard reaction (Eq 2) is endothermic, promoting the formation of CO which increases from 34.2% to 61.9% as CaO/ lignin ratio increase at 750°C. In addition, it can be observed that H₂ composition in syngas changes slightly with the increase of CaO/ lignin ratio. In combination with the trend of H₂ yield at 750°C in Fig.(2b), it can be explained that H₂ production still increases with the increase of CaO/lignin ratio, but the increase is not as obvious as that of CO, so it is difficult to observe the increase of H₂ composition.

(3)

Figure 2. Comparison of yields of syngas obtained under 15%CO₂+85%N₂ atmosphere with different temperatures and CaO/ lignin ratio (a)CO (b)H₂

Figure 3. Comparison of gas composition under 15%CO₂+85%N₂ atmosphere with different temperatures and lignin/CaO ratio (a) 550 °C (b) 650 °C (c) 750 °C

3.2 Influence of CO₂ Concentration in the Gas Mixture on Syngas Production

Fig.4 shows the results related to the influence of CO₂ concentration in the gas mixture (15%CO₂+85%N₂,30%CO₂+70%N₂,45%CO₂+55%N₂) on syngas composition and yield. According to Fig 4(a), with the increase of the volume ratio of CO₂ in the feed gas, the concentration of CO₂ in the syngas increases significantly while

other components decline. Previous research[35] showed that CO₂ yield was reduced with the increase of CO₂ concentration in gasification medium as additional CO₂ can promote water gas shift reaction (Eq 3). Moreover, CaO carbonation (Eq 1) consumed CO₂ to generate heat. This phenomenon can be explained by the fact that the change of CO₂ is much larger than the change of other components.

As can be seen Fig.4(b), CO yield increases from 3.16 (mmol/g lignin) to 5.77 (mmol/g lignin) with the increase of CO₂ concentration in the feed from 15 to 45%. It is suggested that the heat released from CaO carbonization promoted CO production. The yield of H₂ increases firstly and declines with the further increase of CO₂ concentration in the feed indicating that the increase of CO₂ concentration may enhance reverse water-gas shift reaction (Eq 3). The results obtained are consistent with that reported from Shen et al.[36] using 100% air and 85% air +15%CO₂. This indicates that an appropriate increase in CO₂ concentration in the feed facilitates syngas production from biomass gasification. However, high CO₂ concentration in the gas atmosphere will inhibit the production of hydrogen and promote the production of CO due to the Boudouard reaction (Eq 2). This will result in a syngas composed of more CO and less H₂ during autothermal CaO looping biomass gasification.

Figure 4. Influence of CO₂ concentration (a) 15%CO₂+85%N₂ (b) 30%CO₂+70%N₂ (c) 45%CO₂+55%N₂; lignin/CaO ratio: 1/5; temperature: 650 °C

3.3 SEM-EDX Analysis of Reacted samples

Sintering phenomena is a heat-induced mass transport driven by the reduction of free surface energy kinetically controlled by temperature in a particle bed[37]. Once sintering occurs in the process of ash deposition, the deposited ash particles are gradually sintered together, and the particle size and strength increase gradually, eventually forming sintered or molten sediments[38]. The performance of simulated ash was investigated qualitatively by comparing the morphology change of unreacted silica and reacted silica particles with and without CaO at different temperatures.

Fig.5 shows the SEM images of the unreacted silica and reacted silica particles with and without CaO at 650°C and 750°C. As can be seen from Fig.6, The particles after gasification shown in the SEM figures all obtain the silicon peak through EDX, so it can be confirmed that the observed particles are silica. By comparing the morphology of silica particles in conventional biomass gasification (Fig.5(b,d)) with unreacted silica(Fig.5(a)), the size of particles only changes slightly. The unreacted

silica particles are in the shape of a cube, while reacted silica particles obtained at the gasification temperatures of 650°C and 750°C show folds and micropores on the particle surface respectively. It is indicated that temperature can affect the morphology and size of ash particulates [39]. Nevertheless, as shown in Fig.5(b,c) and Fig.5(d,e), the morphology and size of silica particles obtained between conventional and autothermal biomass gasification at the same temperature are different. Compared with the original smooth cube, the size of silica particles reduces, irregular in shape and are attached by many small particles. This can be explained that CaCO_3 generated by CaO carbonation and SiO_2 particles to form calcium silicate change the morphology of the particles[28]. According to the research conducted by Kuo et al.[40], SiO_2+CaO performed a better inhibition effect on ash sintering compared with silica itself as the bed material. Moreover, the released heat from CaO carbonation could be one of the reasons for inhibiting the growth of silica particle size since it can reduce the gasification temperature and thus reduce the ash sintering degree.

Figure 5. SEM morphology images.(a) unreacted silica particle (b) reacted silica particle from Case #5, 650 °C; (c) mixture of particles of Ca species and silica from Case #8, 650 °C; (d) reacted silica particle from Case #9, 750 °C;(e) mixture of particles of Ca species and silica from Case #12, 750 °C.

Figure 6. EDX images of the solid residue: (a) mixture of char and particles of silica from Case #5, 650 °C; (b) mixture of char and particles of Ca species and silica from Case #8, 650 °C; (c) mixture of char and particles of silica from Case #9, 750 °C; (d) mixture of char and particles of Ca species and silica from Case #12, 750 °C.

4. Conclusion

In summary, this paper confirms that the carbonization heat provided by the reaction of CaO-based materials and flue gas can promote the syngas production in biomass gasification. The presence of reaction heat has a certain influence on the morphology and size of simulated silica ash, so it is speculated that autothermal CaO looping biomass gasification has a certain inhibitory effect on ash sintering. The experimental results showed that H₂ yields similar to those of conventional biomass gasification could be obtained by Auto-CaL-Gas technology at lower operating temperatures. Moreover, H₂ concentration increased by 23.29% at 650°C with CaO than at 750°C

without CaO, and 14.11% at 550°C with CaO than at 650°C without CaO, respectively. Autothermal CaO looping gasification has significant advantages over conventional gasification in energy consumption saving and syngas quality improvement.

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