

Performance of a 150 kW chemical looping combustion reactor system for gaseous fuels using a copper-based oxygen carrier

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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 100 – 120 kg/MW, which is low compared to data found in the literature. The total active inventory in both reactors together was then 40 – 45 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 CO₂ capture process because of the potentially low energy penalty when the CO₂ capture takes place within the combustion process itself, as well as low CO₂ 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 oxygen carrier material development 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 reactors, are interconnected through

particle loop seals that works as gas locks to ensure that only the particles get 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 air cooled heat exchangers are mounted in the air reactor. The system is originally designed for operation on methane as fuel gas at a maximum fuel power of 150 kW [3].

The system has two Teledyne 7500 IR gas analysers measuring the CO, CO₂ and CH₄ concentration in the exhaust from each of the two reactors. In addition, a Gasetm DX400 portable FTIR gas analyser with an oxygen-measuring cell was connected to the air reactor exhaust during the experiment. CO₂ and N₂ was used as fluidisation gas for the loop seals, fuel reactor and lifter in this experimental campaign. The system is designed to use steam as fluidisation gas, but there are no steam boiler installed at the site.

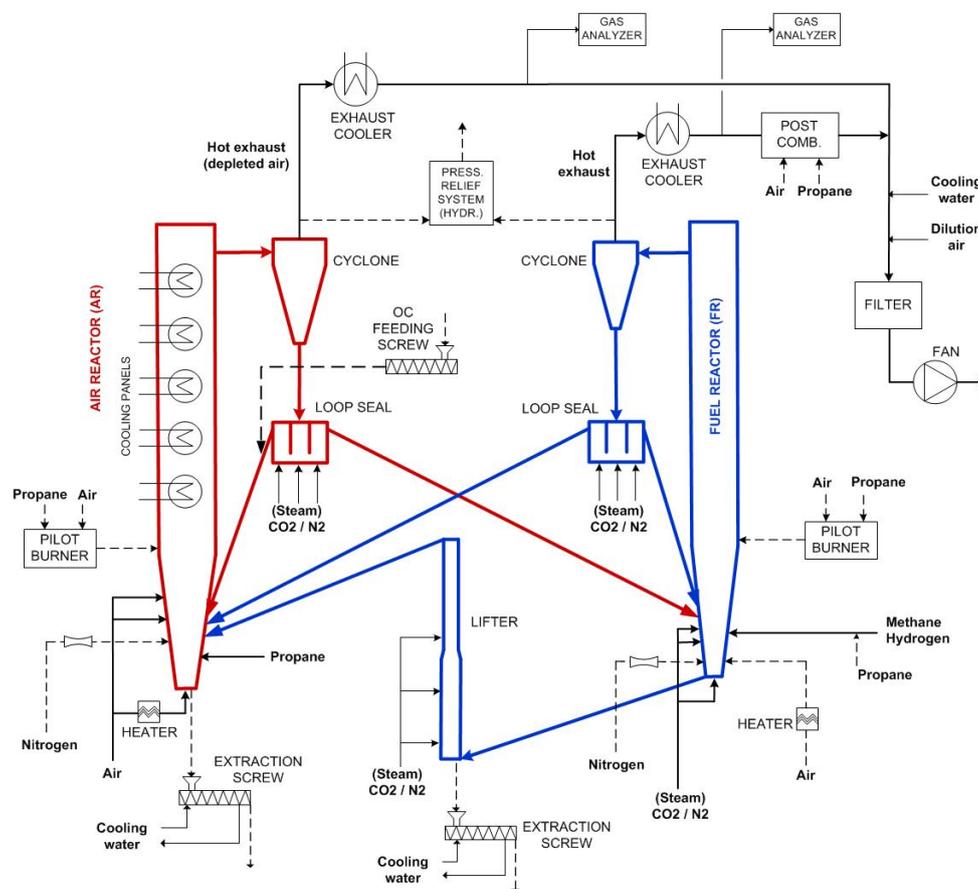


Figure 1: Reactor system layout

2.2 Test conditions

The results in this section are from a one day experiment, where the reactor was run in full CLC mode for a period of 4 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/m³ and the particle density about 1700 kg/m³. The median particle diameter d50 was 149 μ m with a size distribution given by d10 and d90 values of 101 and 218 μ m, 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 fluidisation gas for the fuel reactor, loop seals and lifter was shifted from air to CO₂ 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 CO₂ was used as fluidisation 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 causes a limitation on how high air flow that can be introduced to the air reactor and subsequently on the fuel power. So at 140 kW the system was not operating satisfactory with respect to neither hydrodynamics nor fuel conversion. At about 100 kW, the performance was much better. Different variations in the reactor operation were tested, especially the degree of fluidisation and particle entrainment in the fuel reactor 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 CO₂ to nitrogen as fluidising gas. In a short time interval when doing the change-over, air was introduced as

fluidising 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.

