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Chemical-Looping Combustion of Solid Fuels – Operational Experiences in 100 kW Dual Circulating Fluidized Bed System

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Abstract

Results from the first year of operation of a 100 kW chemical-looping combustor for solid fuels are presented. Gas measurements showed the presence of unconverted gas from the fuel reactor. With bituminous coal the gas conversion was up to 84%, and significantly higher with low-volatile fuel and char. The gas conversion was strongly dependent on solids inventory in the fuel reactor. A CO_2 capture up to 98-99% was reached.

The unit worked well and operation was stable. The operation shows the viability of this technology, which has unique potential for breakthrough in cost and energy penalty of CO_2 capture.

Keywords: CO_2 capture ; chemical-looping combustion ; solid fuel

1. Introduction

Chemical-looping combustion (CLC) has emerged as an attractive option for carbon dioxide capture because CO_2 is inherently separated from the other flue gas components, i.e. N_2 and unused O_2, and thus no energy is expended for the gas separation and no gas separation equipment is needed. The CLC system is composed of two interconnected fluidized bed reactors, an air and a fuel reactor, [1]. Oxygen carriers in the form of metal oxide particles are used to transfer oxygen between the two reactors, Fig. 1.

CLC research has mainly focused on gaseous fuels, but in the last years important work has been dedicated to adapting the process to solid fuels. For more detail a number of reviews are available, [2-5]. First to study solid fuels for CLC was Lewis et al. [6], using copper and iron oxides and fifty years later a number of new laboratory studies emerged, involving the same oxides as well as manganese and nickel, see e.g. [4]. Today there are a number of publications of actual operation in smaller CLC pilots with solid fuel, e.g. [7-15].

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The direct use of solid fuels in CLC could use the circulating fluidized bed (CFB) concept outlined in Fig. 2, but the fuel reactor system would need to be adapted for addition of solid fuels. When using solid fuels, the reaction between the oxygen-carrier and the char remaining after volatiles release is not direct, but involves an intermediate gasification step, Fig. 3. This is determinant for the fuel reactor design and the following key targets have been identified for fuel reactor performance:

- High solid fuel conversion, i.e. minimize loss of unconverted char with flue gas
- High gas conversion, i.e. minimize unconverted gases like H_2, CO and CH_4
- High CO_2 capture, i.e. minimize loss of char to air reactor

As compared to gaseous fuels, CLC with solid fuels will require a different design of the fuel reactor, and likely also oxygen carriers with other properties:

- The ash, normally being part of solid fuels, will make a very long lifetime of the oxygen carrier unlikely, as the ash removal inevitably causing losses of oxygen carrier. Also, the ash might directly affect the oxygen carrier. This means that the oxygen carrier should have low cost.
- The gasification of char is a slow process, which means that the fuel reactor needs a design that provides sufficient residence time, in order to avoid char particles reaching the air reactor. Char burning in the air reactor should be avoided, as it will produce CO_2 that will not be captured.
- In order to achieve high conversion of the volatiles, the fuel needs to be fed to the fuel reactor in a way that allows good contact between bed material and the volatiles released.

