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# CHEMICAL-LOOPING COMBUSTION IN A 100 KW UNIT FOR SOLID FUELS

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**Abstract**: Chemical-looping combustion is a novel technology for combustion of fossil fuels. By using a circulating bed material to transfer oxygen to the fuel, a pure stream of $CO_2$ can be obtained from the flue gas, undiluted by $N_2$ from the air. The main advantage of this capture technology is that there is no direct efficiency loss in obtaining the $CO_2$ in a separate stream. This study describes results from operation in a 100 $kW_{th}$ chemical-looping combustor for solid fuels. The oxygen carrier used was ilmenite, an iron-titanium oxide. Coal is fed directly into a loop seal, leading to the fuel reactor, through a set of screws. All parts of the unit are fluidized with steam, except for the air reactor, which is fluidized with air, and the loop seal with the fuel insertion, which is fluidized with nitrogen. All-in-all, the unit has eleven windboxes, of which four are loop seals. Three experiments have been conducted using a Colombian coal as fuel. Operation was stable and loss of char to the air reactor was small, meaning that the $CO_2$ capture efficiency was high (>90%). Gas concentration measurements showed the presence of unconverted CO, $H_2$ and $CH_4$ corresponding to an oxygen demand of 18.5% at 950°C.

**Keywords**: chemical-looping combustion, fluidization, solid fuels, $CO_2$ capture

## INTRODUCTION

### Background

The concept of chemical-looping combustion was patented by Lewis and Gilliland (1954) for use in the production of high purity $CO_2$ from fossil fuels. However, the process was not commercialized and was not called chemical-looping combustion. The name “chemical-looping” was given by Ishida et al. (1987) as a reference to the analogous human cardiovascular system, confining chemical reactions in circulation. Soon after, Ishida and Jin (1994) recognized the concept as a possibility to capture $CO_2$ from fossil fuels in order to reduce climate impact. More recently, the first tentative chemical-looping combustion design based on the circulating fluidized bed principle was presented by Lyngfelt et al. (2001).

More than 900 materials have been investigated as possible oxygen carrier materials for the chemical-looping process, mostly including active oxides of iron, nickel, copper and manganese (Lyngfelt and Mattisson, 2011). Actual operation for more than 4000 h has been accomplished in 12 units of 0.3-140 kW (Lyngfelt, 2011), although mostly for gaseous fuels. In recent years, both lab investigations (Cao et al., 2004; Cao et al., 2005; Dennis et al., 2006; Gao et al., 2008; Leion et al., 2007; Lyon et al., 2000; Mou et al., 2007; Scott et al., 2006;) as well as studies in continuous operation (Berguerand and Lyngfelt, 2008; Linderholm et al., 2011; Shen et al., 2009) have been made with solid fuels.

### Concept

The principle of chemical-looping combustion (CLC) is described by the circulation of an oxygen carrier particle, usually a metal oxide, between two main reactors, see Fig. 1.

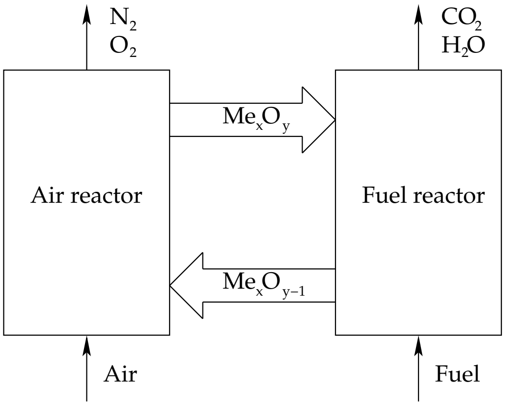


**Fig. 1:** Principal sketch of the CLC process with an air and a fuel reactor, interconnected to allow an exchange of oxygen-carrier material. Here, the oxidized particle is labeled $Me_xO_y$ and the reduced $Me_xO_{y-1}$.

