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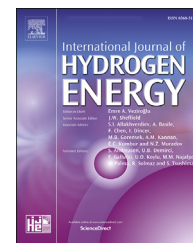
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Hydrogen production from autothermal CO₂ gasification of cellulose in a fixed-bed reactor: Influence of thermal compensation from CaO carbonation

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HIGHLIGHTS

- Autothermal and conventional gasification are compared.
- Higher H₂/CO molar ratio was obtained at 650 °C in the autothermal gasification.
- The gas yield increases with the increase of CaO/cellulose mass ratio.
- The CaO–CO₂ reaction reduces the required energy for cellulose degradation.

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ABSTRACT

Biomass gasification is a promising technology to produce renewable syngas used for energy and chemical applications. However, biomass gasification has challenges of low process energy efficiency, low syngas production with low H₂/CO ratio and the sintering of biomass ash which limit the deployment of the technology. This work investigated the influence of in-situ generated heat from CaO–CO₂ on cellulose CO₂ gasification using a fixed bed reactor, thermogravimetric analysis-Fourier transform infrared spectroscopy (TGA-FTIR) and differential scanning calorimetry (DSC). Experimental results indicate an approximate 20 °C temperature difference in the fix-bed reactor between cellulose CO₂ gasification with the energy compensation of CaO carbonation (denoted auto-thermal biomass gasification) and conventional CO₂ gasification of cellulose after the power of external furnaces were turned off. Around 5 times H₂/CO molar ratio is obtained after switching off the power in the auto-thermal biomass gasification compared with conventional gasification. The gas yield enhances significantly from 0.29 g g⁻¹ cellulose to 0.56 g g⁻¹ cellulose when CaO/cellulose mass ratio increases from 0 to 5. Furthermore, the TGA-FTIR results demonstrate the feasibility of adopting energy compensation of CaO carbonation to reduce the gasification temperature. DSC analysis also proves that the released heat from the CaO–CO₂ reaction reduces the required energy for cellulose degradation.

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Introduction

To tackle climate change caused by greenhouse gas emissions, it is necessary to replace fossil fuels with sustainable green fuels. Among the renewable fuels, biomass has been regarded as a potentially carbon-neutral and abundant energy resource, providing clean fuels to achieve the ambition of negative carbon dioxide emission. Biomass gasification produces syngas that can be applied for energy generation or further conversion into valuable products [1–5]. However, conventional biomass gasification has several limitations for its deployment, such as CO₂ emissions in syngas [6,7], poor syngas quality in gaseous products [8] and low process energy efficiency [9]. One of the main reasons for the low energy efficiency of biomass gasification is that steam is generally used as the gasification agent with high energy consumptions [10,11]. Meanwhile, steam gasification produces a large amount of tar and CO₂. Therefore, efficient heat utilization is essential to improve the energy efficiency of biomass gasification.

To reduce CO₂ emission and enhance the syngas production of biomass gasification, limestone has been added as bed materials and investigated [12–15]. CaO is considered a desirable sorbent for biomass gasification due to its low price and availability [16]. Furthermore, CaO can act as a catalyst for tar reduction and a heat carrier in biomass gasification [12,17,18]. Previous studies [19–22] reported that the concentration of H₂ in the syngas reached 71% and the content of tar reduced 67% when in-situ CO₂ capture with CaO was applied. The increase of H₂ concentration in the syngas is due to CO₂ removal, promoting the equilibrium of the water gas shift reaction (Eq (3)) [23]. However, current work related to sorption enhanced gasification of biomass normally ignores the importance of the in-situ released heat from CaO carbonation which can be utilised to supply energy for biomass gasification.

