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Performance of a NiO-based oxygen carrier for chemical looping combustion and reforming in a 120kW unit

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Abstract

In this study the performance of two different Ni-based oxygen carriers in a 120kW chemical looping pilot rig at Vienna University of Technology is presented. A dual circulating fluidized bed (DCFB) system has been designed with the important characteristics of high solid circulation, very low residence times and a high power to solid inventory ratio. For all presented results the pilot rig is fueled with methane at 140kW fuel power. For both oxygen carriers high CH_4 conversion and CO_2 yield is achieved. Air to fuel ratio and temperature are varied. CH_4 conversion at higher air to fuel ratio as well as at higher temperature seems to decrease. This phenomenon is linked to the Ni/NiO ratio of the particle which determines the catalytic activity and thus influences the CH_4 conversion and the CO_2 yield.

Keywords: Chemical Looping; Oxygen Carrier; Gas-Solid Reactor; Fluidized Bed System; Nickel oxide

1. Introduction

Chemical looping combustion (CLC) and reforming (CLR) are novel fuel conversion technologies allowing inherent CO_2 separation. The main advantage of chemical looping for carbon capture is that there is no gas separation step needed to get a concentrated CO_2 stream. This includes that the energy penalty paid for carbon capture is systematically lower than for pre- or post combustion capture or for oxyfuel combustion. The technology was introduced by Richter and Knoche [1] and Ishida et al. [2] to increase the reversibility of combustion processes. Chemical looping systems consist of two reaction zones in which different gas streams are in contact with circulating solids. The circulating solid transports oxygen and heat from one reaction zone to the other. Metal oxides allow such a transport. In the fuel converting zone, fuel is oxidized by the metal oxide. This reaction zone is called fuel reactor (FR). In the second zone, called air reactor (AR), the metal oxide is reoxidized. Figure 1 shows a setup of chemical looping system. The inlet gases in the two reaction zones are not mixed and solid circulates between them to transport oxygen and heat. A chemical looping system can be operated either as a combustor or as a reformer.

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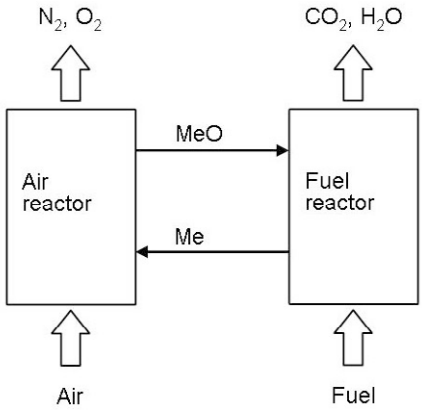

Figure 1. The chemical looping principle

If hydrocarbons are used as fuel in CLC, the main components of the FR exhaust gas are CO_2 and H_2O. After condensation of water, a relatively pure CO_2 stream is left. Therefore this technology has a high potential for CO_2 separation. The AR exhaust gas consists meanly of nitrogen with some excess oxygen.

The global reactions for gaseous fuels are:

fuel reactor

$$C_xH_y + \left(2x + \frac{y}{2}\right)MeO_\alpha \Leftrightarrow xCO_2 + \frac{y}{2}H_2O + \left(2x + \frac{y}{2}\right)MeO_{\alpha\text{-}1} \quad (1)$$

$$CO + MeO_\alpha \leftrightarrow CO_2 + MeO_{\alpha-1} \quad (2)$$

$$H_2 + MeO_\alpha \leftrightarrow H_2O + MeO_{\alpha-1} \quad (3)$$

air reactor

$$MeO_{\alpha\text{-}1} + \frac{1}{2}O_2 \Leftrightarrow MeO_\alpha \quad (4)$$

The AR reaction is exothermal whereas the FR reaction can be exothermal or endothermal. This depends on the fuel and the used oxygen carrier (OC). In the case of Ni-based OC and CH_4 as fuel the AR has an exothermal reaction but an endothermal FR reaction. The total heat release of the system is equal to the heat release of the direct combustion with air. [3]

The characteristic of the gas solid reaction in the FR and AR are

- enough residence time in the reaction zones,
- good gas solids mixing and
- an adequate OC for the used fuel.

At the pilot rig used within the present study, both reactors are designed as circulating fluidized beds with a direct hydraulic link at the bottom. The system is described in detail by Kolbitsch et al. [4].