In one of these main reactors, air is introduced from below. Here, the particles become oxidized in exothermic reactions as they are fluidized. Hence, this reactor is normally called the air reactor. The particles are then transported through a loop seal, entering the other main reactor. As this reactor is where the fuel is inserted, it is called the fuel reactor. Depending on the kind of fuel used, this reactor could be fluidized with either steam, $CO_2$ or the fuel itself. Steam or $CO_2$ must be used if the fuel is in solid form, as they are needed for the gasification process of the char. If the fuel is already in gaseous form, no additional steam or $CO_2$ are needed. The (gaseous) fuel then reacts with oxygen available in the particles, which become reduced. Loop seals prevent gases between the air and fuel reactor to mix, and hence the net effect of the process is a transport of oxygen to the fuel reactor with no nitrogen contamination and without any direct efficiency loss. After subsequent steps of steam condensation and gas cleaning from e.g. sulphur compounds, a pure stream of $CO_2$ is obtained. This $CO_2$ can then be transported to a suitable location for long-time storage.

For solid fuels with in-bed feeding, the (endothermic) reactions in the fuel reactor will be

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1} \tag{1}$$

for the volatiles, and

$$C + H_2O \rightarrow CO + H_2 \tag{2}$$

$$H_2/CO + Me_xO_y \rightarrow H_2O/CO_2 + Me_xO_{y-1} \tag{3}$$

for the (steam-)gasification and subsequent syngas oxidation. In the air reactor, the (exothermic) reactions of oxidizing the ilmenite will be

$$O_2 + 2Me_xO_{y-1} \rightarrow 2Me_xO_y. \tag{4}$$

## EXPERIMENTAL DATA

### Setup of the 100 kW unit

The system includes two interconnected circulating fluidized beds, i.e. the air and the fuel reactor, as well as a carbon stripper. Starting in the fuel reactor, the path of circulation is outlined below. Gas and particles entrained in the fuel reactor (FR) may enter the cyclone (CY2), fall down the downcomer to a loop seal (LS2) and enter the fuel reactor again. Particles not entrained may instead enter the so-called circulation riser (CR), which is placed in between the carbon stripper (CS1–4) and the loop seal (LS3) connected to the fuel reactor. The circulation riser is designed to control the circulation flow of particles from the fuel reactor. The carbon stripper has four chambers separated by weirs. The purpose of the carbon stripper is to gasify or separate the residual char in the particle flow. The particles in the carbon stripper are passed on to a loop seal (LS4), leading to the air reactor (AR). The air reactor will re-oxidize the oxygen carriers before they are transported back to the fuel reactor by passing a cyclone (CY1) and another loop seal (LS1), beginning a new cycle. The air and fuel reactors are separated by loop seals in order to avoid gas mixing. The drawings presented in Fig. 2 show how the different parts are interconnected. The dynamics of the system is also investigated in a cold-flow model (Markström and Lyngfelt, 2011). A film of the cold-flow model that shows the system in operation is available at: http://www.entek.chalmers.se/~anly/co2/CFM.htm

