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NiO supported on Mg-ZrO_2 as oxygen carrier for chemical-looping combustion and chemical-looping reforming

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Abstract

Oxygen-carrier particles consisting of 40 wt% NiO supported on 60 wt% Mg-stabilized ZrO_2 were produced by freeze granulation and examined as oxygen carrier for chemical-looping applications. Firstly, the particles were examined by oxidation and reduction experiments in a batch fluidized-bed reactor. These experiments indicated very high reactivity with CH_4 and low affinity for carbon formation. For highly oxidized particles the products were CO_2 and H_2O, while for reduced particles they were CO and H_2. Secondly, the particles were examined by 40 hours of operation in a small circulating fluidized-bed reactor, using natural gas as fuel. For chemical-looping combustion, there was complete conversion of fuel into products with high selectivity towards CO_2 and H_2O. At 950ºC, a combustion efficiency of 99.3% was achieved, which is only 0.1%-point below the theoretical maximum, i.e. thermodynamic equilibrium. For chemical-looping reforming, the conversion of fuel was 99.9% or higher, with high selectivity towards CO and H_2. Operating at the desired process parameters, which was a fuel reactor temperature of 950ºC and an air ratio of 0.30, worked flawlessly. When only natural gas was used as fuel there was slight formation of solid carbon in the fuel reactor. Adding 30 vol% steam to the fuel removed the carbon formation. The particles retained their physical and chemical structure reasonably well during operation. Approximately 5% of the particles added to the reactor were lost as fines during the first hours of operation. Further, the porosity of the particles increased somewhat during operation. The density was 10% lower for used particles, compared to fresh.

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Abbreviations

CLC	Chemical-looping combustion
CLR	Chemical-looping reforming
C_nH_m	Generic hydrocarbon fuel
f_{CH4}	Fraction of unconverted methane (%)
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
$n_{O,cc}$	Oxygen demand for complete combustion (n_O/n_{fuel})
(O/C)	Oxygen to carbon ratio
p	Partial pressure (Pa)
R_0	Oxygen ratio, i.e. active oxygen content of oxygen carrier (%)
t	Time (s, min)
vol%	Percentage by volume
wt%	Percentage by weight
X	Degree of oxidation of oxygen carrier (%)
x	Dry-gas concentration (%)
y	Wet-gas concentration (%)
Ψ	Air ratio for understoichiometric operation (%)
γ_{eff}	Combustion efficiency (%)

Indexes

ar	Air reactor or batch reactor during oxidation
cc	Complete combustion
fm	Fuel mixture
fr	Fuel reactor or batch reactor during reduction
i	Generic index
oc	Oxygen carrier
ox	Completely oxidized oxygen carrier
red	Completely reduced oxygen carrier
s	Sample of oxygen-carrier particles
tot	Total

1. Introduction

In recent 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, see for example the IPCC report[1].

One way to reduce CO_2 emissions that is receiving significant 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 gas from combustion or industrial processes, and stored in geological formations such as depleted oil fields or deep saline aquifers. CO_2 could also be captured in processes for H_2 generation that uses fossil fuel as raw material, such as partial oxidation, auto-thermal reforming or steam reforming. This procedure could be used to generate H_2, which could be used for vehicle fuel as well as for other applications, without emissions of CO_2 to the atmosphere. An inclusive source for information about carbon sequestration is IPCC:s special report on CO_2 capture and storage[2].

The chemical-looping concept involves oxidation of a fuel using oxygen from a solid oxygen carrier. This way the products are not diluted with N_2, and the need for costly gas separation is eliminated. Hence chemical-looping technologies are interesting both for CO_2 capture applications in combustion processes, and for H_2 generation through gasification and reforming processes. Because of this, chemical-looping technologies could have a significant 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.

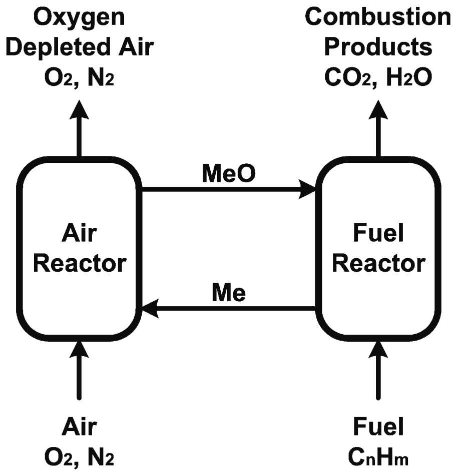

Figure 1. Schematic description of chemical-looping combustion.

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 CO_2 and H_2O according to reaction (1). In the air reactor, it is oxidized to its initial state with O_2 from the combustion air according to reaction (2).

$$C_nH_m + (2n+½m)\ MeO \rightarrow n\ CO_2 + ½m\ H_2O + (2n+½m)\ Me \qquad (1)$$

$$Me + ½\ O_2 \rightarrow MeO \qquad (2)$$

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 must also be used to transfer sensible 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 O_2.

$$C_nH_m + (n+¼m)\ O_2 \rightarrow n\ CO_2 + ½m\ H_2O \qquad (3)$$

The exhaust gas from the air reactor consists 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, see for example Ishida et al[3]. 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. This makes chemical-looping combustion a very attractive technology for power generation with CO_2 capture.

Possible side reactions include formation of solid carbon in the fuel reactor, which could be formed either through the Boudouard reaction, reaction (4), or through hydrocarbon decomposition, reaction (5).

$$2\,CO \rightarrow C + CO_2 \tag{4}$$

$$C_nH_m \rightarrow n\,C + ½m\,H_2 \tag{5}$$

Solid carbon would likely follow the oxygen-carrier particles to the air reactor and burn there, which would reduce the degree of CO_2 capture. Reactions (4-5) can be catalysed by metallic surfaces and could possibly become an obstacle if an oxygen carrier that is reduced directly to a metallic phase, NiO to Ni for instance, is used as oxygen carrier. Carbon formation on oxygen-carrier particles has been specifically examined by Cho et al[4].

In practice, a chemical-looping combustion process could be designed in different ways, for example as moving bed reactors, see Fan et al[5], or as packed-bed reactors, see van Sint Annaland et al[6]. However, the most commonly proposed design is as circulating fluidized-bed reactor with oxygen-carrier particles used as bed material. This design has the advantage of being straightforward, providing good contact between gas and solids and allowing a smooth flow of oxygen-carrier particles between the reactors. Continuous chemical-looping combustion in circulating fluidized-bed reactors has been demonstrated by Lyngfelt et al[7], Ryu et al[8], Johansson et al[9,10], Abad et al[11,12], Adánez et al[13], Linderholm et al[14,15,16], De Diego et al[17], Berguerand et al[18,19] Rydén et al[20], Pröll et al[21] and Kolbitsch et al[22].

The oxygen-carrier particles 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 mass fraction of oxygen which can react according to reaction (1), 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 and 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, SiO_2 or ZrO_2 seem like the most likely candidates to meet those criteria. When NiO is used as oxygen carrier for chemical-looping combustion, there is a thermodynamical constraint for conversion of fuel to CO_2 and H_2O which limits the combustion efficiency to 99.4% at 950°C. Fe_2O_3, Mn_3O_4 and CuO do not have such thermodynamical limitations, so with such oxygen carriers 100% combustion efficiency and CO_2 capture can be achieved. An overview of the research treating such oxygen-carriers can be found in the works of Cho[23], Johansson[24] and Adánez et al[25]. Information about additional potential oxygen-carrier materials can be found in the work of Jerndal et al[26], which includes a theoretical examination of 27 different oxide systems.