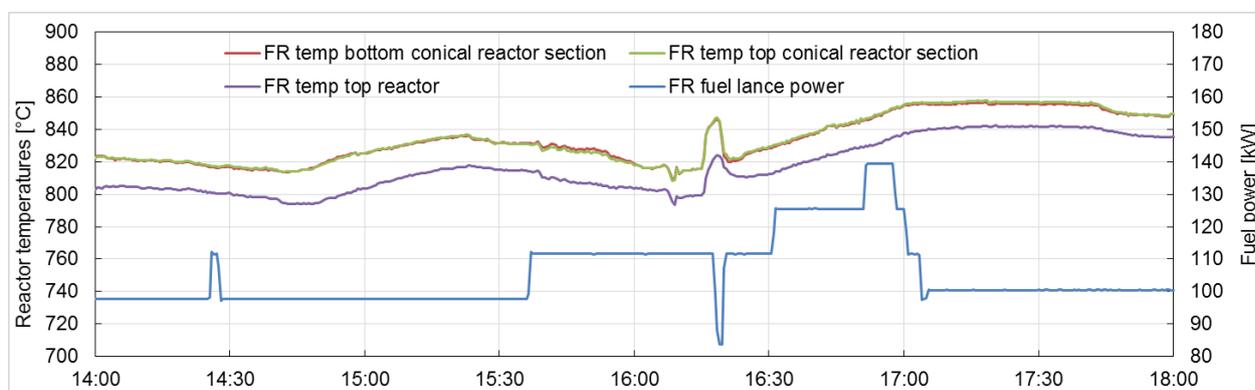


Figure 2: Fuel reactor temperatures and fuel power

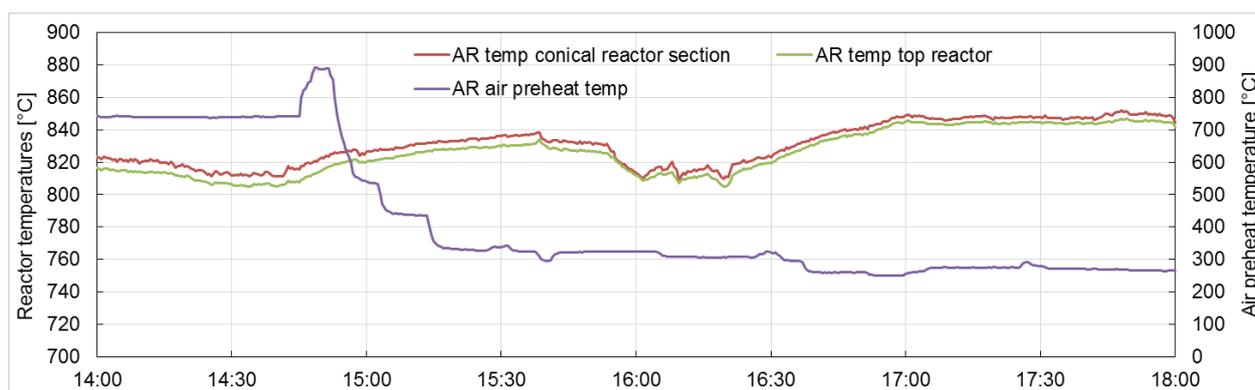


Figure 3: Air reactor temperatures and air preheat

3.1 Emissions

Figure 4 shows the CO and CH₄ concentrations in the fuel reactor exhaust. Also shown is the corresponding overall excess air ratio (λ), which is the ratio of the air introduced in the air reactor to the stoichiometric amount of air needed to fully convert the fuel introduced in the fuel reactor. The CH₄ concentration is generally higher than the CO concentration and represents the highest loss of energy conversion.