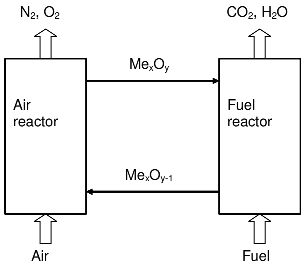


Fig. 1. CLC principle

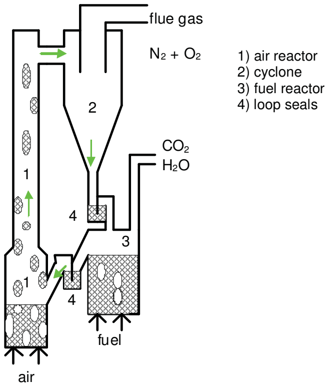


Fig. 2. CFB reactor system for gas

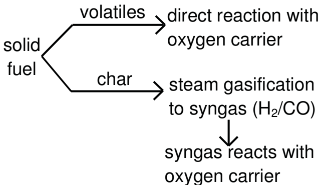


Fig. 3. Sold fuel reactions in CLC

An advantage for CLC with solid fuels is that most oxygen carriers, including low-cost materials, are highly reactive towards the syngas released. However, the syngas is released from char particles inside the fuel reactor, in contrast to gaseous fuels which are introduced from below. Thus, some of the syngas released, e.g. in the upper regions, will have insufficient contact with the bed material. Thus, complete conversion of the gas is difficult to obtain. Measures to reach complete or very high conversion include:

- Introduction of pure oxygen downstream of the fuel reactor, in order to oxidize the remaining unconverted gases H_2, CO and CH_4, so-called ‘‘oxygen polishing”.
- The separation of these unconverted gases from the CO_2 in connection with CO_2 liquefaction, followed by recirculation of these gases to the fuel reactor.
- Using two fuel reactors in series, i.e. leading the incompletely converted gas from the first fuel reactor to a second fuel reactor.
- The use of a CLOU oxygen-carrier, [16], i.e. a material able to release oxygen in the fuel reactor

1.1. Cost and energy penalties

CLC of solid fuels clearly has a potential for a dramatic reduction of energy penalty and costs for CO_2 capture. Thus, the energy penalty for chemical-looping combustion would ideally be equal to the power needed for CO_2 compression of around 2.5%-units.

A power plant using solid fuel CLC would have significant similarities to a CFB power plant, which is a commercial technology for plants up to 460 MWe. The air reactor would be very similar to a CFB, with some notable differences, such as the need for higher solids circulation, and a smaller gas flow as the oxygen is consumed and no combustion products are released. The gas flow through the fuel reactor is the flow that is not going through the air reactor, i.e the combustion products CO_2 and steam, typically 20-25% of the total gas flow, plus the extra flow of gas for fluidization. Thus, the fuel reactor should be considerably smaller than the air reactor. The fuel reactor would also be adiabatic. Clearly, in comparison to a conventional CFB power plant, a CLC plant with an air reactor and a fuel reactor would involve additional costs. Nevertheless, the similarities would be significant, and the cost of the boiler system is typically 30-40% of the total cost of a power plant. So, in all, the additional costs for such an ideal CLC system would be expected to be moderate in comparison to other CO_2 capture technologies.

In the EU project ENCAP a first design of a 455 MWe CLC solid fuel power plant was made. A comparison to a similar fluidized bed combustion power plant indicated a very low efficiency penalty, <3%, as well as a very low capture cost, 10 €/tonne of CO_2, [17]. The major additional costs were associated with the CO_2 compression. This work assumed a conversion of fuel to gas of 97%, and conversion of gas to 95% CO_2 in CO and H_2. If gas conversion would be lower, this will add to the costs. The measures and extra costs needed to reach adequate performance with respect to char conversion, gas conversion and CO_2 capture, are not yet fully understood.

An additional advantage with CLC is that the gas coming out from the air reactor can be expected to be essentially free from harmful emissions such as NO_x and SO_2. Compounds formed from nitrogen and sulphur in the fuel will be concentrated in the smaller gas stream from the fuel reactor, which could facilitate separation.

Although more development work is needed, especially with respect to finding the best design of the fuel reactor system, it is clear that the CLC technology provides a unique potential for avoiding the large costs and energy penalties inherent in gas separation.

1.2. Scope

The paper gives an overview of, and comment to, the operational experiences of the first year of operation of the 100 kW unit. Details are given by Markström et al. [18-21]

2. Design, materials used and evaluation

During the planning of the reactor system, the criteria that led to the final design were:

- The air reactor riser should control the global circulation.
- The fuel reactor should be a circulating fluidised bed, and have a design that can be scaled up.
- A carbon stripper should be implemented after the fuel reactor.
- As a consequence of the stripper needed, a special riser for returning material to the air reactor is needed in order to keep the total height of the reactor system down.
- The operation should be flexible, enabling both large variation in global solids circulation, fuel reactor bed height and fuel reactor fluidisation velocity.
- The system should be stable in operation and run little risk of loss in solids inventory in any part of the system.