The heat produced from CaO carbonation (177.8 kJ per mole of CaO) could provide energy compensation and thus enhance the energy efficiency of biomass gasification. It was reported that syngas production was increased from 0.21 kg h⁻¹ (without CaO) to 0.90 kg h⁻¹ when CaO was utilised to provide heat for biomass gasification via Aspen Plus® simulation. In addition, experimental work resulted in a three-fold CO production by introducing flue gas and CaO into the gasification system [24]. Moreover, a similar H₂ yield was obtained at lower gasification temperature via the CaO carbonation enhanced biomass gasification technology, which can be denoted as auto-thermal biomass gasification [25]. It is suggested that CaO carbonation plays two roles in promoting syngas generation during biomass gasification. Apart from the removal of CO₂ promoting the equilibrium of biomass gasification related reactions, the exothermic reaction is also the energy supply for biomass gasification [26,27]. Therefore, it is necessary to investigate the enhancement of syngas production resulted from CaO carbonation from the perspectives of thermal compensation.

Here, this paper provides insights into heat integration between CaO carbonation and cellulose CO₂ gasification in a lab-scale fixed bed reactor. The effect of CaO carbonation on

the temperature inside the gasifier was studied, and key factors affecting CaO carbonation such as CaO/cellulose mass ratio and holding time were experimentally demonstrated. Meanwhile, TGA-FTIR and DSC were applied to study the thermal degradation and the heat flow of a mixture of cellulose and CaO in CO₂/N₂ and N₂ atmospheres, respectively.

Materials and methods

Materials

Cellulose, a major component of the biomass, was purchased from Sigma-Aldrich Co., Ltd, (CAS number: 9004-34-6). The cellulose used in this work is in white powder. Calcium oxide was purchased from Sigma-Aldrich Co., Ltd without any further purification (CAS number: 1305-78-8). Around 0.5 g cellulose was mixed with different proportions of calcium oxide, and the samples were mixed to achieve good uniformity. The results of proximate and ultimate analysis of cellulose are presented in Table 1.

Experimental

The gasification experiments were conducted in a vertical quartz tubular reactor (24 mm inner diameter and 520 mm height), as shown in Fig. 1. The reactor was externally heated by two adjacent mid-open electric heaters (each has a 200 mm length) using temperature controllers. A mixture of pre-mixed cellulose (0.5 g) and calcium oxide with CaO/cellulose mass ratios of 0, 2 or 5 was evenly placed into the quartz tube and sandwiched by quartz wool (about 0.2 g). A thermocouple was inserted into the reactor from the top of the quartz tubular to the position above the quartz wool. For each experiment, the sample was heated under the nitrogen atmosphere with a flow of 85 ml min⁻¹ to 120 °C at a heating rate of 20 °C min⁻¹ and held for 10 min corresponding to the removal of moisture in the sample. The sample was then heated under 15%CO₂/85%N₂ atmosphere in a total flow rate of 100 ml min⁻¹ at a heating rate of 22 °C min⁻¹ from 120 °C to 650 °C. In particular, the reactor power was turned off when the reactor temperature reached 650 °C and kept at that temperature for 0, 5 or 10 min (holding time), respectively. Subsequently, the temperature was recorded for 10 min to observe the difference of reactor temperature. The final reactor temperature of CaO/cellulose = 5 was compared with the control reference of CaO/cellulose = 0 under the same operating conditions (e.g. carrier gas flowrate and set gasification temperature). The produced

Table 1 – The proximate and ultimate analysis of cellulose sample.

Cellulose Proximate analysis (wt%, d)		Ultimate analysis (wt %, d)	
Moisture	3.9	carbon	50.6
Ash	0.29	hydrogen	5.35
volatile matter	95.36	nitrogen	0.1
fixed carbon	0.45	oxygen ^a	43.95

^a Calculated by weight difference.