2.2 Chemical-Looping Reforming (CLR)

Chemical-looping reforming utilizes the same basic principles as chemical-looping combustion. The difference is that the products desired are not heat but synthesis gas, i.e. a gas mixture consisting mainly of H_2 and CO. Chemical-looping reforming could be described as a process for partial oxidation of hydrocarbon fuels, where a solid oxygen carrier is used as a source of undiluted oxygen. This would eliminate the need for expensive and power demanding air separation. The principles of chemical-looping reforming are illustrated in Figure 2.

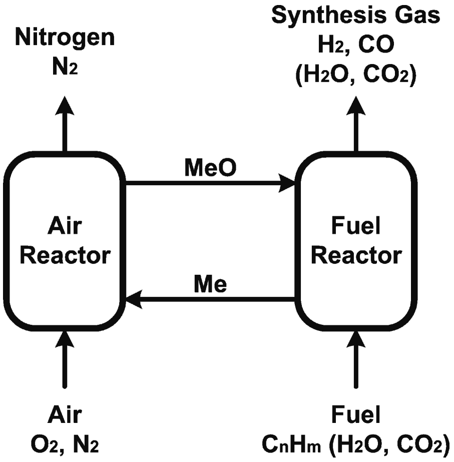

Figure 2. Schematic description of chemical-looping reforming.

Chemical-looping reforming is operated at understoichiometric conditions, i.e. insufficient oxygen is added to the air reactor to completely oxidize the fuel added to the fuel reactor. In the air reactor, reaction (2) will occur, just as in chemical-looping combustion. All added oxygen will be consumed, so the depleted air will consist of only N_2. In the fuel reactor, some fuel may become completely oxidized to CO_2 and H_2O via reaction (1), but the larger share should react according to reaction (6), partial oxidation using oxygen from the oxygen carrier.

$$C_nH_m + n\,MeO \rightarrow n\,CO + \tfrac{1}{2}m\,H_2 + n\,Me \qquad (6)$$

Steam or CO_2 could be added to the fuel to enhance the relative importance of steam reforming, reaction (7), or CO_2 reforming, reaction (8), respectively. This could be useful if synthesis gas with a H_2/CO-ratio that does not correspond to the H/C-ratio of the fuel is desired. Steam or CO_2 also suppress formation of solid carbon via reactions (4-5), which potentially could become an obstacle at understoichiometric conditions.

$$C_nH_m + n\ H_2O \leftrightarrow n\ CO + (n + \tfrac{1}{2}m)\ H_2 \qquad (7)$$

$$C_nH_m + n\ CO_2 \leftrightarrow 2n\ CO + \tfrac{1}{2}m\ H_2 \qquad (8)$$

The overall reaction energy of the reactor system varies as the relative importance between reactions (1-2) and reactions (6-8) is altered. When the fuel and oxygen carrier reacts according to reactions (1) and (2), heat corresponding to the lower heating value of the fuel is released. When the fuel reacts according to reactions (6) and (2), heat corresponding to the reaction energy for partial oxidation of the fuel is released. Reactions (7-8) are strongly endothermic. Therefore, steam reforming and CO_2 reforming can not be allowed to dominate the process since this would result in a process that would require external heating, which would be technically unfavourable at relevant temperatures.

The outlet from the fuel reactor consists of H_2, CO, H_2O and CO_2, and could be used as feedstock for chemical processes or for production of H_2. Due to thermodynamic constraints it is possible that there will be some unreformed CH_4 in the synthesis gas if the reactor temperature is not sufficiently high. A fuel reactor temperature in the order of 800ºC should be sufficient to achieve at least 99% conversion of CH_4 at atmospheric pressure. At elevated pressure, somewhat higher temperature is necessary due to less favourable thermodynamics.

Oxygen-carrier materials for chemical-looping reforming would need to have about the same properties as those for chemical-looping combustion. The main difference is that they must be capable to convert hydrocarbons to CO and H_2 when the air to fuel ratio is reduced, rather than provide CO_2, H_2O and unreacted fuel. A study by Zafar et al[27] indicated high reaction rate and good selectivity towards H_2 and CO for oxygen carriers with NiO as active phase, while oxygen carriers based on Fe_2O_3, Mn_3O_4 and CuO suffered from poor selectivity and produced mostly CO_2, H_2O and unreacted CH_4. Continuously operating chemical-looping reforming in circulating-fluidized bed reactors using NiO-based oxygen carriers has been demonstrated by Rydén et al[20,28,29].

2.3 The aim of this study

The main objective with this study is to examine an oxygen carrier consisting of NiO as active phase, supported on inert Mg-stabilized ZrO_2. This makes the examined oxygen carrier different from most other NiO-based oxygen carriers, which typically have been supported on Al_2O_3-based materials. The aim has been to show that this oxygen-carrier composition also performs well, and is feasible both for chemical-looping combustion of natural gas into CO_2 and H_2O, and for chemical-looping reforming of natural gas into CO and H_2.

3. Experimental

3.1 Oxygen-carrier particles

The oxygen carrier was prepared by dispersing fine chemical powders of NiO (Sigma-Aldrich no. 24.403-1) and Mg-stabilized ZrO_2 (Mandoval MSZ-8) in a water-based slurry, using polyacrylic acid as dispersant. After milling, polyethylene glycol was added as binder to keep the particles intact during freeze-drying and sintering. Spherical particles were produced by pumping the slurry to a spray nozzle where passing atomizing-air produced drops, which were sprayed into liquid nitrogen where they froze instantaneously. The frozen water was removed by sublimation in a freeze-drier. After drying, the resulting particles were sintered for 6 hours at 1400ºC in order to improve their mechanical strength. The density of the resulting oxygen-carrier material was 4.1 g/cm^3, which corresponds to a void fraction of 33%. The average force required to crush a particle with a size of 180-250 µm was 1.7 N, using a Shimpo-5 crushing strength apparatus.

3.2 The batch fluidized-bed reactor

The batch experiments were conducted in an 820 mm long quartz reactor, with an inner diameter of 22 mm. A porous quartz plate, on which the oxygen-carrier sample is applied, is located 370 mm above the bottom of the reactor. During operation, the sample is fluidized by adding gas to the bottom of the reactor, and the porous plate acts as gas distributor. Chemical-looping conditions are simulated by altering between oxidizing and reducing fluidization gas. In order to reach suitable temperature the reactor is placed inside an electrically heated furnace. 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 composition analysed. The concentrations of CO_2, CO and CH_4 are measured using a gas analyzer (Rosemount NGA-2000). Bag sampling, for further examination of produced gas with gas chromatography (Varian Micro-GC CP4900), is also conducted.

3.3 The circulating fluidized-bed reactor

The continuously operating experiments were carried out in a small-scale laboratory reactor. The reactor has been used earlier for similar experiments by Rydén et al[20,29]. A schematic picture of the reactor is shown in Figure 3.