2. General aspects of oxygen carriers

The basic requirements for OC are mechanical stability, lowest possible costs and high oxygen transport capacity. According to the used fuel the OCs has to fulfill other requirements. For hydrocarbon fuel a high catalytic activity is beneficial (especially for natural gas, i.e. methane). Ni- based carriers have a good catalytic activity and are suitable for methane combustion and reforming. Other possible metals beside Ni are: Cu, Fe, Co, Mn and Cd [5-16]. Most oxides have to be supported by other inert materials to gain the necessary strength and attrition stability to be operated in a CFB. Such support materials can be Al_2O_3, TiO_2, yttria-stabilized zirconium or MgO [17].

In the present study, highly active carriers manufactured by VITO, Belgium under the guidance of Chalmers University of Technology, Sweden are used. The oxygen carrier A (OC-A) is based on NiO and α-Al_2O_3. After sintering the particles consist of NiO and inert $NiAl_2O_3$ [18]. The basic components of the second Ni-based oxygen carrier (OC-B) are NiO, α-Al_2O_3 and MgO. These particles are also sintered. More information can be found in the article by Jerndal et al. [18]. The mean particle size of both OCs is approximately 120 μm.

3. The DCFB pilot rig

The chemical looping pilot rig is a DCFB system for gaseous fuels. The pilot rig is designed with respect to the typical properties of large scale installations. The nominal power of the pilot rig is 120kW with natural gas as the fuel. Alternatively, H_2, CO and C_3H_8 can be used as fuel. Loop seals between the reactors avoid mixing of AR and FR gases. These loop seals are fluidized with superheated steam. The flow regime in the AR is fast fluidization and in the FR turbulent fluidization. Downstream of each reactor, gas and solids are separated in cyclone separators. A principle setup is shown in Figure 2.

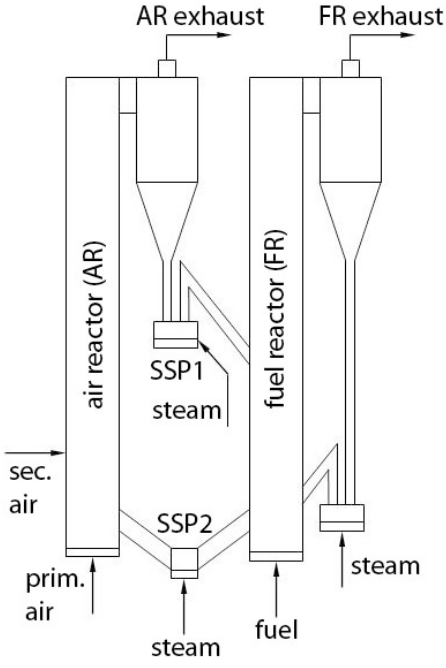

Figure 2 Principle setup of the DCFB reactor system

Depending on the different operating parameter (T, air/fuel ratio, fuel, etc.) of the chemical looping system, the pilot rig has to be cooled (Figure 3).

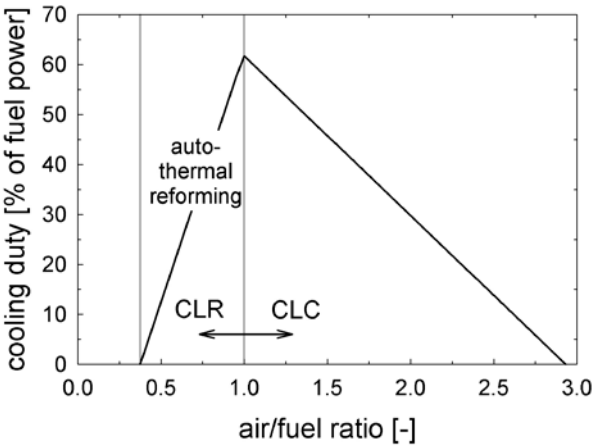

Figure 3 Theoretical cooling duty as a function of air/fuel ratio in case of full conversion to equilibrium [4]

A variable cooling system, consisting of three double jackets, is attached to the AR. A detailed description of the cooling system and the other auxiliary units can be found in Kolbitsch et al. [4].

The 120kW chemical looping pilot rig has been successfully operated since January 2008 at Vienna University of Technology. For the start up of the pilot rig a natural ore (ilmenite $FeTiO_3$) was used. These first results are presented in other contributions to this conference [19, 20]. The present study focuses on the Ni-based particles, for which the pilot rig has actually been designed for.

