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Particle characterisation in chemical looping combustion

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ABSTRACT

In a chemical looping combustion process, as the oxygen carrier circulates the system, it is subjected to morphological and compositional changes such as sintering, attrition and reaction between metal oxides and fuels. These changes may cause the deactivation of the oxygen carrier to decrease over time. This research work is carried out to investigate and characterise the iron oxide and copper oxide particles used in a chemical looping combustion system after 20 reduction–oxidation cycles with 5 different fuels, (i.e. Hambach lignite coal, Hambach lignite char, activated carbon, Taldinski bituminous coal and US bituminous coal). Oxygen carriers used in this study were subjected to analyses with X-ray diffraction (XRD), inductive coupled plasma mass spectrometry (ICP-MS), scanning electron microscope (SEM) and BET surface area and full isotherm analysis.

XRD analysis on these particles showed that the reduced particles were reoxidised back to their original form with trace amounts of impurities such as silicon dioxide (SiO_2) on the iron oxide particles whereas similar impurities plus copper complexes such as copper aluminate were detected on the copper oxide particles. ICP-MS analysis on these particles revealed that the concentration of the core metal elements (iron, copper and alumina) decreased after 20 reaction cycles which in turn decreased the total concentration of the metal elements in the particles. BET surface area analysis on these particles indicated that the total surface area of these particles decreased by more than 50% of their original values. Full isotherm analysis on the copper oxide particles showed that the total pore volume of the particles decreased after 20 reaction cycles even though the pore sizes of the particles increased slightly. SEM analyses showed the iron oxide particles underwent severe attrition whereas the copper oxide particles showed signs of agglomeration due to the high operating temperature.

1. Introduction

It is well known that carbon dioxide is a greenhouse gas that contributes to the global warming. Nowadays, a third of the worldwide anthropogenic CO_2 emissions come from fossil fuels fired power production (Yamasaki, 2003; IEA, 2007). Meanwhile, fossil fuels will continue to be the main source of energy consumption for the foreseeable future (EIA, 2010). The increasing threat posed by enhanced global warming as well as the requirement to secure energy supplies around the world have led to the development of several novel technologies to produce clean energy from fuels (Figueroa et al., 2008). Among these new technologies is chemical looping combustion (CLC) which uses a solid metal oxide (oxygen carrier) to react with fuels (Richter and Knoche, 1983; Ishida et al., 1987). This technology has the potential advantage to produce a pure stream of carbon dioxide (CO_2) which can then be utilised or sequestrated.

In a CLC process, the oxygen carrier is reduced by fuels in one reactor while being reoxidised by air in a separate reactor. The typical operating conditions for a CLC system is 800–1200 °C and under pressurised or atmospheric pressure. The low temperature range used in a CLC system ensures that thermal NO_x does not form as a side reaction in the system (Ishida and Jin, 1996; Son and Kim, 2006).

As the oxygen carrier circulates the system, it is subjected to morphological and compositional changes such as sintering, attrition and reaction between metal oxides and fuels. These changes might cause the reactivity of the oxygen carrier to decrease over time. Earlier studies conducted on CLC focuses on oxygen carriers, reactor design and thermodynamic efficiency of the system with gaseous fuels. Linderholm et al. (2008) studied the performance of $NiO/NiAl_2O_4$ oxygen carrier in a 10 kW reactor for 160 h. They observed no decrease in the reactivity of the oxygen carrier during the test. The particle lifetime was estimated

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to be about 4500 h based on fines loss calculations. Zafar et al. (2006) found that the reactivity of NiO/SiO_2 decreased as a function of the cycle number at 950 °C but this effect was not observed for temperatures below 850 °C. The decay in reactivity is found to be due to the formation of nickel complexes.

Mattisson et al. (2001, 2004) studied the performance of iron ores (haematite) under multiple reduction and oxidation cycle with CH_4 and air at 950 °C. They found that the surface of the particles changes to a coarser texture with cracks and fissures after multiple oxidation–reduction cycles. Copeland et al. (2002) studied unsupported Fe_2O_3 at 720–800 °C and found that it showed good chemical stability and that they observed no loss in reactivity over multiple oxidation–reduction cycle. However, agglomeration was observed at 900 °C at a slow rate. Leion et al. (2008) studied the performance of ilmenite and found that the particles showed no decrease in reactivity after 37 reduction oxidation cycles. Zafar et al. (2005, 2006) studied Fe_2O_3 supported on SiO_2 and found that the particles showed high reactivity during the initial reduction oxidation cycles. However, Fe_2O_3 reacts with SiO_2 to form Fe_2SiO_4, iron silicates which will reduce the amount of available oxygen.

