

# Production of H<sub>2</sub> and synthesis gas by chemical-looping reforming

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## Abstract

Chemical-looping reforming is a novel process for partial oxidation of hydrocarbon fuel where oxygen is brought to the fuel by a solid oxygen carrier. Chemical-looping reforming has been examined in a laboratory reactor consisting of two interconnected fluidized beds. Particles of NiO and MgAl<sub>2</sub>O<sub>4</sub> were used as bed material, oxygen carrier and reformer catalyst. Natural gas was used as fuel. The reactor temperature was 820-930 °C. There was a continuous circulation of oxygen-carrier particles between the fluidized-beds. In the fuel reactor the oxygen carrier was reduced by the fuel, which in turn was partially oxidized to H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. In the air reactor the oxygen carrier was reoxidized with air. Formation of solid carbon was noticed for some cases. Adding 25 vol% steam to the natural gas reduced the carbon formation substantially. H<sub>2</sub> production by chemical-looping reforming with CO<sub>2</sub> capture has also been examined in a process study, where it was found that an overall efficiency of 81% including CO<sub>2</sub> sequestration is possible.

**Keywords:** Chemical-looping reforming, partial oxidation, hydrogen, synthesis gas, carbon capture.

## 1. Introduction

Synthesis gas, the mixture of H<sub>2</sub> and CO, has many uses. It is used for example as feedstock for Fischer-Tropsch synthesis and for production of methanol and ammonia. Synthesis gas is also used for production of pure H<sub>2</sub>, which is an energy carrier with many interesting properties. Combustion of H<sub>2</sub> produces only H<sub>2</sub>O as waste product so it can be used as CO<sub>2</sub>-free fuel for vehicles or other applications. Fossil fuels can be converted to H<sub>2</sub> with high efficiency. If CO<sub>2</sub> is captured within the process an energy carrier that can be utilized without greenhouse gas emissions to the atmosphere is obtained.

## 2. Chemical-looping combustion and chemical-looping reforming

Chemical-looping combustion is an innovative combustion technology that can be used for CO<sub>2</sub> capture in power generating processes. Direct contact between fuel and combustion air is avoided. Instead, a solid oxygen carrier performs the task of bringing oxygen from the air to the fuel. Chemical-looping combustion takes place in two separate reactors. In the fuel reactor the oxygen carrier is reduced by oxidizing the fuel. In the air reactor the oxygen carrier is oxidized with air. The sum of reactions is combustion of the fuel with oxygen. The combustion products are not diluted with N<sub>2</sub> so pure CO<sub>2</sub> can be recovered by condensation, see figure 1.

Suitable oxygen carriers include metal oxides such as Fe<sub>2</sub>O<sub>3</sub>, NiO, CuO and Mn<sub>3</sub>O<sub>4</sub>. An overview of the research dealing with oxygen-carriers for chemical-looping combustion can be found in the works of Cho [1], Johansson [2] and Adánez et al [3]. Information about various subjects regarding chemical-looping combustion such as design of experimental reactors, power production with CO<sub>2</sub> capture and more about oxygen-carriers can be found in the doctoral theses by Brandvoll [4], Johansson [5] and Wolf [6].

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Chemical-looping reforming is similar to chemical-looping combustion, but complete oxidation of the fuel is prevented by using low air to fuel ratio. Hence chemical-looping reforming can be described as a method for partial oxidation of hydrocarbon fuels that it utilizing chemical-looping as a source of oxygen. This is a considerable advantage compared to conventional technology since the need for expensive and power consuming air separation is eliminated, see figure 1.

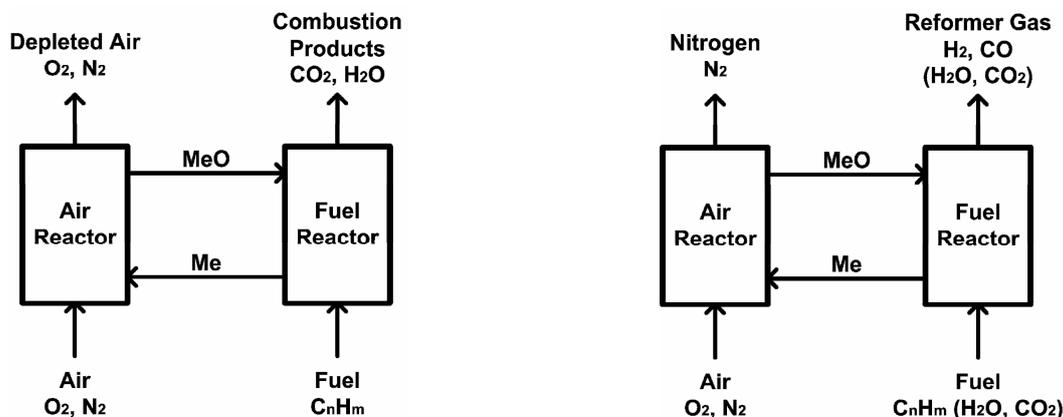
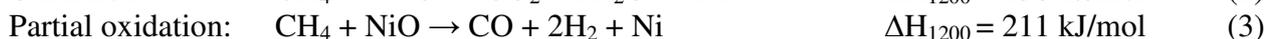


