Performance of Chemical-Looping Combustion for solid fuels

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Chemical-Looping Combustion (CLC) - Introduction

Chemical-Looping Combustion is a novel combustion technology with inherent CO_2 separation, which uses a circulating oxygen-carrier to transfer oxygen from air to fuel. Other capture technologies are burdened with significant *costs and efficiency losses related to gas separation, which can be uniquely avoided in CLC*. The reactor system used involves two interconnected fluidised beds, a fuel reactor where the fuel reacts with the oxygen-carrier to form CO_2 and steam, and an air reactor where the oxygen carrier is regenerated, Figure 1. The metal oxide oxygen-carrier is denoted MeO_x/MeO_{x-1} After condensation of the steam a flow of essentially pure CO_2 is obtained – without any active gas separation.
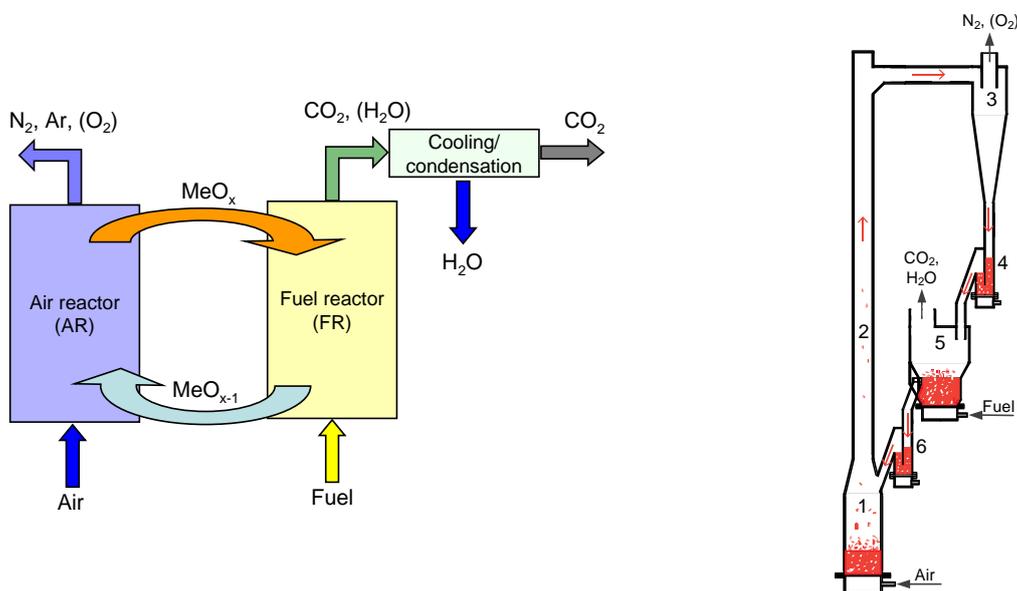

Figure 1. Left: Chemical-looping Combustion principle;
Right: Example of Chemical-Looping combustor, i.e. a 10 kW gas-fired at Chalmers.
1+2) Air reactor and riser, 3) cyclone separator, 5) fuel reactor, 4 + 6) Loop-seals.

The reactor system for CLC has large similarities with conventional circulating fluidized-bed (CFB) boilers, Figure 2.
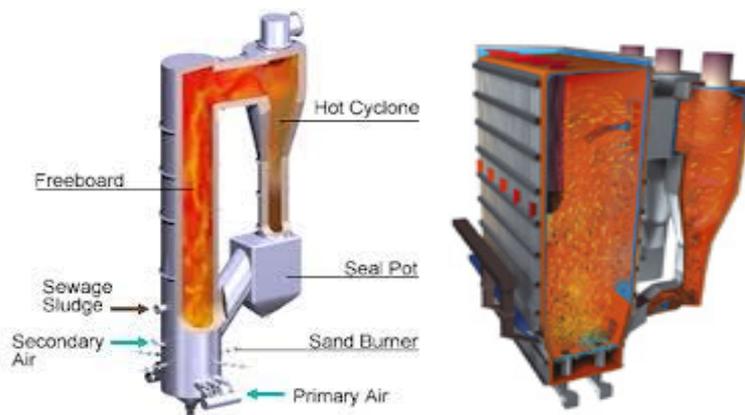

Figure 2. Examples of circulating fluidized bed boilers.
Left: CFB with one cyclone; Right: larger CFB with three cyclones.

Chemical-looping combustion has been shown to work well in 34 pilots of sizes 0.3 kW to 3 MW$_{th}$ as shown in 150 scientific publications, [1]. Totally, operation in these units involves >9000 h with fuel, of which >3000 h with solid fuels.

