

In situ gasification chemical looping combustion of a coal using the binary oxygen carrier natural anhydrite ore and natural iron ore



Min Zheng^{a,*}, Laihong Shen^b, Xiaoqiong Feng^b

^a Engineering Research Center of Metallurgical Energy Conservation and Emission Reduction Ministry of Education, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kun Ming 650093, China

^b Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, China

ARTICLE INFO

Article history:

Received 19 December 2013

Accepted 29 March 2014

Available online 19 April 2014

Keywords:

Chemical-looping combustion

CO₂ separation

Coal

CaSO₄ oxygen carrier

Fe₂O₃ oxygen carrier

SO₂ suppression

ABSTRACT

CaSO₄ is an attractive oxygen carrier for Chemical-looping combustion (CLC), because of its high oxygen capacity and low price. But the utilization of CaSO₄ oxygen carrier suffers the problems of low reactivity, deactivation caused by sulfur loss and the incomplete fuel conversion due to the thermodynamic limitations. To improve the stability and reactivity of CaSO₄ oxygen carrier, a small amount of natural iron ore were added in. The kinetic behavior and thermodynamics of the reduction of the binary oxygen carrier by coal under steam atmosphere were investigated. The results show that Fe₂O₃ improves the performance of coal gasification and the subsequent conversion of coal syngas to CO₂ and H₂O. Besides, the addition of Fe₂O₃ reduces the chance of CaSO₄ reduction to CaO by coal syngas, and the oxygen transfer capacity of CaSO₄ is maintained. The optimal reaction conditions in fuel reactor are shifted from 950 °C without Fe₂O₃ to 900 °C with 7% Fe₂O₃. And the decreases in CO, SO₂ and H₂S environmental factors can be well up to 81.48%, 76.35% and 100%, respectively. Meanwhile, the CO₂ concentration in the dry gas products increases from 81.63% up to 95.35%.

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1. Introduction

Chemical-looping combustion (CLC) has been suggested as a promising combustion technology with inherent CO₂ separation [1,2]. As an alternative to conventional combustion technique, the CLC is an indirect combustion by use of an oxygen carrier. It typically consists of two separate reactors: an air reactor and a fuel reactor [1]. An oxygen carrier, which circulates between the two reactors, transfers oxygen from air to fuel. In the fuel reactor, the fuel (C_xH_y) is oxidized by oxygen carrier to CO₂ and H₂O. Then the reduced oxygen carrier is transferred to air reactor, where the reduced oxygen carrier is oxidized by air and oxygen is transferred from air to the oxygen carrier. In this way, the fuel and air are never mixed during the CLC process. The stream from the air reactor is composed of N₂ and residual O₂, and the stream from the fuel reactor almost consists of CO₂ and H₂O, free of nitrogen

from the air. After the water condensation, almost pure CO₂ can be obtained without costly separation process.

The metal oxides are the main focus of oxygen carriers, because of their high reactivity [2–15]. However, for in situ gasification of a coal and CO₂ separation using CLC with an oxygen carrier, the utilization of the metal oxides may be limited because of high cost, sulfur poisoning, bad environmental sound, and the difficulty in separation metal oxides from coal ash. Besides, there was a loss in metal oxygen carriers, caused by the low-melting-point inert ingredients generated from the reaction of the metal oxides with coal ash [13,16–19].

