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Chemical Looping Combustion of Sulphurous Solid Fuels using Spray-Dried Calcium Manganate Particles as Oxygen Carrier

Matthias Schmitz*, Carl Linderholm, Anders Lyngfelt

Department of Energy and Environment, Chalmers University of Technology, S-41296 Göteborg, Sweden

Abstract

A perovskite material, $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$, has been investigated as oxygen carrier in a 10 kW chemical looping pilot using sulphurous fuels. Operation with inert gas in the fuel reactor showed that the material released significant amounts of gas-phase oxygen, indicating CLOU properties. Stable operation with fuel was performed during 29 hours with performance superior to previously tested oxygen carriers like ilmenite. A slight deterioration of the conversion was detected during the experiments, which can be attributed to the accumulation of sulphur in the oxygen carrier. However, a regeneration test with non-sulphurous fuel showed that this process is reversible and that the oxygen carrier can be regenerated after being subjected to sulphurous fuels.

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Keywords: Chemical looping combustion; CLOU; carbon capture; perovskite; oxygen carrier

1. Introduction

The emissions of anthropogenic CO_2 are widely considered an important contributor to global warming. One possible mitigation strategy is the large-scale implementation of carbon capture and storage (CCS), in which CO_2 from point sources is separated from the flue gas, compressed and stored in deep geological formations. In effect, CO_2 emissions to the atmosphere can be minimized while still using fossil fuels for heat and power generation.

* Corresponding author. Tel.: +46-31-772-1432; fax: +46-31-772-1152.
E-mail address: matthias.schmitz@chalmers.se

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If the gas separation is carried out in a conventional way, for example by the use of cryogenic distillation, adsorption or membrane separation, this step is associated with a considerable loss of plant efficiency.

Chemical looping combustion (CLC) aims at minimizing that loss of efficiency by capturing CO_2 without gas separation. This is possible because fuel and combustion air are not mixed. Instead, the oxygen is transferred to the fuel by means of an oxygen carrier, which typically consists of metal oxide particles. The concept can be realized using two interconnected fluidized bed reactors, the air and the fuel reactor, to ensure that the two reactions incorporating the oxygen carrier, i.e. oxidation with combustion air and reduction with fuel, are unmixed.

If a reaction between oxygen carrier and a solid fuel is to be achieved at the desired rate, solid-solid contact between the reactants is not sufficient. In conventional CLC, the solid fuel therefore has to be gasified prior to reacting with the oxygen carrier. The gasification reaction is comparably slow, which can lead to a loss of char to the air reactor or the fuel reactor exhaust.

Chemical looping with oxygen uncoupling (CLOU) is a way to avoid the gasification step. As opposed to conventional CLC, the oxygen carriers used in CLOU are not only transporting chemically bound oxygen which can be used for the oxidation of gaseous compounds, but are able to release gas-phase oxygen under relevant conditions. The oxygen released can oxidize the solid fuel particles directly, thus eliminating the need for a gasification step, which could facilitate the system design, improve the performance and reduce cost.

Thermodynamics limit the range of possible CLOU oxygen carrier materials, which both have to take up oxygen in the air reactor and release it in the fuel reactor. The structure of perovskites materials, which can be written $ABO_{3-\delta}$, makes those materials suited as CLOU oxygen carriers [1]. In the structural formula, A is a larger and B a smaller cation. δ describes the degree of oxygen deficiency, which among others depends on temperature and pressure and thus provides the above-mentioned CLOU properties. Above that, the same requirements as for conventional CLC oxygen carriers have to be met: the particles should be sufficiently reactive, environmentally benign, non-toxic, mechanically durable and easily fluidized. Especially in the combustion of solid fuels, cost plays an important role because oxygen carrier will be continuously lost in ash separation.

Of all known CLC oxygen carriers, ilmenite has been tested most extensively, which can be attributed to its low cost, high durability and non-toxicity [2, 3, 4, 5, 6, 7]. When used with solid fuels, however, ilmenite could not perform full gas conversion. The need for gasification also slows down the solid fuel conversion, which leads to carbon slip to the air reactor.

In the attempt to improve the overall process performance, the search for new oxygen carriers plays an important role. Experiments with solid biomass fuels and a copper-based CLOU oxygen carrier have been carried out by Adánez-Rubio et.al. [8]. Calcium manganate and variations of that material have been tested in both batch reactors [9, 10] and continuous units with gaseous fuels and solid biomass fuels [11, 12, 13, 14] with promising results concerning fuel conversion and durability. Moreover, the mechanical properties of the material have been investigated in jet-cup attrition tests [15].

The oxygen carrier tested contains large amounts of calcium, which is known to bond with sulphur. As sulphur is present in most solid fossil fuels, the sulphur tolerance of oxygen carriers for CLC/CLOU of these fuels is a crucial point. If the oxygen carrier is irreversibly deactivated by sulphur addition during operation, it might have to be replaced at a higher rate, leading to costs that render the oxygen carrier unsuitable.

Sundqvist [16] and Arjmand [17] have examined the sulphur tolerance of calcium manganates in a batch reactor and found a decrease in reactivity, which is likely to be caused by the formation of $CaSO_4$.

The purpose of this study is the investigation of both the overall performance of calcium manganate in conjunction with sulphurous fuels when used in a continuous chemical looping unit and in particular the effect of sulphur on the oxygen carrier.

2. Experimental

2.1. 10 kW reactor system

The pilot, which was the world's first chemical-looping combustor for solid fuels, 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