

Chalmers Publication Library



This document is the accepted manuscript version of a published work that appeared in final form in *Fuel*, © Elsevier, after peer review and technical editing by the publisher. To access the final edited and published work, see <http://dx.doi.org/10.1016/j.fuel.2010.06.010>

(Article begins on next page)

Ilmenite with addition of NiO as oxygen carrier for chemical-looping combustion

Magnus Rydén^{1,*}, Marcus Johansson², Erik Cleverstam², Anders Lyngfelt¹, Tobias Mattisson¹

¹Department of Energy and Environment
Chalmers University of Technology
SE-412 96, Göteborg, Sweden

²Department of Chemical and Biological Engineering
Chalmers University of Technology
S-412 96 Göteborg, Sweden

Abstract

The naturally occurring mineral ilmenite, FeTiO_3 , has been examined as oxygen carrier for chemical-looping combustion. NiO-based particles have been used as an additive, in order to examine if it is possible to utilize the catalytic properties of metallic Ni to facilitate decomposition of hydrocarbons into more reactive combustion intermediates such as CO and H_2 . Firstly, ilmenite was examined by oxidation and reduction experiments in a batch fluidized-bed reactor. These experiments indicated moderate reactivity between ilmenite and CH_4 , which was used as reducing gas. However, adding 5 wt% of NiO-based particles to the ilmenite improved the conversion of CH_4 greatly, resulting in an increase in combustion efficiency with a factor of 3. Secondly, 83 hours of chemical-looping combustion experiments were conducted in a small circulating fluidized-bed reactor, using ilmenite as oxygen carrier and natural gas as fuel. A wide range of process parameters and different levels of NiO addition were examined. Occasionally, there were problems with the circulation of solids between the air reactor and fuel reactor, but most of the time the experiments worked well. The products were mostly CO_2 , H_2O and unconverted CH_4 . Adding small amounts of NiO-based particles to the reactor increased the conversion of the fuel considerably. For the base case conducted at 900° , the combustion efficiency was 76% for pure ilmenite and 90% for the corresponding experiments with 1 wt% NiO-based particles added to the reactor. The properties of ilmenite were found to change considerably during operation. Used particles had lower density, were more reactive and more porous than fresh particles. These changes appear to have been physical, and no unexpected chemical phases could be identified.

Keywords: Chemical-Looping Combustion; Ilmenite; Natural Gas

*Corresponding author: Tel. (+46) 31 7721457, Email: magnus.ryden@chalmers.se
Fuel 2010; 89: 3523-3533.

Abbreviations

CLC	Chemical-looping combustion
C_nH_m	Generic hydrocarbon fuel
f_{CH_4}	Fraction of unconverted methane (<i>vol%</i>)
F	Volumetric flow (L_n/min)
H_{lhw}	Lower heating value (J/mol)
L_n/min	Normal litres per minute
m	Mass (g)
Me	Generic oxygen carrier, reduced
MeO	Generic oxygen carrier, oxidized
n	Number of moles
R_0	Oxygen ratio, i.e. active oxygen content of oxygen carrier (<i>wt%</i>)
t	Time (s, min)
wt%	Percentage by weight
vol%	Percentage by volume
X	Degree of oxidation of oxygen carrier (<i>%</i>)
x	Dry-gas concentration (<i>vol%</i>)
y	Wet-gas concentration (<i>vol%</i>)
γ_{eff}	Combustion efficiency (<i>%</i>)

Indexes

ar	Air reactor, or batch reactor during oxidation
fr	Fuel reactor, or batch reactor during reduction
i	Generic index
ng	Natural gas
oc	Oxygen carrier
ox	Completely oxidized oxygen carrier
red	Completely reduced oxygen carrier
s	Sample of oxygen-carrier particles

1. Introduction

In later years, concerns that emissions of CO_2 from combustion of fossil fuels may lead to changes in the climate of the earth have been growing steadily. As a consequence, a majority of the scientific community now concludes that global CO_2 emissions would need to be reduced greatly in the future.

One way to reduce CO_2 emissions that is receiving increased interest is carbon capture and storage, which involves capturing of CO_2 in emission sources and storing it where it is prevented from reaching the atmosphere. For example, CO_2 could be captured in flue gases from combustion or industrial processes, and stored in geological formations such as depleted oil fields or deep saline aquifers.

Chemical-looping combustion involves oxidation of a fuel using oxygen from a solid oxygen carrier. This way the products are not diluted with N_2 and pure CO_2 for sequestration is obtained without the need for costly gas separation. Due to this unusual and attractive feature, chemical-looping combustion could have an important role to play in the global task to reduce anthropogenic CO_2 emissions.

2. Technical background

2.1 Chemical-looping combustion (CLC)

In chemical-looping combustion, two separate reactors are used, one for air and one for fuel. A solid oxygen carrier performs the task of transporting oxygen between the reactors. Direct contact between fuel and air is avoided, so the combustion products are not diluted with N_2 , see Figure 1.

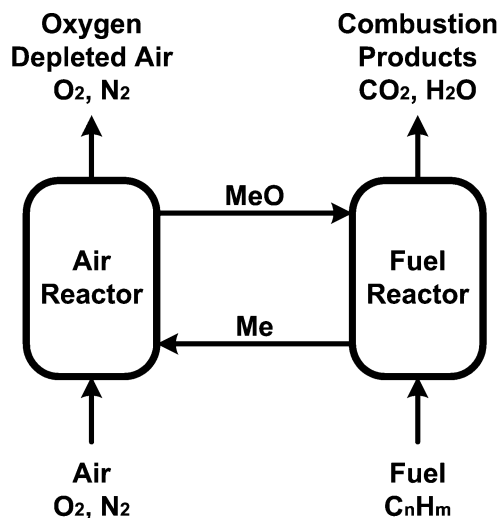
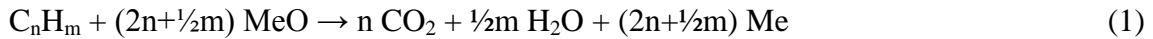


Figure 1. Schematic description of chemical-looping combustion.

Typically, the abbreviation MeO is used to describe the oxygen carrier in its oxidized form, while Me is used for the reduced form. This is because many potential oxygen-carrier materials are metal oxides.

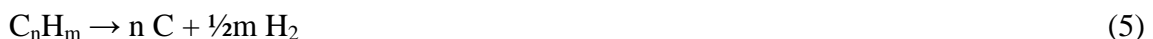
The oxygen carrier circulates between the reactors. In the fuel reactor, it is reduced by the fuel, which in turn is oxidized to CO₂ and H₂O according to reaction (1). In the air reactor, it is oxidized to its initial state with O₂ from the combustion air according to reaction (2).



The amount of energy released or required in each reactor vessel depends on the nature of the oxygen carrier and the fuel. Reaction (2) is always strongly exothermic. For most oxygen-carrier materials, reaction (1) is endothermic if the fuel is a hydrocarbon. Therefore the flow of solid oxygen carrier is also needed to transport heat from the air reactor to the fuel reactor. The net energy released in the reactor system is the same as in ordinary combustion. This is apparent since combining reaction (1) and reaction (2) yields reaction (3), which is complete combustion of the fuel with O₂.



Possible side reactions include formation of solid carbon in the fuel reactor. This is undesired since solid carbon could follow the oxygen-carrier particles to the air reactor and burn there, which would reduce the degree of CO₂ capture. Solid carbon could be formed either through the Boudouard reaction, reaction (4), or through hydrocarbon decomposition, reaction (5).



It is well established that reactions (4-5) can be catalysed by metallic surfaces. Hence carbon formation could possibly become an obstacle, if an oxygen carrier that is reduced directly to a metal phase is used as oxygen carrier.

In practice, a chemical-looping combustion process could be designed in different ways, but circulating fluidized beds with oxygen-carrier particles used as bed material are likely to have an advantage over other alternatives since this design is straightforward, provides good contact between gas and solids and allows a smooth flow of oxygen-carrier particles between the reactors.

Compared with conventional combustion, chemical-looping combustion has several potential benefits. The exhaust gas from the air reactor is harmless, consisting mainly of N_2 and possibly some O_2 . There should be no thermal formation of NO_x since regeneration of the oxygen carrier takes place without flame and at moderate temperatures. The gas from the fuel reactor consists of CO_2 and H_2O , so cooling in a condenser is all that is needed to obtain almost pure CO_2 . Therefore, chemical-looping combustion should be a very attractive technology for power generation with CO_2 capture.

2.2 Oxygen-carrier materials

A feasible oxygen-carrier material for chemical-looping combustion should:

- Have high reactivity with fuel and oxygen.
- Be thermodynamically capable to convert a large share of the fuel to CO_2 and H_2O .
- Have a sufficiently high oxygen ratio, e.g. the mass fraction of the material that is oxygen which can react according to reaction (1) should be high.
- Have low tendency for fragmentation, attrition, agglomeration and other kinds of mechanical or thermal degeneration.
- Not promote extensive formation of solid carbon in the fuel reactor.
- Preferably be cheap and environmentally sound.