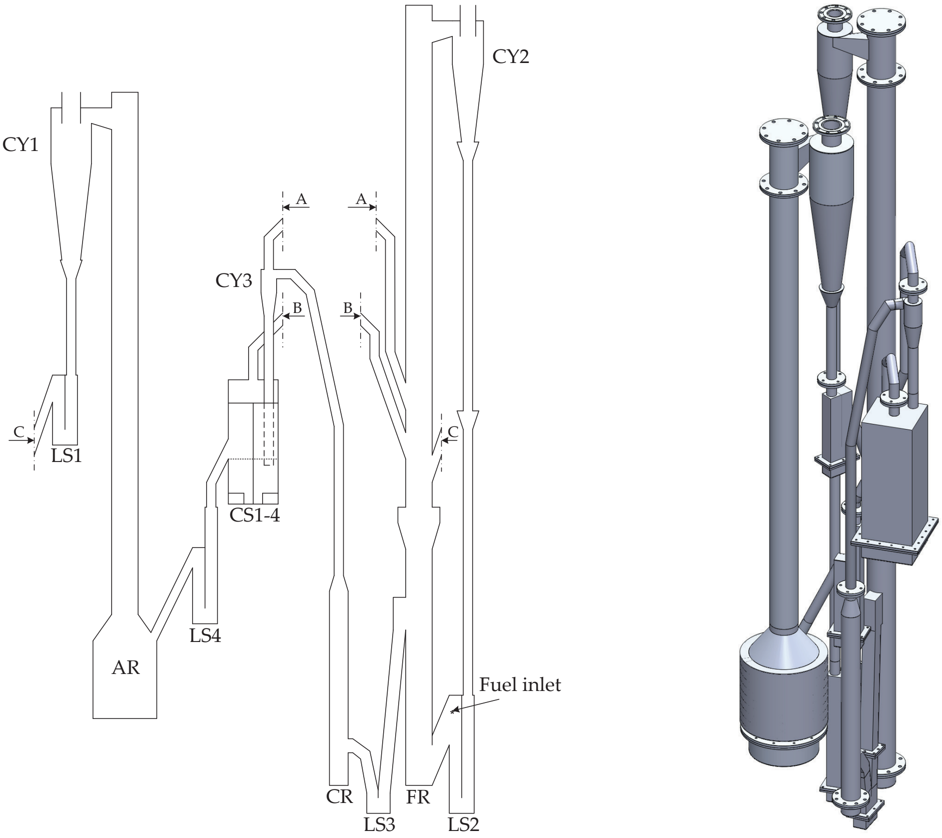


**Fig. 2:** A 2D and 3D sketch of the 100 kW unit. The fuel reactor riser is 5 m tall.

## Fuel

A Colombian bituminous coal was chosen as the first fuel to test in the 100 kW unit. Table 1 shows the composition and Table 2 the distribution of the coal. The lower heating value of the fuel is 29.12 MJ/kg.

**Table 1:** Composition of the Colombian coal. V: volatile matter; M: moisture; A: ash; maf: moisture and ash free.

| Component | Fraction (wt-%) | Comment |
|---|---|---|
| Volatiles | 37.0 | as received |
| Moisture | 3.3 | as received |
| Ash | 5.2 | as received |
| C | 74.0 | maf |
| H | 5.0 | maf |
| O | 10.6 | maf |
| N | 1.4 | maf |
| S | 0.6 | maf |

**Table 2:** Size distribution of the Colombian coal.

| Size (μm) | Fraction (wt-%) |
|---|---|
| <45 | 6.5 |
| 45-90 | 20.4 |
| 90-125 | 17.4 |
| 125-180 | 21.9 |
| 180-212 | 12.4 |
| 212-250 | 13.4 |
| >250 | 8.0 |

## Oxygen carrier

The oxygen carrier used for the first experiments was ilmenite, a natural iron-titanium oxide. It is the most abundant of all titanium minerals and is mined in large quantities. The ilmenite used was 94.3% pure and was supplied by Titania A/S. Table 3 presents some important characteristics of the ilmenite.

Values for sphericity, $\varphi$, were established from SEM images, the minimum fluidization and terminal velocities ($u_{mf}$,$u_t$) were calculated according to relations from Kunii and Levenspiel (1991) and the average particle diameter, $\bar{d}_p$, was calculated from the particle size distribution.

**Table 3:** Characteristics of the oxygen carrier.

| Property | Value |
|---|---|
| Reduced form | $FeTiO_3$ |
| Oxidized form | $Fe_2TiO_5$+$TiO_2$ |
| Average particle diameter, $\bar{d}_p$ | 171 µm |
| Sphericity, $\varphi$ | 0.7 |
| Fresh particle density, $\rho_{p,f}$ | 4.58 g/cm$^3$ |
| Terminal velocity, $u_t$: air, 1000°C | 0.7 m/s |
| Terminal velocity, $u_t$: steam, 950°C | 0.95 m/s |
| Minimum fluidization velocity, $u_{mf}$: steam, 950°C | 0.017 m/s |
| Maximum oxygen transfer capacity, $R_0$ | 0.05 kg $O_2$/kg ox. ilm. |
| Specific heat capacity (ox. form) at 1000°C, $c_p$ | 0.925 kJ/kg,K |
| Specific surface area, BET | 0.11 m$^2$/g |

