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Chemical-looping combustion in a 100-kW unit using a mixture of ilmenite and manganese ore as oxygen carrier

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ABSTRACT

Chemical-looping combustion (CLC) is a novel carbon-capture technology with potential to drastically reduce the cost of CO_2 capture. Relying on interconnected fluidized bed technology, CLC systems can achieve CO_2 capture by using oxygen carrying bed material. This so-called oxygen carrier transports oxygen from combustion air to fuel, thus making carbon capture inherent to the CLC process. In this study, we present findings from a 100 kW chemical-looping combustor for solid fuels. The 100 kW unit uses the dual-CFB concept, where both air reactor and fuel reactor are designed as circulating fluidized beds.

The oxygen carrier material used in this study consisted of a mixture of ilmenite – which has been used in several studies in CLC – and a manganese ore. Previous studies have shown that gas conversion can be significantly increased by using manganese ore particles as oxygen carrier. However, previous testing has also shown that the production of fines, *i.e.* particle attrition, may be high when using manganese ore. The reason for mixing the two materials is thus to obtain an oxygen carrying material that has high reactivity, and yet does not produce too much fines during fuel operation.

The 100 kW unit was operated in total for 18 h with fuel. Three fuels were used in the experiments: two bituminous coals and wood char. Gas conversion was high, and increased with increasing fraction of manganese ore in the oxygen-carrier mixture. At the end of the experiments, the fraction of manganese ore in the bed material was approximately 8%, which also was the highest fraction during all tests. The mixture of ilmenite and manganese ore gave significant improvements in gas conversion in comparison to only ilmenite. The highest gas conversion observed during testing with bituminous coal was 91.5%, as compared to 84% with only ilmenite as oxygen carrier during similar conditions in the 100 kW unit.

These test results indicate that the addition of manganese ore could almost halve the fraction of unconverted gas. Thus, mixing mechanically stable ilmenite with more reactive manganese ore can give reductions in costs as compared to using manganese ore only, and still give significantly reduced oxygen demand as compared to ilmenite. In the present case – mixing of ilmenite and manganese ore – the high reactivity was also possible to combine with improved operability of the material, primarily manifested as lower production rate of fines.

1. Introduction

Chemical-looping combustion (CLC) is a novel carbon-capture technology suitable for large-scale power generation. In normal combustion, flue gases are mixed and the concentration of CO_2 on dry basis is 10–15%, whereas in CLC, CO_2 is obtained in a separate gas stream as an inherent part of the process. This is accomplished by means of metal-oxide particles that transfer oxygen from air to fuel, thus avoiding mixing of the two. Since no active gas separation is needed to obtain a pure stream of CO_2, it is clear that in comparison to other capture technologies, CLC has an indisputable and important advantage, and the potential to drastically reduce the cost of capture. The status of development of CLC has been reviewed e.g. by Adánez et al. [1].

On the road to utility-scale CLC, solutions for optimal reactor design need to be found. An important part of this development is the work carried out in continuous chemical-looping pilot systems. Several researchers have reported the design and operation of chemical-looping combustors in the size 0.5–25 kW for solid fuels [2–12], all of which normally operate under atmospheric conditions. Xiao et al. [13] have made experiments using a 50-kW

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pressurized CLC reactor system. Furthermore, a 1 MW pilot has been built and operated in partial CLC mode [14], *i.e.* with support of air to maintain fuel-reactor temperature. Also, a larger 3-MW_{th} CLC pilot for solid fuels has been erected at Alstom Power Plant Laboratories in Windsor, USA [15]. The first results from the unit look promising. The design of the 100 kW unit used in the present study has been described in a previous work [16]. Operational results from the unit have been reported in e.g. [16–19] and modeling of the gas conversion in the unit has also been accounted for [20].

Even though developed and suggested process schemes for chemical looping differ in a range of operational parameters, a common cornerstone of the CLC technology is the oxygen carrier, which needs to have sufficient reactivity as well as mechanical and chemical stability for long periods of time in continuous CLC systems. Oxygen carrier development has been reviewed by Lyngfelt [21]. In order to find out how particles will behave over time in full-scale applications, evaluation in larger, continuous units is a vital step. The expected lifetime of the oxygen-carrying particles may be a very important parameter when it comes to process up-scaling. The chemical and physical environment in the reactor system during operation is such that particles break and form smaller particles. Using ilmenite as oxygen carrier and bituminous coal as fuel, the expected lifetime of ilmenite particles was investigated in a 100 kW reactor system – also used in the present study – and found to be 700–800 h [19].

1.1. Fate of fuel-N and S

Another important research question is the fate of contaminants such as sulfur and nitrogen. Literature dealing with the fate of sulfur in CLC has been covered in the extensive CLC review by Adánez et al. [1]. The fate of sulfur depends on oxygen carrier, operating conditions, and gaseous environment. Although there are a number of publications on the fate of fuel sulfur in CLC, most studies concern gaseous fuels. A thermodynamic analysis of different oxygen carriers and different gaseous fuels [22] showed that H_2S released from the fuel will be partially or fully oxidized to SO_2 by H_2O, CO_2 or the metal oxide during fuel conversion, and that formation of other sulfur species is generally insignificant.