Metal oxides such as NiO , Fe_2O_3 , Mn_3O_4 and CuO supported on inert carrier material such as Al_2O_3 or stabilized ZrO_2 are likely candidates to meet those criteria. An overview of the research treating these kinds of oxygen-carriers can be found in the works of Cho [1], Johansson [2] and Adánez et al [3]. Information about additional potential oxygen-carrier materials can be found in the work of Jerndal et al [4], which includes a theoretical examination of 27 different oxide systems. Carbon formation on oxygen-carrier particles for chemical-looping combustion has been specifically examined by Cho et al [5]. Continuous chemical-looping combustion in circulating fluidized beds has been demonstrated by Lyngfelt

et al [6], Ryu et al [7], Johansson et al [8, 9], Abad et al [10, 11], Adánez et al [12], Linderholm et al [13, 14, 15], De Diego et al [16], Berguerand et al [17, 18], Rydén et al [19], Kolbitsch et al [20], and Pröll et al [21]. Reaction kinetics for oxygen carriers have been examined by Abad et al [22, 23] and by Zafar et al [24, 25]. The effects of pressure on the behaviour of oxygen-carrier materials have been examined by García-Labiano et al [26]. An overview of various subjects regarding chemical-looping combustion, such as design of experimental reactors, power production with CO₂ capture, chemical looping for production of H₂ and synthesis gas, and more about oxygen-carriers can be found in the doctoral theses by Brandvoll [27], Johansson [28], Wolf [29], Kronberger [30], Naqvi [31], Leion [32] and Rydén et al [33].

2.3 Mixed oxides as oxygen carrier

A mixed-oxide oxygen carrier for chemical-looping combustion consists of more than one active phase, and should be able to take advantage of favourable characteristics of each, i.e. create some kind of positive synergy effect.

Of the commonly suggested oxygen-carrier materials, NiO has shown the highest reactivity with CH₄. When reduced by a fuel, NiO is converted directly into metallic Ni, which is well known to catalyse decomposition of CH₄ and other hydrocarbons. Mattisson et al [34] found that almost complete conversion of CH₄ into CO₂ and H₂O can be achieved with a very small bed of NiO material, and that the reaction proceeds with CO and H₂ as intermediates. Unfortunately, using NiO as oxygen carrier for chemical-looping combustion has some drawbacks. NiO is relatively expensive compared to other possible oxygen carriers and also a health hazard. Further, the conversion of hydrocarbons into H₂O and CO₂ at relevant temperatures will be limited to slightly above 99% due to thermodynamical constraints.

In contrast, Fe₂O₃ is cheap, abundant, non toxic and able to convert hydrocarbon fuel completely into CO₂ and H₂O. The reactivity with CH₄ is low compared to NiO, likely since Fe₂O₃ is reduced to Fe₃O₄ rather than to a metallic phase that could help catalyze the decomposition of hydrocarbons. However, the reactivity of Fe₂O₃ with CO and H₂ has been found to be high, see Mattisson et al [35]. Therefore it seems reasonable to believe that the rate-limiting step for chemical-looping combustion of hydrocarbons using Fe₂O₃ as oxygen carrier is conversion of CH₄ into reactive intermediates such as CO and H₂, see Johansson et al [36].

A mixed-oxide oxygen carrier which combines the low price and high availability of Fe₂O₃ with the catalytic properties of Ni would increase the attractiveness of the chemical-looping

combustion concept, since the cost for and potential environmental impact of highly reactive oxygen-carrier materials could be greatly reduced. Small amounts of NiO would likely be sufficient to facilitate decomposition of hydrocarbons and CH₄ into CO and H₂, which react fast with Fe₂O₃. In a study by Johansson et al [37], it was found that addition of as little as 1 wt% NiO to a sample of Fe₂O₃ improved the capacity of the sample to convert CH₄ into CO₂ and H₂O considerably.

2.4 Ilmenite as oxygen carrier

Ilmenite is a naturally occurring mineral with the approximate chemical composition FeTiO₃. The term is also commonly used for various ores containing more or less of this phase. Ilmenite is cheap, non toxic, and the most abundant of all titanium minerals. It is mined in substantial quantities in many countries, mainly as raw material for TiO₂ production.

Ilmenite could be an attractive oxygen-carrier material for chemical-looping combustion. It has the desired thermodynamical properties and thus could provide close to 100% combustion efficiency. During chemical-looping combustion of hydrocarbons, the reduced level would be ilmenite, FeTiO₃, corresponding to FeO+TiO₂, while the oxidized level would be Fe₂TiO₅+TiO₂, corresponding to Fe₂O₃+2TiO₂.

Details about the possibility to use ilmenite as oxygen carrier for chemical-looping combustion can be found in a study by Leion et al [38]. In the cited study, it was found that while ilmenite reacts fairly slowly with CH₄, it has surprisingly high reactivity with CO and H₂. Therefore, ilmenite appears to be an ideal base material for mixed-oxide oxygen carriers. Ilmenite have also been successfully used as oxygen-carrier material for chemical-looping combustion both of solid fuels, see Berguerand et al [17, 18] and of gaseous fuels, see Kolbitsch et al [20], and Pröll et al [21].

2.5 The aim of this study

The objective of this study is to examine if ilmenite could be a feasible oxygen-carrier material for chemical-looping combustion of natural gas, and also to examine if it is possible to improve the reactivity between ilmenite and natural gas by addition of small amounts of catalytic NiO-based material.

3. Experimental

3.1 Oxygen-carrier materials

Ilmenite was supplied by Titania A/S. It was 94.3% pure and concentrated from a naturally occurring ore containing 40 wt% ilmenite, 37 wt% plagioclase, 8.6 wt% orthopyroxene, 6.5 wt% clinopyroxene, 4.2 wt% biotite and some minor other phases. The iron and titanium molar ratio was close to 1:1. The concentrated material was crushed and grinded into a suitable size distribution. The resulting particles were quite hard, non spherical and relatively non porous. The crushing strength was 3.7 N, if measured on particles of the size 180-250 μm . The apparent density was 3.7 g/cm^3 , which corresponds to a void factor of roughly 20%. The BET surface area for fresh particles was 0.11 m^2/g .

Mixed-oxide samples were prepared by mixing ilmenite particles with particles containing NiO. Two different NiO-based particles were used as additives. N6AM1400 consisted of 60 wt% NiO supported on MgAl_2O_4 , and was produced from fine chemical powders by freeze granulation and sintering for 6 hours at 1400°C. N18- α - Al_2O_3 consisted of 18 wt% NiO supported on Al_2O_3 , and was produced by dry impregnation of $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ onto α - Al_2O_3 , calcination at 550°C for 30 minutes and sintering at 950°C for 60 minutes. These two materials are proven oxygen carriers that have been used in previous experimental work, see for example Johansson et al [8, 9], Rydén et al [19] and de Diego et al [39]. Occasionally, these oxygen carriers will be referred to as simply as N6AM and N18 in this paper.

3.2 The batch fluidized-bed reactor

The batch experiments were conducted in two different quartz reactors. Both reactors were 820 mm long. The first reactor had an inner diameter of 30 mm while the second reactor had an inner diameter 22 mm. In both reactors, a porous quartz plate, on which the oxygen-carrier sample is applied, was located 370 mm above the bottom. During operation, the sample is fluidized by adding gas to the bottom of the reactor, while the porous plate acts as gas distributor.

In order to reach suitable temperature the reactor is placed inside an electrically heated furnace. Chemical-looping conditions are simulated by alternating between oxidizing and reducing fluidization gas. Reactor temperature is measured below and above the porous plate, using thermocouples enclosed in quartz shells. The pressure drop over the bed is measured with pressure transducers. The gas from the reactor is led to a cooler, in which the water is removed. Following this step the volumetric flow of gas is measured, and the gas composition analyzed. The concentrations of CO_2 , CO and CH_4 are measured using infrared analyzers, while O_2 is measured with paramagnetic sensors.

All graphs presented in this paper are from experiments conducted in the 22 mm reactor. Early experiments using the 30 mm reactor often resulted in problems with defluidization of the samples, likely due to insufficient gas velocity. This will be discussed in section 4.1 below.

3.3 The circulating fluidized-bed reactor

The continuously operating experiments were carried out in a small-scale laboratory reactor. The reactor has previously been used for similar experiments by Rydén et al [19, 33], and is a slightly altered version of a reactor that has been successfully used in previous work [8, 9, 10, 11, 28, 33, 40]. A schematic picture is shown in Figure 2.

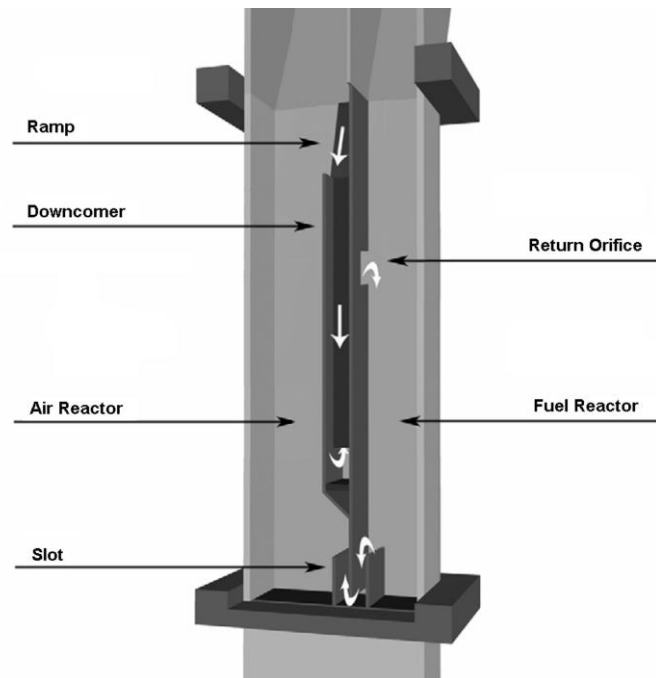


Figure 2. Schematic description of the circulating fluidized-bed reactor. During operation, the downcomer and roughly a third of the air and fuel reactor is filled with oxygen carrier particles in the size range 125-180 μm .

The reactor is designed for chemical-looping combustion experiments using gaseous fuels. Suitable flows are 0.20-0.75 $\text{L}_\text{n}/\text{min}$ natural gas and 3-10 $\text{L}_\text{n}/\text{min}$ air. The solids inventory should be 100-300 g, depending on particle density.