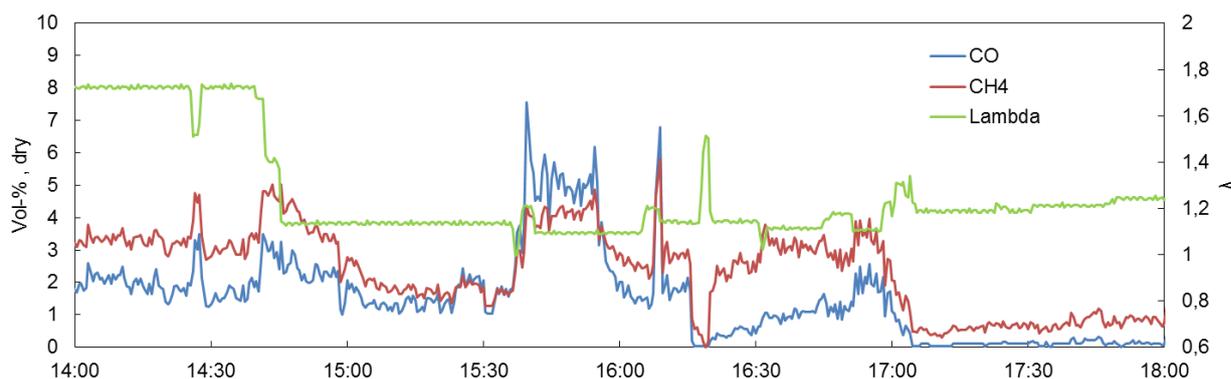


Figure 4: Concentration of CO and CH₄ and excess air ratio, fuel reactor

In periods the emissions are high, representing poor conversion, but in the period after about 17 o'clock the CH₄ concentration was below 1 vol-% and the CO concentration was close to zero. Figure 5 shows the AR riser mass flow, fuel power and FR particle inventory for the same period. In the period of good conversion after 17 o'clock the fuel power was adjusted down to 100 kW, which resulted in the increase in λ seen in Figure 4. 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.

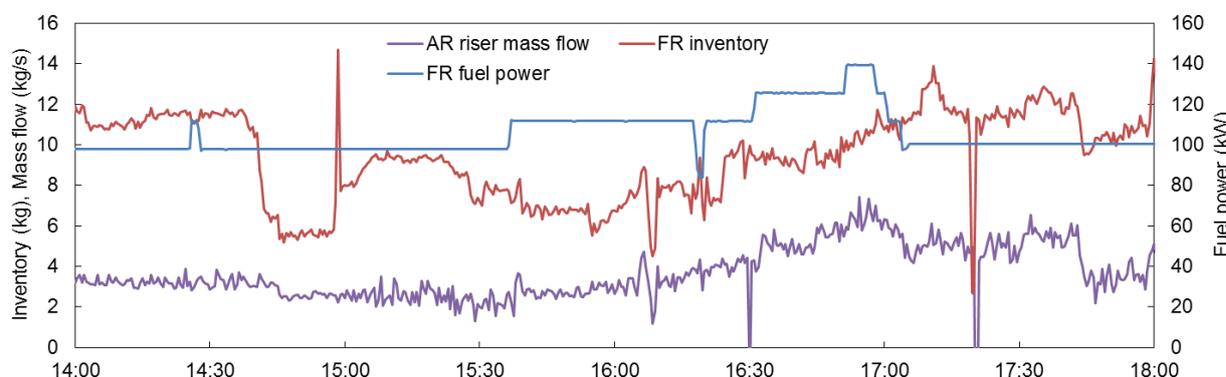


Figure 5: AR riser mass flux, fuel power and FR inventory

Fresh particles were filled into the reactor at 14:15, 14:30 and 15:50. 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.

Hydrogen is also expected to be present in the exhaust, but there was no measuring of hydrogen in this experiment. Penthor et al. also did experiments with a copper based material and methane as fuel in the 120 kW CLC reactor at Vienna University of Technology [5]. In their experiments, the H₂ concentration in the FR exhaust was about 3 times the CO emission, but much lower than the CH₄ emissions. A gas chromatograph (GC) will be used in the next experiment to quantify the H₂ formation.

