



Synthesis gas production from microalgae gasification in the presence of Fe_2O_3 oxygen carrier and CaO additive

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HIGHLIGHTS

- CaO addition in high content improve selectivity for syngas production in BDCL.
- Oxygen carrier with CaO almost keep stable reactivity for BDCL in 10 redox cycles.
- CaO Coverage and $\text{Ca}_2\text{Fe}_2\text{O}_5$ generation result in oxygen carrier reactivity variation.

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ABSTRACT

Microalgae gasification in the presence of Fe_2O_3 oxygen carrier and CaO additive was investigated in a fixed bed reactor to simulate the reactions in direct chemical looping gasification, focusing on the thermal behavior of CaO in synthesis gas production and multiple redox cycles. The results showed that Fe_2O_3 as oxygen carrier improved the synthesis gas but brought much more CO_2 generation, lowering the gas *LHV*. Introducing CaO efficiently inhibited CO_2 release and improved CO and H_2 production, and gasification efficiency and gas *LHV* elevated from 55.2% and 13.27 MJ/N m^3 to 66.2% and 14.85 MJ/N m^3 at 850°C . CaO mainly played as CO_2 absorbent and hardly had catalytic effects on tar crack for synthesis gas production at 650°C . At 850°C , CaO mainly played as catalyst and still had a great selectivity for synthesis gas production. The CaO/C molar ratio of 0.5 was sufficient for achieving its function. The multiple redox experiments showed that the gas efficiency and carbon conversion declined in the second reduction and kept at $60.1 \pm 1.2\%$ and $77.4 \pm 1.5\%$ respectively in 2–10 cycles. XRD and SEM-EDX results showed the coverage of CaO, the formation of calcium ferrites and CaO deactivation accounted for the variation of oxygen carrier reactivity in multiple cycles.

1. Introduction

As the progress of social and economic, developing renewable energy to replace fossil fuels has become the inevitable trend. Due to its wide distribution, stable supply [1] and carbon neutral, biomass energy will be one of the most potential types to replace fossil fuels [2]. Among various biomass, microalgae have the following advantages: shorter growth period and double in 24 h [3,4]; higher production with 5–30 times of traditional oil crops per unit area [5]; cultivated on waste water and non-arable land, no threat to the agricultural production [6]. Therefore, microalgae has been considered as the most potential biomass resource for energy use [4,7]. Also, microalgae is one of important biomass resource in south China because the mild climate condition is suitable for microalgae cultivation.

Synthesis gas production from biomass is a thermal chemical

conversion technology, which can be converted into power, fuels and chemicals [8,9]. In conventional biomass gasification, oxygen-rich air or high temperature steam is needed as gasification agent. Biomass direct chemical looping (BDCL) is a novel technology for converting biomass into synthesis gas, using the lattice oxygen of oxygen carrier for the partial oxidation of biomass, rather than direct oxidized by molecular oxygen or completely oxidation for heat. The process simulation shows that BDCL process is 10–25% more efficient than conventional biomass conversion process [10]. Similar to the chemical looping combustion (CLC) scheme, BDCL system has two reactors for the oxidation and reduction respectively. In the reduction reactor, metal oxide (Me_xO_y) as oxygen carrier is reduced by solid fuel into Me_xO_z ($y > z$) and synthesis gas is produced. In the oxidation reactor, the reduced oxygen carrier (Me_xO_z) is oxidized by air and the lattice oxygen can be regenerated. BDCL has the following advantages

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compared with conventional gasification. Firstly, the lattice oxygen can be regenerated and the cost of oxygen-rich air preparation can be saved [11]; secondly, the partial oxidation and catalytic effects of oxygen carrier facilitates the conversion into synthesis gas [12,13]; thirdly, the oxidation of oxygen carrier is an exothermic process for most metal oxides, and this process can provide the heat for gasification to maintain the continuous reaction [11].

Since iron ore as oxygen carrier has high temperature stability, environmentally friendliness, low cost and extensive source, and its reactivity is acceptable [11,14], most of works for chemical looping conversion was based on Fe-based oxygen carrier or modified by other metal oxides. Also, CaO was a cheap and environmental-friendly metal oxide, and CaO-based chemical looping is also a promising technology for hydrogen-enriched gas production through carbonation ($\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$) and calcination ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) looping [15]. CaO has significant effects on solid fuel thermal conversion. On one hand, CO_2 absorption of CaO made WGS (water-gas shift, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) equilibrium shift to the direction of H_2 production. On the other hand, CaO has catalytic functions for tar crack. Considering that the use of Fe_2O_3 as oxygen carrier do not have ideal reactivity and selectivity for synthesis gas production, resulting the significant increase of CO_2 generation, the introduction of CaO may decrease the CO_2 production and improve the quality of synthesis gas. If CaO directly added in BDCL has a great improvement for synthesis gas production, it will also save the cost in oxygen carrier preparation.

Based on the effects of CaO above, some researchers added it into oxygen carriers for reactivity promotion and CO_2 capture in CLC. Gu, Shen [16] investigated CaO-modified iron ore as oxygen carrier for coal CLC, resulting that CaO enhanced coal conversion. Wang and Zhao [17,18] investigated the reactivity of CaO-decorated Fe_2O_3 oxygen carrier as oxygen carrier for *in situ* gasification chemical looping combustion (iG-CLC) of plastic waste, and used CaO to inhibit the emission of PCDD/Fs and chlorobenzene. Cuadrat, Linderholm [19] and Teyssié, Leion [20] added CaO into ilmenite oxygen carrier for solid fuel CLC, concluding that the addition of CaO improved the char and gas conversion and conversion rate. Qin, Yin [21] and Manovic and Anthony [22] added CaO into CuO oxygen carrier to integrate calcium looping and chemical looping combustion for CO_2 capture.