The reactor is 200 mm high. The base of the fuel reactor measures 25×25 mm. The air reactor is 25×40 mm in the bottom and 25×25 mm in the upper narrow part. Fuel and air enter

the system through separate wind boxes, located in the bottom of the reactor. Porous quartz plates act as gas distributors. In the air reactor the gas velocity is sufficiently high for oxygen-carrier particles to be thrown upwards. Above the reactor there is a separate vessel for particle separation. Here the reactor widens and particles are allowed to fall back into the air reactor. A fraction of these particles falls into the downcomer, which is a J-type loop-seal. From the loop-seal, particles are ejected into the fuel reactor via the return orifice. Particles return to the air reactor through a U-type slot, and this way, a continuous circulation of oxygen-carrier particles is obtained. The downcomer and the slot are fluidized with small amounts of inert gas, such as N₂ or Ar.

In order to make it possible to reach and sustain a suitable temperature, the reactor is placed inside an electrically heated furnace. The temperature in each reactor section is measured with thermocouples located 70 mm above the distributor plates.

On the exit pipe from the fuel reactor there is a water seal that makes it possible to control the pressure in the fuel reactor by changing the height of a water column. Along the reactor sections there are thirteen separate pressure measuring taps. By measuring differential pressures between these spots, it is possible to estimate where particles are located in the system, and to detect disturbances in the fluidization.

Steam can be added to the fuel by means of a steam generator. The fuel-steam mix is transferred to the reactor in a heated tube with a temperature of 150°C. It is also possible to dilute the fuel with N₂, Ar or CO₂.

Prior to analysis, the gas from the reactor passes through particle filters, coolers and water traps. Therefore, all measurements are made on dry gas. CO₂, CO and CH₄ are measured using infrared analyzers, while O₂ is measured with paramagnetic sensors. The gas from the fuel reactor is also examined with a gas chromatograph, which is necessary in order to measure H₂. In addition to this, the gas chromatograph also measures CO₂, CO, CH₄, O₂ and N₂.

3.4 Evaluation of data

For the circulating fluidized bed experiments, the concentration of H₂ in the gas from the fuel reactor was measured with gas chromatography, which provided one measuring point every five minutes. For the batch experiments, H₂ could only be measured by bag sampling, which also provided relatively few measuring points.

In order to facilitate the analysis, an estimated value of the concentration of H₂ in dry gas, $x_{H_2,fr}$, was also calculated, as supplement to the data measured with the gas chromatograph.

This was done by solving the species balance over the reactor, assuming that there was no formation of solid carbon and that the gas composition from the fuel reactor corresponded to thermodynamical equilibrium for the water-gas shift reaction. The calculated numbers for $x_{H_2,fr}$ were close to those measured directly with the gas chromatograph. This could be expected, since the reaction rate for the water-gas shift reaction should be high at the used temperatures. The wet gas concentration was calculated by a species balance, under the assumption that there was no formation of solid carbon in the fuel reactor and that equilibrium conditions were established. A detailed description of the methodology for these calculations can be found elsewhere¹⁹.

The performance of a chemical-looping combustion process can be expressed with the combustion efficiency, γ_{eff} , which is defined in expression [6].

$$\gamma_{eff} = 1 - \frac{n_{CH_4,fr} \times H_{lhw,CH_4} + n_{CO,fr} \times H_{lhw,CO} + n_{H_2,fr} \times H_{lhw,H_2}}{n_{fuel,in} \times H_{lhw,fuel}} \quad (6)$$

In expression (6), n_i is the molar flows of each component, while $H_{lhw,i}$ is its lower heating value. The definition does not take into account the possibility of formation of solid carbon in the fuel reactor or that higher hydrocarbons could be present in the fuel-reactor gas. Neither of these phenomena is believed to have occurred at any significant degree during the experiments presented in this paper.

It can also be of interest to look specifically at the fraction of unconverted CH_4 that slips through the reactor and compare it to the total amount of added carbon, f_{CH_4} , see expression (7).

$$f_{CH_4} = F_{CH_4,fr} / (F_{fuel} \times n_{c,fuel}) = x_{CH_4,fr} / (x_{CO_2,fr} + x_{CO,fr} + x_{CH_4,fr}) \quad (7)$$

The oxygen ratio, R_0 , is defined in expression (8), and the degree of oxidation of the oxygen carrier, X , is defined in expression (9).

$$R_0 = (m_{s,ox} - m_{s,red}) / m_{s,ox} \quad (8)$$

$$X = \frac{m_s - m_{s,red}}{m_{s,ox} - m_{s,red}} \quad (9)$$

In expressions (13-14), m_s is the actual mass of sample, $m_{s,ox}$ is the mass of the sample when fully oxidized, and $m_{s,red}$ the mass of the sample while completely reduced. R_0 describes the mass fraction of the particle that can theoretically be released as oxygen during operation and is about 5 wt% for ilmenite, 21.4 wt% for NiO, 12.8 wt% for N6AM1400 and 3.9 wt% for N18- α -Al₂O₃.

The actual degree of reduction X change during operation, and is calculated in different ways depending on experimental setup. A detailed description for calculation of X during batch experiments can be found elsewhere [2, 36, 37]. For the circulating-fluidized bed experiments, the most feasible way to estimate X is to see how much O₂ that is consumed during reoxidation of the oxygen carrier, see Figure 14 and section 4.2 below.

3.5 Experiments in batch fluidized-bed reactor

The aim of the batch experiment was to examine the general properties of ilmenite as oxygen carrier, and to examine if the reactivity could be improved by adding NiO. A sample of particles was placed on the porous plate. Then the reactor was heated to the desired temperature, which for these experiments was 950°C. During this period the reactor was fluidized with inert N₂.

Chemical-looping combustion was simulated by switching between reducing and oxidizing conditions. The sample was reduced with 0.30-0.45 L_n/min CH₄, with or without steam addition. Most often, the time of the reduction period was 25-30 seconds. Following the reduction, the sample was reoxidized with 1.0 L_n/min of a gas mix consisting of 5 vol% O₂ and 95 vol% N₂. The reason for not using air is that reaction (2) is highly exothermic, so a lower O₂ concentration was used in order to avoid extensive heating of the reactor. The oxidation reaction was fast and at no occasion did any O₂ pass through the sample before it was completely oxidized. To avoid oxygen and methane mixing during the shifts between reduction and oxidation, N₂ was introduced during 180 s after each period.

Although the furnace temperature was set to 950°C for all experiments, the bed temperature changed somewhat during reduction and oxidation due to the endothermic and exothermic nature of these reactions. During reduction, the temperature could be up to 1°C lower, while oxidation resulted in a temperature increase of up to 4°C.

10 samples of ilmenite was examined in the batch-fluidized bed reactor, see Table 1.

Sample	Composition	Size (μm)	Reactor (mm)	Redox Cycles	Reduction (L_n/min)	Dilution (L_n/min)	Reduction time (s)
B1*	15g ilmenite	125-180	30	10	0.3 CH ₄	0.30 H ₂ O	120
B2*	15g ilmenite	90-125	30	14	0.3 CH ₄	0.30 H ₂ O	90
B3	30g ilmenite	125-180	30	8	0.45 CH ₄	0.45 H ₂ O	90
B4	15g ilmenite	125-180	22	93	0.45 CH ₄	0 / 0.19 H ₂ O	30
B5*	14.25g ilmenite 0.75g N6AM1400	125-180	22	8	0.45 CH ₄	-	40
B6*	14.25g ilmenite 0.75g N6AM1400	125-180	22	6	0.45 CH ₄	-	40
B7	14.25g ilmenite 0.75g N6AM1400	125-180	22	11	0.45 CH ₄	-	25
B8	14.25g ilmenite 0.75g N6AM1400	125-180	22	14	0.45 CH ₄	0.19 H ₂ O	25
B9	15 g ilmenite / N6AM1400 ¹	125-180	22	12	0.45 CH ₄	-	25
B10*	15 g ilmenite / N18- α -Al ₂ O ₃ ²	125-180	22	12	0.45 CH ₄	-	25

Table 1. Summary of batch experiments. Samples marked with * experienced problems with defluidization or sintering, which is discussed in section 4.3 below. ¹ used particles from sample C1 in Table 2, with N6AM1400 particles. ² used particles from sample C4 in Table 2, with 10% N18- α -Al₂O₃ particles.

In Table 1, sample B1-B4 consists of fresh ilmenite, sample B5-B8 are fresh ilmenite with 5 wt% N6AM1400 and sample B9-B10 are used particles that have been taken from the circulating fluidized-bed reactor. Sample B4 was pre-treated in 73 redox cycles in order to obtain as stable results as possible, before being carefully examined for 10 cycles with only CH₄ as fuel, and finally 10 cycles with CH₄ diluted with H₂O.

For samples B1, B2, B5, B6 and B10 there were problems with defluidization or sintering, which will be discussed in section 4.3 below. The data presented in graphs in this paper refers only to experiments that did not experience such problems.

3.6 Experiments in circulating fluidized-bed reactor

The aim of the circulating fluidized-bed experiments was to convert natural gas to CO₂ and H₂O during continuous operation. Natural gas with a composition equivalent of C_{1.14}H_{4.25}O_{0.01}N_{0.005} was used as fuel. The fuel flow was 0.17-0.50 L_n/min natural gas and the air flow was 6.30-10.50 L_n/min. At low fuel flows, some N₂ or H₂O was added to the natural gas in order to obtain sufficient gas velocity in the fuel reactor.