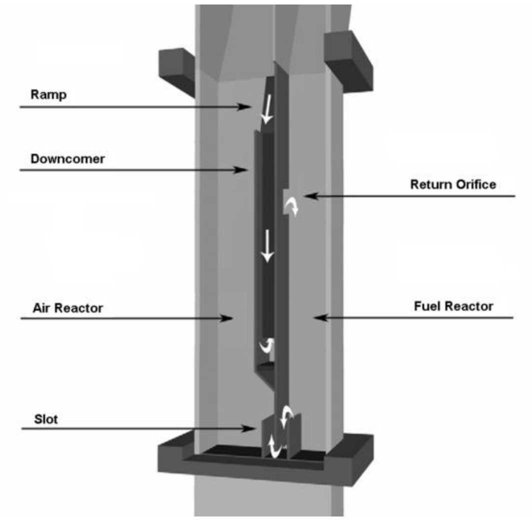

Figure 3. Schematic description of the circulating fluidized-bed reactor. During operation, the downcomer and roughly a third of the air and fuel reactor is filled with oxygen carrier particles in the size range 90-212 μm.

The reactor is designed for chemical-looping combustion experiments using gaseous fuels. Suitable flows are 0.20-0.75 L_n/min natural gas and 3-10 L_n/min air. Chemical-looping reforming experiments are performed by increasing the natural-gas flow to 0.9-1.6 L_n/min, while using a suitable air flow. The height of the reactor is 200 mm. 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 N_2 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 there is a water seal that makes it possible to increase the pressure in the fuel reactor by altering 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 either by means of a steam generator, or by bubble the fuel through water with a temperature of 90ºC and cool the resulting gas mixture to the desirable saturation temperature in a cooling column. The fuel-steam mixture is transferred to the reactor in a heated tube with a temperature of 150ºC.

Prior to analysis, the gas from the reactor passes through particle filters, coolers and water traps. Therefore, all measurements are made on dry gas. CO_2, CO and CH_4 are measured using infrared analyzers while O_2 is measured with paramagnetic sensors (Sick|Maihak S710). The gas from the fuel reactor is also examined with a gas chromatograph (Varian Micro-GC CP4900), which is necessary to measure H_2. In addition to this, the gas chromatograph also measures CO_2, CO, CH_4, O_2 and N_2.

3.4 Evaluation of data

For the circulating fluidized bed experiments, the concentration of H_2 in the gas from the fuel reactor was measured with gas chromatography, which provided one measuring point every five minutes. For the batch experiments, H_2 could only be measured by bag sampling, which also provided relatively few measuring points. So in order to facilitate the analysis, an estimated value of the concentration of H_2 in dry gas, $x_{H2,fr}$, 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 $x_{H2,fr}$ were very close to those measured directly with the gas chromatograph. This could be expected, since Ni is a potent catalyst for the water-gas shift reaction at the used temperatures. Once $x_{H2,fr}$ was calculated, $x_{N2,fr}$ as well as corresponding wet gas concentrations could easily be calculated with a species balance. A detailed description of the methodology for these calculations can be found elsewere[20].

The performance of a chemical-looping combustion process is best expressed with the combustion efficiency, γ_{eff}, which is defined in expression [9].

$$\gamma_{eff} = 1 - \frac{n_{CH4,fr} \times H_{lhw,CH4} + n_{CO,fr} \times H_{lhw,CO} + n_{H2,fr} \times H_{lhw,H2}}{n_{fuel,in} \times H_{lhw,fuel}} \tag{9}$$

In expression (9), 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 carbon formation 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_{CH4}, see expression (10).

$$f_{CH4} = F_{CH4,fr} / (F_{fuel} \times n_{C,fuel}) = x_{CH4,fr} / (x_{CO2,fr} + x_{CO,fr} + x_{CH4,fr}) \tag{10}$$

For chemical-looping reforming, an air ratio Ψ can be calculated with expressions (11-14), using three oxygen to carbon ratios. $(O/C)_{fr}$ refers to the actual gas from the fuel reactor, $(O/C)_{fm}$ refers to the fuel mixture, and $(O/C)_{cc}$ refers to the gas composition that would have been obtained by complete combustion of the fuel. In expressions (12-14), the moles of oxygen in the fuel, $n_{O,fuel}$, is 0.01, the moles of carbon, $n_{C,fuel}$ is 1.14, and the moles of oxygen needed for complete combustion, $n_{O,cc,fuel}$ is 4.41 for one mole of the natural gas used. For CH_4, the corresponding numbers are 0, 1 and 4.

$$\Psi = \frac{(O/C)_{fr} - (O/C)_{fm}}{(O/C)_{cc} - (O/C)_{fm}} \tag{11}$$

$$(O/C)_{fr} = \frac{y_{CO2,fr} \times 2 + y_{H2O,fr} + y_{CO,fr}}{y_{CO2,fr} + y_{CO,fr} + y_{CH4,fr}} \tag{12}$$

$$(O/C)_{fm} = \frac{(1 - y_{H2O,fm} - y_{CO2,fm}) \times n_{O,fuel} + y_{H2O,fm} + y_{CO2,fm} \times 2}{(1 - y_{H2O,fm} - y_{CO2,fm}) \times n_{C,fuel} + y_{CO2,fm}} \tag{13}$$

$$(O/C)_{cc} = \frac{\left(1 - y_{H2O,fm} - y_{CO2,fm}\right) \times n_{O,cc} + y_{H2O,fm} + y_{CO2,fm} \times 2}{\left(1 - y_{H2O,fm} - y_{CO2,fm}\right) \times n_{C,fuel} + y_{CO2,fm}} \tag{14}$$

A Ψ of 1.0 means that sufficient oxygen has been added to the fuel mixture via the oxygen carrier to oxidize it completely to CO_2 and H_2O. For stoichiometric partial oxidation into CO and H_2, Ψ is 0.25 for methane and 0.26 for natural gas. In order for Ψ to be useful for evaluating the results of a chemical-looping reforming experiment, there should be very high conversion of hydrocarbons and no or little formation of solid carbon, and the gas composition should be reasonably close to thermodynamic equilibrium. These criteria were fulfilled for the experiments conducted in this study. The desired value of Ψ for a chemical-looping reforming process depends on factors such as reactor temperature, desired product composition and amounts of H_2O or CO_2 added to the fuel. For a chemical-looping reforming process operating at 950ºC and with 30 vol% steam added to the fuel, a Ψ in the order of 0.30-0.35 seems reasonable, see Rydén et al[29,30].

The oxygen ratio, R_0, is defined in expression (15), and the degree of oxidation of the oxygen carrier, X, is defined in expression (16).

$$R_0 = (m_{s,ox} - m_{s,red}) / m_{s,ox} \tag{15}$$

$$X = \frac{m_s - m_{s,red}}{m_{s,ox} - m_{s,red}} \tag{16}$$

In expressions (15-16), m_s is the actual mass of the 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. The oxygen ratio R_0 is the mass fraction of oxygen in the particle that can be made to react with the fuel. R_0 is 21.4 wt% for unsupported NiO and 8.6 wt% for the oxygen carrier used in the experiments described in this paper.

The degree of reduction, X, change during operation, and is calculated in different ways depending on experimental setup. For the batch experiments, X can be calculated as function of time using expression (17).

$$X_i = X_{i-1} - \int_{t_o}^{t_1} \frac{n_{out,tot}}{n_{o,oc} \times P_{tot}} \times (4p_{CO_2,fr} + 3p_{CO,fr} - p_{H_2,fr})dt \tag{17}$$

In expression (17), X_i is the conversion as a function of time for period i, X_{i-1} is the conversion after the preceding period, t_0 and t_1 are the times for the start and finish of the period respectively, $n_{o,oc}$ is the moles of active oxygen in the unreacted oxygen carrier, $n_{out,tot}$ is the molar flow of the gas leaving the reactor after the water has been removed, P_{tot} is the total pressure, and $p_{CO2,fr}$, $p_{CO,fr}$ and $p_{H2,fr}$ are the outlet partial pressures of CO_2, H_2 and CO after the removal of H_2O. For the circulating-fluidized bed experiments, the best way to estimate X is to see how much O_2 that is consumed during reoxidation of the oxygen carrier, see Figure 9 and section 4.2 below.