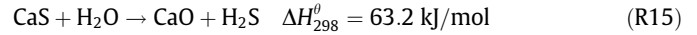
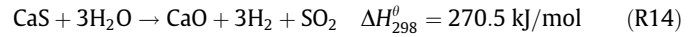
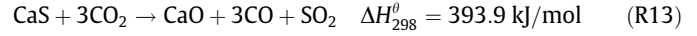
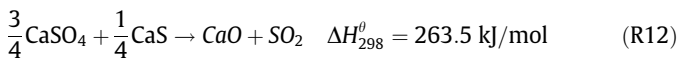
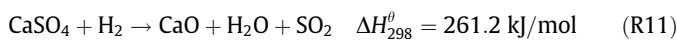
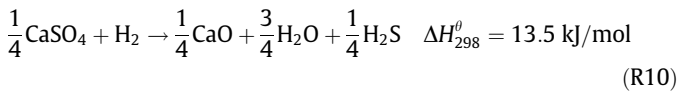
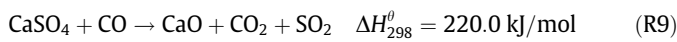
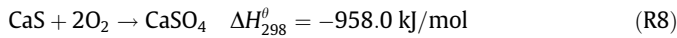
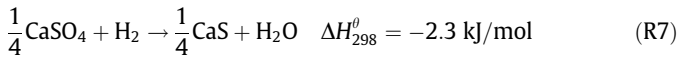
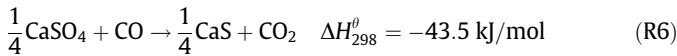
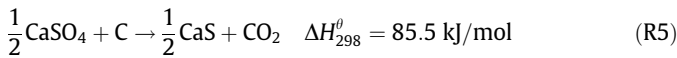
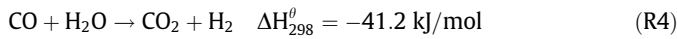
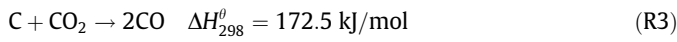
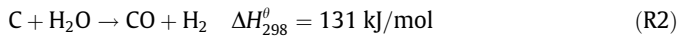
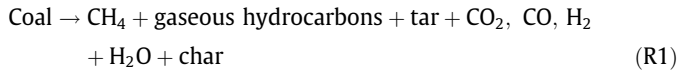
Recently, the inexpensive oxygen carrier natural ore, such as hematite, ilmenite and perovskite attracted considerable attention for future commercial application [20–36]. The Fe₂O₃-based oxygen carrier has resistance to H₂S. For high-sulfur fuels, the oxygen transfer capacity was not affected by H₂S [19]. However, the oxygen transfer capacity of Fe₂O₃-based oxygen carrier is low.

CaSO₄ is becoming an attractive oxygen carrier for the commercial application of CLC because of its easy availability, low price and high oxygen transfer capacity. A few studies have been performed on CaSO₄ oxygen carrier, and many promising results have been obtained [37–44]. Alstom has built a 3 MW_{th} CaSO₄ pilot system for the validation of chemical looping at its Windsor Ct. site [45], and comprehensive data are expected to be obtained for further

* Corresponding author. Address: Engineering Research Center of Metallurgical Energy Conservation and Emission Reduction Ministry of Education, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Wen Chang Lu 68#, Kun Ming 650093, Yunnan, China. Tel.: +86 871 65153405; fax: +86 871 65178347.

E-mail addresses: mzheng.seu@gmail.com, zhengmin1634@163.com (M. Zheng).

evaluation. Fig. 1 shows a schematic of a CLC process of coal using CaSO_4 oxygen carrier. To improve the solid-solid contact between the coal and the oxygen carrier, a small amount of steam is injected in the fuel reactor. Coal is pyrolyzed and gasified with steam into mainly syngas, and then the syngas is oxidized by CaSO_4 to CO_2 and H_2O ((R1)–(R7)); while CaSO_4 is reduced by fuel to CaS , as present in (R5)–(R7). Then in air reactor, CaS is oxidized by air to CaSO_4 (R8). Thus, the oxygen is transferred from air to fuel. Nevertheless, there are thermodynamic limitations for CaSO_4 oxygen carrier that caused the incomplete conversion of fuel, and the loss in CaSO_4 oxygen carrier due to the generation of gas sulfides and CaO . In fuel reactor, the release of gas sulfides are primarily ascribed to the side reactions of CaSO_4 decompositions via reactions (R10)–(R12), and CaS decompositions with CO_2 and H_2O via reactions (R13)–(R15). The sulfur release may be a limit for the use of CaSO_4 oxygen carrier.