Prior to the experiment, the furnace was heated to a temperature slightly above the desired fuel-reactor temperature, which was 780-950°C. During this period both reactor sections were fluidized with air. When sufficiently high temperature was reached, the air to the fuel reactor was replaced by N₂, and after a minute or two, by fuel. Some experiments were done by varying process parameters such as temperature and gas flows, while others were done at as stable conditions as possible.

At the end of each experiment, the oxygen-carrier particles were reoxidized. Most often, the following procedure was used. First, fuel and air was replaced with 1.0 L_n/min N₂ in each reactor part. At such low flow rate the gas velocity in the air reactor is lower than the terminal velocity for the particles, and the solids circulation stops. After a few minutes, N₂ was replaced with 1.0 L_n/min air in both reactor sections. Oxidation of ilmenite is comparably fast, so the time until O₂ breaks through the particle beds can be used to estimate the degree of reduction of the particles in each reactor section, and the magnitude of the solids circulation. Further, if there is accumulation of solid carbon in the system, it can be seen as CO₂ during the reoxidation period.

In total, 81 hours of continuously operating experiments with fuel was recorded. Four samples of ilmenite were used, each of them consisting of 200-300 g particles in the size range of 125-180 μm. NiO-based material was added to two of the samples, in order to examine if any synergy effects could be verified. A summary of the experiments can be found in Table 2.

Sample	Ilmenite (g)	NiO (g)	$F_{ng,fr}$ (L _n /min)	$F_{air,ar}$ (L _n /min)	$F_{H2O,fr}$ (L _n /min)	$F_{N2,fr}$ (L _n /min)	T_{fr} (°C)	Operation (hours)
C1	250	-	0.49	7.6	-	0-0.53	790-910	13
C1	250	2.5 N6AM1400	0.49	7.6	-	-	790-910	8
C2*	250	-	0.21-0.50	7.9	-	0.30-0.53	900	5
C3*	250-300	-	0.20-0.40	8.4-10.5	0-0.54	0-0.40	950	17
C4	200	-	0.17-0.37	6.3-10.5	0.54	-	850-950	20
C4	200	2 N18-α-Al ₂ O ₃	0.17-0.37	6.3-9.5	0.54	-	850-950	7
C4	200	10 N18-α-Al ₂ O ₃	0.17-0.37	6.3-8.4	0.54	-	850-950	8
C4	200	20 N18-α-Al ₂ O ₃	0.17-0.37	6.3-8.4	0.54	-	850-950	3

*Table 2. Summary of circulating fluidized-bed experiments. Each sample designation corresponds to a certain batch of ilmenite particles. For example, all samples with the designation C4 consists of the same ilmenite particles, but with different amounts of N18-α-Al₂O₃ addition. Samples marked with * experienced problems with the circulation of solids, which will be discussed in section 4.3 below.*

In Table 2, each sample designation corresponds to a certain batch of ilmenite particles. For example, all samples with the designation C4 consists of the same ilmenite particles, but with different amounts of N18-α-Al₂O₃ addition.

The reason for using four different samples was problems with the solids circulation. Some trial and error was needed before stable experiments could be carried out. Of the experiments listed in Table 2, sample C1 initially worked well, but eventually problems with formation of

solid carbon in the fuel reactor started to occur. In the end the circulation of solids just stopped. Particle agglomerates were found in the slot section and in the fuel reactor, which explains the stop in the circulation.

For sample C2-C3, the reproducibility of the experiments was not very good due to frequent disturbances in the solids circulation. This phenomenon will be discussed in section 4.3 below.

Sample C4 was a deliberate attempt to get more reproducible data by using milder process parameters. The amount of fuel added to the fuel reactor was reduced. In order to make up for the reduced flow in the fuel reactor, the natural gas was mixed with some steam. Adding steam to the natural gas decreases the partial pressure of reagents in the fuel reactor. This makes comparison with earlier experiments tricky. If the reaction between fuel and oxygen carrier is considered to be a reaction of the first order, the conditions should be roughly comparable to the conditions used for sample C1, and the setup still allowed the examination as to whether it is possible to improve the conversion of fuel into products by adding NiO-material to the ilmenite. Steam also inhibits formation of solid carbon in the fuel reactor, which otherwise could influence the results. Further, by reducing the fuel flow while keeping the same overall gas flow in the fuel reactor as before, the degree of oxidation on the particles in the fuel reactor could possibly be reduced. The experiments using sample C4 worked considerably more smoothly than sample C2-C3.

4. Results

4.1 Results of batch fluidized-bed experiments

The reactivity of fresh ilmenite with CH_4 was quite low. However, the combustion performance increased slightly for each reduction. In this aspect, the results were similar to those presented by Leion et al [38]. After a few redox cycles reasonably stable results could be obtained. The number of cycles needed to obtain stable results varied, and depended on the how far the ilmenite was reduced each cycle. For experiments where the particles was reduced extensively, i.e. with X approaching 0.5, only 4-8 reductions were required. When the degree of reduction each cycle was lower the changes occurred more slowly. This is the reason for why sample B4 was examined for more than 90 redox cycles.

The likely reason for this improvement in reactivity is changes in the physical structure of the particles. Used ilmenite particles was found to have considerably lower density compared

to fresh particles, as will be explained in section 4.4 below. Lower density means higher porosity and larger active surface area, which should increase the reaction rate.

Examples of the resulting gas composition during three typical reduction periods can be found in Figures 3-5.

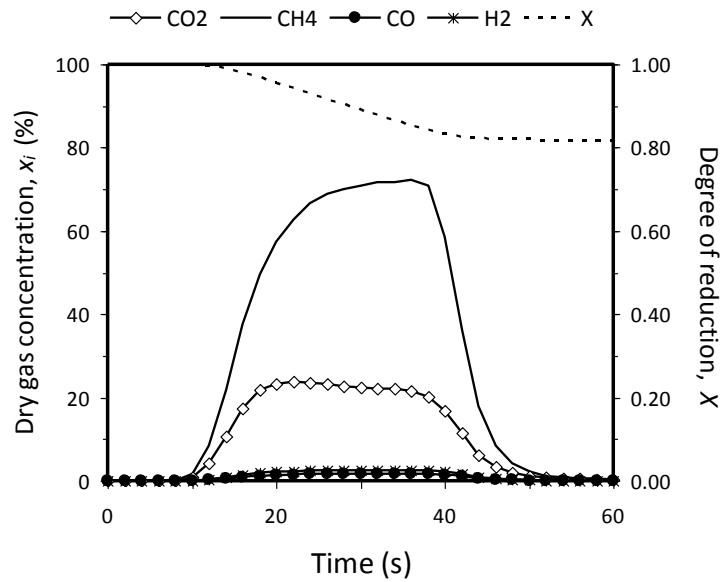


Figure 3. x_i for reduction of 15 g ilmenite with 0.45 L_{N}/min CH_4 at 950°C, sample B4, 48th reduction

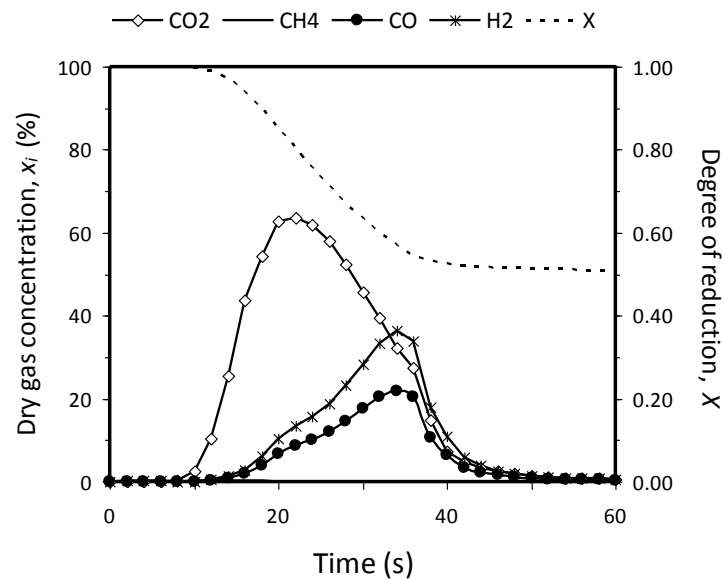


Figure 4. x_i for reduction of 14.25 g ilmenite and 0.75 g N6AM1400 at 950°C with 0.45 L_{N}/min CH_4 , sample B7, 8th reduction.

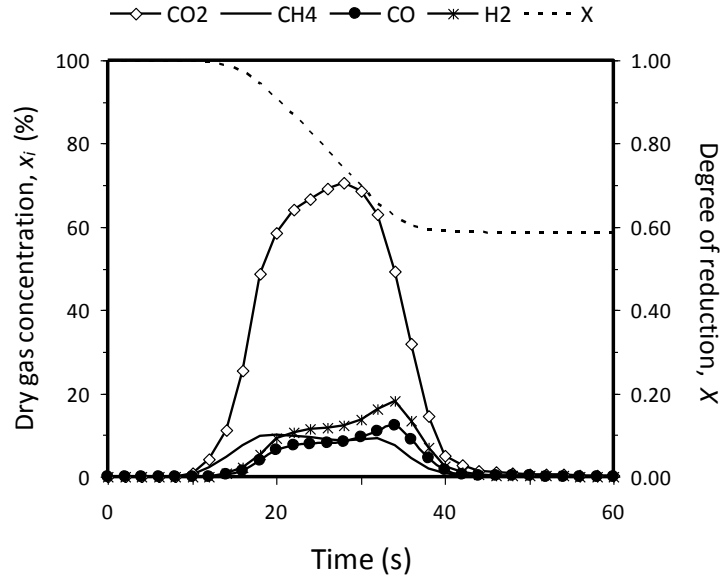


Figure 5. x_i for reduction of 14.85 g ilmenite and 0.15 g N6AM1400 at 950°C with 0.45 L_n/min CH_4 , sample B9, 8th reduction.