However, there are limited literatures focusing on the effects of CaO addition on synthesis gas production through chemical looping conversion, and these researches also indicated the reactivity improvement with CaO addition. Guo, Cheng [23] added CaO into Fe_2O_3 oxygen carrier for chemical looping gasification, concluding that CaO addition could increase the carbon conversion efficiency and gasification rate substantially, and H_2 and CO production were enhanced while decreased CO_2 generation. Guo, Hu [24] added CaO to CaSO_4 oxygen carrier and resulted that CaO addition increased H_2 , CO and CO_2 production, and promoted the reaction performance and catalytic activity. The CaO-decorated CaSO_4 possessed good reactivity and stability in 10 redox cycles. Nevertheless, in these investigations CaO was added in low content, and chemical looping gasification with high content of CaO has not been investigated. Also, the effects of high content CaO additive on the property of Fe-based chemical looping gasification are still not clear. With high CaO content in Fe_2O_3 oxygen carrier, the agglomeration of Fe_2O_3 could be inhibited [25]. Also, the new phase of calcium ferrites, such as $\text{Ca}_2\text{Fe}_2\text{O}_5$ and CaFe_2O_4 , which have high reactivity with solid fuel but low reactivity with synthesis gas [26,27], might be formed in multiple redox cycles through solid phase reactions. Therefore, directly introducing CaO with high content in biomass BDCL with Fe-based oxygen carrier would have an improvement for synthesis gas production, and it is necessary to be investigated.

The aim of this work is to investigate the reactivity and selectivity property of Fe_2O_3 oxygen carrier with CaO additive for microalgae gasification using direct chemical looping. Firstly, characteristics of microalgae gasification using direct chemical looping with Fe_2O_3 oxygen carrier was analyzed. Secondly, CaO was directly introduced

Table 1
The proximate analysis and ultimate analysis of *Chlorella vulgaris* (dry basis).

Ultimate analysis (wt%)					Proximate analysis (wt%)			Q_{net} (MJ/kg)
C	H	N	S	O ^a	Ash	Volatiles	Fixed carbon	
45.49	6.61	10.28	0.21	28.69	8.72	78.98	12.30	18.692

^a Calculated by difference.

into the BDCL reaction at different CaO/C molar ratios and temperatures for discussing the effects of CaO on the reactions. Then the multiple redox cycles experiments were conducted, in order to evaluate its function in microalgae direct chemical looping and discuss its thermal behavior in synthesis gas production and redox cycles.

2. Materials and methods

2.1. Material preparation

Microalgae (*Chlorella vulgaris*) was obtained from Shanxi Baiwei Biotechnology Company, and produced in Zhanjiang region of Guangdong Province. First, the samples were dried for 24 h at 105 °C. Then the *Chlorella vulgaris* sample was sieved into particles with a size of less than 200 μm and loaded in a desiccator before experiments. The proximate analysis and ultimate analysis are shown in Table 1. The composition of microalgae ash was analyzed by XRF (X-ray Fluorescence Spectrometer), and the results were shown in Table 2.

Iron oxide (analytical reagent) was prepared as oxygen carrier, and it was first calcined for 3 h at 800 °C. CaO was prepared by the calcination of CaCO_3 . CaCO_3 in analytical reagent was placed in a tube furnace and calcined at 900 °C for 3 h at nitrogen atmosphere. Both iron oxide and CaO were crushed and sieved with the particle size of less than 200 μm , then also stored in a desiccator.

2.2. Methods

Microalgae gasification experiments were conducted in a U-type fixed bed reactor of quartz with inner diameter of 14 mm, which was shown in Fig. 1. In this experiment setup, argon was used as carrier gas controlled at 50 ml/min by a mass flow controller, while air used for the oxidation of oxygen carrier was set at 200 ml/min. The reactor temperature was controlled by a K-type thermocouple and temperature controller. Drainage method was adopted to measure the volume of gaseous products, and both tanks were filled with saturated sodium chloride solution. The volume of gas could be obtained by measuring the NaCl solution volume in a glass graduated cylinder, and the gaseous products were collected in the left tank.

At the reduction stage, the mixture samples of microalgae (0.250 g), oxygen carrier and CaO additive were filled in a quartz tube with inner diameter of 10 mm and was hanged at the top of the U-type reactor. Then place the U-type reactor into the furnace and set the argon flow at 50 ml/min for 10 min ensuring the inert atmosphere and stable temperature. After 10 min, let the sample quickly fall into the constant-temperature region and the reduction time was set at 30 min. The collected gaseous products in the left tank were transferred into a gas sampling bag by switching the valves. When the reduction stage finished, replace the argon with air in 200 ml/min and the oxidation stage lasted for 30 min. After oxidation, remove the solid residue from the

Table 2
The *Chlorella vulgaris* ash composition (wt%).

P_2O_5	Na_2O	K_2O	SO_3	MgO	SiO_2	Cl	Fe_2O_3	CaO
28.94	27.94	25.77	7.06	3.04	2.72	2.18	1.12	1.08

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