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The operation of chemical-looping combustion in a number of pilots shows that the process works, but what is the performance of the process when it comes to e.g. fuel conversion and CO_2 capture? Below results from the 100 kW pilot at Chalmers will be presented and discussed. As can be seen in Figure 3, there are three possible deviations from the ideal case, which is complete conversion of fuel to CO_2 and H_2O in the fuel reactor:

    i)   loss of combustible gases like H_2, CO and CH_4 in the gas leaving the fuel reactor, leading to a need for adding oxygen to reach full conversion, i.e. oxypolishing.

    ii)   loss of unconverted carbon (char fines) with the gas leaving the fuel reactor

    iii)   loss of unconverted carbon (char) to the air reactor, leading to CO_2 release from the air reactor, *i.e.* incomplete CO_2 capture
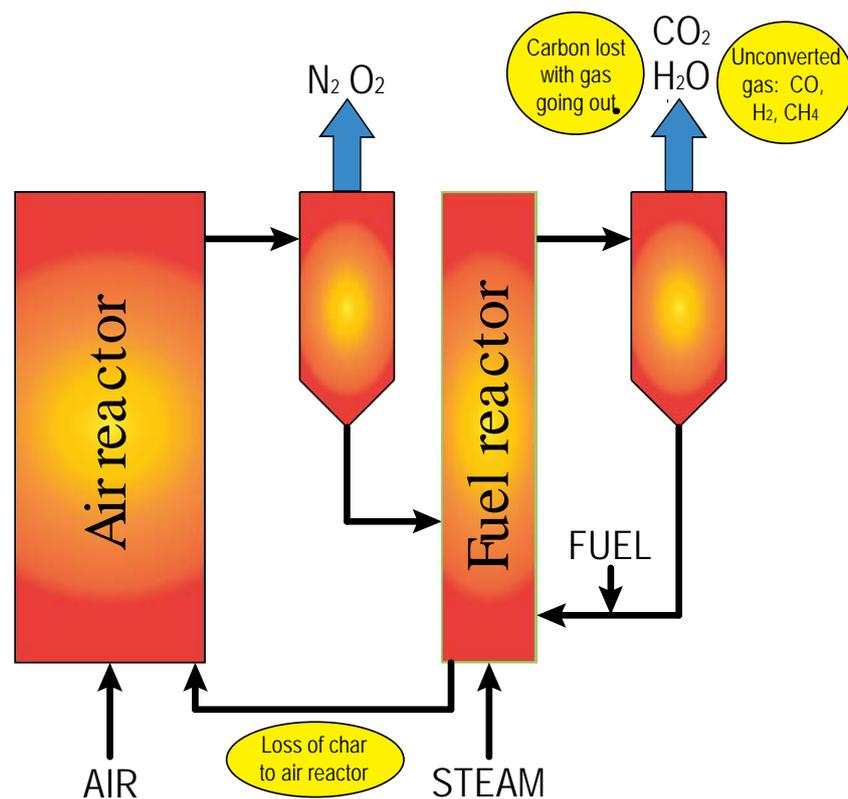

Figure 3. Three potential losses to consider in chemical-looping combustion.

The corresponding performance indicators are:

    i)   Gas conversion, η_{Gas}, indicates how well the gas has been converted in terms of oxygen supplied. Thus, if the gas conversion is 90% it means that 90% of the oxygen needed for the gas to reach full conversion has been supplied by the oxygen carrier, and that the remaining 10% of the oxygen is referred to as oxygen demand, Ω_{OD}. The oxygen demand indicates the oxygen needed to reach full conversion in a subsequent postoxidation or "oxypolishing" step.

ii) Fuel conversion, η_{Fuel}, is used to indicate the char conversion and is defined as the ratio of carbon converted to gaseous compounds in the fuel and air reactors to total carbon added with the fuel. Consequently, $1-\eta_{Fuel}$, is the fraction of total carbon added that is elutriated from the fuel reactor in the form of char

iii) CO_2 capture, η_{CO2}, is the fraction of gaseous carbon leaving the fuel reactor related to the total carbon converted to gas in fuel and air reactors. If no carbon (char) reaches the air reactor the CO_2 capture is 100%. $1-\eta_{CO2}$, represents the release of CO_2 from the air reactor.

Performance in the 100 kW CLC pilot

The performance with coal in the 100 kW pilot at Chalmers is summarized in Table 1. The results are from three publications. The first with ilmenite and pulverized coal (PC) shows high CO_2 capture and reasonable gas conversion, but poor fuel conversion. The second, where manganese ore has been added to the ilmenite bed material, shows similar high CO_2 capture and improved gas conversion, but the same poor fuel conversion. The third shows results for another manganese ore and with an intermediate sized coal (IC) with an average size of 105 µm. This coal has a much smaller fraction of fines with only 35% smaller than 90 µm. As can be seen the CO_2 capture is still very high and the gas conversion is also high, but the important difference is the much higher fuel conversion. Thus, this pilot operation clearly shows that it is possible to reach high performance of gas conversion, fuel conversion and CO_2 capture, at the same time.

