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Chemical looping combustion of high sodium lignite in the fluidized bed: Combustion performance and sodium transfer

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ABSTRACT

The Zhundong coalfield in Xinjiang, China, is the largest integrated coal basin newly found. The present work concentrates on the application of chemical looping combustion (CLC) with a Zhundong lignite, which is characterized by high sodium content. Some experiments in a laboratory scale fluidized bed facility with an active iron ore oxygen carrier, were performed using the lignite as fuel and CO_2 as gasifying agent at a temperature of 900 °C, with the objective of investigating its combustion performance and sodium transfer behavior in CLC. Results indicate that the gasification reactivity of the three coals follows the order of German lignite > Zhundong lignite > American bituminous coal in the current experimental conditions. During reducing stage, the unique product of sodium transfer from coal to the fly ash is albite ($NaAlSi_3O_8$) due to the reactions between sodium and other coal ash. The sodium deposition on the oxygen carrier particles was not found. 40 reducing-oxidizing cycles were performed, and sodium accumulation in the bed materials with cycles was found due to some ash staying in the bed. However, the growth of bed particles due to the sodium accumulation was not observed by determining the particle size distributions of bed materials. This indicates that burning the high sodium Zhundong coal in the present conditions have no influence on the particle agglomeration.

Finally, a literature survey was made and results indicate that the main sodium in the Xinjiang coal basin of China is water soluble with an average value of 64%. The pure salt of NaCl, as one common water soluble sodium phase in Zhundong coals, was introduced to a bed of iron ore particles at 900 °C with regard to investigate the influence of NaCl on fluidization stability. Based on the measurements of pressure drop, bed temperature and SEM-EDS, it was found that NaCl does not react with the iron ore but in fact only acts as glue between iron ore particles. Further, the sodium transfer routes in CLC of Zhundong coal with iron ore based oxygen carrier are given and some discussions are made with regard to practical operation. The corrosion problems on the heating surface in the air reactor can be significantly reduced compared to a conventional Zhundong coal fueled furnace, since most of sodium will release and be converted in the fuel reactor.

1. Introduction

Coal has been one of the most popular solid fuels for Chemical Looping Combustion (CLC) due to its huge amounts in the world (Lyngfelt and Leckner, 2015; Adánez et al., 2012). It normally has lower amounts of alkali metals such as Na, K than biomass. However, some coals as Victorian brown coal from Australia, PRB sub-bituminous coal/Beulah lignite from US, and Zhundong lignite in Xinjiang, Northwest China are found to be characterized by high sodium content. The Zhundong lignite explored in recent years in northwest China is a great energy resource, which has a huge reserve of 390 Gt. Based on the existing annual coal production in China, the vast reserves of the lignite offer a long term supply up to 100 years for power generation of China (Zhang et al., 2013). For Zhundong coal in China, it normally has sodium content in the range of 0.2–1% in raw coals (Yang et al., 2016), and higher than 2% and even 10% in ash (Zhang et al., 2013).

In regard to sodium, as one kind of alkali metals, sodium based substances can catalyze the coal gasification reactions by reducing the activation energy (Ye, 1994). However, besides its positive effect on gasification, other negative effects were also found that gasifying the

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Abbreviations: CLC, chemical looping combustion; PSDs, particle size distributions; SEM-EDS, scanning electron microscope-Energy Dispersive Spectrometer; OES, Optical Emission Spectroscopy; ICP, Inductively Coupled Plasma; XRD, X-ray diffraction

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Nomenclature

R_O	Oxygen transport capacity (%)
m_{ox}	Mass of the oxidized oxygen carrier (g)
m_{red}	Mass of the oxidized oxygen carrier (g)
ρ_s	Apparent density of the bed particles (kg/m^3)
$d_{p,50}$	Median particle diameter (μm)
n_O	Oxygen needed to completely convert the fuel (mol)
N_O	Lattice oxygen from oxygen carrier (mol)
m_{OC}	Weight of oxygen carrier (g)
M_O	Oxygen molar weight (g/mol)
φ	Oxygen carrier to fuel ratio (−)
$y_{i,out}$	Gas molar percentage in the off-gas (%), i = CO_2, CO, H_2, CH_4, O_2
n_{out}	Total molar flows leaving the reactor (mol/s)
n_{in}	Total molar flows entering the reactor (mol/s)
$y_{CO_2,in}$	Inlet CO_2 concentration (%)
r_C	Carbon conversion rate (mol/s)
$X_{C,red}$	Carbon conversion in the reduction stage (%)
m_{batch}	Initial mass of solid fuel added (g)
M_C	Molar weight of C (g/mol)

Greek letter

$\Phi_{C,fuel}$	Mass percentage of carbon in the fuel (wt.%)

coal with high sodium can cause serious agglomeration and even defluidization in case of fluidized beds (Song et al., 2016a).