Some researchers studied CuO supported on Al_2O_3 (Adánez et al., 2004, 2006; Cho et al., 2004; Corbella et al., 2005a, 2005b; de Diego et al., 2004, 2005; Garcia-Labiano et al., 2006; Mattisson et al., 2003). Scanning electron microscope (SEM) images of reduced CuO/Al_2O_3 particles showed the presence of particle agglomeration such that the reactivity of the particles decreased between two consecutive reduction oxidation cycles. At high temperatures, agglomeration decreases the reactivity of the particles and causes the bed to defluidise. Aluminate formation is also another problem found with CuO/Al_2O_3 particles. de Diego et al. (2005) found CuO content in CuO/Al_2O_3 greater than 20 wt% agglomerates whereas CuO content in CuO/Al_2O_3 of less than 10 wt% does not agglomerate. Besides that, the reactivity of CuO/Al_2O_3 was high during the reduction and oxidation and was not affected by the number of cycles.

However, only limited research conducted on chemical looping with solid fuels as the oxygen carrier particles are not easily separable from the fuel or the ash particles. Without separation, the solid fuels would enter the air reactor along with the oxygen carrier and give CO_2 in the off-gas. As a result, a few techniques have been developed (Dennis and Scott, 2010; Brown et al., 2010; Mattisson et al., 2009a, 2009b; Leion et al., 2009a, 2009b; Shulman et al., 2009; Rydén et al., 2010).

The deactivation of the oxygen carries in the chemical looping process with solid fuels due to morphological and compositional have not been studied extensively. Berguerand and Lyngfelt (2008) studied the performance of ilmenite with petroleum coke in a 10 kW_{th} CLC. They observed a low loss of noncombustible fines from the system which indicates low attrition of the ilmenite particles. The main objective of this research work is to investigate and characterise the morphological and compositional changes in oxygen carrier particles such as Fe_2O_3 and CuO after multiple reduction oxidation cycles with solid fuels. The results can then be used to optimise the overall performance of the looping process.

2. Experimental

2.1. Apparatus

Experiments were carried out in a fluidised bed (inner diameter of 25 mm), constructed from 316 stainless steel, heated to a maximum temperature of 1273 K by an external electric furnace. The bed was fluidised with mixtures of nitrogen, air and CO_2 with $U/U_{mf}\sim 7$, with U being the superficial velocity at the temperature of the bed with $U=U_{mf}$ at incipient fluidisation. A screw feeder was used to deliver fuel continuously to the top of the bed. All of the flue gases leaving the reactor were directed to a condenser via a tube, trace-heated to 523 K to prevent the tars and water from condensing. The condenser was cooled with ice water and was packed with glass ballotini to increase the surface area for heat exchange and condensation. When the gases left the condenser, they were passed through a drying tube filled with $CaCl_2$. A fraction of the off gases was then pumped through an infrared analyser measuring 0–100 mol% CO, 0–100 mol% CO_2, and 0–10,000 ppmv SO_2 and a paramagnetic analyser which measured 0–100 mol% O_2. Fig. 1 shows the layout of the CLC system designed for the purpose of this research.

2.2. Procedures

At the start of an experiment, the empty reactor was filled with either 20 g of iron oxide and then heated to 1223 K with the bed fluidised at a rate of 40 mL/s consisting of 50 mol% air in nitrogen [all flow rates are given at standard temperature and pressure (STP)]. Once the operating temperature had been reached, the fluidising gas was switched to 40 mL/s consisting of 50 mol% CO_2 in N_2. When the outlet concentration of CO_2 was steady, Hambach lignite coal was fed continuously into the bed. The continuous feeding was stopped when a carbon monoxide breakthrough was achieved. At the end of the feeding period, CO_2

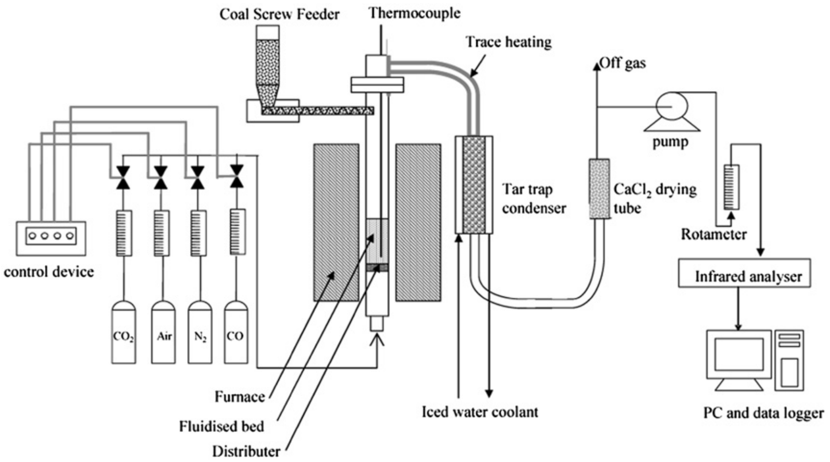

Fig. 1. Schematic of the chemical looping combustion system used in this experiment (Brown et al., 2010).