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Combined oxides of iron, manganese and silica as oxygen carriers for chemical-looping combustion

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ABSTRACT

Spray-dried particles with the chemical compositions of $Fe_{0.66}Mn_{1.33}SiO_3$ and $FeMnSiO_3$ have been examined as oxygen carrier materials for chemical-looping combustion. The experiments were carried out in a fluidized-bed reactor system designed for a thermal power of 300 W. Both materials were able to release gas phase oxygen in inert atmosphere at temperatures between 800 and 950 °C, and with approximately equal oxygen concentrations. $Fe_{0.66}Mn_{1.33}SiO_3$ provided higher conversion of natural gas as compared to $FeMnSiO_3$ and the fuel conversion increased with temperature for both materials. During natural gas operation with $Fe_{0.66}Mn_{1.33}SiO_3$ the conversion reached 100% at around 950 °C with a fuel reactor inventory of 235 kg/MW. The fuel conversion improved when the solid inventory was increased; this improvement could especially be observed for $FeMnSiO_3$ as the fuel conversion was lower for this material. $Fe_{0.66}Mn_{1.33}SiO_3$ also provided higher fuel conversion than $FeMnSiO_3$ when syngas was used as fuel. The fuel conversion increased with temperature for both materials and full conversion was reached above 800 °C with a fuel reactor inventory of 225 kg/MW for $Fe_{0.66}Mn_{1.33}SiO_3$, while $FeMnSiO_3$ was incapable of providing full conversion. A rather large elutriation of fines and a significant change in particle size distribution could be observed during operation for both materials.

1. Introduction

Global warming and the increasing concentrations of greenhouse gases in the atmosphere pose significant threats to today's society [1]. Many different mitigation solutions have been proposed. Carbon dioxide capture and storage (CCS) is often mentioned as an important strategy. CCS is a method to reduce emissions of CO_2 to the atmosphere which involves separation of carbon dioxide in the flue gases from point-sources such as industries and power plants, transportation to a storage location and subsequent long-term storage, for example in depleted gas fields or deep saline aquifers [2].

The aim of this study was to investigate the performance of combined iron, manganese and silica as an oxygen carrier for the carbon capture technology chemical-looping combustion. Combined oxides of manganese–iron and of manganese–silica have promising thermodynamic possibilities to work as oxygen carriers for chemical-looping combustion and for chemical-looping with oxygen uncoupling. Ores with high content of manganese, iron and silica are common and this study could provide an increased level of understanding of how such mixed oxides work as oxygen carriers. One aim is the possible use of natural ores which would provide benefits regarding cost and availability of future oxygen carriers. Another aim is manufacturing high reactivity oxygen carriers from low cost raw materials. Manufactured oxygen carriers of manganese, iron and silica could be fairly cheap and should be neither toxic nor environmentally harmful. These materials would be very favorable for combustion of solid fuels since they would probably not be affected by the sulfur in the fuel and the low cost of the material would be advantageous as material would be lost in the ash removal.

1.1. Chemical-looping combustion

Chemical-looping combustion (CLC) is a carbon dioxide capture technology which has developed fast in the last years. Worldwide more than 700 oxygen carrier materials have been examined and the total continuous operation now amounts to more than 4000 h in chemical-looping units ranging from 300 W to 140 kW, see recent review articles by Lyngfelt [3] and Adanez et al. [4] for an overview. In chemical-looping combustion, the oxygen needed for oxidation of the fuel is supplied by a solid oxygen carrier. The oxygen carrier is oxidized by air in one reactor and reduced by the fuel in another reactor. The oxygen carrier material is continuously circulated between the two reactors. The exhaust gas from the air reactor (AR) consists of oxygen depleted air and the exhaust gas from the fuel reactor (FR) ideally consists only of carbon dioxide and steam, and the latter may easily be

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Nomenclature

AR	air reactor
CCS	carbon capture and storage
CLC	chemical-looping combustion
CLOU	chemical-looping with oxygen uncoupling
F_{AR}	inlet flow to air reactor (L_N/min)
F_{FR}	inlet flow to fuel reactor (L_N/min)
FR	fuel reactor
Me_xO_{y-1}	reduced oxygen carrier
Me_xO_y	oxidized oxygen carrier
x_i	gas concentration, i = CO, CO_2, CH_4, O_2, N_2 (%)
γ_{CO_2}	CO_2 yield (−)

condensed to obtain an almost pure stream of carbon dioxide, see Fig. 1. In this way carbon dioxide is inherently captured without any direct energy penalty for gas separation.

The fuel will react with the oxygen carrier according to:

$$(2n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1} + mH_2O + nCO_2 \quad (1)$$

where Me_xO_y represents a metal oxide and Me_xO_{y-1} represents a metal or reduced metal oxide. The oxygen carrier will then be reoxidized in the air reactor according to:

$$Me_xO_{y-1} + \frac{1}{2}O_2 \rightarrow Me_xO_y. \quad (2)$$

The amount of energy released in the two reactions is equal to that for normal combustion of the same fuel. This is evident since the sum of Eqs. (1) and (2) is the normal combustion of the fuel with oxygen.