### Oxygen demand and $CO_2$ capture efficiency

The oxygen demand, $\Omega_{OD}$, is the fraction of oxygen lacking to achieve a complete combustion of the gases leaving the fuel reactor. As the equipment to measure sulphuric gases like $SO_2$ and $H_2S$ was not available for this study, the oxygen demand was calculated as

$$\Omega_{OD} = \frac{0.5x_{CO,FR} + 2x_{CH_4,FR} + 0.5x_{H_2,FR}}{\Phi_0(x_{CO_2,FR} + x_{CO,FR} + x_{CH_4,FR})}, \tag{5}$$

where $\Phi_0$ is the oxygen/carbon ratio, i.e. the ratio of moles of oxygen needed to convert the fuel completely per moles of carbon in the fuel, and $x_{i,FR}$ is the molar fraction of species $i$ in the fuel reactor. For the Colombian coal used in this study, $\Phi_0 \approx 1.149$. The $CO_2$ capture efficiency, $\eta_{OO}$, is here defined as the amount of oxygen used for oxidizing the particles in the air reactor, divided by the total amount of oxygen consumed in the air reactor. It only depends on the gas concentrations in the air reactor outlet, eliminating any uncertainty due to flows. It is calculated as

$$\eta_{OO} = \frac{0.21 - x_{O_2,AR} - x_{CO_2,AR}}{0.21 - x_{O_2,AR} - 0.21x_{CO_2,AR}}. \tag{6}$$

### Data sampling

All data are sampled at a rate of 1 Hz. The gas analyzer that measures concentrations from the fuel reactor is a ROSEMOUNT NGA 2000, while the analyzer measuring concentrations from the air reactor is a SICK MAIHAK S710. In the plots showing the oxygen demand and $CO_2$ capture efficiency, a floating average of 10 points (seconds) has been applied in order to filter out some of the noise. For all three experiments, fuel was fed at a feed rate of approximately 6 kg/h, corresponding to a thermal power of 50 kW. For the first and second experiment, the total bed inventory was 228 kg of ilmenite. In the third experiment, the inventory was 214 kg of ilmenite.

## RESULTS

### Colombian coal, first experiment

The gas concentrations from the fuel reactor system are shown in Fig. 3. Note that $CO_2$ is diluted by $N_2$ fluidizing LS2 and $N_2$ entering with the coal screw and pressure taps. This fuel feeding lasted for 70 minutes.

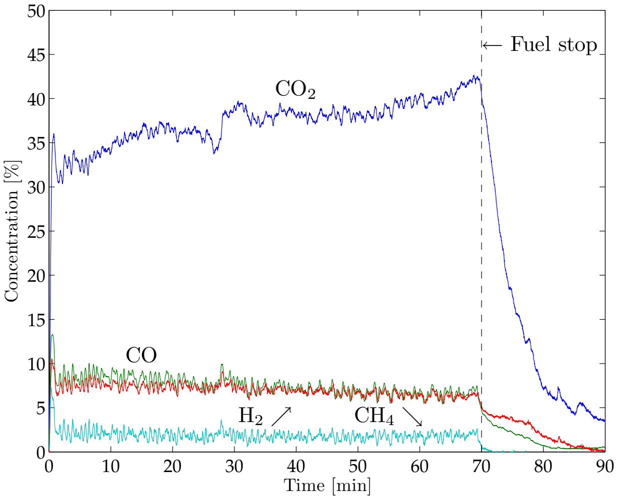


**Fig. 3:** Flue gas concentrations from the first experiment.

As fuel is introduced at 0 min, a drop in fuel reactor temperature of approximately 5°C can be seen, see Fig. 4. Approximately 3.5 minutes later, the temperature starts rising in the air reactor as reduced oxygen carrier particles reach the air reactor. After some additional time, the fuel reactor temperature is regained as warmer particles from the air reactor return. During the last 30 minutes of operation with fuel, the average fuel reactor temperature was 948°C and the average air reactor temperature 992°C. The temperature profile in Fig. 4 shows that it was possible to operate the unit under very stable temperature conditions.

Conversion to $CO_2$ increases as the ilmenite is gradually activated, see Fig. 5. Thus, the oxygen demand drops from approximately 25% to 18.5%, which is the average from the last 30 minutes. The average $CO_2$ capture efficiency found from the last 30 minutes was 94.4%. It is likely that this can be increased by optimizing recirculation flow. Future testing will use smaller fuel particle sizes - cf. Table 2 - which should also increase the capture efficiency.

