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Combustion performance of sewage sludge in chemical looping combustion with bimetallic Cu–Fe oxygen carrier

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HIGHLIGHTS

- Bimetallic Cu–Fe oxides show better performance than hematite for sludge CLC.
- The material with the highest Cu fraction gave the highest sludge conversion.
- NO concentration is below 0.4% of the total nitrogen in sewage sludge during CLC.
- Possible mechanisms for NO emission are presented.

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ABSTRACT

Sewage sludge is the by-product from the wastewater treatment plant. It can be utilized by chemical looping combustion (CLC) for energy conversion and phosphorus recovery. Hematite is an attractive material for CLC due to its abundance, low cost and environmental compatibility. However, hematite shows low reactivity for CLC of solid fuel. The reactivity of hematite can be improved by synthesizing with CuO. This work is to evaluate the combustion performance and NO emission in CLC of sewage sludge in a batch fluidized-bed reactor. The oxygen carrier materials consisted of a mixture of hematite and CuO, which were synthesized using mechanical mixing method. The effect of reduction temperature and the CuO/hematite mass ratio on combustion efficiency and NO emission were investigated. The results show that the mixture of CuO and hematite can give significant improvement in sludge conversion in comparison to only hematite. The oxygen carrier which consisted of 40% CuO and 60% hematite gave the highest sludge conversion with or without steam in fluidizing gas. Most of the nitrogen in sewage sludge was released as N_2 during the reduction period. About 0.4% of N in sewage sludge was converted to NO using the materials containing 10% CuO and 90% hematite. The conversion of fuel-N to NO decreased with the mass ratio of CuO/(CuO + hematite) from 10% to 40%. Additionally, the structural and morphological stability of the oxygen carriers have been examined. The formation of $CuFe_2O_4$ could improve both the reactivity of Fe_2O_3 species through synergetic effect and the physical stability of CuO during redox reactions. Therefore, mixing hematite with CuO could be suitable for CLC of sewage sludge.

1. Introduction

Sewage sludge is the by-product from the wastewater treatment plant [1]. It is a complex mixture of organic and inorganic materials and contains a wide variety of substances and microorganisms in suspended or dissolved form [2]. Some ingredients in the sludge such as phosphorus and organic matter are valuable components. With the growing global urbanization in recent years, the quantity of sewage sludge around the world has increased rapidly [3]. The increasingly stringent sludge reuse/disposal regulations and increasing public concerns demand the reliable and lasting sludge management strategies [4]. Due to the organic nature of sewage sludge, thermochemical process is one of the most attractive methods to produce energy and valuable products from sewage sludge. Chemical looping combustion (CLC) is an innovative combustion technology that could intrinsically separate CO_2 within the process. CLC offers a promising solution for sludge treatment with the target for both energy reuse and phosphorus recovery [5,6].

The CLC system consists of two reactors, a fuel reactor and an air reactor with the oxygen carrier continuously circulating between them. In the fuel reactor, the oxygen carrier in a higher state is reduced by the fuel, which in turn is oxidized to CO_2 and

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H_2O. Subsequently, the reduced oxygen carrier is oxidized to its initial state in the air reactor [7]. In this way, the fuel reactor effluent is comprised of CO_2 and H_2O, therefore a concentrated stream of CO_2 suitable for sequestration can be obtained simply by water condensation. If a solid fuel is used, the main approach is in situ gasification chemical looping combustion (iG-CLC). In this process, the solid fuel is physically mixed with the oxygen carrier in the fuel reactor and gasified by CO_2 or steam. Then the gaseous compounds (volatiles and gasification products) react with the oxygen carrier.

The selection of efficient oxygen carriers is an essential component of the CLC process. The oxygen carrier should exhibit sufficient oxygen transport capacity, high reactivity towards both fuel and air. It should also be mechanically durable, inexpensive and environment-benign [7]. Additionally, it should present resistance to attrition to minimize losses of elutriated solids. Both nickel oxide and hematite have been investigated as oxygen carrier for CLC of sewage sludge [5,6]. Although higher carbon capture efficiency is obtained, the main drawback is the lower CO_2 capture efficiency. When solid fuel is used in CLC process, the CO_2 capture efficiency will be reduced if char particles enter the air reactor with the oxygen carrier stream [8]. Fortunately, our previous work revealed that there were no char particles by-passed to air reactor during CLC of sewage sludge using hematite as oxygen carrier in a 1 kW continuous unit [6]. Thus, it is not necessary to deploy a carbon stripper to separate the char from oxygen carrier. Sewage sludge contains a high volatile content. It may leads to insufficient carrier stability and poor redox kinetics if a low reactivity oxygen carrier is selected.

Among the various metal oxides (CuO, NiO, Fe_2O_3, etc.) tested as oxygen carriers for CLC, iron oxide remains the most favorable due to its abundance, low cost and environmental compatibility [9]. Hematite as a kind of iron oxides has commonly been used as an oxygen carrier [10–12]. However, its low fuel conversion, weak redox characteristics, and low oxygen transport capacity (because of thermodynamic limitation) constitute significant drawbacks. It is possible to resolve the shortcomings by combining hematite with a more reactive metal, such as Cu, Mn and Ni [9,13–15]. The mixed oxides show a good balance between cost, toxicity and reactivity for CLC. One interesting category among these is the combined Cu–Fe oxide as oxygen carrier. The combined Cu–Fe oxygen carriers have low cost, high reactivity and favorable environmental and thermodynamic properties. Thus, the Cu–Fe oxide is significantly relevant for CLC applications.

