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Interaction between biomass ash and iron ore oxygen carrier during chemical looping combustion

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HIGHLIGHTS

- Interaction between biomass ash and iron ore oxygen carrier was carried out.
- SiO_2-rich ash caused particle sintering and reactivity decrease of iron ore.
- K_2O-rich ash promoted the reduction reactivity of oxygen carrier.
- The enhanced reactivity most likely due to the K–Fe–O compound.

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ABSTRACT

Chemical looping combustion (CLC) presents a new method to increase the utilization efficiency of biomass. Due to the existence of ash in biomass, the interaction between biomass ash and oxygen carrier is a significant concern during the biomass CLC process. Three typical biomass ashes were added into an iron ore oxygen carrier, and their effects on the performance of oxygen carrier were carried out during the CLC process. The effects of some key variables on the performance of oxygen carrier were evaluated, including biomass ash type, ash addition ratio (0–20%) and cycle number. The results indicate that fuel conversion was significantly influenced by the addition of biomass ash. The addition of SiO_2-rich wheat straw ash (WSA) was likely to be converted into potassium silicates, and it caused serious particle sintering of oxygen carrier. It led to a reactivity decrease of oxygen carrier and its reduction extent was slighter. In contrast, fuel conversion was always promoted by the addition of corn stalk ash (CSA) and rape stalk ash (RSA), i.e., K_2O-rich ashes with a relatively lower SiO_2 content. A slight reactivity decrease was also observed at a high CSA ratio (20%). Cycle experiments indicate that the iron ore activated by CSA and RSA has a relatively stable reactivity promotion. Finally, possible mechanisms for the enhanced performance of iron ore by biomass ash were explored.

1. Introduction

In view of the increasing concern about the global warming, biomass conversion technologies have received intensive attention because of the minimized CO_2 emission. The utilization of biomass mainly includes biochemical and thermochemical methods [1]. The biochemical method involves a large consumption of water [2] and a stringent requirement for the feedstock. The thermochemical treatments, particularly include combustion, gasification and pyrolysis, have been demonstrated to produce fuels and chemical from biomass [3]. All these traditional technologies present an intensive energy penalty and therefore, the utilization efficiency of biomass decreases.

Chemical looping combustion (CLC) is proposed as a novel technology increasing the combustion efficiency with the inherent separation of CO_2 with low energy penalty [4,5]. Principally, the process contains the cycle of reduction and oxidation of oxygen carrier in two separated reactors, i.e., air reactor and fuel reactor to transport oxygen from air to fuel, avoiding the contact between them. The reduced oxygen carrier is first oxidized in the air reactor to obtain molecular oxygen from the air and then, the oxidized oxygen carrier is reduced in the fuel reactor to provide lattice oxygen for the fuel. Based on the two-step reaction, this novel process could reduce the exergy loss [6]. The CO_2-rich flue gas from the fuel

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reactor is not diluted by N_2, favoring the subsequent utilization or capture of CO_2.

For the solid fuel CLC process, the in situ gasification chemical looping combustion (IG-CLC) is one of the most accepted routes [7]. The gasification process is recognized as the rate-limiting step in the process, especially when a Fe-based oxygen carrier was used [8]. Therefore, highly reactive solid fuels, e.g., bituminous coal and biomass are proposed for the IG-CLC.

The biomass-fueled chemical looping process has at least three advantages: (1) higher utilization efficiency of biomass in comparison with traditional gasification or combustion; (2) negative CO_2 emission (3) lower NO emission in comparison with that in air-fired process. Biomass has been investigated in different chemical looping processes. Research team of Shen investigated the biomass fueled [9] and biomass/coal fueled [10] CLC process in a continuous reactor using $NiO/NiAl_2O_4$ and iron ore oxygen carriers, respectively, and the biomass shows a high reactivity. Mendlara et al. [11] investigated the biomass CLC process using calcium manganate as an oxygen carrier in a 10 kW pilot. GarcÍa-labiano and Adánez [12] and Adánez-Rubio et al. [13] focused on the biomass process using chemical looping with oxygen uncoupling (CLOU) technology. Furthermore, the biomass chemical looping technology has also been extended to chemical looping gasification (CLG) [14,15] and chemical looping reforming (CLR) [16,17].

Due to the existence of ash in the solid fuels, the interaction between ash and oxygen carrier is a significant issue in the IG-CLC process. The thermodynamic calculation indicates that reactions between the ash and the oxygen carrier could occur at a high temperature with a low rate [18]. Also, the coal ash deposition on the oxygen carrier and the interaction between them have been demonstrated with a Fe-based oxygen carrier during the CLC process [19–22]. However, the ash deposition on the oxygen carrier or some eutectic with low-melting point could cause reactivity decrease. Furthermore, some ashes with high content of Fe_2O_3, $CaSO_4$ could enhance the reactivity of oxygen carrier because these materials could also be used as an oxygen carrier [22].