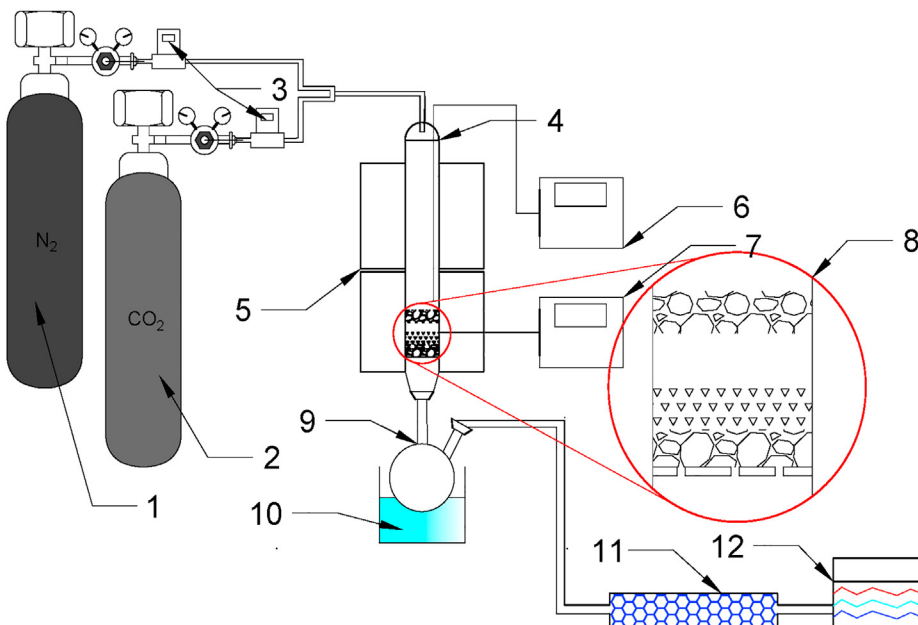
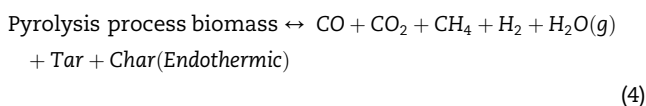
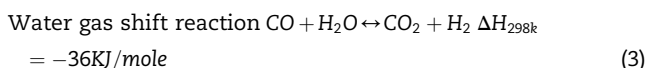
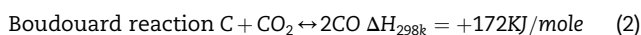
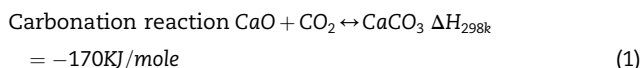


Fig. 1 – Schematic diagram of auto-thermal biomass gasification technology reactor system. (1) Nitrogen cylinder (2) CO₂ cylinder (3) Mass flowmeters (4) Quartz reaction tube (5) Heating furnace (6) Thermocouple (7) Temperature control (8) Reaction layer: Quartz wool + sample + quartz wool (9) Condensing flask-2-neck (10) Ice bath (11) Drying tube (12) Gas analyser.

gas was collected for analysis using a gas analyser after passing through a condensation system, including an ice bath and a drying tube. The important chemical reactions involved are summarized as follows:



set temperature (650 °C). Subsequently, the different holding times at 650 °C correspond to the extent of CO₂ sorption of CaO. As once CaO is saturated, it cannot provide heat for cellulose gasification through the carbonation reaction.

Product analysis

The composition of the gas product was examined and displayed in real-time by online gas chromatography (ETG Ltd., Italy). Besides, analysis of gaseous products was performed off-line using gas chromatography (GC7900, Tianmei Ltd., China) to quantify the concentration of produced gases such as CO, CO₂, CH₄ and H₂. Based on the volume of nitrogen in the carrier gas, the yield of syngas was calculated by a standard external method. All the syngas values shown in the results section are the average values obtained after three repeated experiments.

It is difficult to distinguish between CO₂ in the carrier gas and CO₂ from biomass pyrolysis, the gas yield (Eq (4)) is

$$\text{Gas yield} = \frac{M_{\text{biomass}} + M_{\text{CaO}} - M_{\text{tar}} - M_{\text{residue}}(1 - (\text{desorbed CO}_2 - \text{unreacted char}))}{M_{\text{biomass}}} \quad (5)$$

