Chemical looping combustion of biomass using metal ferrites as oxygen carriers

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HIGHLIGHTS

- $CuFe_2O_4$ has the highest reactivity and a lower initial reaction temperature in biomass CLC.
- $NiFe_2O_4$ has the highest catalytic reactivity for tar cracking and reforming.
- $CoFe_2O_4$ is easily reduced to FeO and three metal ferrites can be regenerated completely after five redox cycles.
- Both $CuFe_2O_4$ and $CoFe_2O_4$ have remarkable thermal stability.
- The reactivity of $NiFe_2O_4$ decreases significantly after five redox cycles due to sintering.

ARTICLE INFO

ABSTRACT

The evaluation of chemical looping combustion (CLC) for CO_2 capture was conducted via a thermogravimetric analyzer (TGA) and a laboratory-scale fluidized bed using pine sawdust (PS) as fuel and metal ferrites, MFe_2O_4 (M = Cu, Ni and Co), as oxygen carriers. Metal ferrites were prepared by sol-gel method. The fresh, reduced and after five redox cycles oxygen carriers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and accelerated surface area porosimetry. Thermodynamic simulation was performed using software HSC Chemistry 6.0. The TGA results indicated that $CuFe_2O_4$ shows a lower initial reaction temperature, and $CoFe_2O_4$ has a faster oxygen uptake rate. Both carbon conversion (x_c) and carbon capture efficiency (η_{CO2}) increased with temperature. The maximum values of x_c and η_{CO2} were 96.86% and 95.48%, 95.45% and 94.25%, and 95.17% and 94.04% for $CuFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$ at 900 °C, respectively. The $CuFe_2O_4$ shows higher reaction reactivity, while $NiFe_2O_4$ has a higher catalytic activity for decomposition of tar in fluidized bed tests. The XRD results show $CoFe_2O_4$ is more readily reduced to FeO, which agreed with the results of thermodynamic simulation, and three metal ferrites can be regenerated completely after five cycles. The values of x_c and η_{CO2} remained high for both $CuFe_2O_4$ and $CoFe_2O_4$, while a significant decrease in x_c and η_{CO2} for $NiFe_2O_4$ was observed after five cycles due to significant sintering. Both $CuFe_2O_4$ and $CoFe_2O_4$ are more applicable as oxygen carriers in biomass CLC compared with $NiFe_2O_4$.

1. Introduction

The concerns of global warming and climate change have resulted in efforts to reduce carbon dioxide (CO_2) emissions by adopting carbon capture and storage (CCS) technologies or increasing the utilization of renewable energies [1]. The purpose of CCS technologies is to capture and store pure streams of CO_2 from the atmosphere [2]. Currently, in order to capture CO_2, there are three main approaches: post-combustion, oxy-fuel combustion, and pre-combustion [3]. Although these methods can reduce the CO_2 emissions effectively, they typically involve large-scale gas separations, which require significant energy and economic investments. The chemical looping combustion (CLC) has been considered a promising technology for low-cost CO_2 emissions reduction [4]. In general, the CLC process consists of an air reactor (AR) and a fuel reactor (FR). An oxygen carrier is utilized to transfer

oxygen from AR to FR. Thus, the CLC process does not require a gas separation unit because the air and fuel are never mixed.

In recent years, a lot of work has been done concerning CLC with gaseous fuels [5–7]. More recently, CLC has shown great potential for better utilizing solid fuels, such as coal [8], petroleum coke [9], sewage sludge [10], and biomass [11], because of abundant solid fuel resources.

As a renewable and carbon neutral resource, biomass is expected to significantly contribute to global energy and environmental demands [12]. What is noteworthy is that carbon emissions in CLC will be negative when replacing fossil fuels with biomass because the generated CO_2 is previously absorbed by photosynthesis. Furthermore, biomass CLC has additional advantages, such as higher carbon conversion efficiency [13,14] as well as lower NO_x [15] and SO_2 emissions [16].

Oxygen carrier is the backbone of the CLC process. Ideally, the oxygen carrier should have high transport capacity, reactivity, and thermal stability, with low production costs and no environmental impacts [17]. Transition single metal oxides, such as Cu, Ni, Co, Mn and Fe, have been widely investigated in CLC despite some disadvantages and inability to fully meet the requirements of CLC. More specifically, CuO readily agglomerates due to its lower melting point; NiO and CoO have adverse environmental effects and are expensive; and MnO and Fe_2O_3 have poor oxygen transfer capacity and low reactivity. In order to find a perfect oxygen carrier, an increasing number of studies have focused on combined or mixed-metal oxides. For example, Fe_2O_3 has been widely used in combined or mixed-metal oxide oxygen carrier systems due to its low cost, environmental friendliness and abundance. Metal ferrites, MFe_2O_4, yielded favorable results in CLC when using combined or mixed Fe_2O_3 and another metal oxide as oxygen carrier.