Adánez-Rubio et al. [23] studied the fate of fuel-N and S in CLC and CLOU experiments using lignite as fuel. In the CLOU experiments, the only sulfur containing gas from the FR was SO_2. In the CLC experiments, there was also some H_2S from the FR, approximately 15% of the S-containing gas from the FR. The same study also showed that the fuel-N balance in the CLOU experiments closes with 65% N_2 in the FR, around 17% NO in the FR, and around 17% NO in the AR. Finally, the fuel-N balance in the CLC experiments showed a little more than 80% N_2 from the FR, and around 5% NO in the AR. Hence, there seemed to be no HCN or NH_3 from the fuel-N in the CLC experiments.

Experimental results from a 1 kW unit [24], using a hematite oxygen carrier suggested that N_2 was the sole product of fuel-N conversion in the fuel reactor. Another study by the same research group looked at the nitrogen transfer of fuel-N using a Ni-based oxygen carrier and different coals as fuel in the same CLC unit [25]. Here, too, it was found that all fuel-N released from the fuel reactor is in the form of N_2.

In a recent study [19], the fate of sulfur and nitrogen in the 100 kW unit was investigated through a mass-balance approach, where all in and outgoing mass flows were carefully monitored, sampled, and analyzed. The sulfur balance showed that the conversion in FR of inbound sulfur is around 72%, and that around 2/3 of S-containing gas produced in the fuel reactor exits with the condensate. Furthermore, it was found that 75% of the S-containing gas is SO_2, and only 25% was H_2S. The nitrogen analysis indicated that 62% of the nitrogen fed with the coal was converted to gas, and that the *mass* of nitrogen in this gas was distributed as follows: 1% HCN, 11% NO, 0% NO_2 and 26% NH_3, with the balance, 62% probably being mostly N_2.

1.2. Purpose of study

Ilmenite has been widely used as oxygen carrier in CLC applications. Here, we investigate the potential to improve performance by mixing ilmenite with manganese ore. Compared to ilmenite, manganese ore has shown higher reactivity with syngas. This was demonstrated in a study by Sundqvist et al. [26] who investigated 11 manganese ores in a laboratory fluidized bed, and estimated the rate constant for the 8 most reactive ores to be 3–6 times higher as compared to ilmenite. Moreover, the presence of manganese ore has also been shown to give a higher rate of steam gasification of char in both lab tests [27] and a continuous unit [7]. An additional purpose of the study was to investigate the fate of sulfur, nitrogen and carbon by making rigorous material balances of in- and outgoing flows of gas, particles, and water from the FR flue gas condensation.

Using a mixture of the two materials could be preferable to use only manganese ore as oxygen carrier. It has been shown that manganese ore produces a lot of fines when used as oxygen carrier. The rationale for mixing the two materials is thus to obtain an oxygen carrying material that has high reactivity, and yet does not produce too much fines during fuel operation. Higher reactivity gives higher fuel conversion and thus lowers the demand for oxy-polishing. Lyngfelt and Leckner [28] showed that aside from the inevitable costs of CO_2 compression, oxy-polishing is likely the largest added cost for a full-scale CLC-CFB (circulating-fluidized bed) boiler.

2. Experimental

2.1. Reactor system

The 100 kW system, shown in Fig. 1, is designed as to allow operational flexibility. The system includes two interconnected circulating fluidized beds, *i.e.*, air reactor (AR) and fuel reactor (FR), as well as a carbon stripper. The circulating fluidized bed in the fuel reactor adds flexibility. Variation of the fluidization regime in the fuel reactor could have consequences on gas–solid contact. Moreover, by controlling the flows to the air reactor and the so-called circulation riser it is possible to control the fuel reactor inventory and the global circulation independently. The pilot design in Fig. 1 appears complex, but a full-scale CLC boiler would have a simpler design and be more similar to a state-of-the-art CFB boiler, confer for example Lyngfelt and Leckner [28].

Starting in the fuel reactor, the path of solids circulation is outlined below and is numbered from 1 to 28 in Fig. 1. Gas and particles entrained in the fuel reactor (FR) enter the cyclone (CY2), fall down the downcomer to a loop seal (LS2) and enter the fuel reactor again. Particles not entrained may instead enter the circulation riser (CR), which is placed in between the carbon stripper (CS1–4) and the loop seal (LS3) connected to the fuel reactor. The circulation riser is designed to return varying mass flows of particles to the air reactor. The carbon stripper has four chambers separated by weirs. The purpose of the carbon stripper is to gasify or separate residual char in the particle flow. The particles in the carbon stripper are passed on to a loop seal (LS4), leading to the air reactor (AR). The air reactor re-oxidizes the oxygen carriers before they are transported back to the fuel reactor by passing a cyclone (CY1) and another loop seal (LS1), thus beginning a new cycle. The air reactor and fuel reactor are separated by loop seals in order to avoid gas mixing. The fuel reactor, with an inner height of 5.0 m,