4. Results

4.1 Experiments in batch fluidized-bed reactor

A sample of 15 g of oxygen-carrier particles in the size range 125-180 μm was added to the reactor, which corresponds to a bed height of ≈1.5 cm. During heating to this temperature, the reactor was fluidized with N_2. Chemical looping was simulated by altering between reducing and oxidizing conditions. The experiments can be divided into two subcategories:

- **Continuous experiments**
  The particles were exposed alternately to reducing and oxidizing conditions. The reduction was conducted in one single period, lasting 60-180 seconds. The gas flow was 0.45 L_n/min CH_4, with or without 30 vol% steam addition. Some reductions with 11-33% CH_4 in N_2 were also conducted. The sample was reoxidized by a mixture of 5% O_2 and 95% N_2. A low oxygen concentration was used in order to avoid excessive heating of the bed. In between oxidation and reduction, the reactor was fluidized with N_2 for 180 s, in order to avoid oxygen and methane mixing.
- **Pulse experiments**
  Similar to above, but the reduction period was divided into pulses of 2, 4 or 6 seconds. Between each pulse, the reactor was fluidized with N_2 for 60 seconds. A more detailed description of the procedure can be found in a study by Johansson et al[31].

In total, 4 separate samples were examined. A summary of the batch experiments can be found in Table 1.

Sample	Experiment	Cycles	Reduction (L_n/min)	Oxidation (L_n/min)
1	Continuous	13	0.45 CH_4	0.05 O_2 / 0.95 N_2
2	Continuous	1	0.45 CH_4	0.05 O_2 / 0.95 N_2
2	Continuous	2	0.15 CH_4 / 0.30 N_2	0.05 O_2 / 0.95 N_2
2	Continuous	1	0.05 CH_4 / 0.40 N_2	0.05 O_2 / 0.95 N_2
2	Continuous	8	0.45 CH_4 / 0.19 H_2O	0.05 O_2 / 0.95 N_2
3	Continuous	2	0.45 CH_4	0.05 O_2 / 0.95 N_2
3	Pulses (2, 4, 6 s)	6	0.45 CH_4	0.05 O_2 / 0.95 N_2
4	Continuous	2	0.45 CH_4 / 0.19 H_2O	0.05 O_2 / 0.95 N_2
4	Pulses (2, 4, 6 s)	4	0.45 CH_4 / 0.19 H_2O	0.05 O_2 / 0.95 N_2

Table 1. Summary of batch experiments.

All batch experiments were conducted with a furnace temperature of 950°C. Since reactions (1), (3) and (6-8) are endothermic, the actual reactor temperature decreases slightly during the reduction phase. For extended reduction periods with steam addition, the temperature reduction could be 15°C. During reoxidation, the exothermic reaction (2) resulted in a temperature increase of up to 10°C.

An example of the produced gas composition during a typical continuous reduction is shown in Figure 4, while Ψ and f_{CH4} have been plotted as a function of X for the same experiment in Figure 5.

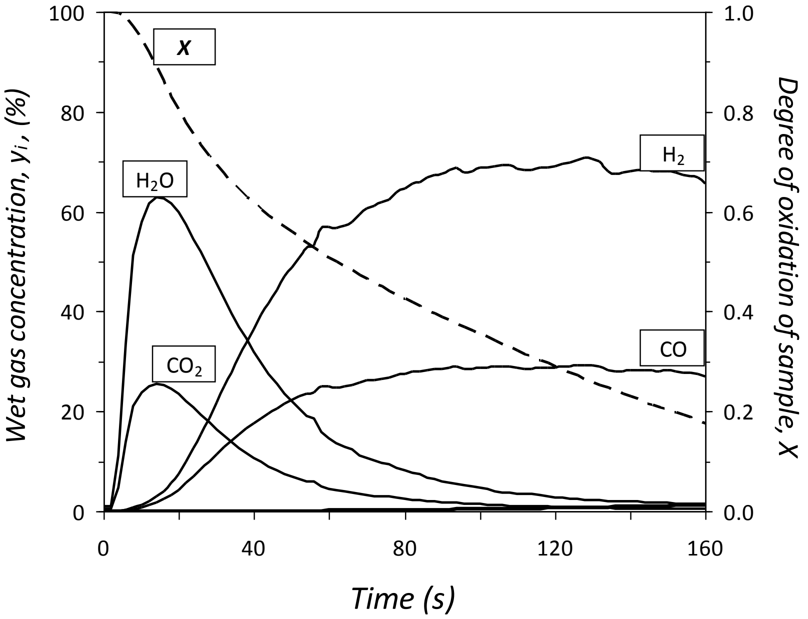

Figure 4. Calculated wet-gas composition during reduction with 70 vol% CH_4 and 30 vol% steam, sample 2, 12th cycle.

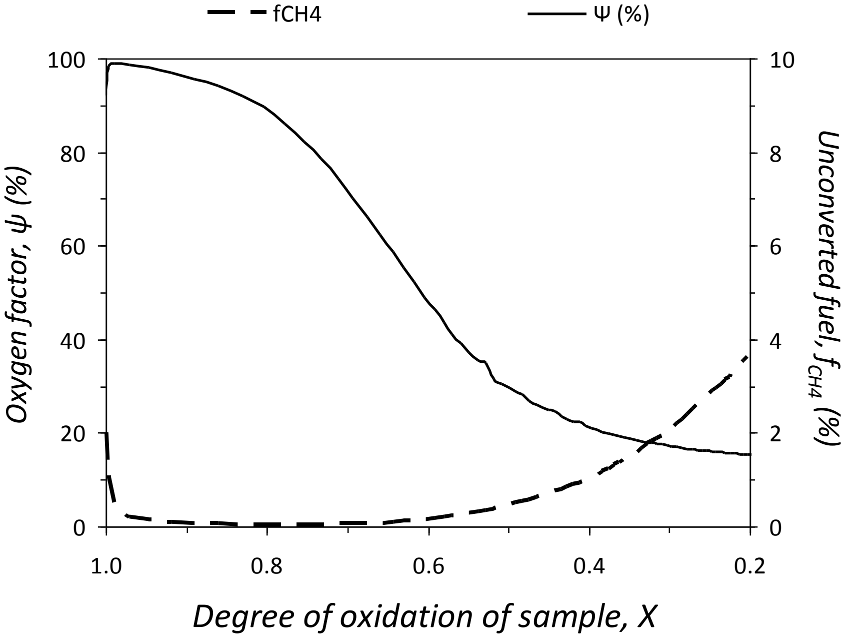

Figure 5. Ψ and f_{CH4} as function of X for the reduction described in Figure 4, sample 2, 12th cycle.

In Figures 4-5, it can be seen that the reduction of the sample initially resulted in almost complete oxidation of CH_4 into CO_2 and H_2O. However, some minor amounts of CH_4 slip through the reactor when X is very close to 1. In Figure 6, x_{CH4} has been plotted as a function of X for a comparable pulse experiment, and it can be seen that there is a small CH_4 peak for the first pulse here as well.

