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Chemical looping combustion of four different solid fuels using a manganese-silicon-titanium oxygen carrier

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ABSTRACT

In chemical looping combustion, solid metal oxide particles are utilized to transport oxygen from the air reactor to the fuel reactor. As fuel and air are never mixed, the energy penalty typically associated with gas separation in first-generation carbon capture and storage technologies can be avoided. To be considered as oxygen carrier for this process, a material should be reactive at relevant conditions, environmentally friendly, non-toxic, mechanically durable and have potential to be produced at low cost in large scale. Combined oxides of manganese and silicon have previously shown promise to meet these requirements.

In this study, a spray-dried oxygen carrier based on a combined oxide of manganese, silicon and titanium was examined with respect to its performance in continuous chemical looping combustion of solid fuels. The experiments were carried out in a 10 kW chemical looping pilot unit which uses interconnected fluidized beds for oxygen carrier cycling. Prior to these experiments, the attrition rate was determined in a jet-cup rig. As the particles were comparably small and light, elutriation from the air reactor was high.

The fuels used during a total experimental duration of 32 h were wood char, devolatilized hard coal, pet coke and lignite. In addition to varying fuels, the influence of fuel power, solids circulation and fuel reactor temperature were investigated.

Gas conversion performance correlated clearly with the volatile content of the fuels, peaking at 97.8% for wood char and 94.6% for pet coke, which is the highest value ever reached for this particular fuel in this unit. Higher temperatures and solids circulation rates increased gas conversion. No decrease in performance over time, in particular no loss of reactivity due to sulphur accumulation, could be detected. The oxygen carrier released gaseous oxygen at relevant conditions. The particles were easily fluidized and fines production was low, suggesting a sufficient lifetime for the purpose.

1. Introduction

Anthropogenic emissions of CO_2 are widely considered the major driver for global warming. Climate mitigation strategies thus aim at reducing or eliminating the emission of greenhouse gases. Capturing the CO_2 from big point sources to store it underground (Carbon Capture and Storage, CCS) can be a means of reaching this goal in an economically reasonable manner.

Conventional CCS technologies employ an active gas separation step, which inevitably leads to a decrease in overall plant efficiency. Chemical looping combustion (CLC) has been proposed as a way of avoiding the losses associated with the gas separation step (Lyngfelt et al., 2001). To do so, solid metal oxide particles are used as oxygen carrier which is reduced by fuel in one reaction chamber (i.e. the fuel reactor) and reoxidized in a second chamber (i.e. the air reactor). For process related reasons such as high mass- and heat transfer as well as good gas-solids contact, the system is often designed as a dual fluidized bed (Adanez et al., 2012). A so-called carbon stripper can be utilized to separate and recycle non-converted char particles from the bulk flow of reduced oxygen carrier material before they can enter the air reactor, see Fig. 1. After condensation of water produced during fuel conversion and gas cleaning, the flue gas consists of almost pure CO_2 and can be deposited in a designated storage site. As air nitrogen is never in contact with the fuel, it does not have to be separated from the flue gas stream.

If a gaseous fuel is burnt, the fuel itself can be used to fluidize the fuel reactor bed. In solid-fuel CLC, no direct reaction between the solid fuel particles and the oxygen carrier is expected, which is why the fuel has to be gasified by steam or CO_2, as seen in Fig. 1. This step can be executed in the same reactor as the subsequent reaction between the gas produced by gasification and the oxygen carrier particles. Compared to combustion, char gasification is a slow process. However, in chemical looping combustion the presence of an oxygen carrier can

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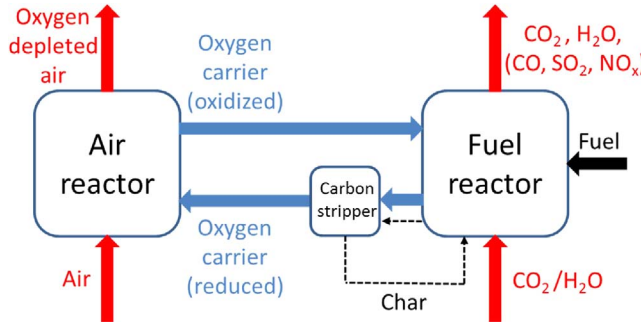

Fig. 1. Schematic of the solid fuel CLC process.

increase the gasification rate significantly (Leion et al., 2008). Apart from that, fuel conversion can also be increased by using chemical looping with oxygen uncoupling (CLOU). In this process, the oxygen carrier releases gaseous oxygen, thus opening a second route for solid fuel conversion through direct combustion rather than gasification (Mattisson et al., 2009).

Oxides of manganese, iron, copper and nickel have been identified as feasible alternatives with respect to expected fuel conversion performance in thermodynamic analyses (Jerndal et al., 2006; Imtiaz et al., 2013).

Apart from showing high fuel conversion rates and sufficient lifetime, the material of choice should be environmentally friendly, non-toxic and cheap. Oxygen carrier cost is especially sensitive in solid fuel applications, where some oxygen carrier material will be lost in ash removal. Also, an inert behaviour towards fuel impurities such as sulphur is desired. Whereas most operational experience to date has been gathered with the iron-titanium material ilmenite, e.g. (Thon et al., 2014; Berguerand and Lyngfelt, 2009; Cuadrat et al., 2011; Ströhle et al., 2014; Linderholm et al., 2014a), research is directed towards the identification of alternatives.

