



Application of calcium ferrites as oxygen carriers for microalgae chemical looping gasification

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ABSTRACT

Calcium ferrites (CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$) are adopted as oxygen carriers for microalgae chemical looping gasification (CLG), and their reactivity is tested through TG-FTIR and fixed-bed reactor. Thermodynamics data show the ideal temperature for calcium ferrites, at which they can react with carbon but not with CO/H_2 . TG-FTIR tests indicate that calcium ferrites have lower oxidizability than Fe_2O_3 , according to the higher reduction temperature, lower CO_2 production and higher CO production. The great selectivity of calcium ferrites is also verified by fixed-bed tests. With steam, the efficiency can be elevated from 82.95% (with Fe_2O_3) to 92.49% (with $\text{Ca}_2\text{Fe}_2\text{O}_5$) at 850 °C. In one typical cycle, the synthetic calcium ferrites can be oxidized into the initial state after air oxidation, and $\text{Ca}_2\text{Fe}_2\text{O}_5$ keeps a better surface structure than CaFe_2O_4 . In summary, calcium ferrites have great selectivity for synthesis gas production, and are suitable for microalgae CLG, especially for $\text{Ca}_2\text{Fe}_2\text{O}_5$.

1. Introduction

Due to the consumption crisis of fossil fuel and its pollutant emission problem, developing the renewable energy to replace the fossil fuel is an irresistible trend of energy use. Biomass energy is a great candidate for renewable energy due to its renewability, carbon neutral [1] and abundant resource. Microalgae biomass is a very promising feedstock for energy use, owing to the following reasons: (1) higher growth rates and double in 24 h [2,3]; (2) higher yields per unit area with 5–30 times of traditional oil crops [4–6]; (3) no threat to the agricultural production [7]; (4) high solar energy conversion and high efficiency for CO_2 capture [8,9].

Biomass gasification is an important thermal conversion technology for energy use. The conventional gasification technology requires a large amount of pure oxygen as gasification agent to obtain high quality synthesis gas, which causes high cost for air separation. Chemical looping gasification (CLG) is novel technology to convert solid fuel into combustible gas, with no need for pure oxygen carrier preparation. It uses the lattice oxygen in oxygen carriers for partial oxidation, rather than direct oxidized by molecular oxygen or completely oxidation for heat. Oxygen carrier is a crucial factor for the performance of CLG. For chemical looping process, ideal oxygen carriers need high temperature stability, environmentally friendliness, low cost and great lattice oxygen transportation ability. Up to now, there are many researchers investigating the use of oxygen carrier in solid fuel CLG. Among these

investigations, the oxygen carrier mainly includes Fe_2O_3 -based [10–18], nickel-based [19], CaSO_4 -based [20–22], CuO and Mn_2O_3 [23,24] material. Since Fe_2O_3 oxygen carrier has the advantages of low cost, extensive source, environmentally friendliness and high temperature stability, most of works mentioned above are based on Fe-based oxygen carrier, or added other metal oxides [25–28], such as NiO and Al_2O_3 , to promote its reactivity.

For CLG, it is better to have a great selectivity for synthesis gas production, which needs the oxygen carrier to have a great reactivity for fuel thermal conversion, but weak reactivity with CO/H_2 . Previous studies [21] showed that addition of small amounts of CaO into oxygen carrier increased synthesis gas production, with lower CO_2 production [29]. If CaO added into Fe_2O_3 oxygen carrier in high content and the new phases of calcium ferrites (CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$) were formed, there would be a potential selectivity for synthesis gas production from biomass CLG [30].

The use of calcium ferrites for chemical looping process have been investigated. Some researchers [31–33] used $\text{Ca}_2\text{Fe}_2\text{O}_5$ as oxygen carrier for chemical looping hydrogen production (CLH) through steam-iron process. They found that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ as oxygen carrier had a higher conversion ability of steam to hydrogen, compared to unmodified iron oxide. But these studies did not investigate the thermal reactions between solid fuel and $\text{Ca}_2\text{Fe}_2\text{O}_5$ oxygen carriers. Sirwardane, Riley [28] used CaFe_2O_4 and BaFe_2O_4 as oxygen carrier for coal char CLG, resulting that these two oxygen carriers had high

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reactivity with coal but low reactivity with synthesis gas. They also studied the kinetics of CLG reactions between coal char and CaFe_2O_4 oxygen carriers [34]. Zhang, He [30] investigated the chemical looping partial oxidation of carbon using CaFe_2O_4 , CaFe_2O_5 and FeAl_2O_4 as oxygen carriers, and the thermodynamics and TG-MS results indicated CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ had large oxygen-carrying capacity, high CO selectivity and good regeneration performance. But it did not apply to real solid fuel and the synthesis gas production performance is not clear. Therefore, the effects of calcium ferrites on solid fuel CLG is not completely clear, especially for microalgae biomass. The use of calcium ferrites as oxygen carriers for microalgae biomass CLG is necessary to be investigated.

The present work is aimed to investigate the reactivity and selectivity of calcium ferrites (CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$) as oxygen carriers in CLG. First, thermodynamic analysis is used to discuss the reactivity of oxygen carrier - C/CO/ H_2 reaction, then thermogravimetric-Fourier transform infrared spectroscopy (FTIR) is used to discuss the interactions between oxygen carrier and biomass in the whole CLG process, and synthesis gas production performance and the phase evolution of oxygen carrier is evaluated in a fixed-bed reactor.