Figure 1. Schematic description of chemical-looping combustion (left) and chemical-looping reforming (right). MeO is the oxygen carrier in its oxidized form while Me is the reduced form.

If the fuel is CH<sub>4</sub>, the oxygen carrier is NiO and the reactor temperature is 1200 K, reaction (1) occurs in the air reactor.



In the fuel reactor, reactions (2-5) may occur, depending on the air ratio. Steam or CO<sub>2</sub> could be added to the fuel to enhance the relative importance of reaction (4) or reaction (5) respectively. This could be used to adjust the H<sub>2</sub>/CO ratio in produced synthesis gas or to suppress formation of solid carbon in the fuel reactor. For chemical-looping combustion as much fuel as possible should be completely oxidized according to reaction (2).



Chemical-looping processes could be designed in several ways but circulating fluidized beds are likely to have an advantage over other alternatives since this design provides good contact between gas and solids and allows a smooth flow of oxygen carrier between the reactors. Continuous chemical-looping combustion in circulating fluidized beds has been demonstrated by Lyngfelt et al [7], Ryu et al [8], Johansson [5] and Abad et al [9].

Oxygen carrier particles for chemical-looping reforming have been experimentally examined by Zafar et al [10], who made tests in a fluidized-bed reactor with oxygen-carrier particles as fluidizing agent, and by Mattisson et al [11]. These two studies indicates high reaction rate and good selectivity towards H<sub>2</sub> and CO for oxygen carriers with NiO as active phase, while oxygen carriers based on Fe<sub>2</sub>O<sub>3</sub>, CuO and Mn<sub>3</sub>O<sub>4</sub> suffered from poor selectivity and produced CO<sub>2</sub>, H<sub>2</sub>O and unreformed CH<sub>4</sub> rather than CO and H<sub>2</sub>.

Here results from an experimental study of chemical-looping reforming in a continuous laboratory reactor are presented. In addition to this, the opportunity to use chemical-looping reforming for H<sub>2</sub> production with CO<sub>2</sub> capture is briefly described. Additional information on the subject chemical-looping reforming can be found in the work of Rydén et al [12, 13, 14].

### 3. Experimental study of chemical-looping reforming

The laboratory reactor was built up from two interconnected fluidized beds. In order to reach the desired temperature of reforming the test reactor was located inside a furnace. A schematic description of the reactor is found in figure 2. A detailed description can be found in the work of Johansson [5] or Rydén et al [14].