In Figures 3-5, the reason why the sum of the gas components differs from 100% in the beginning and the end of each reduction is due to back mixing of inert N_2 , which is added to the reactor in between reduction and oxidation periods.

A closer look on the combustion efficiency for the reduction periods in Figures 3-5 can be found in Figure 6, while the corresponding fraction of unconverted CH_4 can be found in Figure 7.

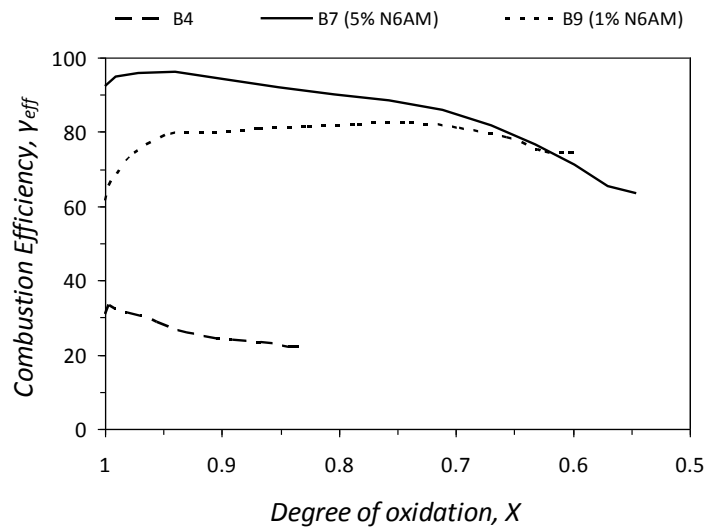


Figure 6. Combustion efficiency, γ_{eff} , as function of degree of oxidation, X , for the reductions presented in Figures 3-5, i.e. for reduction of 15 g sample with 0.45 L_n/min CH_4 at 950°C.

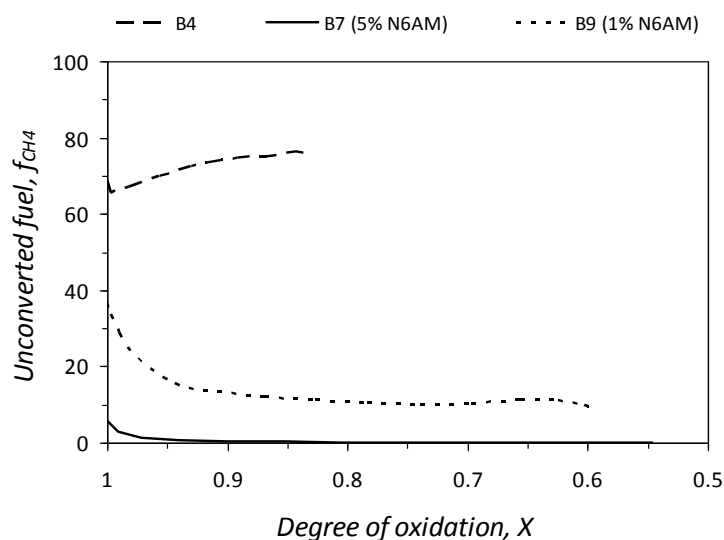


Figure 7. Fraction unconverted fuel, f_{CH_4} , as function of degree of oxidation, X , for the reduction periods presented in Figures 3-5.

In Figure 3 and Figure 7, it can be seen that there is only moderate conversion of CH_4 in the sample with only ilmenite. The products are mainly CO_2 and H_2O . As the sample is reduced, the outlet concentration of CH_4 increases steadily. The concentration of CO and H_2 remains very low during the whole reduction period.

In Figure 4, where 5 wt% N6AM1400 has been added to the sample, there is almost complete conversion of CH_4 . Initially, the products are mainly CO_2 and H_2O . As the sample is reduced the products shift towards H_2 and CO . The concentration of CH_4 is too small to be seen in Figure 4, but in Figure 7 it can be seen that there is a slight slip of CH_4 in the beginning of the reduction period. However, once sufficient amounts of metallic Ni is obtained there is 100% conversion of CH_4 .

The reduction shown in Figure 5, which is for ilmenite with 1 wt% N6AM1400 which have experienced 21 hours of operation in the circulating fluidized bed reactor (sample C1 in Table 2). The reactivity is in between that of pure ilmenite and ilmenite with 5 wt% N6AM1400 addition, which could be expected. Here complete conversion of CH_4 is not achieved.

In Figure 6, it can be seen that the apparent combustion efficiency was tripled by adding 5 wt% N6AM1400 to the sample. In fact, as little as 1 wt% N6AM1400 appears to have more than doubled the combustion efficiency.

In Figure 8, the accumulated amount of CO_2 produced during reduction of the same samples as is referred to in figures 3-7. Included in the figure is also the maximal theoretical amount of CO_2 that could be produced by added N6AM1400, if it is assumed that all oxygen present in the NiO material is used to oxidize CH_4 to CO_2 and H_2O .

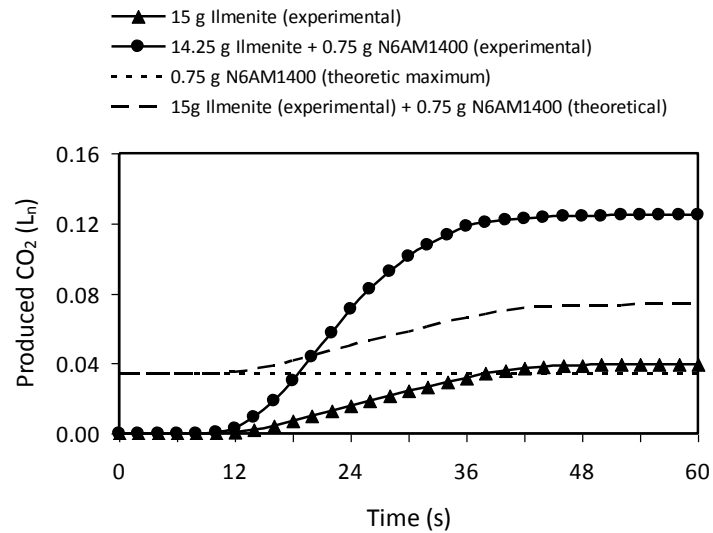


Figure 8a) CO_2 produced vs time for ilmenite at 950°C with/without adding 5 wt% N6AM1400, with $F_{\text{CH}_4}=0.45 L_n/\text{min}$. Dashed lines show maximum CO_2 from N6AM1400.

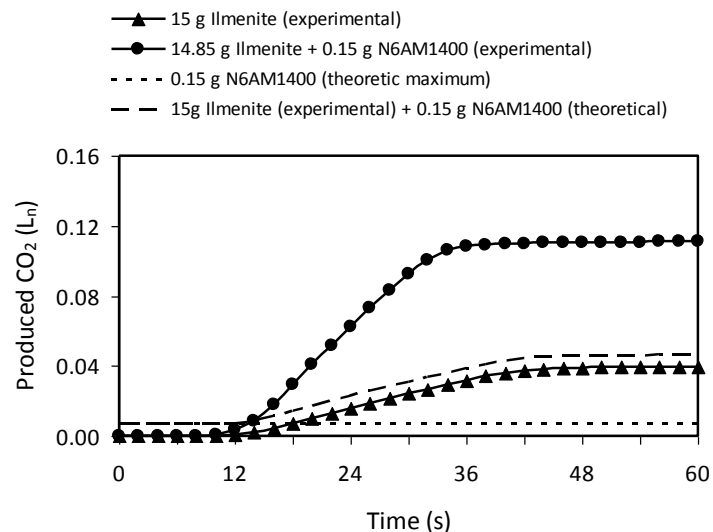


Figure 8b) CO_2 produced vs time for ilmenite at 950°C with/without adding 1 wt% N6AM1400, with $F_{\text{CH}_4}=0.45 L_n/\text{min}$. Dashed lines show maximum CO_2 from N6AM1400.

In Figure 8, it can be seen that there apparently is a considerable synergy effect of adding N6AM1400 to ilmenite. 70-130% more CO_2 was produced for actual mixed oxide experiments, compared to the base case plus the theoretical contribution from added N6AM1400. Therefore it seems safe to conclude that there is a synergy effect of adding NiO to ilmenite, i.e. obtained Ni catalyses decomposition to CO and H_2 , which reacts further with Fe_2O_3 to CO_2 and H_2O .

4.2 Results of circulating fluidized-bed experiments

As was shown in the batch experiments, fresh ilmenite has comparably low reactivity with natural gas. The same was true for the experiments conducted in the circulating fluidized-bed reactor. Just as for the batch experiments the conversion of fuel was found to increase as a function of time, when the ilmenite was exposed to fuel. The improvement was fast in the beginning of a test series, and then proceeded more slowly until a steady-state condition was obtained after 4-5 hours. Following this initial period, the experiments using sample C1 and C4 performed reasonably well. All data presented are from experiments with these samples. An example of the gas composition produced during an hour of operation is shown in Figure 9.