In order to characterize the performance of the chemical looping system, the fuel conversion in terms of CH_4 and the yield of CO_2 based on total carbon supplied are used:

$$X_{CH_4} = \left. \frac{y_{CO} + y_{CO_2}}{y_{CO} + y_{CO_2} + y_{CH_4}} \right|_{FRout} \tag{6}$$

$$\gamma_{CO_2} = \left. \frac{y_{CO_2}}{y_{CO} + y_{CO_2} + y_{CH_4}} \right|_{FRout} \tag{7}$$

In these definitions, the y_i are mole fractions of the gas species measured in the FR exhaust stream.

4. Operation results

The performance of the NiO-carriers (OC-A & OC-B) is demonstrated at the 120 kW pilot rig. Temperature and global air to fuel ratio are varied. The results shown in Figure 4 and Figure 5 are performed at 900°C, at an average fuel load of 140kW CH_4 and a total solids inventory of 65kg.

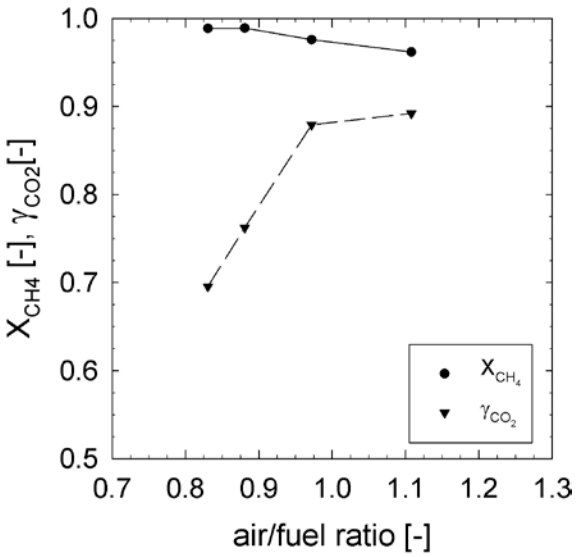

Figure 4 OC-A: CH_4 conversion and CO_2 yield vs. air to fuel ratio

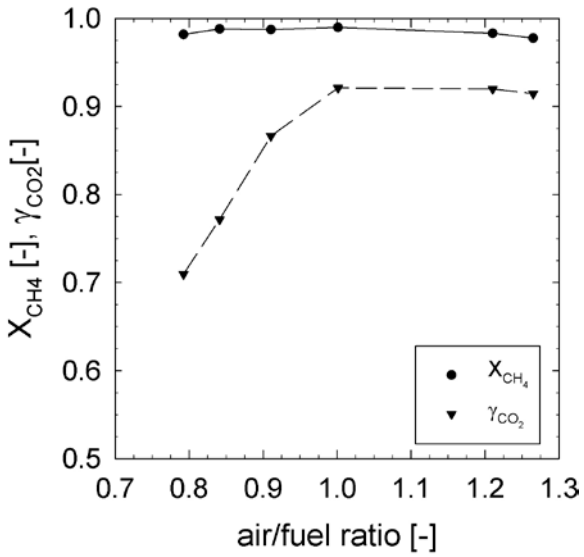

Figure 5 OC-B: CH_4 conversion and CO_2 yield vs. air to fuel ratio

The CH_4 conversion is high for both OCs but decreases with higher air to fuel ratio. This phenomenon seems to be linked to the Ni/NiO ratio in the particle [21]. With increasing air/fuel ratio the Ni/NiO ratio decreases. This seems to limit the catalytic activity of the OC and leads to the decrease in CH_4 conversion. With OC-B, which was optimized for high CH_4 conversion, this phenomenon is less pronounced. The CO_2 yield at global air/fuel ratios below one is limited mainly by the availability of oxygen. At an air/fuel ratio of one, the steep increase of the CO_2 yield flattens significantly for both OCs. There are different constraints in the pilot rig, which limit the CO_2 yield for global air/fuel ratios above one:

1. A low mean oxidation state of the OC entering the fuel reactor [21], which is welcome for good CH_4 conversion, limits the CO_2 yield.
2. The reactor height which limits the gas-solids contact time in the reactors (this could not be increased due to limiting laboratory height).
3. A relatively high solids circulation rate causes the age distribution of the particles in the reactors to be very narrow compared to other installations with lower circulation rates and higher specific solids hold up. This leads to a pronounced trade-off between satisfactory CH_4 conversion and high CO_2 yield.