With a decrease in reaction temperature, the sulfur release from CaSO_4 can be partially eliminated [44], while the conversion efficiency of coal to CO_2 and H_2O dropped. To maintain the formation efficiency of CO_2 at low temperatures, a small amount of active components were added in CaSO_4 oxygen carrier. In the literature [46–48], the synthesized oxygen carriers were prepared by chemical impregnation with the NiO and Fe_2O_3 additives. The reactivity of the synthesized oxygen carriers were tested by the use of gaseous fuels and coal char. As a whole, the application of the synthesized oxygen carriers enhanced the CO_2 generation, and suppressed the sulfur release. Nevertheless, the reaction mechanism was still unknown, and some low-melting-point inert ingredients, such as Ni_3S_2 , $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_3\text{Fe}_4\text{S}_3\text{O}_6$, were generated. Efforts should be taken to improve the reactivity and stability of CaSO_4 -based oxygen carrier.

The binary mixture of nature anhydrite ore and natural iron ore was proposed as oxygen carrier for CLC of coal in this study. Compared with CaSO_4 oxygen carrier, Fe_2O_3 oxygen carrier has higher reactivity but lower oxygen transfer capacity [41]. And the oxygen transfer capacity of Fe_2O_3 was not affected by H_2S species [19]. Thus, CaSO_4 and Fe_2O_3 are mutually complementary in oxygen transferring. The bi-oxygen carrier, composed largely of nature anhydrite ore and a very small proportion of natural iron ore, was prepared through mechanical mixing. In the bi-oxygen carrier, the oxygen is supposed to be transferred by the chemical looping of CaSO_4 to CaS and Fe_2O_3 to Fe_3O_4 . The Fe_2O_3 fraction in the bi-oxygen carrier is defined as the ratio of the oxygen transferred by the chemical looping of Fe_2O_3 – Fe_3O_4 to the whole. The investigation was conducted in the condition that the oxygen transfer capacity of the bi-oxygen carrier was kept constant.

In CLC of coal with CaSO_4 oxygen carrier, both steam and CO_2 are optional intermediate for coal gasification. Between the two, steam is prior to CO_2 as a gasification intermediate, where both the higher reactivity and less gas sulfide release were ensured [44]. Therefore, the kinetic and thermodynamics of the reaction between the bi-oxygen carrier and coal were investigated in the present work, with the use of steam as gasification intermediate.

The investigation of the kinetic of the chemistry process were explored in a batch reactor at different reaction temperatures and different ratios of CaSO_4 to Fe_2O_3 , with respect to the reactivity, CO_2 generating efficiency, gas emissions, phase characterization and surface morphology of the used oxygen carrier. Product characterization analysis was performed by gas analyzers, X-ray diffraction (XRD) and scanning electron microscope (SEM) to investigate the reaction reactivity. The relationship between the CO_2 generation and other gas emissions is assessed by the environmental factor.

2. Reaction principles

The chemistry reaction process of the bi-oxygen carrier with coal under steam atmosphere is complicated, where the coal is gasified with steam and the bi-oxygen carrier reacted with coal syngas simultaneously.

2.1. Thermodynamic of the competitive reduction of the bi-oxygen carrier

Chemical reaction thermodynamics generally concerns with systems in equilibrium. Whether a reaction can happen

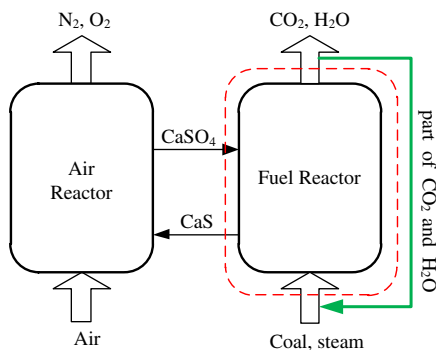


Fig. 1. Schematic illustration of a chemical-looping combustion of coal with a dual fluidized bed.

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