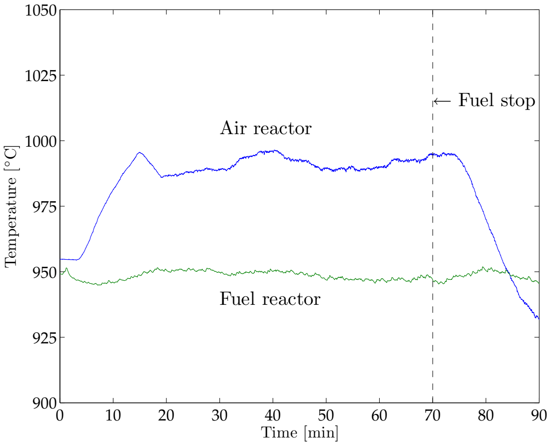


**Fig. 4:** Temperatures in the air and fuel reactor from the first experiment.

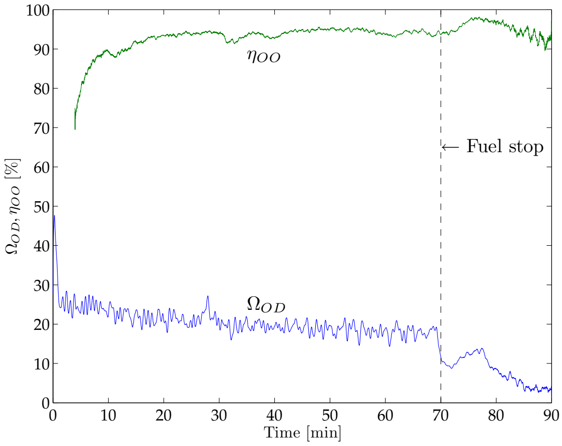


**Fig. 5:** $CO_2$ capture efficiency ($\eta_{OO}$) and oxygen demand ($\Omega_{OD}$) from the first experiment.

The oxygen demand is highly dependent on the oxygen carrier reactivity. Experiments in smaller units have clearly shown that it can be reduced with more reactive oxygen carrier material. These data can be compared to previous results from a 10 kW chemical looping combustor, where the oxygen demand obtained was around 23% with the same coal, although partially devolatilized (Linderholm et al., 2011). As fuel addition stops, oxygen demand drops significantly. This is a result of volatiles not being released any more, and indicates that the oxygen demand for char combustion is significantly lower.

### Colombian Coal, second experiment

In the second experiment, the gas concentrations in Fig. 6 show a similar profile as in Fig. 3, but this time the $CO_2$ rate of increase is slower than before. This fuel feeding lasted for 28 minutes. The $CH_4$ concentration reflects the release of volatiles, and is consequently a good measure of the fuel feeding rate. Similar to the first experiment, the $CH_4$ concentration is stable. The much lower level and slower rise in $CO_2$ concentration, as well as total carbon-containing gas, can therefore best be interpreted as a much slower conversion of the char. Thus, the $CO_2$ concentration during the first minutes originates to a large effect from the oxidation of the volatiles.

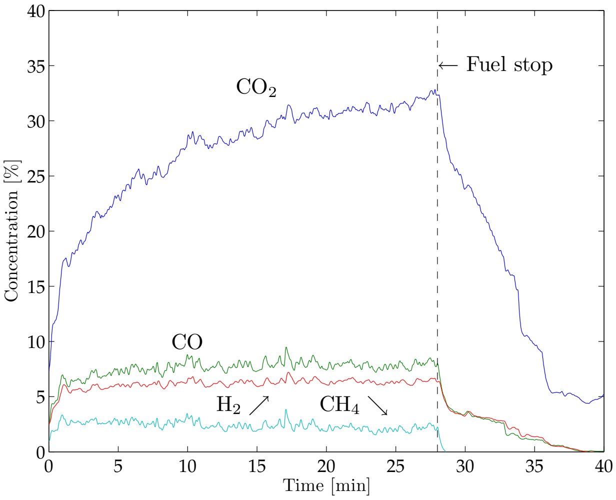
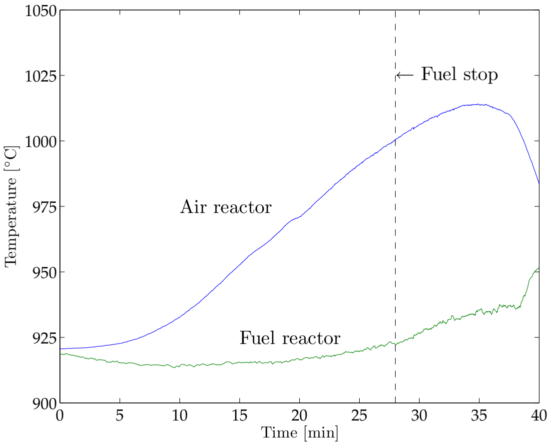