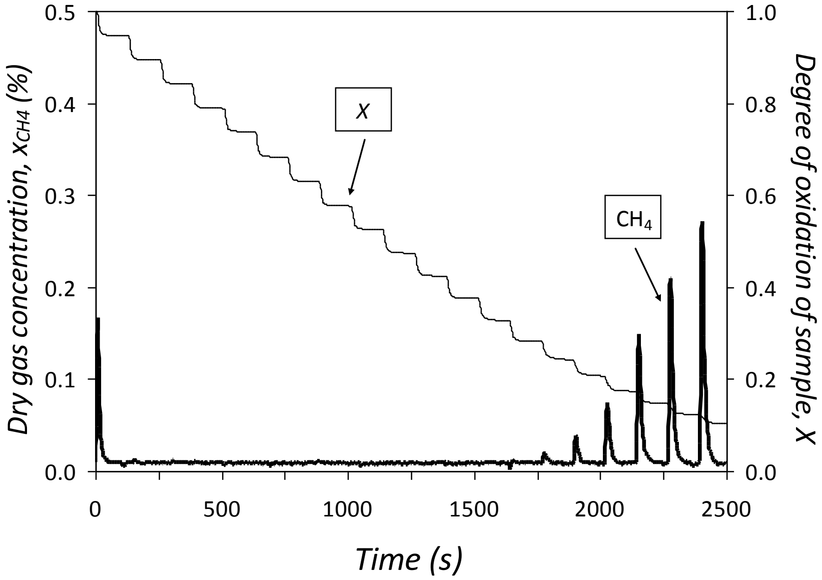

Figure 6. x_{CH4} and X for reduction with 70 vol% CH_4 and 30 vol% steam in 6 s pulses, sample 4, 3rd cycle.

The reason for this phenomenon is likely that there is no metallic Ni present in the fully oxidized sample. It is well established that metallic Ni catalyzes the decomposition of CH_4 and other hydrocarbons into more reactive components such as CO and H_2. Consequently, it is not surprising that there is no CH_4 present in the gas from the reactor once the sample is reduced somewhat and metallic Ni is obtained, as can be seen in Figures 5-6. This implies that it is not necessarily a good idea to operate a chemical-looping combustion process with the highest possible rate of solids circulation, since this would result in a value of X close to 1 in the fuel reactor, which could lead to incomplete conversion of CH_4 or other hydrocarbons.

In Figures 4-5, it can be seen that the products start to shift towards H_2 and CO when X is reduced to below 0.85-0.90. This could be expected, since less O_2 will be available for the oxidation reactions. A chemical-looping combustion process would need to operate above this number. In order to obtain a product composition that corresponds to the desired Ψ value for chemical-looping reforming of 0.30, an X of slightly below 0.5 is needed at these particular conditions. However, it should be pointed out that the composition of produced gas likely will depend upon factors such as fuel to oxygen-carrier ratio, temperature, pressure etc.

In Figures 5-6, it can be seen that minor amounts of CH_4 slip through the bed when the oxygen carrier have been reduced to very low numbers. This can be connected to the composition of produced gas, since there is a thermodynamical limitation for how high CH_4

conversion there can be when the degree of oxidation of the gas product, Ψ, approaches 0.30. At the desired conditions, with Ψ=0.30 at 950°C with 30 vol% steam addition, the equilibrium concentration of CH_4 is below 0.01 vol%. However, this number increases rapidly as Ψ approaches 0.25 or below.

The reduced samples were reoxidzed by a mixture of 5 vol% O_2 in 95 vol% N_2. The reason for not using air is that reaction (2) is highly exothermic, so a lower O_2 concentration is needed in order to avoid overheating of the reactor, which lacks external cooling. The oxidation reaction was fast and at no occasion did any O_2 pass through the sample before it was completely oxidized.

If CH_4 without addition of H_2O was used for the reduction, small amounts of solid carbon were formed in the reactor if the oxygen carrier was reduced to below X≈0.50. During the reoxidation, this coke was burnt into CO_2. Adding 30 vol% H_2O to the sample removed this tendency. There were no problems with defluidization or agglomeration of the particles, at any occasion.

4.2 Experiments in circulating fluidized bed

A sample of 240 g of particles in the size range of 90-212 μm was added to the two-compartment reactor, which resulted in a bed height in the fuel reactor of ≈4.0 cm. Later, another 60 g of particles was added, which increased the bed height to ≈5.5 cm. The reason why the modest increase in the amount of particles in the reactor results in a comparably large increase in bed height is that when only the smaller amount is used, a comparably larger share will be located to the downcomer. Natural gas with a composition equivalent of $C_{1.14}H_{4.25}O_{0.01}N_{0.005}$ was used as fuel. The experiments in the continuously operating reactor can be divided into two subcategories:

- **Chemical-looping combustion (CLC)**
  The aim of a CLC experiment was to convert as large share of the fuel as possible to CO_2 and H_2O. The fuel flow was 0.35-0.90 L_n/min natural gas and the air flow was 6.30-10.50 L_n/min. The reactor temperature was 670-950°C.
- **Chemical-looping reforming (CLR)**
  The aim of a CLR experiments was to convert the fuel to CO and H_2. This was achieved by using an air to fuel ratio below the stoichiometric requirement for combustion, i.e. a fuel flow of 1.20-1.50 L_n/min natural gas and an air flow of 3.80-6.50 L_n/min. Most of the time, 30 vol% steam was added to the natural gas in order to

suppress formation of solid carbon in the fuel reactor and to obtain a process that, from a thermodynamic point of view, resembles conventional auto-thermal reforming.

Prior to the experiment, the overpressure in the fuel reactor was set to 200-250 Pa by adjusting the level in the water seal. The furnace was heated to a temperature slightly above the desired fuel reactor temperature. 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 N_2, and after a minute or two, by fuel. Steady-state conditions were reached after a few minutes, depending on the fuel and air flow.

Most data referred to in this paper are from the period following the start-up sequence. Typically, this period was 1-3 hours. 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. Fuel and air was replaced with 1.0 L_n/min N_2 in each reactor part, which reduced the gas velocity in the air reactor to below the terminal velocity for the particles, and hence there should be no solids circulation. After a few minutes, N_2 was replaced with 1.0 L_n/min air in both reactor sections. The reoxidation provided some information about accumulation of solid carbon in the system, the degree of reduction of the particles in each reactor section and subsequently the magnitude of the solids circulation. In total, 40 hours of operation with fuel were recorded. A summary can be found in Table 2.

	Experiment (Type)	**Bed mass (g)**	F_{ng} **(L_n/min)**	F_{H2O} **(L_n/min)**	F_{air} **(L_n/min)**	T_{fr} **(°C)**	**Operation (hours)**
1	CLC	240	0.50		6.30-10.50	850-950	6
2	CLC	240	0.50	0.21	8.40	950	2
3	CLR	240	1.40		5.20-6.50	950	3
4	CLR	240	1.40	0.60	3.80-6.00	850-950	9
5	CLC	300	0.35-0.90		6.30-10.50	670-950	8
6	CLR	300	1.20-1.50		5.20	950	3
7	CLR	300	1.40	0.60	3.80-6.00	850-950	9

Table 2. Summary of circulating fluidized-bed experiments.