In view of the composition differences between the biomass ash and the coal ash, the interaction between biomass ash and oxygen carrier would also be different from that between coal ash and oxygen carrier. For example, the biomass ash often contains a large amount of potassium species, depending on the biomass type. The low melting point of the biomass ash because of the alkali metal, e.g., K and Na, may cause the particle sintering and the subsequent defluidization of the bed material. Furthermore, the K-containing species would be heated and released in gas phase, which would be captured and react with the oxygen carrier. Gu et al. [10] also confirmed the transport of biomass ash compositions into the oxygen carrier during the coal/biomass fueled CLC process. Therefore, the performance of oxygen carrier could be affected due to the interaction between the biomass and the oxygen carrier. This interesting issue motivated the present investigation.

The present article focused on the interaction between three typical biomass ashes and iron ore oxygen carrier during chemical looping combustion. The effect of biomass ashes addition, the ash ratio and the reaction cycle on the fuel conversion were evaluated. BET, SEM–EDX, XRD and XRF were used to characterize the oxygen carrier. The results are important to the development of biomass CLC process.

2. Experimental section

2.1. Preparation of oxygen carrier

An Australia iron ore was selected as the oxygen carrier material. To obtain the maximum oxidation state and to improve the mechanical strength, the iron ore was initially calcined in air atmosphere for 3 h. According to the XRF analysis (ARL-9800), the iron ore after calcinations was composed of 83.21% Fe_2O_3, 7.06% SiO_2 and 5.37% Al_2O_3, as is shown in Table 1. The particles of iron ore were crushed and double sieved to a size range of 0.3–0.45 mm.

2.2. Preparation of biomass ash

In the biomass CLC process, the gasification ash would be produced in the fuel reactor and then reacted with oxygen carrier. However, combustion ash was used because the main compositions of combustion ash are similar to those of the gasification ash [23]. The biomass ash was prepared by calcining the biomass in a muffle oven at 600 °C for 2 h. Three typical Chinese biomasses, i.e., corn stalk, rape stalk and wheat straw were selected, and the corresponding ashes were corn stalk ash (CSA), rape stalk ash (RSA) and wheat straw ash (WSA), respectively. The XRF results in Table 2 display the compositions of these three ashes. The main component of CSA is K_2O, with less content of SiO_2, CaO and Cl. RSA mainly consists of K_2O, CaO and less content of Cl. In contrast, WSA has a much higher SiO_2 content but lower contents of K_2O and CaO.

2.3. Experimental setup and procedure

The effect of the addition of biomass ash into oxygen carrier on the interaction between them was evaluated in the CLC process. Although the contact efficiency is low, the reactions between ash and oxygen carrier would occur and their effect could be enhanced during the continuous operation period in a biomass CLC process. Moreover, the fluidization of biomass ash could not be well regulated in a fluidized bed of oxygen carrier. Therefore, a lab-scaled fixed bed was employed to evaluate the interaction between ash and oxygen carrier, as is shown in Fig. 1. The system consists of inlet gas controller, reaction chamber and gas analyzer, as is described in previous work [24].

In each case, a batch sample of 40 g oxygen carrier particles was initially mixed with biomass ash at a fixed ratio. To eliminate the interference effect of carbon in biomass ash, the mixture was then added into the reactor and heated in 5% O_2/N_2 at 1000 ml/min to reaction temperature. When the char in the ash was completely converted, the gas was switched to pure N_2 (1 L/min) to purge the reaction chamber for 10 min. Afterwards, the purging gas was switched to the reaction gas, i.e., 10% CO/N_2 at 500 ml/min. Simultaneously, the reduction of oxygen carrier started and maintained for 80 min. In the cycle experiments, a mixture of 7% O_2/N_2 at 1000 ml/min was used in the oxidation process. The N_2 purge duration between the reduction and oxidation process maintained for 10 min. When the experiment finished, the reactor was cooled down to room temperature in N_2 atmosphere. The particles of the reduced oxygen carrier were sampled, and XRD, BET, SEM–EDX and XRF were employed to characterize the surface structure and the composition of oxygen carrier.

Table 1
Chemical composition of the Australian iron ore after calcinations.

Composition	Content (wt.%)
Fe_2O_3	83.21
SiO_2	7.06
Al_2O_3	5.37
MgO	1.9
CaO	0.236
P_2O_5	0.38
Na_2O	1.4
SO_3	0.213
Others	0.231