Chemical looping combustion of methane using a copper-based oxygen carrier in a 150 kW reactor system

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Abstract

Chemical looping combustion experiments have been conducted in the 150 kW CLC reactor at SINTEF Energy Research in Trondheim with good results. Methane was used as fuel and porous copper oxide based particles, with a bulk density of 800 kg/m³ were, used as oxygen carrier. At a fuel power of 140 kW the methane conversion was limited to about 90%, but at 100 kW a methane conversion of up to about 98% was achieved with an oxygen deficit of about 3% compared to the stoichiometric amount. At the same time, the specific fuel reactor inventory was just above 120 kg/MW, which is low compared to data found in the literature. The total active inventory in both reactors together was then 44 kg and the overall excess air ratio was about 1.2.

1. Introduction

The development of the chemical looping combustion (CLC) technology has been moving forward the later years, but further development is still needed before commercialisation. However, the process is proven in several lab scale and pilot scale setups around the world [1] and successful operation of such systems have been obtained for durations of up to several weeks. The process is a promising CO_2 capture process because of the potentially low

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energy penalty when the CO_2 capture takes place within the combustion process itself, as well as low CO_2 capture cost [2]. The process can be described as an oxy-fuel process with inherent air separation where a metal oxide is alternately oxidised and reduced, and in this way takes up oxygen from the air and supplies it to the fuel. Much work has been conducted on the development of oxygen carrier materials as it is critical to develop particles with high oxygen transport capacity that at the same time are long lasting and cheap to produce. It is also important to develop reactors that utilize the properties of the particles in the best way. In this work, the special design of the CLC reactor at SINTEF Energy Research in Trondheim is tested with a copper oxide based oxygen carrier.

2. Experimental setup

2.1. Overview of the CLC pilot plant

The CLC reactor system consists of two interconnected circulating fluidized bed reactors as shown in Figure 1. The two reactors, the air and fuel reactor respectively, are interconnected through particle loop seals that works as gas locks to ensure that only the particles are transferred between the reactors. In addition, particles are also transferred from the fuel reactor to the air reactor through the lifter, which is fed from the bottom of the fuel reactor. The air and fuel reactors are 6 m tall of which the first 1 m is a conical bottom section. The remaining 5 m cylindrical sections have an internal diameter of 230 mm and 154 mm, respectively. The system has three particle transport screws, one feeding screw and two extraction screws, which makes it possible to refill and extract particles during operation. The reactors are heated up by hot air and fuel that are introduced into the particle beds, and pilot burners are mounted above the bed to ensure safe ignition of the injected fuel. During CLC operation, the reactor temperature is controlled by adjusting the air preheat temperature to the air reactor. In addition, five cooling panels are mounted within the air reactor. The system is originally designed for operation on methane as fuel gas at a maximum fuel power of 150 kW [3].
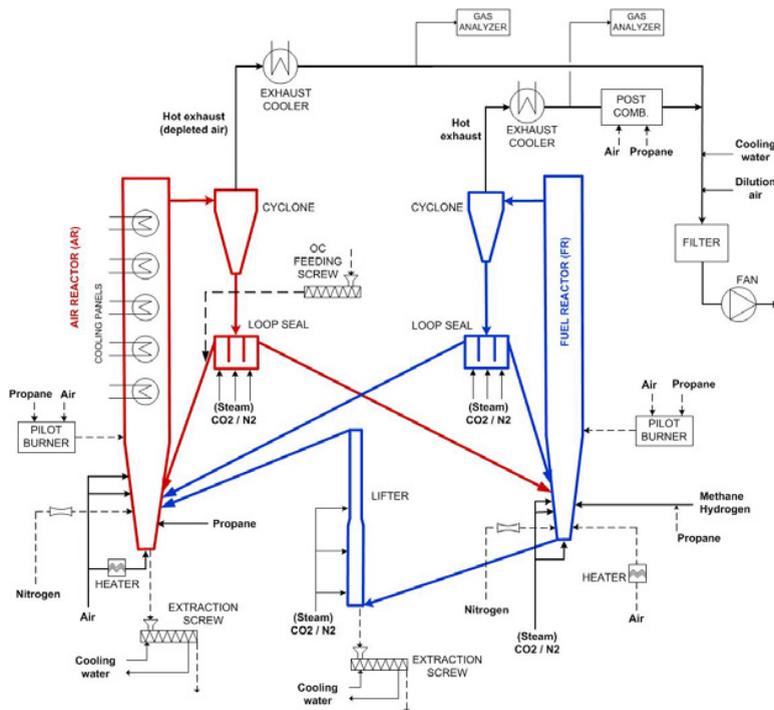
Fig. 1. Reactor system layout.

