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Full Length Article

Performance of an iron based oxygen carrier in a 120 kW_{th} chemical looping combustion pilot plant

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ABSTRACT

Chemical looping combustion is an unmixed combustion process with inherent separation of CO_2. CLC technology has the capability to generate concentrated CO_2 as further use for carbon capture and storage and thus reduce CO_2 emissions. Since the use of cheap and non toxic oxygen carriers is favourable, iron is a potential candidate as active component.

The performance of iron oxide impregnated on alumina (called Fe17) as oxygen carrier is investigated. Fe17 is tested in a 120kW_{th} chemical looping combustion pilot plant at TU Wien. Various tests are carried out, the influence of active solid inventory, temperature, used gaseous fuel and oxygen carrier to fuel ratio are in the focus of the investigation. Post-experimental tests with thermogravimetric analysis, X-ray fluorescence analysis, particle size distribution and scanning electron microscope are used to characterize Fe17. The oxygen carrier shows attrition and a loss of iron. This leads to a drop of fuel conversion. The energy based fuel conversion is approx 40% to 60 %. For good fuel conversion, high inventories are needed in both reactors. Furthermore, high solid circulation rates and a high iron content on the particles show better fuel conversion.

1. Introduction

Carbon dioxide has been identified as greenhouse gas quite a long time ago. To slow down global warming a reduction of CO_2 emission has to be realized. According to the International Panel on Climate Change most of the CO_2 is produced in the industrial sector, especially during power generation [1]. Power plants emit huge streams of CO_2, which are very focused geographically. Such sites have a great potential for carbon capture and storage (CCS) [2].

The intention of CCS is the avoidance of CO_2 emission to the atmosphere by separation of CO_2 from a flue gas stream. The gas is compressed and stored consecutively. The main steps are separation, compression, transport and storage of the CO_2 [3]. The gas separation can be achieved through post-process capture, syngas/hydrogen capture, oxy-fuel combustion or inherent separation [3]. Chemical looping combustion (CLC) features inherent separation. It is the process investigated in this work and uses the principle of unmixed combustion to produce a pure CO_2 stream.

1.1. Chemical looping combustion (CLC)

The chemical looping combustion (CLC) process divides the combustion reaction into two steps, avoiding a mixing of combustion air and fuel. The unmixed combustion is realized with oxide based materials. These materials are called oxygen carrier. The highly irreversible combustion reaction is split up into two reactions. The oxidation of the oxygen carrier, as shown in (1), and the reduction of the oxygen carrier by the fuel, as shown in (2). The process is visualized in Fig. 1.

$$MeO_{\alpha-1} + \frac{1}{2}O_2 \rightarrow MeO_{\alpha} \quad (1)$$

$$4MeO_{\alpha} + CH_4 \rightarrow 4MeO_{\alpha-1} + CO_2 + 2H_2O \quad (2)$$

CLC has been identified as highly suitable for CCS applications. The CO_2 capture from the flue gas of a conventional fossil fuel based combustion process is combined with high energy loss. However, the technology of chemical looping combustion has the advantage that the net released heat is the same as in a regular combustion process and the CO_2 is already separated from the combustion air [4]. The CLC process can be realized with two fluidized beds, as proposed by Lyon and Cole [5] and Lyngfelt et al. [6]. To avoid leakage or dilution of CO_2, the fluidized beds are connected via loop seals (fluidized with inert gas or steam).

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Nomenclature

ΔX_S	difference in degree of oxidation between particles in AR and FR [–]
ϕ	Oxygen carrier to fuel ratio [–]
$\dot{m}_{O_2, AR_{feed}}$	massflow of oxygen to the AR [kg/h]
$\dot{m}_{O_2, AR_{fuel}}$	massflow of oxygen needed for stoichiometric conversion of additional fuel fed to the AR [kg/h]
$\dot{m}_{O_2, FR_{fuel}}$	massflow of oxygen needed for stoichiometric conversion of the fuel fed to the FR [kg/h]
λ_{eff}	Effective air equivalence ratio [–]
AR	Air reactor
CCS	Carbon Capture and Storage
CLC	Chemical Looping Combustion
d_{50}	Mean Particle diameter [µm]
DCFB	Dual circulating fluidized bed
FR	fuel reactor
LSi	loop seal internal
LSl	loop seal low
LSu	loop seal up
m_{ox}	mass of fully oxidized sample [kg]
m_{red}	mass of fully reduzed sample [kg]
$m_{spec,FR}$	fuel power specific FR inventory [kg/MW]
XRF	X-ray fluorescence
m	Mass of sample [kg]
R_{OC}	Oxygen transport capacity [–]
SEM	scanning electron microscope
TGA	thermo gravimetric analyzer
X_{CH4}	Methane conversion [%]
X_S	degree of oxidation [%]
Y_{CO_2}	carbon dioxide yield [%]
$\dot{m}_{O_2, OC}$	massflow of available oxygen to the FR [kg/h]

1.2. Oxygen carriers

Oxygen carriers have to fulfil some requirements. High reactivity in the oxidation reaction with air and the reduction reaction with the fuel are of great importance. The particles must not agglomerate and be resistant against attrition and fragmentation, as they are exposed to high physical stress through the circulation in the chemical looping combustion unit. Oxygen carriers also have the demand of being cheap, no danger for the human health, and environmentally friendly [7]. Common oxygen carrier materials are iron oxide, cobalt oxide, copper oxide, manganese oxide and nickel oxide.