3.2 Particle circulation

Unfortunately, there is no suitable method to measure the particle circulation directly. 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 and the other part goes through the lifter in the bottom. However, the circulation may be estimated by the pressure measurements in the AR riser. 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):

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

However, because the particles tend to flow upwards in the central part of the riser and fall downwards close to the walls, the 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 Markström 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. The 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 circulation rate was somewhere between 0.4 and 1.4 kg/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 ΔX_s , which is the difference in solid conversion between the reactor inlet and outlet [1]. A TGA 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 oxidised state. Figure 6 shows the calculated particle circulation rate for solid conversion differences from 0.2 to 1 as function of the CO_2 yield.

Depending on what the actual solid conversion difference ΔX_s was during the experiment, the real circulation rate can be within a quite large range. If one assumes that the circulation rate was between 0.4 and 1.4 kg/s, as indicated from the riser flow estimation, ΔX_s should be in the range between about 0.6 and 0.2. The solid conversion strongly depends on the kinetics and residence time of the oxygen carrier particles. During the most stable operation, between 17:10 and 17:40, the particle residence time in the FR is about 15 sec. when calculated using the FR inventory and the riser mass flow. If, however, the real mass flow is 29% of the riser mass flow, the residence time will be about 50 - 55 sec in this period. If the real mass flow is only 8% of the calculated riser mass flow, the residence time will be about 200 – 250 sec.

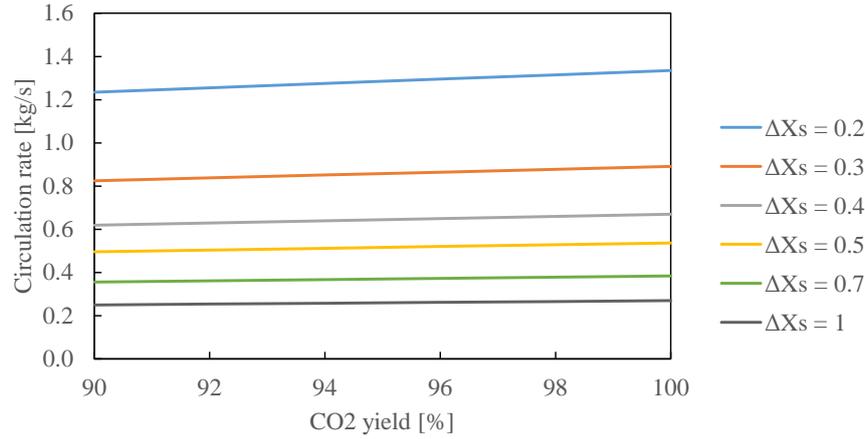


Figure 6: Particle circulation rate as function of the CO₂ yield for different ΔX_s

These residence time values can be compared with the values provided by de Diego et al. [6] for the reduction of a rather similar impregnated copper oxide in a small fluidized bed reactor using 25 vol-% methane in nitrogen and a temperature of 800°C. In the present case the methane-nitrogen mix is 32 vol-% methane in nitrogen, if it is assumed that the primary and secondary nitrogen fluidisation of the FR makes a mixture with the methane fed into the same part of the reactor. The data from de Diego et al. shows that about 30 sec is needed for a solid conversion of 0.2 when starting with fully oxidised particles. For a solid conversion of 0.6 the time needed is about 85 – 90 sec, and if the reduction stage is driven even further, to about 100 sec, the solid conversion is above 0.7 and it will be a sharp drop in CO₂ concentration and quite large amounts of CH₄, H₂ and CO will appear in the outlet gas. Based on this, a rough estimate is that the real mass flow in the present test, during the most stable period, is far closer to 29% than 8% of the calculated riser mass flow, and that solid conversion should be about 0.4. Particle sampling out of the reactors will be needed in order to predict this more accurately.