Evaluation of temperature influence

Based on our pre-experimental commissioning, the maximum amount of CaO (2.5 g) packed in the reactor is not sufficient to capture CO₂ (15 ml min⁻¹) for more than 35 min. Therefore, a concept of holding time is defined as the reaction time after an immediate shut down of the reactor power when reaching the

calculated on the mass balance of the process where CO₂ sorption is the amount of CO₂ captured by the addition of commercial CaO (M_{CaO}) as CaCO₃. The mixture of CaO/cellulose feedstock minus the liquid products (M_{tar}) and solid products (M_{residue}), where solid products are required to remove the weight of the adsorbed CO₂ from CaCO₃ and to discharge CO₂ from unreacted cellulose, and then divide by

the cellulose (M_{biomass}). Around 10 mg of samples were heated in a TGA-FTIR (EXSTAR TG/DTA6300) (Irafinity1s, Japan) with a heating rate of $15\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $900\text{ }^{\circ}\text{C}$ under N_2 atmosphere and kept for 5 min to determine the percentage of CO_2 desorption in residue and the composition of the decomposed gas, thus determining the amount of CO_2 captured by CaO as CaCO_3 .

Thermal decomposition of the mixture of cellulose and CaO was carried out with a TGA-FTIR. Around 15 mg of feed-stock samples were heated with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $100\text{ }^{\circ}\text{C}$ to $750\text{ }^{\circ}\text{C}$ under CO_2/N_2 atmosphere and kept for 0 min, allowing for displaying the performance of thermal degradation and the tendency of CO_2 sorption with temperatures.

TGA/DSC analysis of biomass was carried out by an SDT Q600-TA instrument simulating the auto-thermal biomass gasification process and traditional biomass gasification. Around 15 mg of the mixed samples of cellulose and CaO were heated with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $100\text{ }^{\circ}\text{C}$ to $750\text{ }^{\circ}\text{C}$ under CO_2/N_2 and N_2 atmosphere, respectively, allowing for comparing the difference between thermal degradation and exothermic reactions.

Results and discussion

Influence of CaO/cellulose mass ratio on syngas production

Fig. 2 indicates the results of gas composition and syngas yield using various mass ratios of CaO to cellulose. Regarding the composition of gaseous products, abundant CaO captures CO_2 from the gasification agent and enhances the generation of CO and H_2 with the increase of CaO/cellulose mass ratio. The yield of H_2 increases with the increase of CaO/cellulose ratio and reaches around 4 mmol g^{-1} at a CaO/cellulose mass ratio of 5:1, almost 8 times higher than the yield without the addition of CaO. Likewise, CO yield achieves 3-fold enhancement compared to the experiment without CaO. This is due to the multiple functions of CaO, including catalysis and adsorption during biomass gasification [28]. CO_2 was captured by CaO via carbonation reaction (Eq. (1)), shifting the equilibrium of the reactions of biomass decomposition (Eq. (4) to syngas production [29,30]. At the same time, the Boudouard reaction typically occurs at 700 or higher temperatures, the energy compensation from CaO carbonation allows Eq. (2) to occur at lower temperature ($650\text{ }^{\circ}\text{C}$), which facilitates CO production during this process. Previous studies have reported that syngas production was enhanced with the increase of CaO addition under CO_2/N_2 atmosphere at $700\text{ }^{\circ}\text{C}$ [31], while the increase of the addition of limestone also improved syngas yield at $850\text{ }^{\circ}\text{C}$ under O_2/CO_2 atmosphere [32]. These two aspects indicate that the thermal compensation of CaO carbonation might play a crucial role in improving syngas production when CO_2 is rich in the gasification agent.

To calculate the total gas yield of this process, TGA under the N_2 atmosphere was applied to desorb the captured CO_2 from the collected solid residue, while the corresponding FTIR was used to analyse the released gaseous compounds [33]. The results in Fig. 3(a) show that there is dramatic weight loss

at around $600\text{ }^{\circ}\text{C}$, which is the decomposition of CaCO_3 . Compared to CaO/cellulose = 5, there is also a slight weight loss at about $350\text{ }^{\circ}\text{C}$ for CaO/cellulose = 2, which can be attributed to the weight loss of unreacted cellulose. The corresponding FT-IR spectrum supports the above observation. As shown in Fig. 5(b), the intensity of the infrared vibrational peak with a wavenumber of 2342 cm^{-1} varies with increasing temperature. A clear desorption peak of CO_2 occurs at around $600\text{ }^{\circ}\text{C}$.