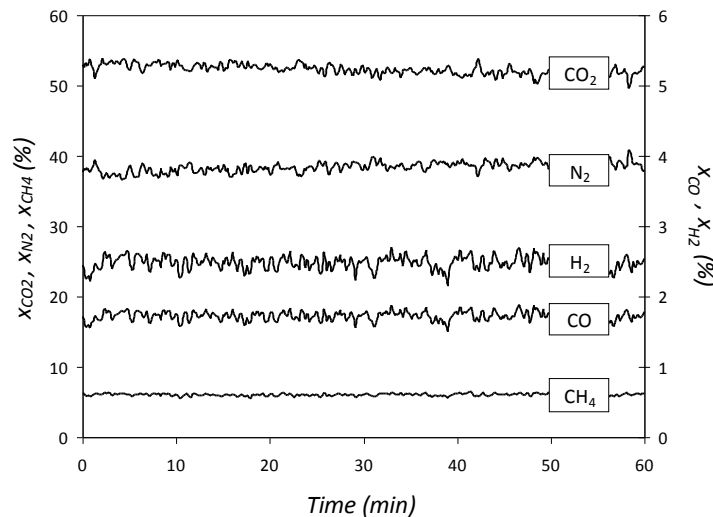


Figure 9. Dry-gas concentration during chemical-looping combustion at 900°C for sample C1 with addition of 1 wt% N6AM1400. $F_{ng}=0.49 \text{ L}_n/\text{min}$, $F_{air}=7.60 \text{ L}_n/\text{min}$. N_2 is present because it is used as fluidization gas in slot and downcomer. Note that x_{CO} and x_{H_2} has a separate y-axis.

Figure 9 represents the best conditions that were achieved during the test series presented in this paper, which was when 1 wt% N6AM1400 had been added to the ilmenite and natural gas without addition of steam was used as fuel. It can be seen that the conversion of natural gas into reagents for was about 90%, and that the selectivity towards CO₂ and H₂O was high. The concentration of CO and H₂ was low, in the order of 2 vol% on dry basis. This was true for all experiments in the circulating fluidized-bed reactor, with or without NiO addition. Typically, the CO₂/CO ratio was 25-30.

The difference between experiments with and without N6AM1400 was not as big in the circulating fluidized-bed reactor as in the batch reactor. But it was still possible to obtain considerable improvements in combustion efficiency by adding NiO-based particles. In Figures 10-11, the combustion efficiency, γ_{eff} , is shown as a function of reactor temperature for experiments with sample C1 and sample C4. In Figures 10-11, each data point represents average values of the combustion efficiency for stable experiments at a particular process parameter.

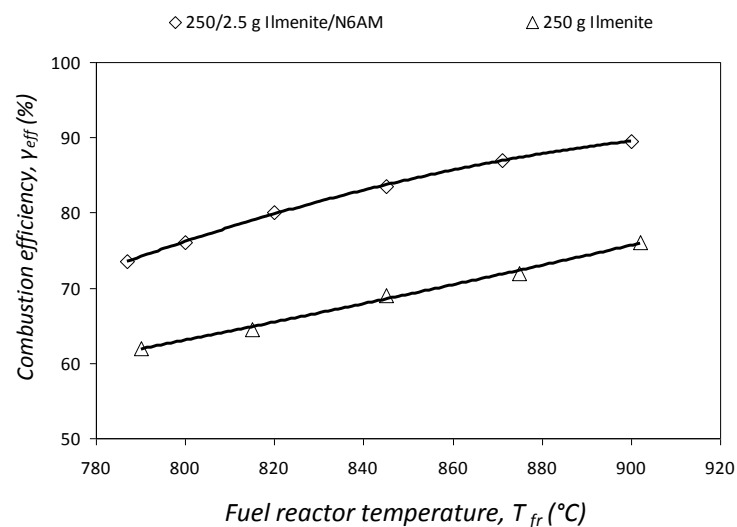


Figure 10. Combustion efficiency as function of fuel reactor temperature for ilmenite with addition of N6AM1400. Sample C1, $F_{ng}=0.49 L_n/min$, $F_{air}=7.60 L_n/min$.

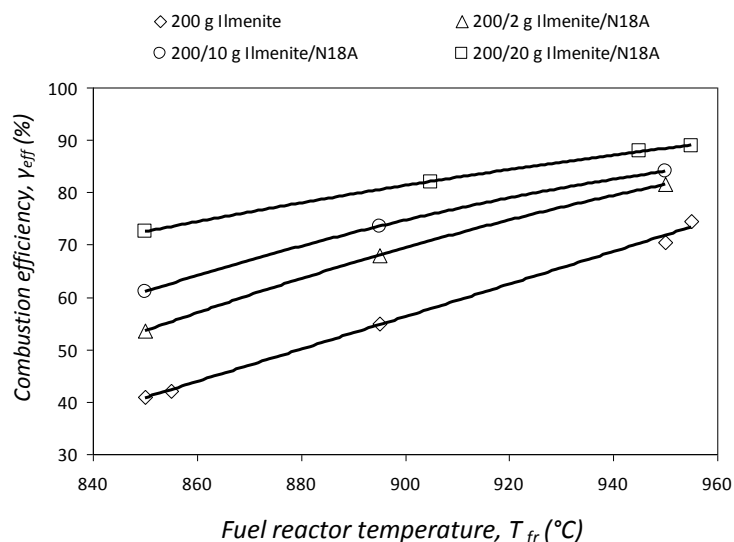


Figure 11. Combustion efficiency as function of fuel reactor temperature for ilmenite with addition of N18- α -Al₂O₃. Sample C4, $F_{ng}=0.27$ L_n/min, $F_{H_2O}=0.54$ L_n/min, $F_{air}= 8.40$ L_n/min.

In Figures 10-11, it can be seen that high fuel reactor temperature was positive for the reactivity of the oxygen carrier. This is expected, since high temperature speeds up chemical reactions in general. It can also be seen that adding NiO-based material improved the conversion of CH₄ considerably. However, not to the same degree as was indicated in the batch experiments, see Figure 5 above.

With sample C4, experiments were also conducted using varying fuel and air flow. A reduced fuel flow resulted in better fuel utilization, see Figure 12. An increased air flow also resulted in slightly better fuel utilization, see Figure 13. In Figures 12-13, each data point represents average values of the combustion efficiency for stable conditions at a particular process parameter.

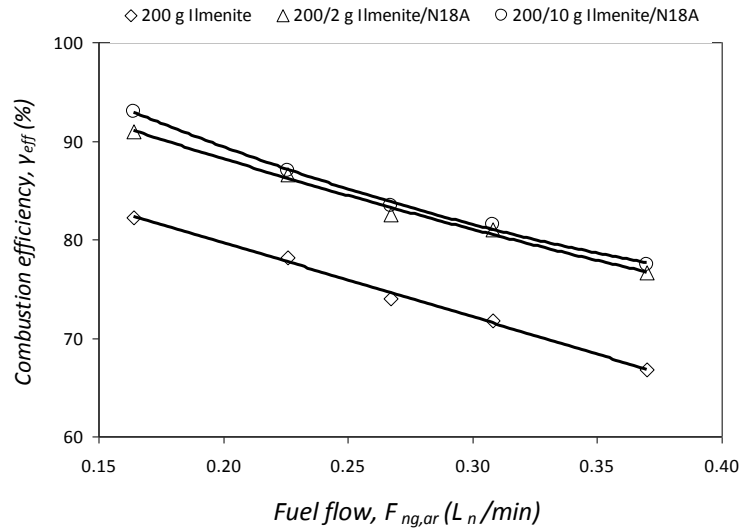


Figure 12. Combustion efficiency as function of fuel flow for ilmenite with addition of $N18-\alpha-Al_2O_3$. Sample C4, $T_{fr}=950^\circ C$, $F_{H_2O}=0.54 L_n/min$, $F_{air}= 8.40 L_n/min$.

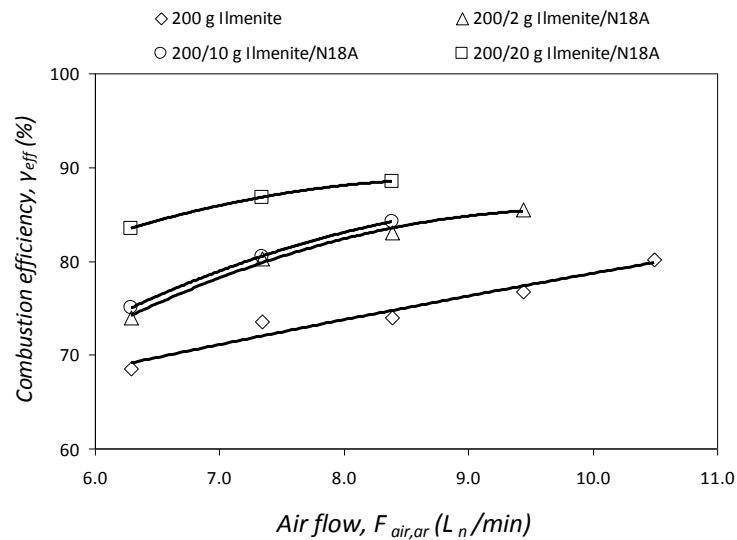


Figure 13. Combustion efficiency as function of air flow for ilmenite with addition of $N18-\alpha-Al_2O_3$. Sample C4, $T_{fr}=950^\circ C$, $F_{ng}=0.27 L_n/min$, $F_{H_2O}=0.54 L_n/min$.

These effects of varying the inlet gas flows could be expected. Reducing the fuel flow means that there will be more oxygen available for the fuel to react with, as well as a longer residence time for the fuel in the fuel reactor. Hence improved combustion efficiency could be expected when the fuel flow is decreased. However, it shall be pointed out that by comparing Figures 10-11 it can be seen that experiments with a lower natural gas flow which have been diluted with steam provided slightly worse results compared to a higher fuel flow without

steam addition. Therefore, it can be concluded that the partial pressure of the fuel and reagents also is important for the reaction rate in the fuel reactor.

Increased air flow should result in an increased circulation of solids between the reactor parts, which in turn increases the degree of oxidation of the oxygen carrier in the fuel reactor, which makes oxygen more readily available here. In Figure 6, it can be seen that a modest increase in the degree of oxidation has a positive effect on the combustion efficiency, as long as the process is not operated at a degree of oxidation, X , very close to 1.