Chemical-looping with oxygen uncoupling (CLOU) is a process closely related to chemical-looping combustion, which was originally proposed by Mattisson et al. [5]. The combustion of the fuel takes place in two steps. First the oxygen carrier releases gas phase oxygen according to:

$$Me_xO_y \rightarrow Me_xO_{y-1} + \frac{1}{2}O_2. \quad (3)$$

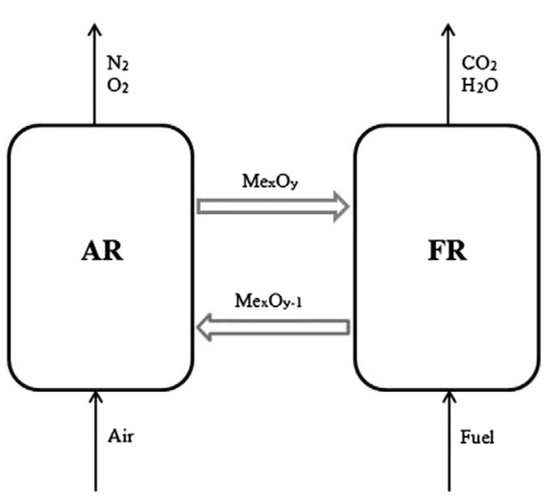

Fig. 1. A schematic overview of the CLC process.

The fuel may then be oxidized by gaseous oxygen released by the oxygen carrier, rather than by direct reaction with the oxygen carrier. This is especially beneficial for solid fuels where char otherwise needs to be gasified to be able to react with the solid oxygen carrier, and char gasification is slow compared to direct reaction between char and oxygen. In chemical-looping with oxygen uncoupling the char instead reacts directly with gaseous oxygen released by the oxygen carrier. The use of an oxygen carrier capable to release gas phase oxygen could decrease or even eliminate the need for additional measures such as oxygen polishing to reach full conversion of the fuel. This has been demonstrated during continuous operation with bituminous coal by Abad et al. [6]. CLOU could also prove to be favorable for oxidation of gaseous fuels, since the presence of gas phase oxygen could be expected to facilitate full combustion even with insufficient mixing of gases and solids. Presence of small amounts of gaseous oxygen in the freeboard can effectively oxidize any combustible gases that pass the bed because of bubbles or poor mixing. Azimi et al. showed the impact of the oxygen release during combustion of wood chips in inert atmosphere and could compare this to the combustion of methane with the same oxygen carrier particles [7]. Continuous operation with natural gas as fuel with complete conversion of the fuel and excess oxygen in the outlet stream has been reported by Källén et al. [8].

In order to illustrate the possible advantages of an oxygen carrier which releases oxygen, a comparison between a very reactive material without CLOU properties and a less reactive material with CLOU properties can be made. The two materials are a spray-dried nickel oxide material here referred to as N-Vito which has been used during 1000 h of operation in a 10 kW unit [9] and a calcium manganate material, here referred to as C14, which has been examined in the same 10 kW unit [8]. A kinetic determination of the two materials was made at CSIC under similar conditions, whereby conversion versus time was studied in TGA in e.g. 15% methane [10,11]. A reactivity comparison indicates that methane reacts more than three times faster with N-Vito, as compared to C14. In theory, the N-Vito material could reach full conversion with a solid inventory of 10–20 kg [11], whereas in reality it reached 97% conversion in the 10 kW unit with a solid inventory corresponding to around 500 kg/MW [9], and 89% conversion in a 120 kW unit with around 133 kg/MW [12]. The discrepancy has been attributed to the inadequate contact between gas and solids due to by-passing gas in the bubble phase. Despite the markedly lower reactivity of C14, it has been possible to reach full conversion in the 10 kW unit [8] as well as in the 120 kW unit [13].

There are a number of requirements which an oxygen carrier material should fulfill. Firstly, oxidation and reduction must occur at sufficient rate at the desired temperature level. This is important in order to minimize the amount of material required in each reactor. The oxygen transfer capacity, i.e. the amount of oxygen (measured in wt.%) which the oxygen carrier can deliver to the fuel per cycle, should be sufficient. If the oxygen carrier is used for chemical-looping with oxygen uncoupling, the rate of oxygen release is also an important parameter. The oxygen carrier particles also need to have sufficient mechanical and chemical integrity to keep attrition and elutriation of fines at low rates. The particles should also be inert towards fuel impurities in order to avoid deactivation and loss of reactivity. Furthermore, the cost and the environmental impact of the material should be at reasonable levels.

The most commonly proposed way to realize chemical-looping combustion is using two interconnected fluidized beds. In this case, the oxygen carrier in the form of particles with good fluidization properties is circulated between the two fluidized beds. By using this method much of the knowledge and experience from fluidized bed boilers (CFB) can be utilized.

1.2. Combined iron–manganese–silica oxygen carriers

The most investigated oxygen carrier materials for chemical-looping combustion are based on oxides of nickel, copper, iron and manganese.