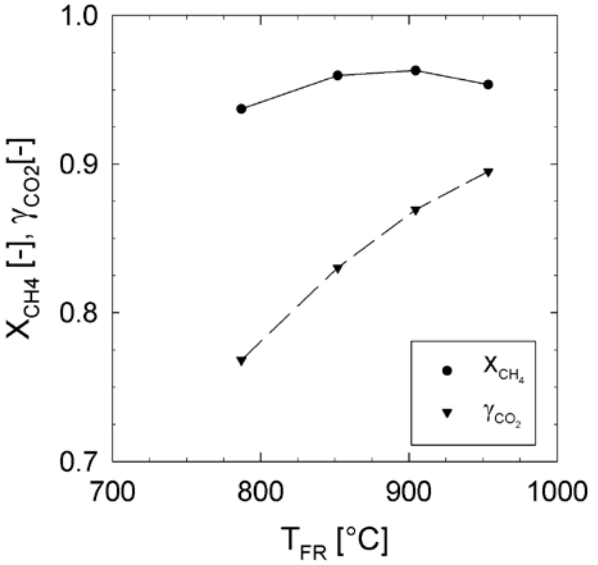

Figure 6 OC-A: CH_4 conversion and CO_2 yield vs. FR temperature

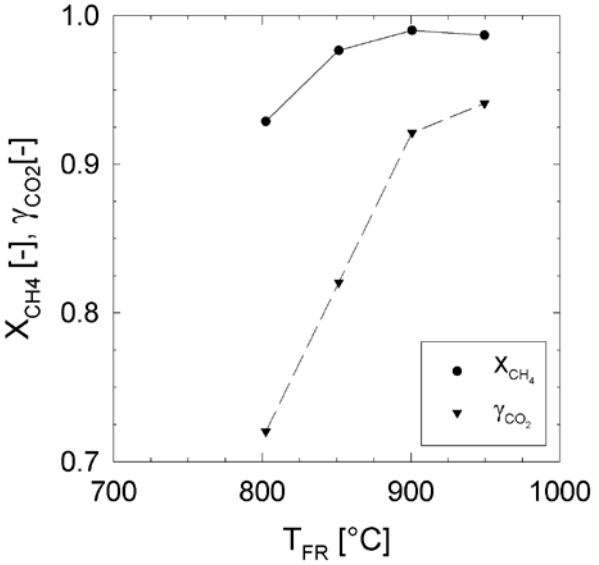

Figure 7 OC-B: CH_4 conversion and CO_2 yield vs. FR temperature

Figures 6 and 7 demonstrate the influence of the FR temperature on the CH_4 conversion and the CO_2 yield. In both cases, Figures 6 for OC-A and Figure 7 for OC-B, the pilot rig is operated at a fuel load of 140kW CH_4 and an air/fuel ratio of approximately 1.10. In general the conversion becomes better with high temperature. The absolute numbers are higher for OC-B compared to OC-A. The CH_4 conversion shows a maximum around 900°C. This can be explained by the increasing degree of oxidation of the oxygen carrier particles with increasing temperature. The CO_2 yield increases over the whole temperature range. Possible reasons are increased reactivity and improved fluid dynamic regime in the fuel reactor.

5. Conclusion

More than 90 hours of CLC and CLR operation experience with Ni-based OC at different bed inventories have been reached at a 120 kW test rig. The unit can be fueled with CH_4, CO, H_2, C_3H_8 or mixtures of these gases and can be operated with different oxygen carriers. The pilot rig design allows high solids circulation, low solids inventories and low solids residence time. The DCFB reactor system has a high potential for scale up. Therefore, the results obtained can be assigned to large plants to some extent. Two Ni-based OCs are compared and discussed for CH_4 fueled operation. These particles achieve high CH_4 conversion and high CO_2 yield. For high air/fuel ratio and high temperature the CH_4 conversion decreases. This is most likely caused by reduced catalytic activity due to reduced presence of metallic nickel at the surfaces of more oxidized particles. The CO_2 yield increases over the investigated temperature range and with increasing air/fuel ratio. This phenomenon is also linked to the Ni/NiO ratio of the particles and has some relevance for larger scale CLC units, where high circulation rates and low solids inventories may reduce operating costs. Further investigation of the observed trade-off between CH_4 conversion and CO_2 yield is surely required.

Acknowledgements

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