**Fig. 6:** Flue gas concentrations from the second experiment.

The much slower char conversion is not unexpected as the temperature in the fuel reactor was around 30°C lower than in the first experiment, see Fig. 7. During the last 10 minutes of fuel operation, the average temperature was 919°C in the fuel reactor and 984°C in the air reactor.

Due to the lower temperature, the oxygen demand and $CO_2$ capture efficiency did not reach the levels of the first experiment, see Fig. 8. The discontinuity of $\eta_{OO}$ was due to an interruption of the air reactor gas measurements.



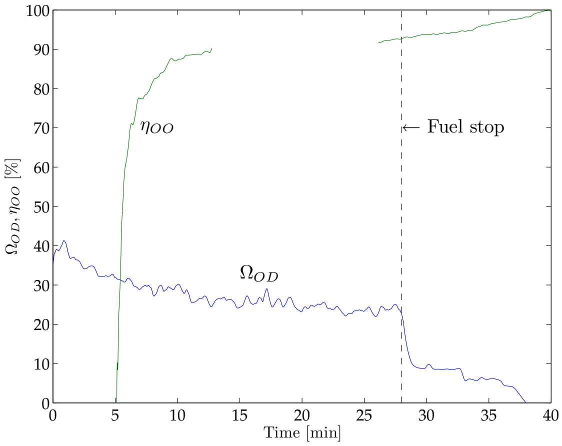


**Fig. 7:** Temperatures in the air and fuel reactor from the second experiment.

**Fig. 8:** $CO_2$ capture efficiency ($\eta_{OO}$) and oxygen demand ($\Omega_{OD}$) from the second experiment.

As char gasification is a process strongly dependent on temperature, more char is expected to reach the air reactor, hence yield a lower $CO_2$ capture efficiency, see Eq. (6). As previously noted, the oxygen demand for char combustion is significantly lower. Therefore, as the relative amount of volatiles converted is increased due to slower char conversion, a higher oxygen demand is expected. Averages from the last 10 minutes yield an oxygen demand of 24.0%, while an average from the last 2 minutes yield a $CO_2$ capture efficiency of 92.3%.

### Colombian Coal, third experiment

In the third experiment, gas concentrations show a similar trend as in the second experiment. The rate at which $CO_2$ is increasing is the same as in Fig. 6. This time, fuel was fed during 42 minutes.

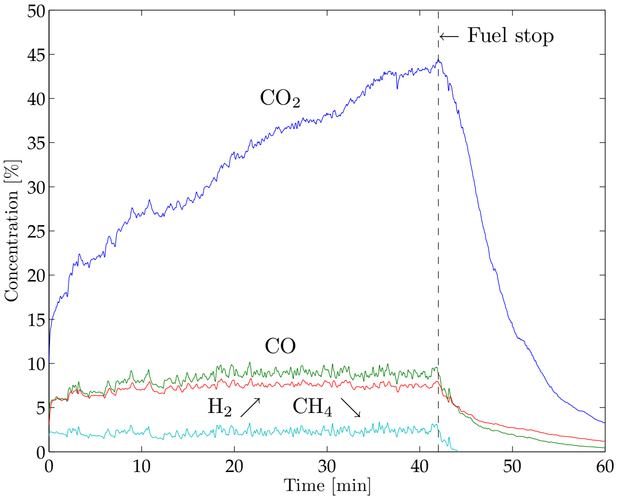


**Fig. 9:** Flue gas concentrations from the second experiment.

As seen in Fig. 10, the fuel reactor temperature during the third experiment is in between the first and the second experiment. During the last 10 minutes of fuel operation, the temperature was 932°C in the fuel reactor and 1020°C in the air reactor.