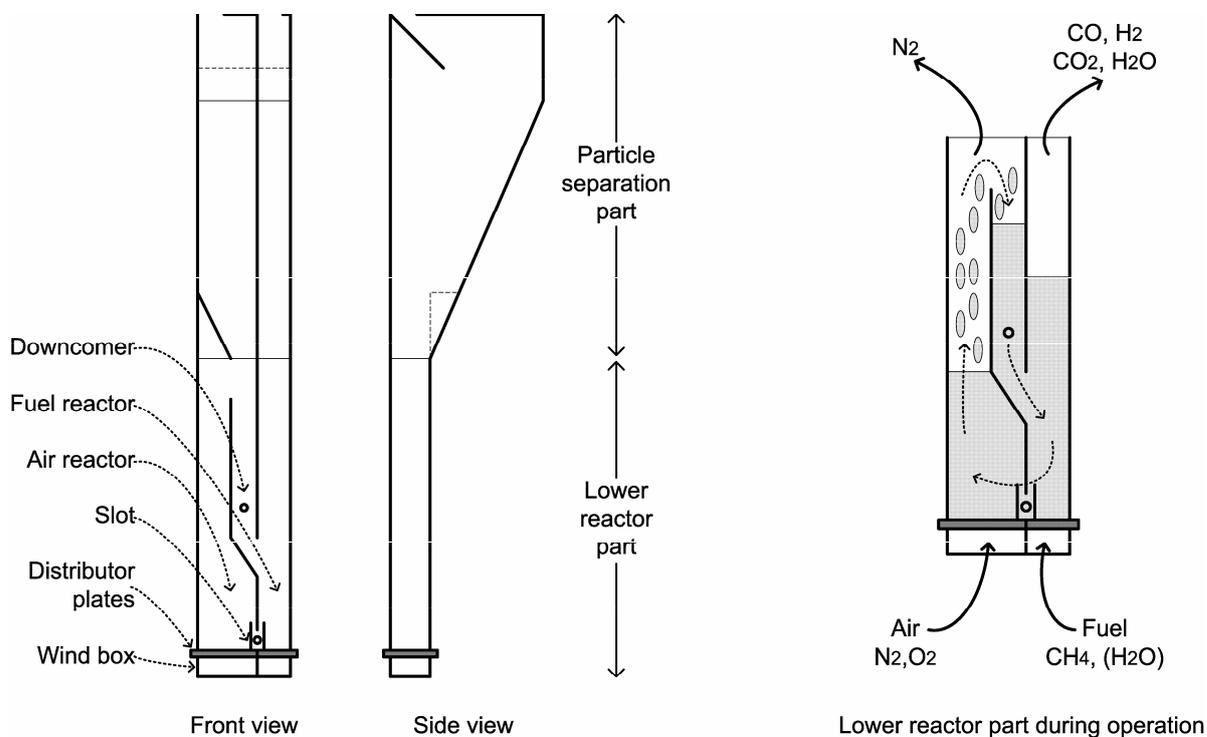


Figure 2. Schematic description of the laboratory reactor used for the experimental study.

350 g of particles consisting of 60 wt% NiO and 40 wt% MgAl<sub>2</sub>O<sub>4</sub> was used as bed material, oxygen carrier and reformer catalyst. The particles were prepared by freeze granulation and sintered at 1300 °C for 6 hours before they were sieved to a size of 90-212 μm. Natural gas was used as fuel, in some of the experiments together with 25 vol% steam. There was a continuous circulation of oxygen-carrier particles between the reactors. In the fuel reactor, the particles were reduced by the fuel, which in turn was partially oxidized to H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O according to reactions (2-5). In the air reactor the reduced oxygen carrier was reoxidized with air according to reaction (1). 33-44% of the available NiO on the oxygen-carrier particles was reduced to Ni during operation. In total, 24 hours of reforming with dry natural gas and 17 hours with 75 vol% natural gas and 25 vol% steam were recorded.

The oxygen-carrier particles did not agglomerate, but soft lumps were found in the air reactor after the experiments had been finished. A likely explanation for this is the low gas velocity used, 0.1-0.5 m/s. Carbon formation was apparent for some of the experiments with dry natural gas since small amounts of solid carbon were accumulating in the fuel reactor, likely in the pressure measurement taps. All measurements were made on dry gas, after cooling and condensation. The H<sub>2</sub>O concentration in the reformer gas could be estimated either by a species balance where it was assumed that there was no carbon formation, or by assuming that the reformed gas was at thermodynamic equilibrium. By comparing the results of these two assumptions it was possible to estimate the order of magnitude of the carbon formation. For one experiment with dry natural gas and all experiments with natural gas and 25 vol% steam there was no or very small accumulation of carbon in the reactors and the composition of the reformer gas was very close to thermodynamic equilibrium if it was assumed that there was no carbon formation, see figure 3 for an example. This indicates that the carbon formation was very low for these occasions.