4.2.1 Chemical-looping combustion results

Natural gas without steam addition was used as fuel for all chemical-looping combustion experiments. These experiments worked flawlessly. The conversion of natural gas was always very close to 100% and the selectivity towards CO_2 and H_2O was high. An example of the concentration of the outlet gas from the fuel reactor, using the base case process parameters, is shown in Figure 7.

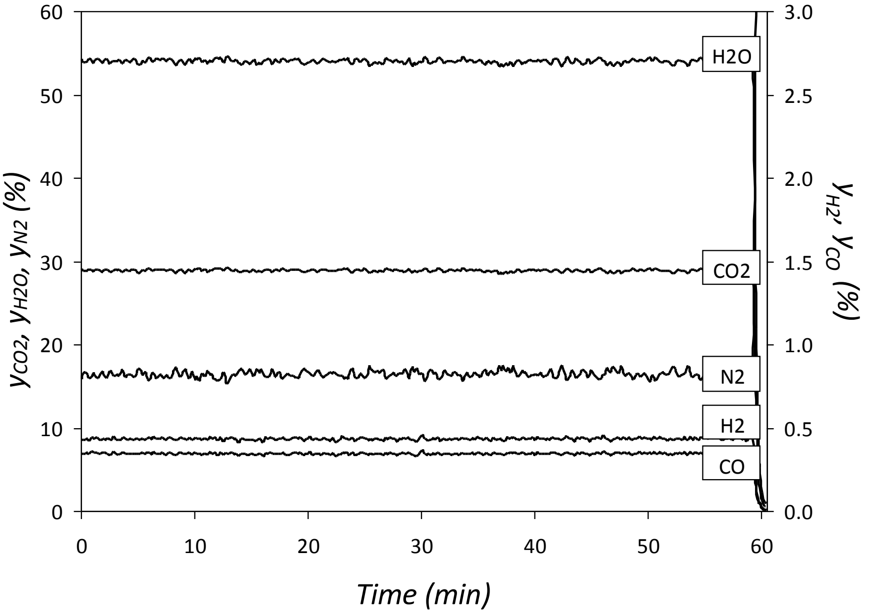

Figure 7. Wet gas concentration, y_i, during chemical-looping combustion at 950°C with 300 g N4MZ1400 and F_{ng} =0.50 L_n/min, F_{air} =8.40 L_n/min. y_{CH4} was to low to measure. N_2 is present because it is used as fluidization gas in slot and downcomer. Note that y_{CO} and y_{H2} are displayed on a separate y-axis.

In Figure 7, it can be seen that H_2 and CO were present only in very small proportions, 0.5 vol% or below. The concentration of CH_4 was too low to measure, and since higher hydrocarbons are expected to be at least as reactive with NiO as CH_4, it can be assumed that the conversion of hydrocarbons was very close to 100%.

The results were remarkably stable for variations in process parameters. Due to thermodynamic constraints, NiO is incapable to fully convert natural gas into CO_2 and H_2O and the highest possible value of γ_{eff} at 950°C is 99.4%. With base case parameters, as in Figure 7, γ_{eff} was 99.2%. Varying the air factor between 1.15 and 1.60 did not have any measurable impact on the results. Reducing the natural gas flow to 0.35 L_n/min improved γ_{eff} to 99.3%, while increasing the natural gas flow to 0.90 L_n/min reduced it to 99.1%. Reducing the amount of bed material to 240 g reduced γ_{eff} to 99.0%.

It can be concluded that the resulting gas concentration at 950°C are close to the theoretical maximum. When the reactor temperature was reduced below 800ºC, γ_{eff} did decrease somewhat. There was still complete conversion of CH_4, but some CO and H_2 were produced instead of CO_2 and H_2O, see Figure 8.

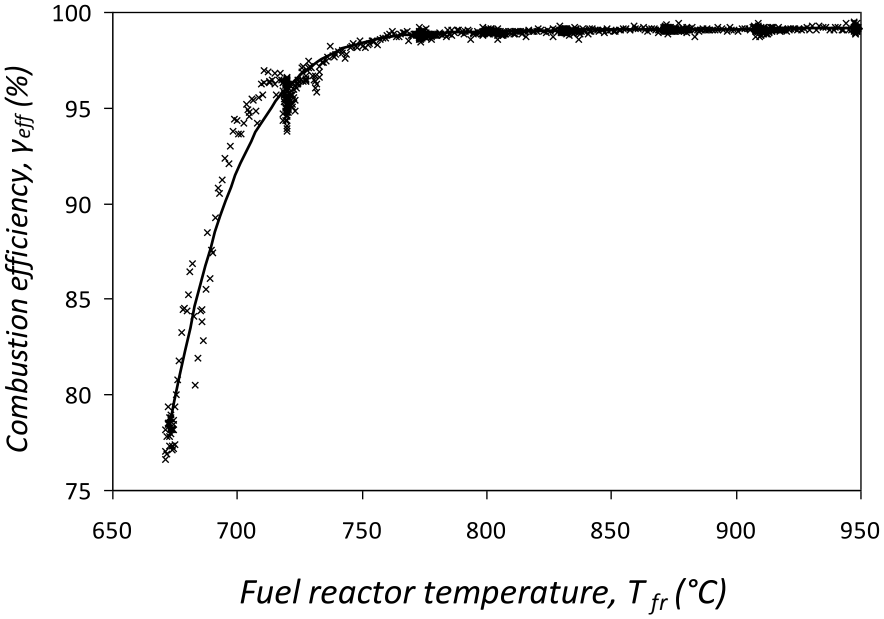

Figure 8. Combustion efficiency as function of fuel reactor temperature with 300 g N4MZ1400 and F_{ng} =0.50 L_n/min, F_{air} = 8.40 L_n/min. Summary of data from a 3 h experiment.

The reduction in γ_{eff} as function of temperature, as can be seen in Figure 8, is likely due to slower reaction kinetics at lower temperatures. From a thermodynamical equilibrium point of view, reducing temperature would have improved γ_{eff} slightly.

It was not possible to measure the circulation of solids between the reactor halves directly. However, it was possible to do estimations, using the difference in the degree of reduction between the particles in the air reactor and the particles in the fuel reactor, which in turn could be estimated from the reoxidation data, such as is shown in Figure 9.

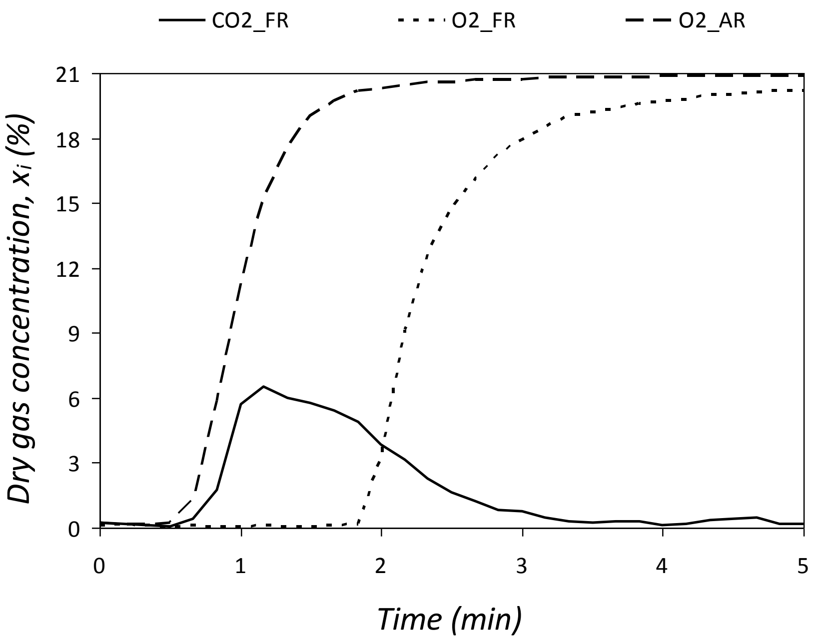

Figure 9. Reoxidation following a typical chemical-looping combustion experiment with dry natural gas as fuel. Prior to t=0 the reactor is fluidized with N_2. At t=0 the N_2 is replaced with 1.0 L_n/min air in each reactor section.