From Table 2, the percentage of the desorbed CO_2 per mg CaO decreases from 29% to 22% when the CaO/cellulose ratio increases from 2 to 5. It is suggested that a higher CaO/cellulose mass ratio results in more uncarbonated CaO in the solid residue. After the mass balance calculation (Eq. (4)), the gas yield enhances significantly from 0.29 g g^{-1} cellulose to 0.56 g g^{-1} cellulose when CaO/cellulose mass ratio increases from 0 to 5. Muhammad et al. [34] also found the conversion of biomass during steam gasification varied from 0.69 to 0.91 by modifying the CaO/cellulose mass ratio and temperature, supporting the results of this research. For ideal biomass gasification, a higher gasification temperature increases the yield of gas [35]. However, it is necessary to limit the gasification temperature to reduce the energy consumption of the process. This contradiction restricts the development of biomass gasification [36]. Therefore, the auto-thermal biomass gasification has the advantages of higher gas yield under lower gasification temperature that is more favourable for scale-up.

Evaluation of thermal compensation of CaO carbonation on temperature differences

Fig. 4 exhibits the online syngas production of cellulose and CaO/cellulose mass ratio = 5 in $15\%\text{CO}_2+85\%\text{N}_2$ atmosphere as well as the corresponding relationship between reactor temperature and reaction time. As shown in Fig. 4(a), upon the introduction of CaO in $15\%\text{CO}_2+85\%\text{N}_2$ atmosphere, the thermochemical conversion of auto-thermal biomass gasification shows a significant difference as compared to conventional CO_2 gasification of cellulose. The generation of H_2 shifted to lower temperatures ($450\text{ }^{\circ}\text{C}$) when CaO participated in the cellulose pyrolysis. Furthermore, the second peak of CO and H_2 , due to thermal compensation of CaO carbonation, was observed in the auto-thermal biomass gasification process after the temperature reached $650\text{ }^{\circ}\text{C}$, while the syngas yield from conventional gasification gradually decreased after $650\text{ }^{\circ}\text{C}$ without the supply of reactor power. In addition, around 5 times H_2/CO molar ratio is obtained at $650\text{ }^{\circ}\text{C}$ for auto-thermal biomass gasification compared with conventional gasification. It is suggested that the first H_2 peak is caused by the cracking of cellulose (Eq. (4)) and the second peak is due to the impact of CaO carbonation since Eq. (1) can release peak heat at this temperature. Also, it was reported that CaO catalysed the volatiles from cellulose to produce more H_2 at $650\text{ }^{\circ}\text{C}$ and achieved higher carbon conversion [37]. The above observations reveal that the production of H_2 could be dramatically enhanced when integrating CaO carbonation into biomass gasification.

Subsequently, as observed in Fig. 4(b), the impact of different holding times was compared in the auto-thermal