The average oxygen demand from the last 10 minutes was 21.2%, i.e. higher than for the first experiment, but lower than for the second. This is consistent with the temperature being in between the temperatures of the two previous experiments. As the lower bed inventory resulted in lower circulation, the $CO_2$ capture efficiency is higher. The average from the last 10 minutes before fuel stop is 96.0%, i.e. less char reached the air reactor compared to the first two experiments.

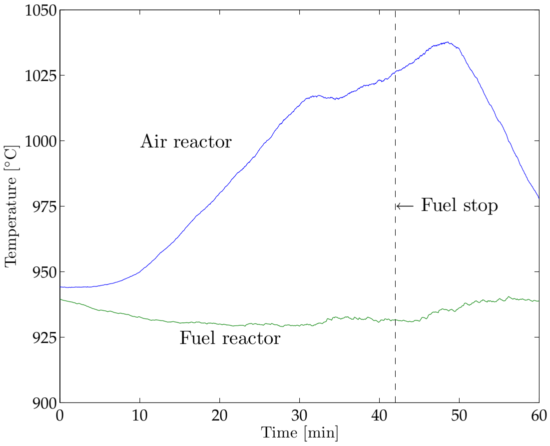


**Fig. 10:** Temperatures in the air and fuel reactor from the third experiment.

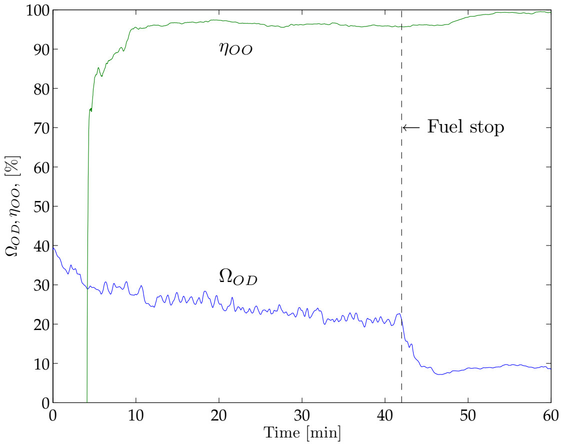


**Fig. 11:** $CO_2$ capture efficiency ($\eta_{OO}$) and oxygen demand ($\Omega_{OD}$) from the third experiment.

## CONCLUSIONS

Three experiments were conducted with a Colombian coal in a 100 kW chemical-looping combustor. All experiments were successfully conducted for 28, 42 and 70 minutes of continuous fuel feeding. The experiments showed that stable conditions could be reached and maintained. Results of the average oxygen demand and $CO_2$ capture efficiency can be summarized as

- At 948°C, the oxygen demand was found to be 18.5% and the $CO_2$ capture 94.4%.
- At 919°C, the oxygen demand was found to be 24.0% and the $CO_2$ capture 92.3%.
- At 932°C, the oxygen demand was found to be 21.2% and the $CO_2$ capture 96.0%.

The results demonstrate the possibility to use solid fuels in chemical-looping combustion. The presence of unconverted gas after the fuel reactor is expected, and can be remediated in three ways:

- By oxygen polishing, i.e. addition of oxygen at the outlet of the fuel reactor.
- By separation and recycling of the unconverted gas after $CO_2$ compression.
- By the use of an oxygen carrier that releases oxygen, i.e. using the principle of CLOU (Chemical-Looping with Oxygen Uncoupling).

## NOTATION

| | | | | | |
|---|---|---|---|---|---|
| $x_i$ | molar fraction of species $i$ | - | $\Phi_0$ | oxygen/carbon ratio | - |
| $\Omega_{OD}$ | oxygen demand | % | $\eta_{OO}$ | $CO_2$ capture efficiency | % |

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