Table 1. Performance in the 100 kW pilot at Chalmers.

	100 kW at Chalmers		
	PC, ilmenite [2]	PC, ilmenite + Mn ore 1 [3]	IC, Mn ore 2 [4]
i) Gas conversion, η_{Gas}, [%]	75-83	82-**91.5**	84-**91**
ii) Fuel conversion, η_{Fuel}, [%]	~65	54-74	**86-95**
iii) CO_2 capture, η_{CO2}, [%]	98-99	99	99
Pressure drop fuel reactor, kPa	14-25		
Solids inventory in fuel reactor, kg/MW	300-500		
T FR, ºC	965-980	960-974	970-980

The operational results from the 100 kW unit, which involves 170 h with fuel addition, also shows that the gas conversion significantly increases with lowered volatiles content, i.e. up to 95% for wood char, [5].

Discussion

The important question is how relevant these performance results are for the assumed full-scale application. Up-scaling means higher velocities and increasing the riser height by one order of magnitude, *e.g.* 5 to 50 m. This should have the following effects:

Gas conversion. From the very high conversion of low volatile fuels, it is clear that the fuel mixes well with the bed material and that the unconverted gas is mainly unconverted volatiles. In the bottom bed, higher gas velocities would result in less efficient contact between volatiles, assumed to be released mainly in the bubble phase, and the oxygen carrier in the dense particle phase. On the other hand, the high velocities will increase the solids inventory above the bottom bed, which in combination with the much higher riser, can be expected to significantly improve the gas-solids contact above the bottom bed.

Thus, it is not unlikely that gas conversion will improve in full-scale.

Fuel conversion. The effect of a higher riser should definitely improve the conversion of the char, based on the simple fact that a ten times higher riser height will mean increased residence time for the char fines. Furthermore, the cyclone efficiency of the 100 kW pilot is poor, and it is likely that the full-scale would capture and recycle fines more efficiently.

Thus, it is most likely that the full-scale will provide significantly longer residence time for the fines and consequently a higher fuel conversion.

CO_2 capture. The somewhat larger char particles that remain in the bed material and are not carried away with the gas as fines will eventually follow the circulating bed material to the air reactor. Therefore, the CO_2 capture is determined by the conversion time of these char particles in relation to the bed material residence time in the fuel reactor. As the circulation per MW needs to be the same independent on scale to fulfil the heat balance, it will be the solids inventory that controls the residence time. The pilot operation was made with 300-500 kg/MW in the fuel reactor plus an additional 400-500 kg/MW in the so-called carbon stripper. Additional material is present in the loop seals. For the full-scale the solids inventory and accordingly the residence time can be increased by adding a carbon stripper, i.e. a low-velocity bubbling fluidized-bed between the fuel reactor and the air reactor. The optimum size of such a unit would be given by the desired CO_2 capture.

Thus, the CO_2 capture is linked with the solids inventory and can be improved, if needed, by adding a so-called carbon stripper. It can be noted that the CO_2 capture in the 100 kW unit is much higher than would be realistic with normal post-combustion capture like amine scrubbing.

Comparison

The results in the 100 kW unit are similar to the results presented from a 50 kW unit, [6]. On the other hand lower performance has been found in the 1 MW CLC unit in Darmstadt, especially when it comes to fuel conversion. The reasons for lower performance are well understood, however, and should be possible to amend, as discussed in [7].

Consequences

Gas conversion. The consequence of incomplete gas conversion is that oxygen needs to be added to reach full conversion. This means that the process needs to be complemented by an oxyfuel step. Based on the gas conversion reached in pilots it is expected that the need for oxygen will be at least 5-10 times lower as compared to oxyfuel combustion.

Fuel conversion. Fuel conversion is expected to be high in full-scale. Unconverted char fines will either add to the need for oxygen produced, or result in unconverted fuel in filters.

CO_2 capture. The CO_2 capture can be increased by adding a carbon stripper. The larger the solids inventory in the carbon stripper, the higher the residence time and thus the CO_2 capture.

Conclusion

Pilot operation with CLC shows good performance, and the performance in full-scale is generally expected to be better. Deviations from the ideal case will involve some added costs and the largest cost is associated with oxygen production. When included in the cost estimation the added cost of CLC with solid fuels is nevertheless estimated to be as low as 20 €/tonne, [8].

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