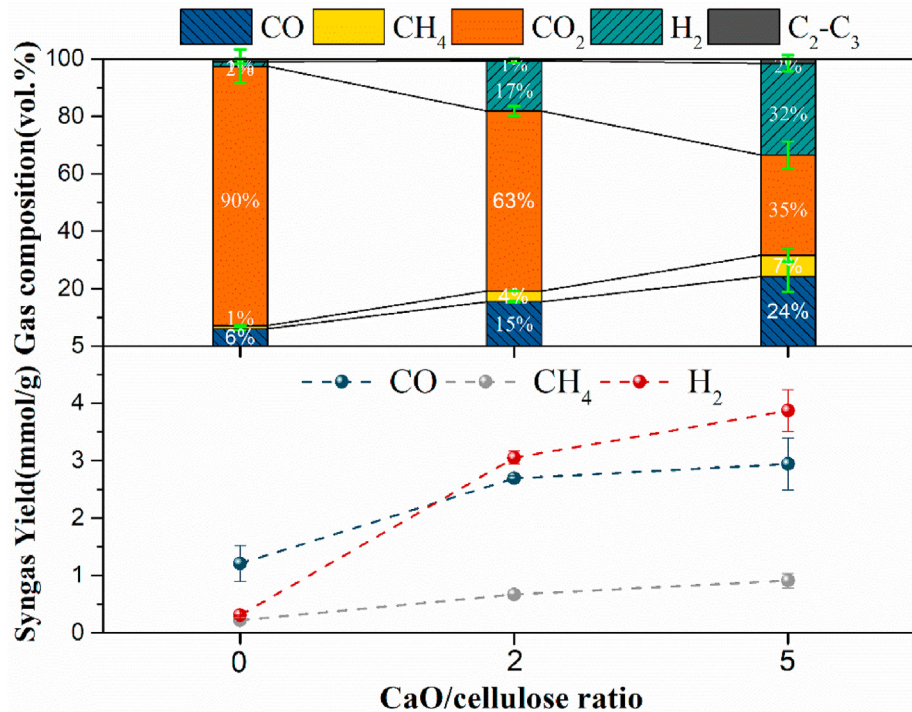


Fig. 2 – Influence of CaO/cellulose ratio on syngas production at 650 °C under 15%CO₂+85%N₂ atmosphere with 0 min holding time.

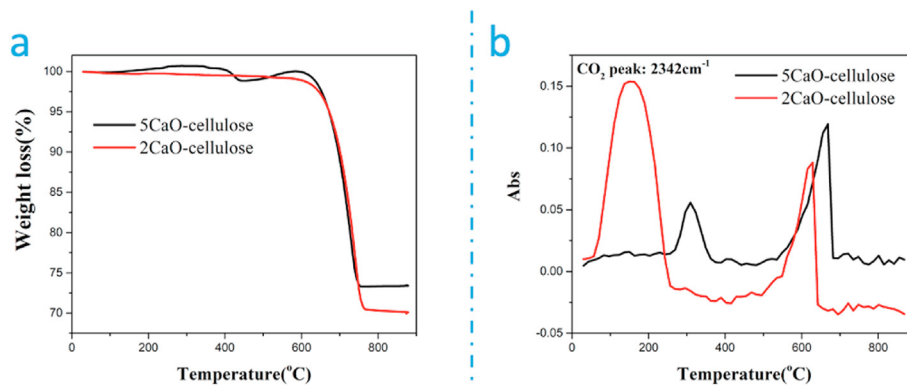


Fig. 3 – Weight loss curve of solid residue in N₂ atmosphere (a) and the intensity profile of CO₂ peak at wavenumber of 2342 cm⁻¹ in the corresponding FT-IR spectrum (b).

Table 2 – Gas yield calculation based on process mass balance.

CaO:cellulose	Cellulose	CaO	Tar	Residue	Unreacted cellulose	Desorbed CO ₂ from CaCO ₃	Total CO ₂ sorption	Gas yield
	(g)	(g)	(g)	(g)	(%/mg)	(%/mg)	(g)	(g/g)
5	0.51	2.48	0.59	2.71	2	22	0.60	0.56
2	0.50	1.02	0.49	1.09	0	29	0.32	0.52
no CaO	0.49	–	0.3	0.08	–	–	–	0.29

biomass gasification. The reactor temperature decreases from 650 °C to 570.6 °C in 10 min after the power off. Final reactor temperatures are 555.4 and 548.2 °C for the auto-thermal biomass gasification after keeping 650 °C for 5 and 10 min, respectively. This indicates that the CaO reacts with

the CO₂ in the carrier gas to release heat and the energy provided by CaO carbonation depends on the extent of the conversion from CaO to CaCO₃. This difference in temperature after the power off (around 20 °C) confirms that the thermal compensation of CaO carbonation was used to