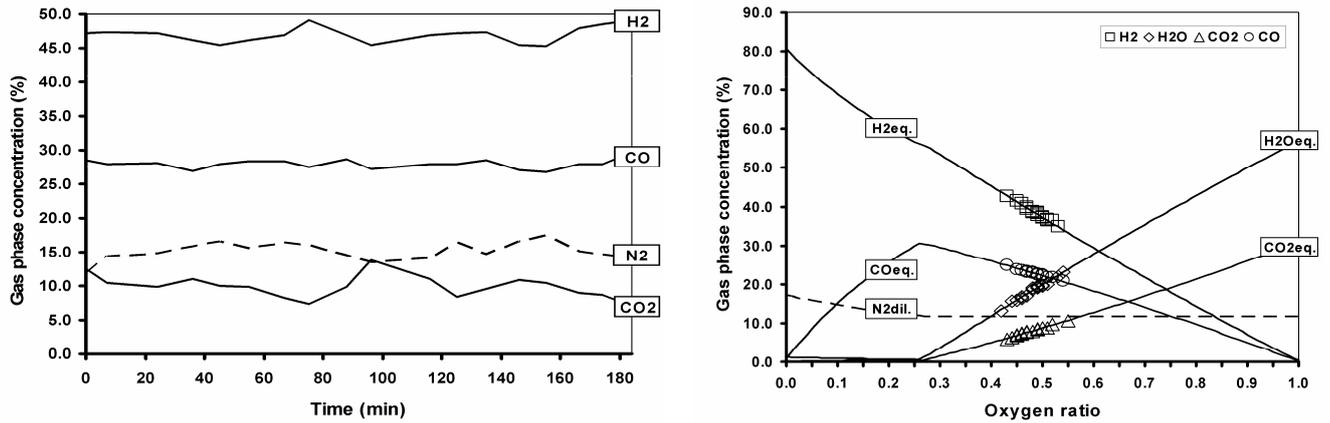


Figure 3. Dry gas composition after the fuel reactor (left), and measured point values compared to thermodynamic equilibrium when the H<sub>2</sub>O concentration is calculated with a species balance (right), for case 3D. The temperature is 900-920 °C. The oxygen ratio is the amount of oxygen that has reacted with the fuel divided by the amount that is needed for complete combustion. N<sub>2</sub> is present due to leakages from the air reactor.

The results of the experimental study are summarized in table 1. Details can be found in the work of Rydén et al [12, 14],

Table 1. Summary of performed chemical-looping reforming experiments.

Case	FR $x_{\text{CO}_2, \text{dry}}$ (average %)	FR $x_{\text{CO}, \text{dry}}$ (average %)	FR $x_{\text{H}_2, \text{dry}}$ (average %)	Estimated oxygen ratio	Estimated carbon (average %)	Accumulated carbon (%)
1D	13.6	26.7	50.5	0.50-0.54	7.7	No data
2D	5.3	26.5	58.2	0.30-0.42	19.9	2.6
3D	9.9	28.0	47.0	0.48-0.48	-0.7	0.1
4D	4.6	27.4	53.4	0.34-0.39	10.1	0.6
5D	7.9	29.6	53.0	0.41-0.44	5.0	1.6
6D	11.4	26.7	51.5	0.46-0.54	14.3	1.8
7S	16.9	25.7	48.3	0.54-0.55	1.3	0.3
8S	11.2	26.6	54.3	0.44-0.46	4.2	0
9S	11.0	26.7	52.2	0.45-0.46	0.9	0
10S	11.5	26.7	51.8	0.46-0.46	-0.7	0
11S	21.7	23.2	49.4	0.58-0.59	3.0	0
12S	15.5	24.5	51.7	0.50-0.51	1.3	0
13S	10.9	25.8	55.1	0.42-0.43	0.9	0

#### 4. Process study of chemical-looping reforming

In addition to the experiments, a process study has been done to investigate the potential for large scale production of H<sub>2</sub> with CO<sub>2</sub> capture. A schematic description of the proposed process is shown in figure 4. Air is compressed (AC) before entering the air reactor (AR). The fuel which is considered to be CH<sub>4</sub> is mixed with one third steam before the fuel reactor (FR). The outlet from the reformer reactor is cooled and extra steam is added to obtain a H<sub>2</sub>O/CO ratio of 2.5 before high-temperature shift (HTS) and low-temperature shift (LTS). H<sub>2</sub>O is removed from the shifted gas in a condenser (COND) before CO<sub>2</sub> is captured by absorption with MDEA solvent (MDEA). If wanted, some of the H<sub>2</sub> produced could be burned in a separate combustor (COMB) to increase the power output of the gas turbine (GT).