Niu et al. [18] studied Cu-Fe oxygen carrier for CLC using sewage sludge as fuel. They found that the presence of $CuFe_2O_4$ enhanced the performance of Fe_2O_3 and improved the thermal stability of CuO. Similar results were published by Wang et al. [19]. Bhavsar et al. [20] investigated the performance of bimetallic oxygen carriers in thermogravimetric analyzer (TGA) and a fixed-reactor using H_2 and CH_4 as fuels. They concluded that the reactivity of $NiFe_2O_4$ was higher than Fe_2O_3 but lower than NiO. Kuo et al. [21] also confirmed that $NiFe_2O_4$ withstood higher cycle numbers and had greater stability than those of NiO and Fe_2O_3 using CH_4 as fuel. The research results of Huang et al. [22] showed that the presence of $NiFe_2O_4$ improved the reaction reactivity of the oxygen carrier with biochar. Wang et al. [23] indicated that $CoFe_2O_4$ exhibited higher reactivity than CoO and Fe_2O_3 in TGA using coal as fuel. Evdou et al. [24] demonstrated that $CuFe_2O_4$ showed high reactivity towards CH_4 while $CoFe_2O_4$ exhibited excellent thermal stability.

In general, metal ferrites with a spinel structure have high thermal stability and magnetic properties [25]. High thermal stability is favored as it increases the lifetime of the oxygen carrier, while magnetic properties of spinel metal ferrites could allow for the separation of the oxygen carrier from ash via magnetic separation technique. Therefore, metal ferrites exhibit great potential as oxygen carriers in solid CLC. To date, metal ferrites have been predominantly used as catalysts [26–29], and to authors' knowledge, the utilization of metal ferrites in biomass CLC remains few.

In this study, three metal ferrites, MFe_2O_4 (M = Cu, Ni and Co), were evaluated in CLC using pine sawdust (PS) as fuel. TGA was used to analyze the reaction reactivity of PS with MFe_2O_4. The effects of temperature on carbon conversion (x_c), CO_2 capture efficiency (η_{CO2}) and tar yield were measured in fluidized bed reactor. Thermodynamic simulation was performed to elucidate the conversion of MFe_2O_4 (M = Cu, Ni and Co) during reduction reaction. The metal ferrites were investigated by a series of characterization techniques including XRD, SEM and BET. Finally, cyclic

performances of the metal ferrites were also evaluated via five redox cycle tests.

2. Methods

2.1. Materials

Raw pine sawdust (PS) was collected from a wood factory in Bijie City, Guizhou Province, China. The pine sawdust was naturally dried for seven days, then crushed and sieved to 75–250 μm for use. The ultimate and proximate analysis of PS are given in Table 1.

2.2. Synthesis of oxygen carrier

Three metal ferrites, MFe_2O_4 (M = Cu, Ni and Co), were prepared by the sol-gel combustion method [30]. First, stoichiometric amounts of $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $C_6H_8O_7 \cdot H_2O$ (citric acid) were dissolved in deionized water. Metal nitrates and the citric acid solution were mixed at a 1:1 M ratio of total metal cation (Fe^{3+} and M^{2+}) to citric acid. The citric acid was used as a chelating/fuel agent. Next, the precursor mixture solution was slowly stirred at 80 °C for 6 h, and the sol-gel was obtained. After that, the sol-gel was dried in a dryer at 105 °C for 12 h and ignited in the preheated muffle furnace at 650 °C for 10 min, followed by calcination at 900 °C for 6 h in air. Finally, metal ferrites samples were cooled, ground, and sieved to 75–250 μm for use.

2.3. Thermogravimetric analysis

Thermogravimetric analysis of the mixture of PS and oxygen carrier was performed under atmospheric pressure by using a TGA/DTA analyzer (SDT Q600, TA instruments). The PS and metal ferrite were homogenized via mortar and pestle with a mass ratio of 1:15 biomass to oxygen carrier. Then, approximately 15 mg of mixture was loaded in TGA and heated to 900 °C at 30 °C/min in nitrogen atmosphere with a flow rate of 100 ml/min. Once the temperature reached 900 °C, the samples were held this temperature for 15 min. Finally, the nitrogen flow was switched to air flow at 100 ml/min for 15 min in order to oxidize the reduced oxygen carrier.

2.4. Fluidized bed tests

CLC experiments with PS were conducted in a fluidized bed reaction system, as shown in Fig. 1. The reaction system consisted of a biomass feeder, carrier gas unit, fluidized bed reactor, cyclone separator, condenser, gas flow meter and gas analyzer. A stainless steel tube (i.d. = 26 mm, length = 1000 mm) was used as the fluidized bed reactor. A porous distributor plate was placed in the reactor 600 mm from the top. A K-type thermocouple was used to measure the temperature of the reactor.

At the start of each run, 2.0 g of PS feedstock was load in the biomass feeder (PEF-90AL, Sanki Co. LTD, Japan). The feeding rate was set to 0.20 g/min by a digital controller. A sample of 30.0 g of oxygen carrier particles was loaded on the porous distributor plate in the reactor. Then, the fluidized bed reactor was heated from room temperature to the desired temperature by an electrical furnace with a ramp rate of 10 °C/min in air (600 ml/min). After achieving the desired temperature, the fluidized bed reactor was flushed using nitrogen (99.99%, 600 ml/min) for 5 min to ensure an inert atmosphere. Subsequently, the biomass feeder was turned on, and the PS (2.0 g) was continuously fed into the fluidized bed reactor at a rate of 0.20 g/min. During the feeding period, a nitrogen flow (about 80 ml/min) was used as balance which was intro-