In Figure 9, it can be seen that once air was added to the reactor, there was an almost immediate breakthrough of O_2 in the air reactor. The time delay in the system was approximately 30 seconds, so it can be concluded that the oxygen carrier was close to completely oxidized in the air reactor. After another minute 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 was 4-6%, i.e. X_{fr} was 0.94-0.96. According to the batch experiments, this is probably close to the ideal conditions for chemical-looping combustion, since there would be metallic Ni present to catalyze decomposition of hydrocarbons, while oxygen would still be readily available. The numbers corresponds to a solids circulation between the reactor halves of 5-10 g/s, and a residence time in the fuel reactor of 10-20 s.

In Figure 9, it can also be seen that was some CO_2 released when air was added. This was likely due to minor amounts of solid carbon formed in the fuel reactor via reactions (4-5), which accumulated at stagnant locations such as inside the pressure measurement taps. The amount of CO_2 produced in Figure 9 corresponds to approximately 0.1 wt% of the total amount of carbon added to the reactor during the experiment, which in this case lasted for 2 hours. If 30 vol% steam was added to the natural gas, there was no detectable accumulation of solid carbon in the system.

In order to put the results into some perspective, it is worth comparing them to an earlier series of experiments by Rydén et al[20], where three NiO-based oxygen carrier materials were examined in a reactor setup very similar to the one used here. These materials had considerably lower NiO content compared to the oxygen carrier used here, and the resulting γ_{eff} varied between 40-98.5%. In another series of experiment, Linderholm et al[15], used the same reactor setup to examine oxygen-carrier material made from commercially available NiO, Al_2O_3 and production methods, rather than using particles manufactured with laboratory-grade chemicals. The maximum γ_{eff} for these experiments appears to have been in the order of 99%. Further, Johansson et al[9,10] examined chemical-looping combustion of natural gas using a reactor system comparable to the one used in this paper. Two NiO-based oxygen carriers were examined, which both provided γ_{eff} up to 99%.

4.2.2 Chemical-looping reforming results

The chemical-looping reforming experiments also worked well. The conversion of natural gas into reagents was very high. Minor amounts of CH_4 could be expected due to thermodynamical constraints at low Ψ values. Measured $x_{CH4,fr}$ was most often to low to measure, and always below 0.1 vol%.

With 30% steam added to the natural gas, it was possible to conduct experiments at Ψ values below 0.30 with no formation of solid carbon in the fuel reactor. An example of a typical experiment is shown in Figure 10.

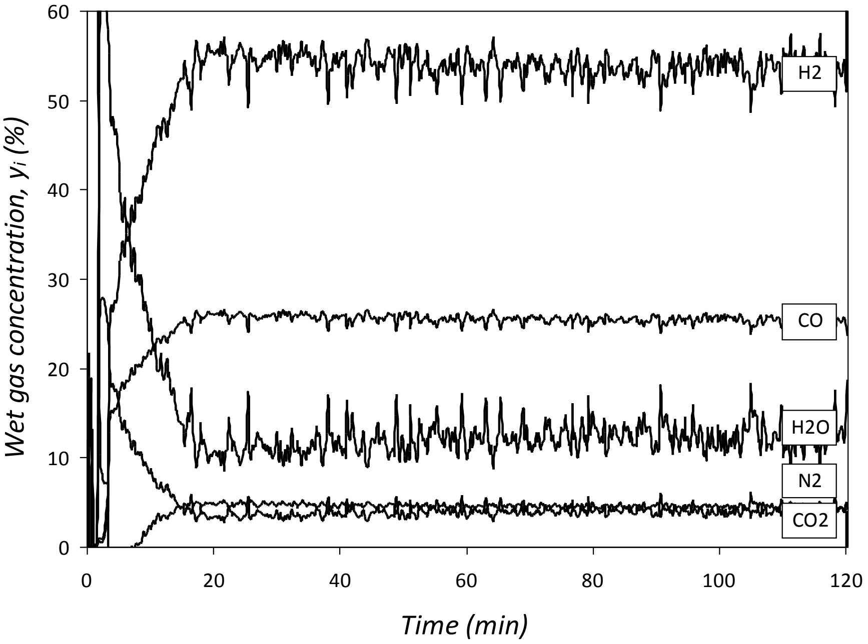

Figure 10. Wet gas concentration during chemical-looping reforming at T_{fr}=940ºC with 300 g N4MZ1400 and Ψ=0.30, F_{ng} =1.40 L_n/min, F_{H2O}=0.60 L_n/min, F_{air} =4.30 L_n/min. y_{CH4} was to low to measure. N_2 is present since it is used as fluidization gas in slot and downcomer.

In Figure 10, it can be seen that the natural gas initially was completely oxidized to CO_2 and H_2O. However, since the oxygen added to the air reactor is insufficient to reoxidize the oxygen carrier completely, the overall degree of oxidation of the particles in the system slowly decreases, and the products shifts towards CO and H_2. In the example presented in Figure 10, steady state is achieved after about 20 minutes. This means that the particles are in a reduced state not only in the fuel reactor, but in the air reactor as well. Using reoxidation experiments similar to the one shown as in Figure 9, X_{ar} was estimated to 0.40-0.60 and X_{fr} to 0.20-0.35, depending on process conditions. This corresponds to a solids circulation in the range of 0.7-1.5 g/s, and a residence time in the fuel reactor of 60-100 s. So in order to give the desired product composition, the oxygen carrier needed to be reduced somewhat further here compared to the batch experiments. The likely reason is that the oxygen carrier to fuel ratio, residence time etc was higher for the experiments in the circulating-fluidized bed reactor compared to the batch reactor.

It should be noted that the solids circulation apparently was much lower for chemical-looping reforming experiments compared to chemical-looping combustion experiments. The likely reason for this is that much lower air flows were used. The air flow is the force that transports particles into the downcomer, and thus creates the solids circulation.

For chemical-looping reforming experiments where only natural gas was used as fuel, there was some carbon accumulation in the fuel reactor. The numbers were larger than for chemical-looping combustion, in the order of 0.3 wt% of the total amount of carbon added during the experiment. Still, this is small compared to earlier experiments using similar methodology[20,28,29]. If 30% steam was added to the natural gas, there were no indications that there was any formation of solid carbon within the reactor system. It can be concluded that the used oxygen carrier seems less prone to propagate carbon formation in the fuel reactor compared to oxygen carriers examined in the studies cited above.

4.2.3 Effects on the oxygen-carrier particles

Following the experiment, the reactor was opened and the particles examined. It was found that some of the particles had elutriated. Of the 300 g particles added to the system, about 280 g remained in the reactor. 3 g was collected in the water seal after the fuel reactor. 2 g of particle dust was found in the filters to the gas analyzing equipment. A few grams of particles could possibly have been lost during handling. The most likely explanation is that the remaining ≈10-15 g was lost as fines, which possibly could have blown out of the reactor system via the air reactor.