2. Materials and methods

2.1. Materials

Microalgae (*Chlorella vulgaris*) is Jiangmen Yuejian Biotechnologies Co., Ltd, and the samples are dried for 24 h at 105 °C. Then the *Chlorella* sample is 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.

Calcium ferrites ($\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_2O_4) are prepared by combustion method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR) are mixed in the molar ratio of Ca:Fe = 1:2 and Ca:Fe = 1:1 and dissolved in deionized water. Then add appropriate urea into the solutions as fuel and stirred at 70 °C until a viscous material was formed. The obtained viscous material is placed into muffle furnace and combusted at 250 °C, then calcined it at 900 °C for 5 h. The calcined materials are crushed, sieved and marked as CF and C_2F respectively. For comparison, Fe_2O_3 material is also calcined at 900 °C for 5 h as oxygen carrier, and labeled as F. The XRD patterns of oxygen carriers prepared were shown in Fig. 1. All the peaks could be indexed by $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_2O_4 . Thus, over combustion method, mono-calcium ferrite (CaFe_2O_4) and di-calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) could be formed without the impurity of Fe_2O_3 and CaO.

2.2. Experiment setup and procedure

A thermogravimetric analyzer (METTLER TOLEDO) coupled with Fourier transform infrared spectrometry (TGA-FTIR) is adopted to investigate the reactivity of calcium ferrites with microalgae. At each test, mixtures of oxygen carrier and 7 mg *Chlorella* are filled into an alumina crucible and heated from 105 to 850 °C at a heating rate of 20 °C/min, then keep at 850 °C for 20 min at argon atmosphere. Argon is controlled at 50 ml/min. The gaseous products, including CO, CO_2 , CH_4 and others were detected by FTIR spectrometer. The scanning range of IR was set at 4000–500 cm^{-1} , and its resolution was 4 cm^{-1} .

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	
49.99	7.39	9.48	0.500	27.40	5.25	81.84	12.91	19.576

^a Calculated by difference.

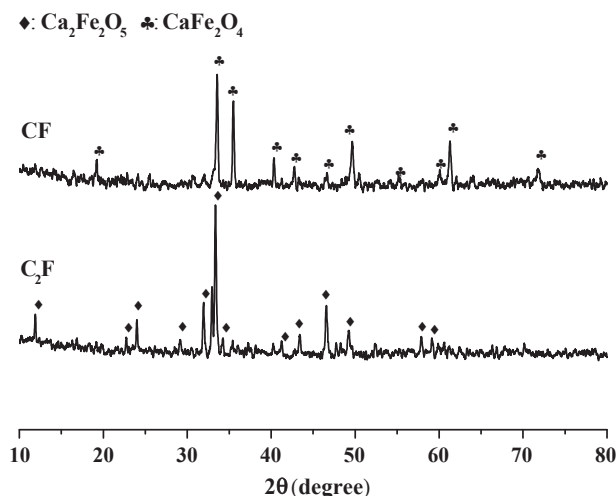


Fig. 1. XRD patterns of fresh oxygen carriers.

The fixed-bed reactor setup is shown in Fig. 2. The reactor is a U-type tube made by quartz, with inner diameter of 14 mm and heated by an electric furnace, whose temperature is controlled by a K-type thermocouple and PID controller. Argon as purge gas is controlled at 50 ml/min by a mass flow controller, and steam as gasification agent is derived from deionized water, whose flow is controlled by a constant flow pump. The volume of gaseous products is measured by drainage method. The gaseous products from reactor are purged by argon and collected in the left tank, which is initially full filled with saturated NaCl solution, and its volume is obtained by measuring the NaCl solution volume in a glass graduated cylinder. Before each test, the furnace temperature is required to keep at the target values. At first, 0.5 g *Chlorella* and various oxygen carriers are mixed and filled in a basket made by copper mesh, then hanged it at the top of the U-type reactor. Subsequently, place the U-type reactor into the electric furnace and turn on the constant flow pump for 10 min, in order to remove air, and maintain a stable steam partial pressure and stable temperature in reactor. After 10 min, let the samples drop into the constant-temperature region and begin to collect the gas products. The gasification reaction lasts for 30 min. Then turn off the pump and remove the reactor from furnace, and let the samples cool at inert atmosphere. The gaseous products collected in the left tank is transferred into a gas sampling bag by the NaCl solution in the right tank through switching the valves. In thermogravimetric and fixed-bed tests, the ratio of oxygen carrier to biomass is consistent with the stoichiometric oxygen supply to produce CO, with the fully reduction to metallic Fe. For example, the molar ratio of $\text{Fe}_2\text{O}_3/\text{C}$ is 1/3, corresponding to the stoichiometric reaction $\text{Fe}_2\text{O}_3 + \text{C} = 2\text{Fe} + 3\text{CO}$.

The gas products collected in sampling bag were analyzed by gas chromatograph (Agilent Gas Chromatograph, 7890B) with TCD (Thermal Conductivity Detector), and the results were quantified by standard sample gas. The phase of solid residue was analyzed by XRD (X-ray diffraction, X'pert3 Powder) with the scanning range of 10–80°, and the surface morphology was observed in SEM (scan electron microscope, LEO 1530VP) with 5000 times.

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