Understanding the mechanisms related to these negative effects is significant with respect to find some solutions. With regard to sodium in the coal, sodium mainly exists in the coal as sodium carboxylates (organic sodium) and as soluble ionic salts dissolved in the coal moisture. On heating, volatilization of the compounds takes place. Some of the sodium within the coal particle including both organic and soluble sodium is transferred into the gaseous phase, and the other reacts with other components in the coal and is fixed in ash (Song et al., 2016a,b; Wang et al., 2015). As shown in Fig. 1, several mechanisms regarding to the agglomeration of the bed particles due to sodium are (Song et al., 2016a,b; Wang et al., 2015; Sevonius et al., 2014): (1) the sodium vapors can condense on surface of bed particles in case of SiO_2 in the bed materials, resulting in sticky coating on bed particles; (2) some sodium vapors can react with the SiO_2 in the bed particles to form some eutectics with low melting points, such as $SiO_2{\cdot}nNa_2O$ ($1 < n < 3.75$, $SiO_2{\cdot}2Na_2O$ has a melting point of 874 °C); (3) the fuel ash contains some substances with low melting points, such as CaO-SiO_2-Na_2O (720 °C), Na_2SO_4 (840 °C) and so on, which can be directly adhered to bed particles.

Oxygen carriers in CLC use both active metal oxides and inert supports such as SiO_2 and Al_2O_3. The role of inert supports is significant for carrying the metal oxides and heat. The present work concentrates on the application of this latter high sodium Zhundong lignite for CLC with iron ore as oxygen carrier, which has been known as an attractive candidate for CLC due to its low price and sufficient reactivity (Lyngfelt and Leckner, 2015; Adánez et al., 2012). Most iron ores contain Al_2O_3 and SiO_2 as the gangue materials which are usually used as additives to trap the alkali (particularly sodium) into the solid phase (Kosminski et al., 2006). The objectives of the present work are: (1) to compare the combustion performance of the Zhundong coal to another two coals (American bituminous coal and German lignite); (2) to investigate the sodium transfer and the corresponding mechanisms.

2. Experimental

2.1. Solid bed materials

In this work, an iron ore from Norway was used for the CLC experiments. Before experiments, the iron ore was calcined in a muffle oven at 950 °C for 3 h, which was then defined as fresh oxygen carrier. The elements were quantitatively determined by Optical Emission Spectroscopy (OES) with Inductively Coupled Plasma (ICP, Perkin Elmer Optima 8300 DV). Two subsamples were prepared and the average results are reported in Table 1. The mass fraction of Fe in the ore is 521 g/kg, corresponding to the fraction of Fe_2O_3 in the iron ore of about 74.4 wt.%.

The oxygen transport capacity (R_O, %), defined as the mass fraction of oxygen that can be used in the oxygen transfer, was calculated as $R_O = (m_{ox} - m_{red})/m_{ox}$, where m_{ox} and m_{red} are the masses of the oxidized and reduced form of the oxygen carrier, respectively. The value of the oxygen transport capacity (R_O) depends on the final oxidization state after reduction. Although iron compounds have different oxidization states ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$), only the transformation from Fe_2O_3 to Fe_3O_4 is favored for industrial CLC systems (Adánez et al., 2012; Leion et al., 2009; Song et al., 2013). To calculate R_O, the transformation from Fe_2O_3 to Fe_3O_4 is considered with a theoretical value of R_O of 3.3%. The apparent density (ρ_s) of the iron ore was measured as 2400 kg/m^3. Particle size distributions (PSDs) were determined using the measurement of CAMSIZER-XT (Retsch Technology GmbH, Germany), as shown in Fig. 2. Particle diameter was determined from the smallest of all maximum chords of the particle projection. The median ($d_{p,50}$) for the iron ore is 170 μm. The minimum fluidization velocity of the iron ore is 2.9 cm/s, which was measured under ambient conditions (1 bar, 20 °C) using air as the fluidizing gas in a laboratory fluidized bed. At a temperature of 900 °C and using the mixture gas (19.2 vol.% CO_2 and 80.8 vol.% N_2) as fluidizing gas, the minimum fluidization velocity of the iron ore is calculated as 1.1 cm/s based on Ergun's equation (Ergun, 1952).

2.2. Solid fuels

Three coals were used in this investigation namely a Zhundong lignite from Xinjiang of China, an American bituminous coal, and a German lignite. The proximate and ultimate analyses (determined by vario MARO cube, Elementar) of the coals are shown in Table 2. The diameter of the coal particles in the samples is 200–400 μm. The ash compositions of the Zhundong coal after calcination in a muffle oven at 900 °C for 2 h can be found in Ref. Ge et al. (2015), with a Na content of 7.5 wt.% in the ash. It is much higher than that in other Chinese coals with normally have sodium content below 1% (Zhang et al., 2013).

The sodium in the fuels can be classified as water soluble, ammonium acetate soluble, acid soluble and insoluble. The water soluble sodium mainly consists of dissolved Na^+, while the one of ammonium acetate soluble primarily contains organically-bounded sodium based

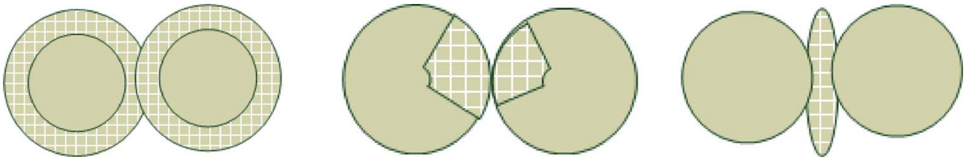

Fig. 1. Mechanisms regarding to the agglomeration of the bed particles due to sodium.