The system has two Teledyne 7500 IR gas analyzers measuring the CO, CO_2 and CH_4 concentration in the exhaust from each of the two reactors. In addition, a Gasmet DX400 portable FTIR gas analyzer with an oxygen-measuring cell was connected to the air reactor exhaust during the experiment. CO_2 and N_2 were used as fluidization gas for the loop seals, fuel reactor and lifter in this experimental campaign. The system is designed to use steam as fluidization gas, but there are presently no steam boiler installed at the site.

2.2. Test conditions

The results in this section are from a one day experiment, where the reactor where run in full CLC mode for a period of nearly 4.5 hours. The oxygen carrier material used in the experiment was a copper oxide based material impregnated on a commercially available γ-alumina support with a CuO content of 14.7 wt-%. The particle porosity was about 53% [4], the poured bulk density was 800 kg/m^3 and the particle density about 1700 kg/m^3. The median particle diameter d50 was 149 μm with a size distribution given by d10 and d90 values of 101 and 218 μm, respectively. At the present temperature levels it is anticipated that the redox system will be CuO – Cu [5, 6]. The oxygen transport capability, R_{OC} [1], then becomes 0.029 kg oxygen per kg particle.

The reactor system was filled with a total amount of 88 kg of oxygen carrier particles before the experiment started. Thereafter followed a heat-up sequence for about 5 hours using the air pre-heaters and the fuel gas lances in each reactor. This also included feeding hydrogen to the FR fuel lance from a reactor temperature of about 300°C in order to improve combustion and heat-up rate. When reactor temperatures were above 800°C the pilot burners, the AR fuel lance and the air to the FR reactor were closed. At the same time the fluidization gas for the fuel reactor, loop seals and lifter was shifted from air to CO_2 in order to achieve full CLC mode. The reactor system was in full CLC mode from 13:45 until 18:05, when the experiment was shut down. From 13:45 to 16:20 CO_2 was used as fluidization gas whereas from 16:20 it was shifted to nitrogen for the rest of the experiment.

The methane fuel power during the CLC mode period was varied between 100 kW and 140 kW, while the overall air excess ratio (λ) was varied from 1.1 to 1.7. The particle density is low compared to the reactor design value and this cause a limitation on how high air flow that can be introduced to the air reactor and subsequently on the fuel power. At 140 kW the system was not operating satisfactory with respect to neither hydrodynamics nor fuel conversion whereas at about 100 kW, the performance was much better. Different variations in the reactor operation were tested, especially the degree of fluidization and particle entrainment up the fuel reactor riser vs. particle transport through the lifter. However, during the last part of the experiment, from 17:10 to 17:40, constant operating conditions were maintained for which the system showed very stable performance with high degree of fuel conversion.

3. Results

The system performance has been evaluated from measured exhaust gas concentrations, measured inlet gas flows and from calculations of fuel conversion efficiency, solids inventory and riser mass flow. It should be noted that particle losses could not be measured during operation, but the total losses from each reactor were measured afterwards. However, fresh particles were filled into the reactor at three occasions during the CLC mode period to compensate any particle losses and to increase the inventory.

