CHEMICAL ENGINEERING RESEARCH AND DESIGN 86 (2008) 1017–1026

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

The use of ilmenite as an oxygen carrier in chemical-looping combustion

Henrik Leion[a,*], *Anders Lyngfelt*[b], *Marcus Johansson*[a], *Erik Jerndal*[a], *Tobias Mattisson*[b]

[a] *Department of Environmental Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden*
[b] *Department of Energy and Environment, Chalmers University of Technology, S-412 96 Göteborg, Sweden*

ABSTRACT

The feasibility of using ilmenite as oxygen carrier in chemical-looping combustion has been investigated. It was found that ilmenite is an attractive and inexpensive oxygen carrier for chemical-looping combustion. A laboratory fluidized-bed reactor system, simulating chemical-looping combustion by exposing the sample to alternating reducing and oxidizing conditions, was used to investigate the reactivity. During the reducing phase, 15 g of ilmenite with a particle size of 125–180 μm was exposed to a flow of 450 mL_n/min of either methane or syngas (50% CO, 50% H_2) and during the oxidizing phase to a flow of 1000 mL_n/min of 5% O_2 in nitrogen. The ilmenite particles showed no decrease in reactivity in the laboratory experiments after 37 cycles of oxidation and reduction. Equilibrium calculations indicate that the reduced ilmenite is in the form $FeTiO_3$ and the oxidized carrier is in the form $Fe_2TiO_5 + TiO_2$. The theoretical oxygen transfer capacity between these oxidation states is 5%. The same oxygen transfer capacity was obtained in the laboratory experiments with syngas. Equilibrium calculations indicate that ilmenite should be able to give high conversion of the gases with the equilibrium ratios $CO/(CO_2 + CO)$ and $H_2/(H_2O + H_2)$ of 0.0006 and 0.0004, respectively. Laboratory experiments suggest a similar ratio for CO. The equilibrium calculations give a reaction enthalpy of the overall oxidation that is 11% higher than for the oxidation of methane per kmol of oxygen. Thus, the reduction from $Fe_2TiO_5 + TiO_2$ to $FeTiO_3$ with methane is endothermic, but less endothermic compared to NiO/Ni and Fe_2O_3/Fe_3O_4, and almost similar to Mn_3O_4/MnO.

Keywords: Chemical-looping combustion (CLC); Oxygen carrier; Ilmenite; Iron oxide; Titanium oxide

1. Introduction

Chemical-looping combustion (CLC) has been introduced as a technique where the greenhouse gas CO_2 is inherently separated during combustion. The CLC-process is composed of two fluidized bed reactors, an air and a fuel reactor, shown in Fig. 1. The fuel is introduced to the fuel reactor where it reacts with an oxygen carrier to CO_2 and H_2O, reaction (1). The reduced oxygen carrier is transported to the air reactor where it is oxidized back to its original state by air, reaction (2). In this paper, when oxidation and reduction is mentioned, it refers to oxidation and reduction of the oxygen carrier.

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

$$O_2 + 2Me_xO_{y-1} \leftrightarrow 2Me_xO_y \quad (2)$$

The fuel never mixes with air, resulting in a stream of oxygen-depleted air from the air reactor, and a stream of combustion gases from the fuel reactor, which mainly consists of CO_2 and H_2O. The water is easily condensed and, after compression, the CO_2 can be transported to a suitable underground storage location. The total amount of heat resulting from reactions (1) and (2) is the same as for a normal combus-

* *Corresponding author*. Tel.: +46 31 7722886; fax: +46 31 7722853.
E-mail address: Leion@chalmers.se (H. Leion).
Received 16 November 2007; Accepted 31 March 2008
0263-8762/$ – see front matter
doi:10.1016/j.cherd.2008.03.019

Nomenclature

m	mass of oxygen carrier (g)
m_{ox}	mass of oxygen carrier for in its most oxidized state (g)
m_{red}	mass of oxygen carrier for reduced oxygen carrier (g)
R_o	the oxygen transfer capacity
x_{CH_4}	fraction of CH_4 in the outgoing gases after the water has been removed
x_{CO}	fraction of CO in the outgoing gases after the water has been removed
x_{CO_2}	fraction of CO_2 in the outgoing gases after the water has been removed
X	degree of conversion

Greek symbols

γ	gas yield
ω	mass-based conversion

tion where the fuel is in direct contact with air, thus a pure stream of CO_2 has been produced without any direct energy penalty for the separation of gases.