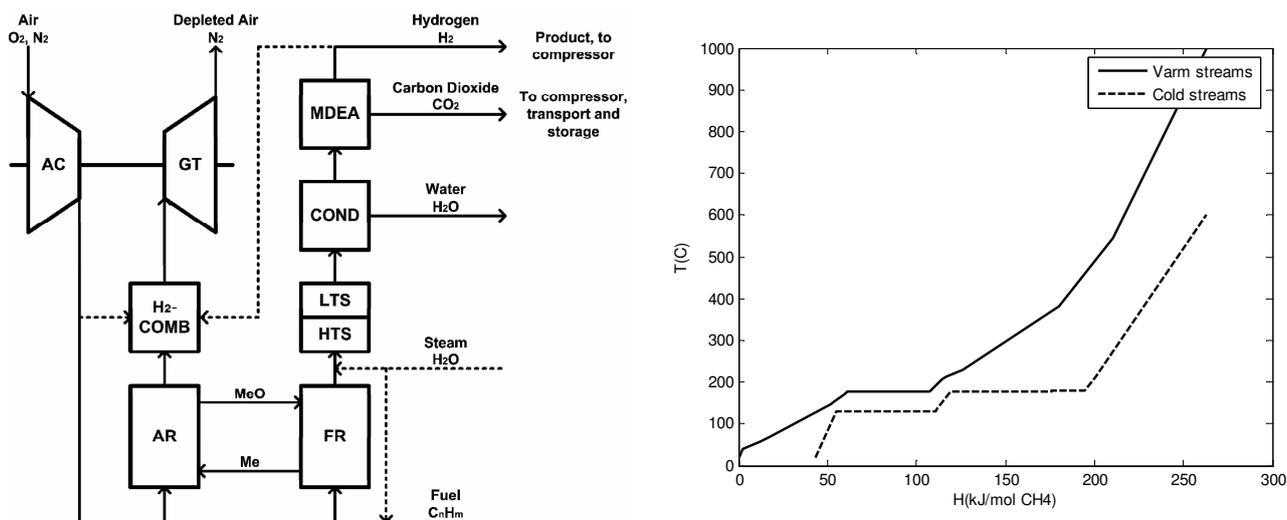


Figure 4. Schematic description excluding heat exchangers for  $H_2$  production with  $CO_2$  capture by chemical-looping reforming at elevated pressure (left), and thermal profile as grand composite curve for the particular case described below (right).

With a fuel reactor temperature of  $1000\text{ }^\circ\text{C}$ , preheating of fuel and air to  $600\text{ }^\circ\text{C}$  and a system pressure of 10 bar, 2.74 moles  $H_2$  is produced per mole  $CH_4$ . The overall reformer efficiency is about 81%, excluding heat losses but including capture and compression of  $CO_2$  to 100 bar. Increasing preheating to  $650\text{ }^\circ\text{C}$ , fuel reactor temperature to  $1060\text{ }^\circ\text{C}$  and reactor pressure to 16 bar would increase the overall efficiency about 1% and make the process self sustaining with power.

$H_2$  production by chemical-looping reforming at atmospheric pressure is possible but would result in lower efficiency. Reforming involves large volumetric increase so the power consumption for compression of  $H_2$  to a suitable product pressure would be large. Additional fan power would be needed to overcome pressure drop in the water-gas shift reactors. If  $CO_2$  capture is required an atmospheric process would need either a strong absorbing solvent such as MEA due to the low  $CO_2$  partial pressure in produced synthesis gas, or gas compression prior to the  $CO_2$  capture. Both these options that would increase the energy penalty for  $CO_2$  capture compared to the pressurized process described in figure 4. See the work of Rydén et al [12, 13] for further discussion about pressurized and atmospheric chemical-looping reforming.

## 5. Conclusions

It can be concluded that chemical-looping reforming of natural gas is feasible. The concept has been successfully demonstrated in a continuous laboratory reactor built up of two circulating fluidised-beds. The reactor was operating at atmospheric pressure and a temperature of  $820\text{--}930\text{ }^\circ\text{C}$ . Freeze-granulated particles of  $NiO/MgAl_2O_4$  were used as oxygen carrier. The particles were found to have the desired characteristics. They did not break apart or agglomerate and there was complete conversion of  $CH_4$  and higher hydrocarbons to  $H_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$ . Formation of solid carbon was identified as a potential problem. This was most apparent for reforming of dry natural gas. Adding 25 vol% steam to the natural gas removed or at least reduced the carbon formation.

From the process study it can be concluded that chemical-looping reforming is an interesting process concept for  $H_2$  production with  $CO_2$  capture. Chemical-looping reforming at atmospheric pressure is a possibility but it would be favourable to pressurize the reactor system. For pressurized systems integration with a gas turbine would be beneficial. The overall reformer efficiency could be in the order of 80%, including  $CO_2$  capture and  $CO_2$  compression.

## 6. Acknowledgements

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