Time series of reactor and air preheat temperatures and fuel power are shown in Figure 2 and Figure 3. During the CLC mode of operation, the reactor temperatures were generally slightly above 800°C. The temperature jump at 16:20 is due to the shift from CO_2 to nitrogen as fluidizing gas. In a short time interval when doing the changeover, air was introduced as fluidizing gas. In the FR the temperature difference between the bottom conical reactor section and top reactor is within 15 – 20°C during the CLC operation. In the most stable operational period between 17:10 and 17:40 the FR bottom temperature is 857°C while the top temperature is 841°C. In the same period the AR bottom temperature was 848°C with a very low difference to the top of the reactor where the temperature was 844 – 845 °C.
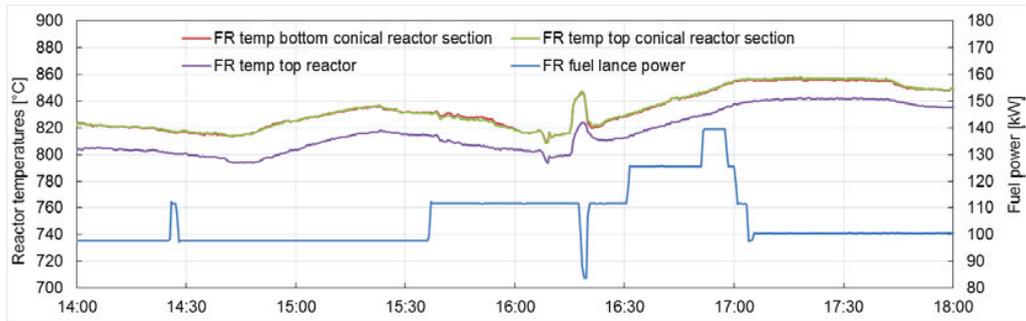
Fig. 2. Fuel reactor temperatures and fuel power.
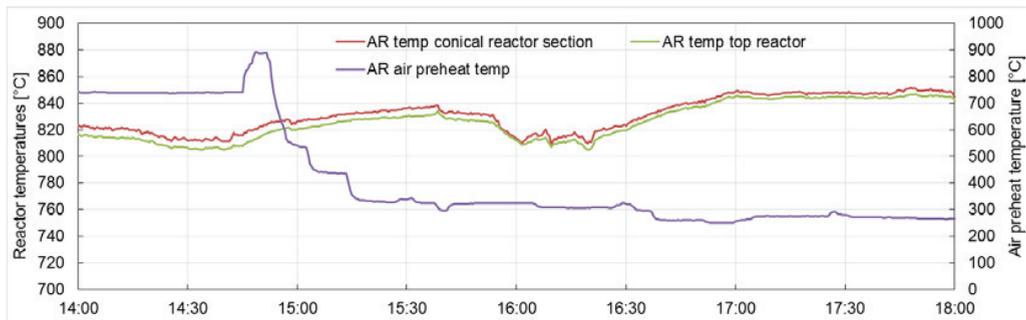
Fig. 3. Air reactor temperatures and air preheat.

3.1. Emissions

Figure 4 shows the CO, CH$_4$ and CO$_2$ concentrations in the fuel reactor exhaust as well as the O$_2$ concentration out from the air reactor. The large drop in CO$_2$ concentration at 16:20 is due to the shift from CO$_2$ to N$_2$ as fluidizing gas. The CH$_4$ concentration is generally higher than the CO concentration and represents the highest loss of energy conversion.

In periods the emissions are high, representing poor conversion, but in the period after about 17 o'clock the CH$_4$ concentration was below 1 vol-% and the CO concentration was close to zero. Figure 5 shows the calculated AR riser mass flow, fuel power and FR particle inventory for the same period. The inventory is calculated from the pressure recordings at different heights in the reactor system. The peaks and dips in the inventory is caused by disturbances in the pressure recordings, caused by pressure transducer flushing or sudden changes in gas velocity. Fresh particles were filled into the reactor at 14:15, 14:30 and 15:50. It should be noted that the calculated AR riser mass flow is an ideal value not taking into account particle recirculation along the walls. The actual value will be considerably lower as will be discussed in Chapter 3.3.