3.3 Conversion efficiency

Figure 7 shows the oxygen demand, CO₂ yield, methane conversion and λ during the experiment. The oxygen demand 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 needed for full conversion. The parameter is calculated from the FR exhaust composition according to [7];

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

Where Φ_0 represent the number of moles of O₂ needed to convert one mole of fuel (=2 for CH₄) 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 CH₄ conversion represent the fraction of the fuel that is converted to either CO₂ or CO. This is calculated by [9]:

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

The CO₂ yield represent how much of the carbon in fuel is fully converted to CO₂, which is calculated according to [9] as:

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

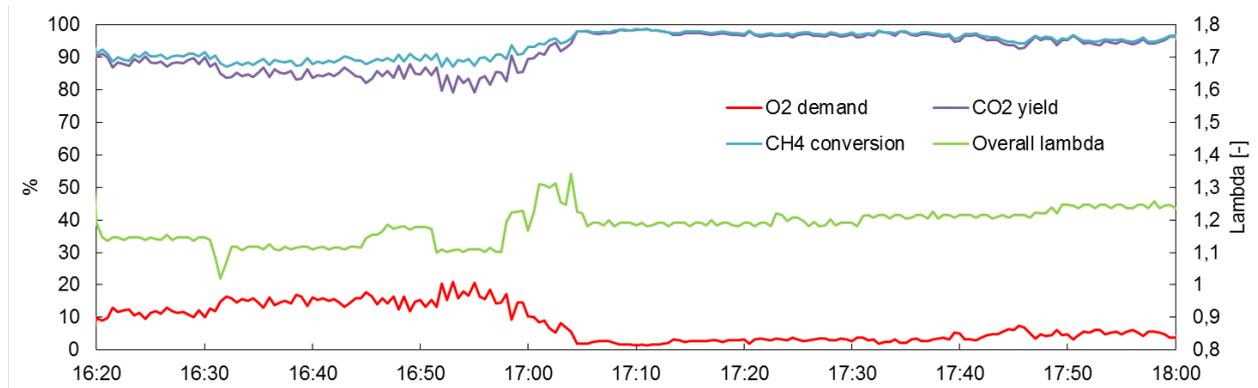
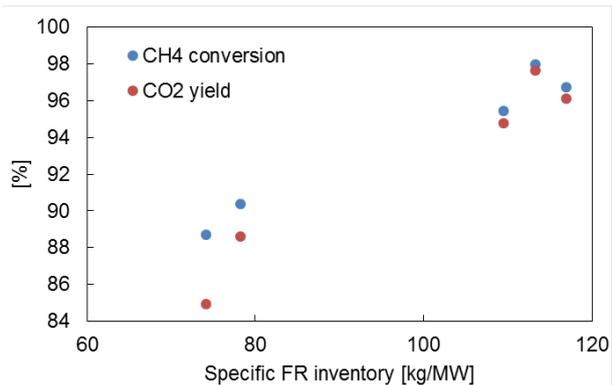
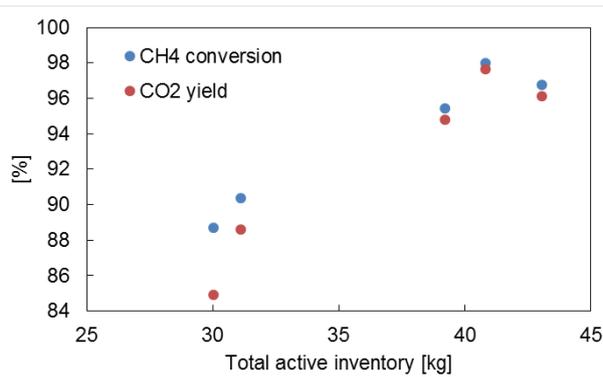


Figure 7: Oxygen demand, CO₂ yield, CH₄ conversion and overall lambda (excess air ratio) for the period when nitrogen was used as fluidisation gas

The O₂ 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 CO₂ yield and CH₄ conversion, which stays within 95 – 98% in this period.

The fuel conversion is also dependent on the amount of particles in the reactors, especially the fuel reactor inventory. Figure 8 and Figure 9 shows the CH₄ conversion and CO₂ 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 CH₄ conversion and CO₂ yield at low specific inventory. The difference between CH₄ conversion and CO₂ yield is a measure of CO. This difference is decreasing with the higher inventories and the higher CH₄ conversion indicating that almost all the CH₄ that is converted is converted fully to CO₂.

Figure 8: CH₄ conversion vs specific FR inventoryFigure 9: CH₄ conversion vs total active inventory

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 shut-down was 9.58 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/m³ 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 100 – 120 kg/MW, which is low compared to data found in the literature. The total active inventory in both reactors together was then 40 – 45 kg, and the overall excess air ratio was about 1.2.

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