The oxidizing behaviour of common oxygen carrier materials is depicted in Fig. 2. The illustration shows the redox behaviour of the different oxygen carrier materials as a function of temperature and oxygen partial pressure [8,9]. It is noticeable that there is a difference between pure iron oxides and iron aluminate.

1.2.1. Iron oxide as oxygen carrier

Compared to other oxygen carriers, iron oxide is a relatively cheap [10]. Other advantages of iron based oxygen carriers are low toxicity and they environmentally friendly [11]. Furthermore, the oxidation to Fe_2O_3 is not thermodynamically limited in the chemical looping combustion environment (compare Fig. 2). Reduced forms of Fe_2O_3 can be Fe_3O_4, FeO and Fe [6,12]. Sakata et al.[13,14] investigated the ion mobility in iron based catalysts. They identified that iron ions are diffusing during the redox process while lattice oxygen is not very mobile. Monazam et al.[15] proposed a reaction mechanism for the conversion of methane, assuming Fe_2O_3 as fully oxidized species: First, an initial reduction of hematite to wustite occurs on the surface. Second, with reduced species present on the surface, two reactions take place. Further reduction of hematite to wustite giving CO and H_2 and reduction of hematite to magnetite leading to CO_2 and H_2O. The proposed overall reaction of hematite to wustite with CH_4 is:

$$7CH_4 + 27Fe_2O_3 \longrightarrow 10Fe_3O_4 + 24FeO + 4CO_2 + 3CO + 6H_2O + 8H_2 \quad (3)$$

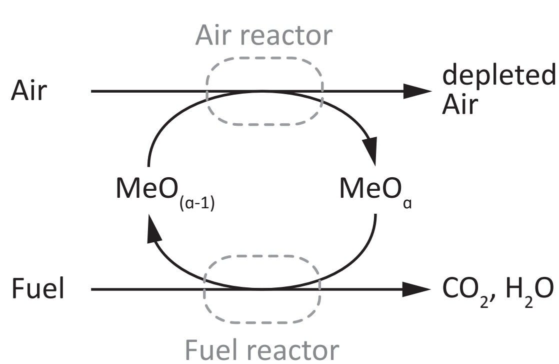

Fig. 1. Scheme of the Chemical Looping Combustion process.

It has to be mentioned that Monazam et al.[15] investigated the hematite reduction in a temperature range of 700 °C to 825 °C. The proposed mechanism corresponding to (3) leads to a mixture of magnetite and wustite in the oxygen carrier and incomplete conversion to CO_2. Abad et al. [16] investigated the use of iron oxide as oxygen carrier in a small scale CLC unit ($100W_{th}$ to $300W_{th}$). They did not observe any carbon formation on the bed material during the reduction step. Full fuel conversion was not reached with methane, though. The performance of an iron based oxygen carrier with focus on carbon formation has been investigated by Cho et al. [17]. Even under conditions with low fuel conversion, carbon formation on the oxygen carrier was not observed.

The oxygen carrier used in this study is a mixture of Fe_2O_3 and Al_2O_3 (Fe17). The synthetic material was developed at the Instituto de Carboquímica (CSIC) in Zaragoza and produced by Johnson Matthey. Fe17 was tested earlier in the 500 W_{th} CLC continuous unit at CSIC using methane as a fuel [18]. A determination of the kinetic parameters, relevant for CLC, has been performed by Cabello et al. [19] with a material of similar composition. Since Fe17 contains a significant amount of alumina as support material, the ternary system Fe-Al-O is used to describe the oxygen carrier. The phase relationships of Fe-Al oxides have been investigated by Turnock et al. [20]. A more recent description of the system is given by Kubaschewski et al. [21]. Both report that above 860 °C a spinel solid solution of $FeAl_2O_4$ (hercynite) and magnetite is formed. Below this temperature a miscibility gap leads to iron rich and aluminium rich solid solutions. This effect is also reported by Kapelyushin et al.[22]. Dreval et al.[23] investigated the Al_2O_3 - Fe_2O_3 - FeO system. They report that hematite and also alumina are soluable in the spinel solid solution at elevated temperatures. Since the Fe17 material is produced by impregnation, it is expected that fresh particles show a high concentration of iron on the particle surface. This iron gradient is expected to disappear with operating time under CLC conditions, leading to more or less homogeneous particles. Furthermore, hercynite is expected to be present in the reduced form of the oxygen carrier. Zhang et al.[24] proposed the following reactions for an iron based oxygen carrier with alumina support:

$$CH_4 + 4Fe_2O_3 + 8Al_2O_3 \longrightarrow 8FeO \cdot Al_2O_3 + CO_2 + 2H_2O \quad (4)$$

$$8FeO \cdot Al_2O_3 + 2O_2 \longrightarrow 4Fe_2O_3 + 8Al_2O_3 \quad (5)$$