In the period of good conversion after 17 o'clock the fuel power was adjusted down to 100 kW. At the same time, the FR inventory increased and the AR riser mass flow was high, indicating a high particle circulation. All these parameters influence the fuel conversion, but the most immediate response on the emissions seem to be due to changes in fuel power which will lead to a higher specific fuel reactor inventory.
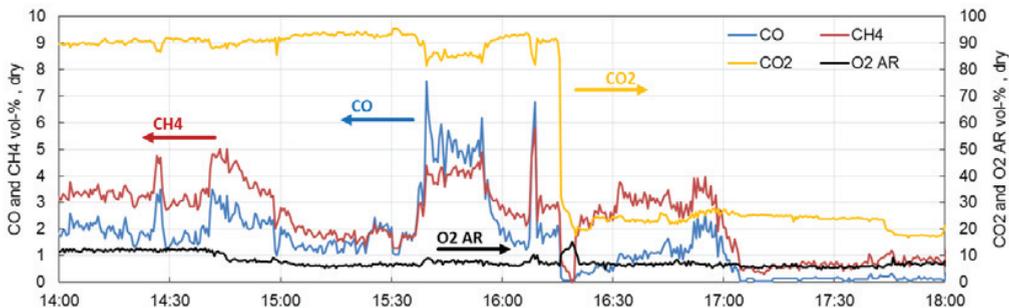
Fig. 4. Concentration of CO, CH₄ and CO₂ in the FR exhaust and O₂ concentration out from the AR.
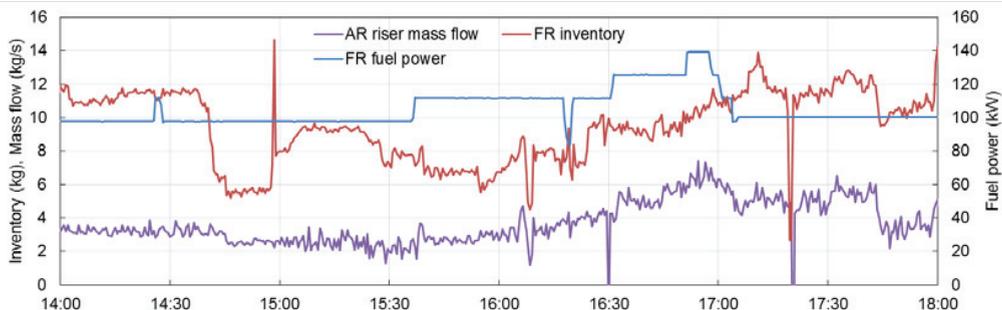
Fig. 5. Calculated AR riser mass flow, fuel power and FR inventory.

Hydrogen is also expected to be present in the exhaust, but there was no measuring of hydrogen in this experiment. Penthor et al. [5] also did experiments with a copper-based oxygen carrier and methane as fuel in the 120 kW CLC reactor at Vienna University of Technology. In their experiments, the H_2 concentration in the FR exhaust was about 3 times the CO emission, but much lower than the CH_4 emissions.

3.2. Conversion efficiency

Figure 6 shows the oxygen demand, methane conversion, CO_2 yield and the overall excess air ratio λ during the period of the experiment where N_2 was used as fluidization gas. The oxygen demand Ω_{OD} represent the ratio of oxygen lacking to achieve complete combustion to the stoichiometric amount of oxygen needed. In this way it represent the amount of "oxygen polishing" which will be needed in the downstream exhaust system for full conversion. The parameter is calculated from the fuel reactor exhaust composition according to [7];

$$\Omega_{OD} = \frac{0.5 x_{CO,FR} + 2 x_{CH_4,FR} + 0.5 x_{H_2,FR}}{\Phi_0 \left(x_{CO_2,FR} + x_{CO,FR} + x_{CH_4,FR} \right)} \tag{1}$$

where Φ_0 represent the number of moles of O_2 needed to convert one mole of fuel (=2 for CH_4) and x_i represent the mole fractions of the different species in the fuel reactor (FR) exhaust. Because hydrogen was not measured, the hydrogen concentration was assumed to be 3 times the CO concentration as roughly indicated by [5].

The CH_4 conversion X_{CH4} represent the fraction of the fuel that is converted to either CO_2 or CO, whereas the CO_2 yield Y_{CO2} represent how much of the carbon in fuel is fully converted to CO_2. They are calculated using the following expressions [9]:

$$X_{CH_4} = 1 - \frac{x_{CH_4,FR}}{x_{CH_4,FR} + x_{CO_2,FR} + x_{CO,FR}}. \tag{2}$$