The CLC process has in a few years grown from a paper concept to a promising technique for CO_2-capture and a number of prototypes have been designed. The first successful demonstration with 100 h of operation was in a 10-kW prototype at Chalmers in 2003 (Lyngfelt and Thunman, 2005; Lyngfelt et al., 2004). Now the process has been demonstrated in reactor units ranging from 300 W to 50 kW using natural gas or syngas as fuel (Abad et al., 2006, 2007a; Adanez et al., 2006; de Diego et al., 2007; Johansson et al., 2006a,b; Linderholm et al., accepted for publication; Lyngfelt and Thunman, 2005; Lyngfelt et al., 2004; Ryu et al., 2004). Furthermore a 10-kW unit at Chalmers designed for solid fuel has been operated with coal and petroleum coke (Berguerand and Lyngfelt, accepted for publication, 2008). Various aspects of the oxygen carriers needed in the CLC-process have been investigated such as

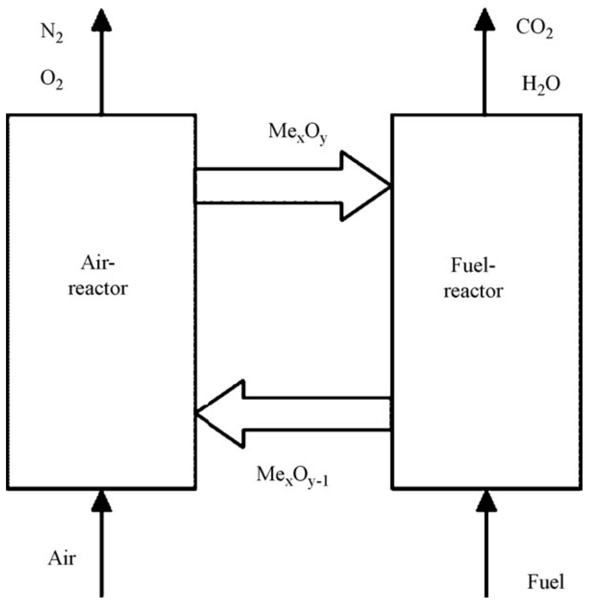

Fig. 1 – Schematic picture of the CLC-process. Two interconnected fluidized bed reactors, an air and a fuel reactor, with circulating oxygen-carrying particles.

different combination of active oxides and support materials and the effect of sintering temperatures (Adanez et al., 2004, 2005; Johansson, 2007; Mattisson et al., 2004), different manufacturing processes (Ishida et al., 1996) and thermodynamic restrictions (Jerndal et al., 2006). An overview of literature concerning CLC including over 100 publications is given by Johansson et al. (2006c).

A majority of the publications concerning CLC have used gaseous fuel such as natural gas or methane. Since solid fuels are considerably more abundant and often less expensive than natural gas, it would be highly advantageous if the CLC-process could be adapted for solid fuels. Lyon and Cole (2000) studied the conversion of coal with Fe_2O_3 in a small fluidized bed reactor and found that SO_2 enhances the conversion rate. Pan et al. (2004) proposed a design for a CLC unit with solid fuel. Cao et al. (2005) performed TGA experiments showing that it is possible to reduce CuO using coal as fuel. Moreover, Dennis et al. (2006) and Scott et al. (2006) demonstrated that lignite char could be oxidized using Fe_2O_3 as oxygen carrier in a small bed reactor fluidized with steam and CO_2. Leion et al. (2007) used Fe_2O_3 supported with $MgAl_2O_4$ as oxygen carrier and petroleum coke as fuel to investigate the effect of different reaction parameters such as temperature and different composition of the fluidizing gas. Mattisson et al. has also proposed a novel combustion technique utlilizing chemical-looping, i.e. chemical-looping with oxygen uncoupling (CLOU), for combustion of solids fuel (Mattisson et al., accepted for publication). In this technology, the solid fuel is actually burnt with gas-phase oxygen, released from an oxygen carrier in the fuel reactor. There are also a few publications on CLC using syngas as fuel (Abad et al., 2006; Copeland et al., 2002; Johansson et al., 2006b; Mattisson et al., 2006) which are of relevance, because solid fuels during gasification produce CO and H_2, which are important reaction intermediates in CLC with solid fuel. Moreover, Gupta et al. (2005) have performed TGA experiments where Fe_2O_3 supported with TiO_2 is used to produce syngas from coal.

In all these publications, except Berguerand and Lyngfelt (accepted for publication, 2008), the oxygen carrier has been manufactured using pure chemicals. These are high-cost materials and may not be well suited for solid fuels since lifetime of the oxygen carrier in a CLC-system with solid fuels may be restricted by deactivation caused by ash or by loss of material with the ash when separated from the oxygen carrier. Therefore, low-cost materials with sufficient reactivity towards H_2 and CO are of interest when using solid fuels in CLC. An example of such an oxygen carrier is the natural mineral ilmenite which will be the focus of this paper. Ilmenite has recently been tested by Berguerand and Lyngfelt (accepted for publication, 2008) and Leion et al. (2008).

In this paper, the reactivity of ilmenite towards methane and syngas as well as the fluidization properties of ilmenite were investigated experimentally in a laboratory setup. This included both long-term experiments to verify that particles can sustain multiple cycles of oxidation and reduction, as well as test where the length of the reducing period was gradually increased in order to investigate whether the degree of reduction has any effect on fluidization of particles. The ilmenite used in these experiments has been compared with unused ilmenite using X-ray diffraction (XRD) as well as with scanning electron microscope (SEM). Thermodynamic properties of ilmenite were calculated and compared with results from experiments.