Copper-based materials exhibit high fuel conversion rates (Adánez-Rubio et al., 2014; Abad et al., 2012) but are expensive and of uncertain long-term stability (Rydén et al., 2014a). While the use of pure manganese oxide is limited by slow re-oxidation and a low equilibrium temperature (Mattisson et al., 2009), combined oxides of manganese and iron, calcium and/or silicon have shown their suitability as oxygen carriers in numerous studies, e.g. (Ksepko et al., 2012; Bhavsar et al., 2014; Cabello et al., 2014; Jing et al., 2014; Frick et al., 2015; Larring et al., 2015). Azimi et al. (2013) tested iron-manganese oxides and concluded that essentially full conversion of syngas and methane was possible. Abad et al. (2014) modelled CLOU operation with a calcium manganite and validated against a 120 kW unit using gaseous fuels. The same unit was used to test copper, iron and manganese oxygen carriers (Mayer et al., 2015). Källén et al. (2013) tested calcium manganite in a 10 kW unit and iron/manganese/silicon oxygen carriers in a 300 W unit (Källén et al., 2015). Both groups of materials performed well with respect to gas conversion, but while the calcium manganite showed high durability, the lifetime of the tested iron/manganese/silicon materials was limited.

Among the tested materials, combined oxides of manganese and calcium can be susceptible to sulphur poisoning (Arjmand et al., 2014a; Schmitz et al., 2014; Pishahang et al., 2016). As sulphur is a common impurity in fossil fuels, this could limit the applicability of these materials to the combustion of sulphur-free fuels. Combined oxides of manganese and silicon might be an option to avoid this problem because they feature both favourable thermodynamic properties, sulphur tolerance and potentially low cost (Arjmand et al., 2014b). Hanning et al. (2016) found that adding titanium to the formulation of the oxygen carrier can increase its mechanical durability.

In the present study, a combined oxide of manganese and silicon with addition of titanium was evaluated with respect to its performance and long-term stability in continuous solid-fuel chemical looping combustion. To obtain a robust database for potential future evaluations of the material, four different fuels are tested.

2. Experimental

Experiments were conducted in Chalmers' 10 kW solid fuel chemical looping unit during operation with continuous fuel feeding.

2.1. 10 kW pilot

The pilot is based on interconnected fluidized-bed technology. In the riser, which constitutes the upper part of the air reactor, high gas flows in combination with a small cross-section area ensure high gas velocities which provide the driving force for the circulation. The entrained oxygen carrier particles enter a cyclone, where they are separated from the air flow and fall into the fuel reactor via a loop seal to avoid gas mixing. The fuel reactor is designed as a bubbling bed and consists of several parts: in the main section, fuel is oxidized to CO_2 and H_2O. The char remaining after devolatilization is gasified followed by oxidation of the gasification products by the oxygen carrier. The main section is usually fluidized with steam. The particles are forced to pass under a vertical wall, see Fig. 2. The carbon stripper (CS), which is fluidized by nitrogen, is supposed to separate coal and oxygen carrier particles by making use of their different density and size. The particles entrained in the carbon stripper can be reintroduced to the low velocity section, whereas the partly reduced oxygen carrier particles continue to the air reactor via a loop seal to be regenerated.

Fuel is introduced into the fuel-reactor bed via a coal screw and a fuel chute. The operating temperature is measured via three thermocouples located in the air reactor, fuel reactor and air reactor cyclone. Fluidization behaviour, solids circulation and inventory can be estimated from numerous pressure measurements. The exhaust gas streams from both air and fuel reactor are passively cooled before entering filter bags (air reactor exhaust) or a water seal (fuel reactor exhaust). The water seal is used both to collect condensate from fuel conversion and steam fluidization and to impose a hydrostatic pressure on the fuel reactor exhaust, thus creating a pressure difference between the outlets of the fuel reactor and air reactor. This is necessary to avoid inadequate pressure differences over the loop seals connecting the reactors.

A fraction of the exhaust gas streams from the AR and FR is cooled, filtered for removal of fines, led through gas conditioning systems to condense remaining steam and then analysed by infrared- (CO, CO_2 and CH_4), thermal conductivity- (H_2) or paramagnetic analysers (O_2).

As the heat losses are higher than the thermal power generated by fuel addition, the unit is enclosed in an electrically heated furnace, which also is used for initial heat-up. During heat-up, all parts of the unit are fluidized by air before switching to steam-/nitrogen fluidization of the fuel reactor, the loop seals and the carbon stripper.

Previous operational experience in this unit has been achieved using different natural minerals like ilmenite and manganese ores, e.g. (Berguerand and Lyngfelt, 2009, 2010; Linderholm et al., 2012), and a spray-dried calcium manganite (Schmitz et al., 2014, 2016).

2.2. Oxygen carrier

The oxygen carrier material was produced by spray-drying a slurry made from 66.7% Mn_3O_4, 22.2% SiO_2 and 11.1% TiO_2. Upon attrition testing, it was concluded that the particles were not sufficiently durable. As it is known that the calcination temperature had a strong influence on particle stability in a previously tested material (Jing et al., 2016), it was decided to re-calcine the particles in small batches. The best compromise of sufficient calcination and as little sintering as possible was found to be 1130 °C for a time of 12 h. After that, the batch was sieved to the desired size, see Fig. 3. The average diameter was 104 μm and the bulk density 1.35 g/cm^3.