$$Y_{CO_2} = \frac{x_{CO_2,FR}}{x_{CH_4,FR} + x_{CO_2,FR} + x_{CO,FR}} \tag{3}$$

The O_2 demand varies during the experiments but is quite low, about 3% in the period after 17 o'clock when the emissions were at the lowest. This is also reflected in the CO_2 yield and CH_4 conversion, which stays within 95 – 98% in this period.
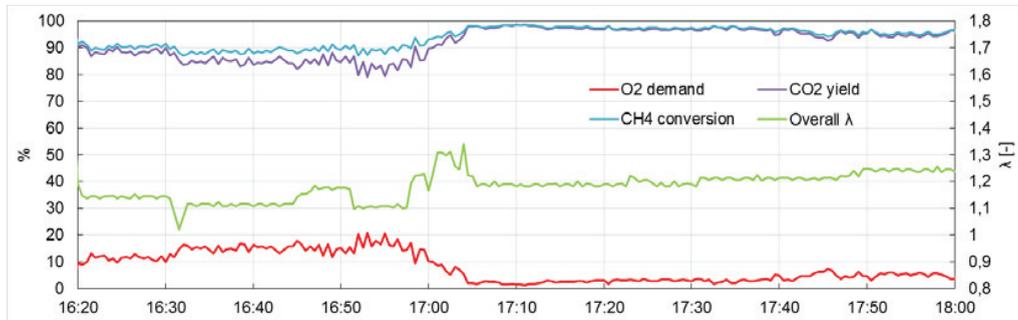
Fig. 6. Oxygen demand, CO_2 yield, CH_4 conversion and overall excess air ratio λ for the period when N_2 was used for fluidization.

The fuel conversion is also dependent on the amount of particles in the reactors, especially the fuel reactor inventory. Figure 7 shows the CH_4 conversion and CO_2 yield as function of the specific particle inventory in the fuel reactor and the total active particle inventory in both the reactors. There is a clear increasing trend with increased inventory, as expected. The results are good compared to e.g. [5], who did experiments with similar particles. The results show high CH_4 conversion and CO_2 yield at rather low specific inventory. The difference between CH_4 conversion and CO_2 yield is a measure of CO. This difference is decreasing with the higher inventories and the higher CH_4 conversion indicating that almost all CH_4 converted is converted fully to CO_2.
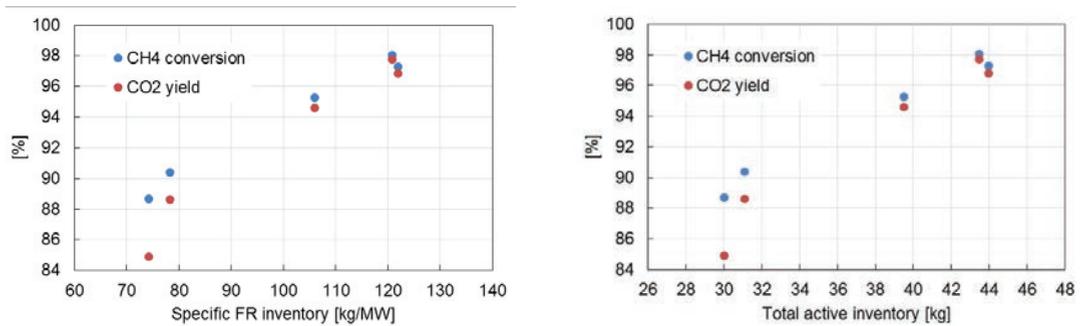
Fig. 7. CH_4 conversion and CO_2 yield vs specific FR inventory (left) and total active inventory (right).

3.3. Particle circulation

Unfortunately, there is no suitable method to directly measure the solid circulation rate (SCR) between the two reactors. The flow from the FR to the AR is also split in two, as part of the flow goes up the riser, through the cyclone and loop seal to the air reactor, whereas the other part goes through the lifter in the bottom. However, the circulation may be estimated by the pressure measurements up along the riseres. A riser particle mass flow can be

estimated by the pressure difference between the two upper pressure transducers (Δp), the difference in height between the transducers (Δh), superficial velocity (gas velocity, u_0) the terminal velocity of the particles (u_t) and the reactor riser flow area (A) and gravitational acceleration (g):

$$\dot{m}_{riser} = \frac{A}{g} \frac{\Delta p}{\Delta h} (u_0 - u_t) \qquad (4)$$

However, because the particles tend to flow upwards in the central part of the riser and fall downwards close to the walls, this calculated riser mass flow is larger than the real net mass flow out of the reactor. The fraction of the calculated riser mass flow that enters the cyclone and is transferred to the other reactor has been reported by Markstöm et al. ([7], [8]) to be about 29% in one case and as low as 8% in another case. The fraction is expected to be different for different reactor geometries, superficial velocity and concentration.

As shown in Table 1 the calculated AR riser flow was on average about 5 kg/s in the period after 17 o'clock when the fuel conversion was good. If one uses the two fractions found by Markström et al. as a lower and higher limit, the real solid circulation rate between the reactors were somewhere between 0.4 and 1.4 kg/s.