For the continuously operating experiments, the degree of oxidation in the fuel reactor, X , could be estimated from reoxidation data, such as shown in Figure 14.

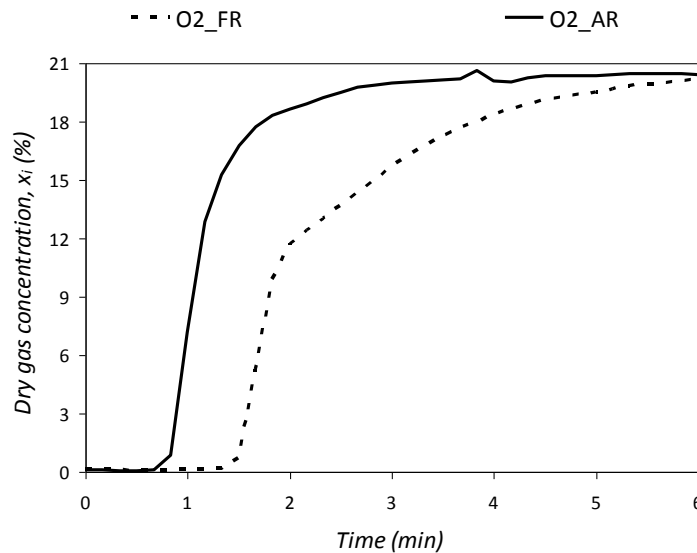


Figure 14. Reoxidation following a typical chemical-looping combustion experiment with Sample C4, using natural gas diluted with steam as fuel. Prior to $t=0$ the reactor is fluidized with N_2 . At $t=0$ the N_2 is replaced with $1.0 L_n/min$ air in each reactor section.

In Figure 14, it can be seen that once air was added to the reactor, there was a fast response in the air reactor. The time delay in the system was approximately 30-40 seconds, so it can be concluded that the oxygen carrier was close to fully oxidized in the air reactor. After another 20-30 seconds or so, the oxygen carrier in the fuel reactor is reoxidized and O_2 starts to slip through here as well. From this data it can be estimated that the degree of reduction in the fuel reactor during chemical-looping combustion most often was in the order of 3-5%, i.e. X was 0.95-0.97. These numbers corresponds to a solids circulation of 4-10 g/s, and a residence time in the fuel reactor of 10-25 s. There are some uncertainties in these estimations. The exact distribution of solids in the system is unknown and there is also a few seconds delay when

inert gas is shifted to air. It is also possible that small amounts of oxygen carrier could be transferred between the reactor parts during the inert period via the slot. However, the order of magnitude should be correct.

In some cases, small amounts of CO₂ were emitted from the fuel reactor during the reoxidation. This is due to minor amounts of solid carbon which is formed in the fuel reactor via reactions (4-5) and accumulates at locations such as the pressure measurement taps. However, most often no CO₂ could be seen during reoxidation.

Gas leakage between the reactor sections via the slot and the downcomer during operation was a possibility. Gas leakage from the air reactor to the fuel reactor could be calculated by measuring N₂ after the fuel reactor with gas chromatography, while using Ar as inert gas for fluidization. The leakage this way was found to be low. Typically it was 0.4-0.6 vol%. In practice, this means that at least 99% of the oxygen present in the gas from the fuel reactor originates from the solids circulation. The leakage from the fuel reactor to the air reactor could be calculated directly from the measured concentration of CO₂ following the air reactor. The leakage this way was in the order of 0.04-0.10 L_n/min, which corresponds to 3-7 vol% of the fuel-reactor flow in chemical-looping combustion experiments. Leakage this way is believed to have little impact on the experimental results.

Further, 0.40-0.50 L_n/min N₂ or Ar was needed for fluidization of the downcomer and the slot. This resulted in a slight dilution of the gas from the fuel reactor and the air reactor. It seems unlikely that this dilution would have had any major impact on the experimental results. 80% of the inert gas was added to the downcomer, which has an exit that is located above the particle bed, which is where the chemical reactions should take place. Typically, 50-70% of added inert gas ended up in the fuel reactor and the rest in the air reactor.

The experiments in the circulating fluidized-bed reactor seem to verify that ilmenite should be a feasible oxygen carrier for chemical-looping combustion of natural gas. They also strengthen the theory that the reactivity of ilmenite can be improved considerably by adding small amounts of NiO to help catalyze the decomposition of hydrocarbons into more reactive combustion intermediates such as CO and H₂

4.3 Fluidization properties

As is shown in Table 1 and Table 2, performing experiments with ilmenite as oxygen carrier was a learning experience, and there were a few problems associated with these experiments.

Firstly, there was a tendency towards defluidization during the batch experiments, which could be seen as a loss of pressure fluctuations over the bed. Defluidization occurred during reduction when ilmenite was extensively reduced, below $X=0.5$ or so. Defluidization could also occur during the inert phase, when superficial gas velocities below 0.1 m/s were used. Further, there were fluidization problems for sample B10, which consisted of ilmenite with 10 wt% N18- α -Al₂O₃ that had been used for 38 hours of experiments in the circulating fluidized-bed reactor. However, these particles had changed physical properties quite dramatically compared to fresh material, as will be explained in section 4.4 below.

Secondly, there were some problems with the solids circulation of particles for the circulating fluidized-bed experiments, especially for sample C2 and C3. Such problems have not been experienced in earlier experiments using the same circulating fluidized-bed reactor [14, 19, 33], which have been working flawlessly. However, in the cited experiments synthetic NiO-based oxygen-carrier particles were used as oxygen carrier, which have higher sphericity and a better defined chemistry. It is believed that the problems were related to the downcomer, for which odd fluidization behaviour was indicated at certain conditions. The condition could easily be detected, and involved a radical decrease in pressure drop over the downcomer, and a sharp increase in the fraction of inert gas that found its way to the fuel reactor. This condition resulted in sudden reduced circulation of solids between the reactors and reduced conversion of natural gas in the fuel reactor. For sample C4 and most often for sample C1, there were no or only minor problems. Therefore, all data presented in the paper are taken from these two series of experiments, and from occasions when the experiments was running smoothly.

In the batch experiments, agglomerations typically could be found in samples that defluidized. Further, the continuous experiments with sample C1 was stopped because of forming of agglomerations that blocked the slot section of the reactor. No signs of agglomerations were found during other experiments in the circulating fluidized-bed reactor or experiments in the batch reactor which fluidized in all cycles.

It can be concluded that very low fluidization velocities and extensive reduction should be avoided. None of these conditions seem likely to become a problem in a real-world chemical-looping combustor, which will operate with higher gas velocities and faster solids circulation, and after some trial and error the experiments worked quite well.

4.4 Effects on ilmenite during operation

Following each series of experiment, the reactor was opened and the particles examined. Typically, about 80% of the particles remained in the original size span of 125-180 μm , while the remaining 20% had eroded into somewhat finer fractions. The particles had become notably more porous and the apparent density typically was only 75% of that of fresh particles. It seems reasonable to believe that the increase in porosity happens during the first few hours of operation, and that it was related to the continuous improvement in fuel conversion that could be seen here, as was mentioned in section 4.1 above.

The particles from the batch experiments showed similar physical changes. Here up to 50% of available oxygen is removed each reduction cycle, compared to only 3-5% in the circulating fluidized-bed. A handful such extensive reduction and oxidation cycles appear to be sufficient to obtain the same effect as several hours of continuous operation. Increased porosity of ilmenite as a result of reduction and oxidation has been noticed in other studies as well. Leion et al [38] reported an increase in BET surface from 0.11 m^2/g for fresh particles to 0.28 m^2/g for particles that had experienced a handful redox cycles.

Sample C4 changed physical properties more dramatically than other examined samples. It had even lower density, only 50% of that of fresh particles. It also changed colour quite considerably, from dark grey to brown. As have been explained above, the solids circulation eventually stopped for this sample. And when the used particles were examined in the batch reactor, sample B10, the particles barely fluidized.

Fresh ilmenite, as well as used particles from several samples, has been examined with X-ray diffraction. The numerous impurities present in natural ilmenite make analysis complicated, but no major unexpected phases have been identified. So the deformation of the particles only seems to be a change in the physical structure, rather than changes in chemistry.

The change in physical properties raises some questions about the expected life time for natural ilmenite as oxygen carrier. However, it shall be pointed out that ilmenite has been used for as oxygen carrier both in a 10 kW chemical-looping combustion reactor for solid fuels [17, 18] and in a 120 kW chemical-looping combustion reactor for gaseous fuels [20, 21], in both cases with good results.

5. Summary and conclusions

Ilmenite has been examined as oxygen carrier for chemical-looping combustion by performing experiments both in a batch fluidized-bed reactor and in a circulating fluidized-bed reactor. CH_4 and natural gas have been used as fuel. It has also been examined whether it

is possible to improve the reactivity of ilmenite with hydrocarbons by adding small amounts of NiO-based particles, utilizing obtained metallic Ni to catalyze decomposition of CH₄ into more reactive combustion intermediates such as CO and H₂.

The batch experiments indicated modest reactivity between ilmenite and CH₄. Adding 5 wt% of a NiO material to the ilmenite improved the overall reactivity greatly. The experiments in the circulating fluidized-bed reactor strengthened these impressions. Adding NiO material to the reactor was found to increase the conversion of the fuel considerably. For the base case conducted at 900°C, the combustion efficiency was 76% for pure ilmenite, and 90% for the corresponding experiments with 1 wt% N6AM1400, corresponding to a NiO content of 0.6 wt%. The products were mostly CO₂, H₂O and unconverted CH₄, while the concentrations of CO and H₂ were low.