The phase diagram of CuO–Fe_2O_3 bimetallic system is shown in Fig. 1 [16]. It can be seen that a solid solution of CuO–Fe_2O_3 is formed at the temperature above 761 K. If the mole concentration of Fe_2O_3 is higher than CuO, Fe_2O_3 and $CuFe_2O_4$ can coexist. Similarly, CuO can be observed when CuO concentration is higher than Fe_2O_3.

Several combined Cu–Fe oxides have been examined as oxygen carriers in both CLC and CLOU process [17,18]. Compared with the single metal oxygen carriers, the combined Cu–Fe oxides displayed high reaction rate, better solid conversion, greater oxygen usage and improved physical stability [16]. Additionally, Cu–Fe mixed oxides has a higher catalytic activity for CO oxidation even at low temperature [19]. The addition of Cu into iron oxide promoted the structure and enhanced the catalytic activity through a synergistic effect. The results by Yang et al. indicate that 6% Cu (6CuHem) has better reactivity with the gasification products and can accelerate the gasification rate of anthracite char [17].

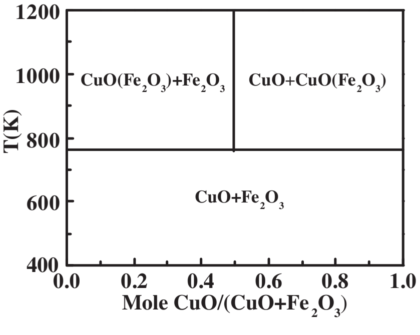

Fig. 1. Thermodynamic analysis of interaction between CuO–Fe_2O_3 systems.

It is a crucial technical obstacle that high nitrogen content in sewage sludge could cause a high NO_x emission during combustion process. The high NO_x emissions from sludge combustion are not only because of their high nitrogen content but also the high contents of metal oxides in the ash [20,21].

Shimizu et al. [20,21] investigated the emissions of NO_x and N_2O during combustion of dried sewage sludge in both bubbling fluidized bed combustor (BFBC) and circulating fluidized bed combustor (CFBC). The results show that the increase in NO_x with the sludge ash accumulation in the reactor is less for the CFBC than the BFBC. It can be due to the higher attrition rate of sludge ash in CFBC resulting from the higher gas velocity. The combustion process in the CFBC presents a high concentration of NO_x (400–600 mg/Nm^3) at 1123 K. To reduce NO_x emission, a combined gasification and incineration process for the disposal of sewage sludge was proposed [22]. The results indicate that the conversion of fuel-N to NO_x is 1 ± 0.04%. Even with the combined gasification and incineration process, high NO_x concentrations are emitted in sewage sludge air-combustion process. However, during CLC of coal in a 1 kW unit, N_2 is the sole product of fuel-N conversion in the fuel reactor using either hematite or Ni-based oxide as oxygen carrier [12,23]. Thus, it can be speculated that both the inlet fuels and the combustion conditions have a great influence on the NO emission [24]. As a result, the viability of sewage sludge for CLC, to a large extent, will be determined by the NO emission level.

The objective of this work is to explore the combustion performance and NO emission in CLC of sewage sludge using bimetallic Cu–Fe oxide as oxygen carrier. The experiment was conducted in a batch fluidized-bed reactor. The effects of operating conditions including reduction temperature and the CuO/hematite mass ratio on the combustion characteristics were investigated. The combustion characteristics such as carbon conversion and NO emission were analyzed. SEM and XRD analyses were also conducted to reveal the reaction mechanism of during sewage sludge in CLC.

2. Experimental

2.1. Manufacture and characterization of oxygen carriers

The oxygen carriers used in this work were particles with a CuO:hematite mass ratio of 10:90, 20:80, 30:70 and 40:60. The particles were manufactured by mechanical mixing method in Southeast University. Hematite (Nanjing Steel Manufacturing Company, <0.05 mm) and CuO (Jiangsu Teho Metal Industrial Company, >99%, <0.05 mm) were mixed thoroughly and deionized water was added to the mixture to obtain a paste. The paste was then extrusion molding in a tablet machine and dried at room temperature for 24 h. The dried particles were crushed and sieved to 0.2–0.3 mm. After this, the samples were calcined at 980 °C for 3 h in a muffle oven to completely oxidize and increase the mechanical strength. The elemental compositions of the synthesized oxygen carrier were performed by X-ray fluorescence (XRF), as summarized in Table 1. Here, Cu denotes CuO and the digits after Cu represents the mass fraction of CuO in the sample. Further, Fe denotes hematite and the following digits show the mass fraction of hematite. Fig. 2 shows the size distribution of the fresh oxygen carrier using Cu20Fe80 as an example.