Table 1. Values from the best point in Fig. 7 (10-minutes averaged values).

Fuel reactor particle inventory	12.1 kg
Calculated AR riser flow $\dot{m}_{riser}$	5.1 kg/s (*)
Calculated FR riser flow $\dot{m}_{riser}$	1.6 kg/s
Gas velocity top AR u_0	3.4 m/s
Gas velocity top FR u_0	3.8 m/s

To make more certain evaluations of the particle circulation, a calculation based on the amount of oxygen released in the FR and the oxidation state of particle samples from each reactor can be made. The oxidation state of the particles can be found by thermogravimetric analyses (TGA) and the amount of oxygen released in the FR is found by the fuel consumption and the FR exhaust analysis. Comparing the TGA results with the theoretical maximum oxygen capacity determines the parameter ΔXs, which is the difference in solid conversion between the reactor inlet and outlet [1]. However, such a TGA evaluation has not been performed for this experiment, but the theoretical oxygen capacity of the particles, R_{OC}, is known to be 0.029 kg oxygen per kg particles in fully oxidized state. Using this value, Figure 8 shows the calculated solid circulation rate (SCR) for solid conversion differences ΔXs from 0.2 – 1, as well as calculated FR residence time based on the calculated SCR and the fuel reactor inventory as given in Table 1.
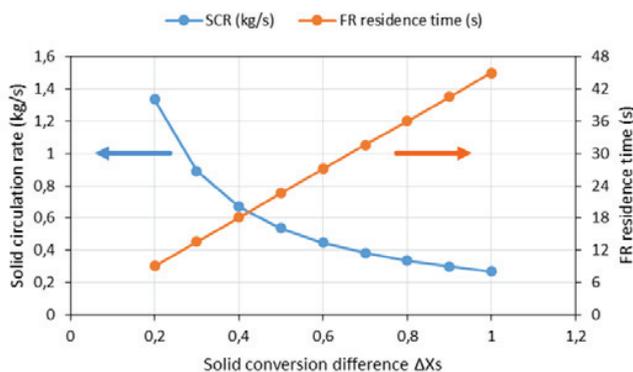
Fig. 8. Solid circulation rate and FR residence time as function of solid conversion difference ΔXs.

A solid circulation rate between 0.4 and 1.4 kg/s, as indicated above, means that the solids conversion difference (ΔXs) should be between about 0.2 and 0.7 according to Figure 8. Diego et al. found from experiments with similar oxygen carrier particles and fuel that solid conversion values higher than 0.7 resulted in a large increase in unconverted fuel. Based on this, one can conclude that the real solid circulation rate was above 0.4 kg/s in the periods of good conversion as 0.4 kg/s corresponds to a value of about 0.7.

3.4. Particle losses

Total particle inventory at the start of the test was 88 kg. During the test, a total of 30 kg of fresh particles were filled in three separate filling sequences. Particle losses were evaluated after the test and the total loss was 16.9 kg. The total test duration including heat-up, CLC mode and shutdown was 9.5 hours. The average particle losses then was 1.7 wt-% per hour, when using the remaining net reactor system inventory at the end of the test as basis (101 kg). The reason for this high loss is mainly due to the fuel reactor since 79% of the losses are from the FR. This is a clear trend of this specific reactor system, particle losses from the FR are much larger than from the AR and the FR cyclone should be investigated more in detail to solve this problem. It should be noted that during the test, about 12 % of the particle loss went out through the AR hydraulic pressure relief system. This is not the normal case, indicating that at some period the operation of the AR was upset or far outside the operational window. If this had been avoided an even higher share of the losses would have been from the fuel reactor.

4. Conclusions

Chemical looping combustion experiments have been conducted in the 150 kW CLC reactor at SINTEF Energy Research in Trondheim with very good results. Methane was used as fuel and porous copper oxide based particles with a bulk density of 800 kg/m^3 was used as oxygen carrier. At a fuel power of 140 kW, the methane conversion was limited to about 90%, but at 100 kW a methane conversion of above 98% was achieved. This corresponds to an oxygen demand of 1 – 2%. At the same time, the specific fuel reactor inventory was just above 120 kg/MW, which is low compared to data found in the literature. The total active inventory in both reactors together was then 44 kg, and the overall excess air ratio was about 1.2.

Acknowledgements

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