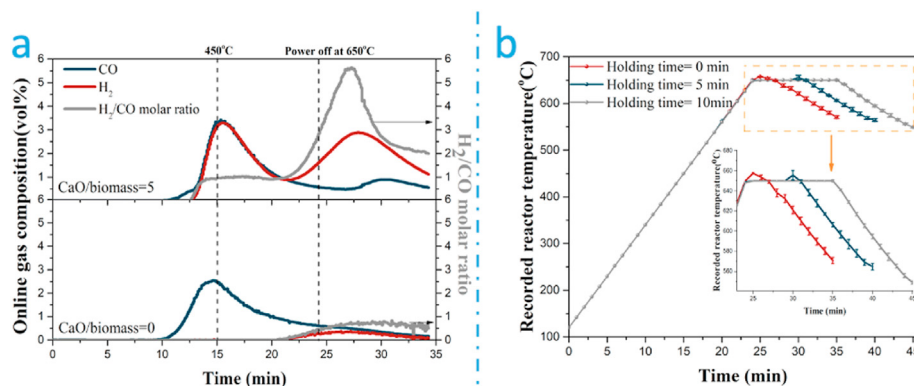


Fig. 4 – Comparison of online syngas composition between auto-thermal biomass gasification technology and traditional CO₂ gasification of biomass under 15%CO₂+85%N₂ atmosphere at 0 min holding time (a) and the impact of different holding times on reaction temperature (b).

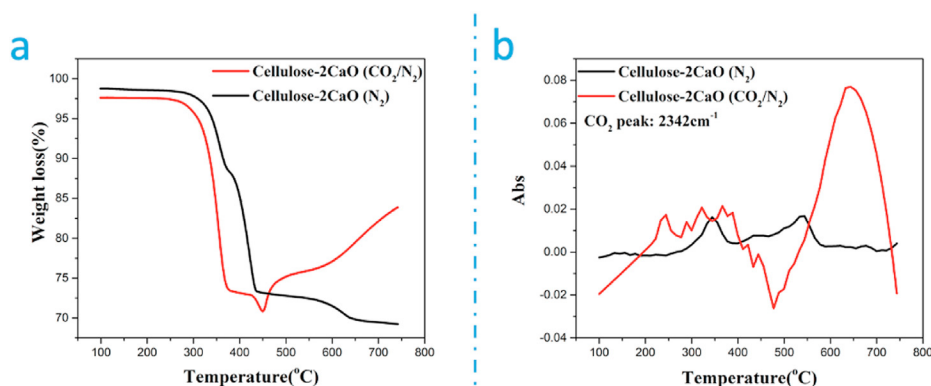


Fig. 5 – Thermal degradation of the mixture of CaO/cellulose under different atmospheres (a) and the intensity profile of CO₂ peak at wavenumber of 2342 cm⁻¹ in the corresponding FT-IR spectrum (b).

support biomass gasification on the promotion of syngas production. This is beneficial for biomass gasification that generally has a higher gas yield at higher temperature [38]. While the above results are from lab-scale experiments, the correlation between the heat released by tonnes of commercial CaO and large-scale biomass gasification needs to be further studied [39].

TGA-FTIR analysis

Fig. 5 exhibits the thermal degradation of the mixture of cellulose and CaO under CO₂/N₂ and N₂ atmosphere, respectively. A sharp weight loss can be observed for samples in both CO₂/N₂ and N₂ atmospheres at temperatures above 350 °C, which is the degradation of cellulose. Under CO₂/N₂ atmosphere, the weight loss curve of the sample first decreases smoothly until 450 °C and gradually accumulates weight. In addition, the weight loss of the sample in N₂ atmosphere loss mitigates in the temperature range of 450–600 °C. It can be attributed to CaO, which starts to adsorb CO₂ and thus gains weight or mitigates weight loss.

Fig. 5(b) shows the relationship between the peak intensity of CO₂ at wavenumber of 2342 cm⁻¹ and temperature that corroborates the above-observed phenomena in TGA. The results suggest that CO₂ production at 350 °C and 550 °C for

samples under N₂ atmosphere corresponds to the degradation of cellulose and the conversion of CO to CO₂ in the water gas shift reaction (Eq (3)), respectively. There is a clear inverted peak of CO₂ occurring at 450–600 °C, consistent with TGA results in Fig. 5(a), indicating the CaO carbonation reaction (Eq (1)) is in action. Previous studies also support the use of CaO as both a CO₂ absorbent and a catalyst at lower temperatures (550 °C), while only as a catalyst at high temperatures [28]. Therefore, it is feasible to use the thermal compensation of CaO carbonation to reduce the gasification temperature, as CaO carbonation is more efficient at relatively low temperatures.