The properties of ilmenite were found to change considerably during operation. Used ilmenite particles had lower apparent density, and were more reactive and more porous than fresh. The changes appear to have been in the physical structure of the particles, and no unexpected chemical phases could be identified.

6. Acknowledgements

The authors wish to thank our financiers, supporters and co-workers within the CACHET project, which is contract 019972 under the 6th framework programme funded by the European Commission. A special thanks to our colleagues at CSIC-ICP in Zaragoza, who manufactured the N18- α -Al₂O₃ oxygen carrier.

7. References

- [1] P. Cho, Development and characterization of oxygen-carrier materials for chemical-looping combustion. Chalmers University of Technology, Göteborg, Sweden, 2005.
- [2] M. Johansson, Screening of oxygen-carrier particles based on iron-, manganese-, copper- and nickel oxides for use in chemical-looping technologies. Chalmers University of Technology, Göteborg, Sweden, 2007.
- [3] J. Adánez, L.F. de Diego, F. García-Labiano, P. Gayán, A. Abad, Selection of oxygen carriers for chemical-looping combustion, *Energy & Fuels* 18 (2004) 371-377.
- [4] E. Jerndal, T. Mattisson, A. Lyngfelt, Thermal Analysis of Chemical-Looping Combustion, *Chemical Engineering Research and Design* 84 (2006) 795-806.

- [5] P. Cho, T. Mattisson, A. Lyngfelt, Carbon Formation on Nickel and Iron Oxide-Containing Oxygen Carriers for Chemical-Looping Combustion, *Industrial & Engineering Chemistry Research* 44 (2005) 668-676.
- [6] A. Lyngfelt, B. Kronberger, J. Adánez, J.X. Morin, P. Hurst, The GRACE project. Development of oxygen carrier particles for chemical-looping combustion. Design and operation of a 10 kW chemical-looping combustor. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 2004.
- [7] H.J. Ryu, G.T. Jin, C.K. Yi, Demonstration of inherent CO₂ separation and no NO_x emission in a 50 kW chemical-looping combustor - continuous reduction and oxidation experiment. Poster presented at the 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 2004.
- [8] E. Johansson, T. Mattisson, A. Lyngfelt, H. Thunman, Combustion of Syngas and Natural Gas in a 300 W Chemical-Looping Combustor, *Chemical Engineering Research and Design* 84 (2006) 819-827.
- [9] E. Johansson, T. Mattisson, A. Lyngfelt, H. Thunman, A 300 W laboratory reactor system for chemical-looping combustion with particle circulation, *Fuel* 85 (2006) 1428-1238.
- [10] A. Abad, T. Mattisson, A. Lyngfelt, M. Rydén, Chemical-looping combustion in a 300W continuously operating reactor system using a manganese-based oxygen carrier, *Fuel* 85 (2006) 1174-1185.
- [11] A. Abad, T. Mattisson, A. Lyngfelt, M. Johansson, Using continuous and pulse experiments to compare two promising nickel-based oxygen carriers for use in chemical-looping technologies, *Fuel* 86 (2007) 1021-1035.
- [12] J. Adánez, P. Gayán, J. Celaya, L. de Diego, F. García-Labiano, A. Abad, Chemical Looping Combustion in a 10 kWth Prototype Using a CuOAl₂O₃ Oxygen Carrier: Effect of Operating Conditions on Methane Combustion, *Industrial & Engineering Chemistry Research* 45 (2006) 6075-6080.
- [13] C. Linderholm, A. Abad, T. Mattisson, A. Lyngfelt, 160 hours of chemical-looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier, *International Journal of Greenhouse Gas Control* 2 (2008) 520-530.
- [14] C. Linderholm, E. Jerndal, T. Mattisson, A. Lyngfelt, Investigation of Ni-based mixed oxides in a 300-W chemical-looping combustor, *Fuel*, in press.
- [15] C. Linderholm, T. Mattisson, A. Lyngfelt, Long-term integrity testing of spray-dried particles in a 10-kW chemical-looping combustor using natural gas as fuel, *Fuel*, in press.

- [16] L. de Diego, F. García-Labiano, P. Gayán, J. Adánez, J. Celaya, J.M. Palacios, Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO–Al₂O₃ oxygen carrier, *Fuel* 86 (2007) 1036-1045.
- [17] N. Berguerand, A. Lyngfelt, Design and Operation of a 10 kWth Chemical-Looping Combustor for Solid Fuels – Testing with South African Coal, *Fuel* 87 (2008) 2713-2726.
- [18] N. Berguerand, A. Lyngfelt, The Use of Petroleum Coke as Fuel in a 10 kWth Chemical-Looping Combustor, *International Journal of Greenhouse Gas Control* 2 (2008) 169-179.
- [19] M. Rydén, A. Lyngfelt, T. Mattisson, Chemical-Looping Combustion and Chemical-Looping Reforming in a Circulating Fluidized-Bed Reactor Using Ni-Based Oxygen Carriers, *Energy & Fuels* 24 (2008) 2585-2597.
- [20] P. Kolbitsch, T. Pröll, J. Bohlar-Nordenkamp, H. Hofbauer, Operating experience with chemical looping combustion in a 120kW dual circulating fluidized bed (DCFB) unit, *Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies*, Washington, United States, 2008.
- [21] A. Pröll, M. Mayer, J. Bohlar-Nordenkamp, P. Kolbitsch, T. Mattisson, A. Lyngfelt, H. Hofbauer, Natural minerals as oxygen carriers for chemical-looping combustion in a dual circulating fluidized bed system. *Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies*, Washington, United States, 2008.
- [22] A. Abad, F. García-Labiano, L. de Diego, P. Gayán, J. Adánez, J. Reduction Kinetics of Cu-, Ni-, and Fe-Based Oxygen Carriers Using Syngas (CO + H₂) for Chemical-Looping Combustion, *Energy & Fuels* 21 (2007) 1843-1853.
- [23] A. Abad, J. Adánez, F. García-Labiano, L. de Diego, P. Gayán, J. Celaya, Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion, *Chemical Engineering Science* 62 (2007), 533-549.
- [24] Q. Zafar, A. Abad, T. Mattisson, B. Gevert, Reaction kinetics of freeze-granulated NiO/MgAl₂O₄ oxygen carrier particles for chemical-looping combustion, *Energy & Fuels* 21 (2007) 610-618.
- [25] Q. Zafar, A. Abad, T. Mattisson, B. Gevert, M. Strand, Reduction and Oxidation Kinetics of Mn₃O₄/Mg-ZrO₂ Oxygen Carrier Particles for Chemical-Looping Combustion, *Chemical Engineering Science* 62 (2007) 6556-6567.
- [26] F. García-Labiano, L. de Diego, P. Gayán, J. Adánez, A. Abad, Effect of pressure on the behavior of copper-, iron-, and nickel-based oxygen carriers for chemical-looping combustion, *Energy & Fuels* 20 (2006) 26-33.
- [27] Ø. Brandvoll, *Chemical looping combustion: fuel conversion with inherent CO₂ capture*, Norwegian University of Science and Technology, Trondheim, Norway, 2005.

- [28] E. Johansson, Fluidized-bed reactor systems for chemical-looping combustion with inherent CO₂ capture, Chalmers University of Technology, Göteborg, Sweden, 2005.
- [29] J. Wolf, CO₂ mitigation in advanced power cycles, The Royal Institute of Technology, Stockholm, Sweden, 2004.
- [30] B. Kronberger, Modelling analysis of fluidised bed reactor systems for chemical-looping combustion, Vienna University of Technology, Vienna, Austria, 2005.
- [31] R. Naqvi, Analysis of gas-fired power cycles with chemical looping combustion for CO₂ capture, Norwegian University of Science and Technology, Trondheim, Norway, 2006.
- [32] H. Leion, Capture of CO₂ from solid fuels using chemical-looping combustion and chemical-looping oxygen uncoupling, Chalmers University of Technology, Göteborg, Sweden, 2008.
- [33] M. Rydén, Hydrogen production from fossil fuels with carbon dioxide capture, using chemical-looping technologies, Chalmers University of Technology, Göteborg, Sweden, 2006.
- [34] T. Mattisson, M. Johansson, E. Jerndal, A. Lyngfelt, The reaction of NiO/NiAl₂O₄ particles with alternating methane and oxygen, *The Canadian Journal of Chemical Engineering* 86 (2008) 756-767.
- [35] T. Mattisson, M. Johansson, A. Lyngfelt, CO₂ capture from coal combustion using chemical-looping combustion – Reactivity investigation of Fe, Ni and Mn based oxygen carriers using syngas, *Proceedings of the Clearwater Coal Conference*, Clearwater, United States, 2006.
- [36] M. Johansson, T. Mattisson, A. Lyngfelt, Investigation of Fe₂O₃ on MgAl₂O₄ support for chemical-looping combustion, *Industrial & Engineering Chemistry Research* 43 (2004) 6978-6987.
- [37] M. Johansson, T. Mattisson, A. Lyngfelt, Creating a synergy effect by using mixed oxides of iron- and nickel oxides in the combustion of methane in a Chemical-Looping Combustion reactor, *Energy & Fuels* 20 (2006) 2399-2407.
- [38] H. Leion, A. Lyngfelt, M. Johansson, E. Jerndal, T. Mattisson, The use of ilmenite as an oxygen carrier in chemical-looping combustion, *Chemical Engineering Research and Design* 86 (2008) 1017-1026.
- [39] L. de Diego, M. Ortiz, F. García-Labiano, J. Adánez, A. Abad, P. Gayán, Hydrogen production by chemical-looping reforming in a circulating fluidized bed reactor using Ni-based oxygen carriers, *Journal of Power Sources*, in press.
- [40] M. Rydén, A. Lyngfelt, T. Mattisson, Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor, *Fuel* 85 (2006) 1631-1641.