A comparison of the size distribution between fresh particles and particles which have been used for 40 hours of operation in the continuously operating reactor can be found in Table 3. The size of the particles apparently increased somewhat during the experiments. This is likely an effect of an increase in porosity during repetitious oxidation and reduction. The apparent density of the particles had decreased from 4.1 g/cm^3 to 3.7 g/cm^3.

Size (μm)	**Fresh (wt%)**	**Used (wt%)**
212+		7
180-212	20	22
125-180	46	44.5
90-125	32	23
45-90	1.5	3
-45	0.5	0.5

Table 3. Size distribution of fresh and used oxygen carrier.

Minor changes in surface properties and porosity for oxygen-carrier particles, as well as loss of fines during the initial hours of operation, have been reported for other oxygen carriers in similar experiments. In order to verify the long term stability, more comprehensive experiments in a setup that emulates industrial conditions better would need to be done.

Linderholm et al[16] reports an expected life span of 33 000 hours for spray-dried particles consisting of 40 wt% NiO supported on Al_2O_3, based on more than 1000 hours of operation in a 10 kW chemical-looping combustor. In this extensive test series, it is reported that the major loss of fines was in the first 100 hours of operation.

4.2.4 Gas leakage between reactor sections

The slot and the downcomer were fluidized with N_2. This resulted in a slight dilution of the gases from the fuel reactor and the air reactor. In addition to this, gas leakage between the reactor sections via the slot and the downcomer is a possibility. These phenomena were examined by performing leak tests, during which the loaded reactor was operated at relevant temperatures but without fuel. Air was fed to the air reactor, N_2 to the slot and the downcomer, and CO_2 to the fuel reactor, and it could be calculated how the different gas components distributed themselves within the reactor system. Later, the estimated numbers have been verified during operation using Ar as fluidization gas, and gas chromatography to measure the leakage of N_2 to the fuel reactor. These experiments used similar process parameters, but a different oxygen carrier, compared to the experiments presented in this paper.

Both methods indicate that the leakage of air from the air reactor to the fuel reactor was close to zero, or at most 0.5 vol% of the air flow. This means that at least 99%, and in most cases close to 100%, of the oxygen present in the combustion products leaving the fuel reactor originates from the solids circulation.

The leakage from the fuel reactor to the air reactor was in the order of 0.04-0.08 L_n/min. This corresponds to 1-2 vol% of the fuel-reactor flow in chemical-looping reforming experiments and 3-7 vol% of the fuel-reactor flow in chemical-looping combustion experiments. Gas leakage this way is believed to have very little impact on the experimental results. The leakage could be estimated by leak tests, as well as by measuring the concentration of CO_2 in the gas from the air reactor. It can not be ruled out that a small share of the measured CO_2 from the air reactor could be due to coke formation in the fuel reactor, which could be transferred to the air reactor via the solids circulation. This is not believed to have happened to any larger extent though.

A flow of 0.40 L_n/min N_2 was needed for fluidization of the downcomer and the slot. 80% of the N_2 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. Hence it seems unlikely that the

N_2 dilution would have had any significant impact on the experimental results. Typically, 50-75% of added N_2 ended up in the fuel reactor and the rest in the air reactor.

5. Discussion

Freeze-granulation is not a suitable method for large-scale production of oxygen-carrier particles. However, it has been shown by Jerndal et al[32] that particles produced by spray drying have essentially the same properties as particles produced by freeze granulation, as long as similar ingredients and process parameters are used. This is important since spray drying is a cheap and well established method to produce particles. This means that particles with properties similar to those examined here likely could be produced at low cost. Lyngfelt et al[33] estimated the production cost for NiO-based particles to €4/kg. With a life span of 33000 hours and a solids inventory of 200 kg/MW, this would correspond to a particle cost in the order of €0.1/ton CO_2 captured.

As has been mentioned earlier, there appears to have been limited formation of solid carbon in the reactor at some occasions. This is not necessarily a problem. If the carbon follows the oxygen-carrier particles to the air reactor it would burn there and release heat that could be used for the endothermic reactions in the fuel reactor. This would dilute the N_2 from the air reactor with some CO_2 though, and if the chemical-looping process is to be utilized for production of heat, power or H_2 with CO_2 capture, carbon formation in the fuel reactor would lead to slightly reduced capture efficiency. It also can be speculated that carbon formation could affect the integrity of the oxygen carrier, as is the case for example with carbon formation on NiO-based steam reformer catalysts. This would need to be further examined though. And unlike in the steam reforming case, any solid carbon on the oxygen carrier would immediately be removed by combustion in the air reactor in the chemical-looping case.

The degree of carbon formation during the experiments could probably not have exceeded a few tenths of a %-point of added carbon. Otherwise it would have been possible to measure higher values of $x_{CO2,ar}$ and $x_{H2,fr}$ than what is expected. The little carbon that was formed could very well be due to reactor specific factors, for example accumulation of carbon in stagnant sections of the reactor, such as the pressure measurement taps. Several experiments undertaken in other reactors indicate no formation of solid carbon for chemical-looping combustion using NiO-based oxygen-carrier materials, see Lyngfelt et al[7] and Linderholm et al[14,16]. Further, adding 30 vol% steam to the fuel removed all signs of carbon formation, i.e. the slight accumulation of carbon within the reactor system.

Finally, it shall be pointed out that reforming of hydrocarbons results in a very large volumetric increase, see reactions (6-8). Therefore, the power required for compression of produced H_2 or synthesis gas to suitable product pressure becomes considerable for any process working at atmospheric pressure. As a consequence, elevated pressure during the reforming process would be highly beneficial for the overall efficiency, see Rydén et al[29,30]. If the process is pressurized, the thermodynamics indicate that higher reactor temperature would be necessary in order to achieve complete conversion of the fuel.

6. Summary and conclusions

The experiments presented in this paper show that NiO supported on Mg-ZrO_2 could work well as oxygen carrier in chemical-looping applications.

The batch experiments indicate very high conversion of CH_4 once some metallic Ni is obtained. The selectivity towards combustion and partial oxidation can be controlled by altering the degree of reduction of the particles. Combustion is favoured at X above ≈0.90, while partial oxidation is favoured at X below ≈0.50.

The circulating fluidized-bed experiments worked flawlessly. 40 hours of operation were recorded. There were no problems with defluidization, agglomerations etc, despite the sometimes harsh experimental conditions. For chemical-looping combustion, γ_{eff} up to 99.3% was obtainable, which is very close to the theoretical maximum at 950ºC and slightly better than results obtained with NiO-based oxygen carriers supported on Al_2O_3-based materials, using similar reactor setup[9,10,15,20]. For chemical-looping reforming, complete conversion of natural gas and very high selectivity towards H_2 and CO was achieved. Operating the reactor at the desired process parameters, i.e. Ψ=0.30 and T_{fr}=950ºC, worked well.

When only CH_4 or natural gas was used as fuel, very small amounts of solid carbon were found to accumulate in the reactor. Adding 30 vol% steam or CO_2 to the fuel removed this tendency.

The particles retained their physical and chemical structure reasonably well during operation. Used particles were found to be slightly more porous than fresh, and there was also a small loss of fines during operation. This is to be expected though.

7. Acknowledgements

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