DSC analysis

Heat flows of thermal conversion of the mixture of cellulose and CaO under CO₂/N₂ and N₂ atmosphere was determined by DSC. The results are shown in Fig. 6. An endothermic and an exothermic peak are observed in Fig. 6(a) for the pure cellulose at around 350 °C and CaO at about 450 °C, respectively, when the gas atmosphere is CO₂+N₂. The endothermic peak can be attributed to the degradation of cellulose, while the exothermic peak is due to the heat released from the reaction of CaO with the CO₂ in the carrier gas. A previous work [40] also reported that the endothermic peak of CaCO₃

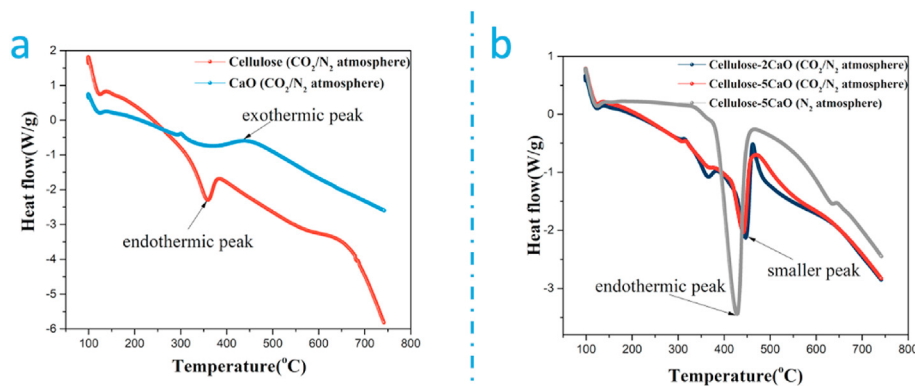


Fig. 6 – DSC analysis of cellulose between auto-thermal biomass gasification technology and traditional biomass gasification.

decomposition detected by DSC analysis was stronger in the atmosphere of 21%O₂/79%CO₂ than in the atmosphere of 21% O₂/79%N₂. The results suggest that more Ca reacts with CO₂ to release heat when the atmosphere is rich in CO₂.

Fig. 6(b) shows the effect of CaO/cellulose ratios (2 and 5) and gas atmospheres (CO₂/N₂ and N₂) on the thermal chemical conversion of cellulose. The endothermic peak under the CO₂/N₂ atmosphere was smaller than that under the N₂ atmosphere when CaO/cellulose ratio is 5, indicating that the heat released by CaO carbonation reduces the energy required for cellulose degradation. Compared with the mass ratio of CaO/cellulose = 5, there are two stronger endothermic peaks at around 350 °C and about 500 °C, respectively, when CaO/cellulose ratio is 2. It is illustrated that the obtained curves are related to cellulose degradation and CaO carbonation, respectively. Besides, an increase in the amount of cellulose requires more energy for decomposition and a decrease in the weight of CaO releases less heat.

Conclusion

In summary, the influence of the thermal compensation from CaO carbonation for biomass gasification is studied. Experimental results demonstrate that the final reactor temperature of biomass gasification after power off was increased by 20 °C due to the thermal compensation of CaO carbonation, resulting in 5 times H₂/CO molar ratio compared with CO₂ gasification of biomass without CaO. The gas yield enlarges significantly from 0.29 g g⁻¹ cellulose to 0.56 g g⁻¹ cellulose when the mass ratio of CaO/cellulose increases from 0 to 5. Furthermore, TGA-FTIR results confirm that the employment of the energy compensation of CaO carbonation can be applied to reduce the gasification temperature. In addition, DSC results indicate that the heat released from CaO carbonation reduces the energy input for the thermal conversion of cellulose. Therefore, it is suggested that this promising auto-thermal biomass gasification process could facilitate a syngas yield with a higher H₂/CO ratio at lower energy consumption. However, the application of this concept for large-scale biomass gasification needs to be further investigated by process modelling.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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