The system includes two interconnected circulating fluidised beds, i.e. the air and the fuel reactor, as well as a carbon stripper. Starting in the fuel reactor, the path of solids circulation is outlined below and is numbered from 1–28 in Fig. 4.

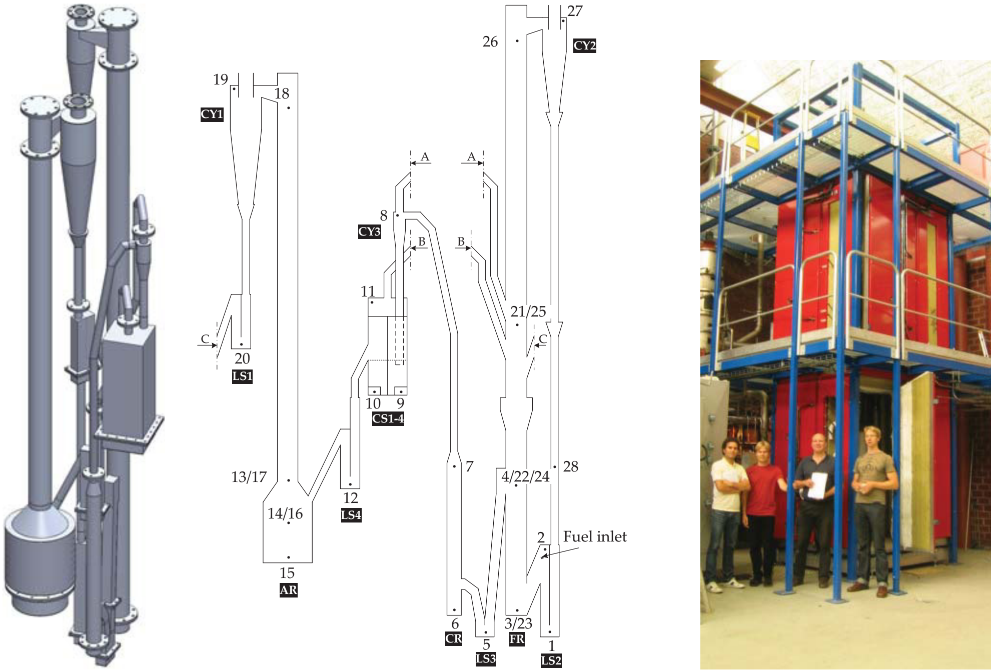


Fig. 4. 100 kW CLC for solid fuels. Left: 3-D representation; Middle: 2-D representation; Right: photo.

Gas and particles entrained in the fuel reactor (FR) 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 return varying mass flows of particles to the air reactor. The carbon stripper has four chambers separated by weirs. The purpose of the carbon stripper is to gasify or separate 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-oxidise 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. It is the fuel reactor, with an inner height of 5.0 m, that determines the overall height of the unit. The fluid dynamics of the system have also been investigated in a cold-flow model [22]. A film of the model in operation is available on http://www.entek.chalmers.se/~anly/co2/CFM.htm

The oxygen carrier used was ilmenite, a natural iron-titanium oxide supplied by Titania A/S at 94.3% purity. For this study, a pulverized bituminous coal from the Cerrejón coal mine in Colombia. Further data on the coal and ilmenite used is given by Markström [20].

The oxygen demand, Ω_{OD}, is the fraction of oxygen lacking to achieve a complete combustion of the gases leaving the fuel reactor, see e.g. Markström et al. [12, 20]. The gas conversion, γ, is given from the oxygen demand as $\gamma = 1 - \Omega_{OD}$.

The CO_2 capture efficiency, η_{OO}, is defined as the amount of oxygen used for oxidising the particles in the air reactor, divided by the total amount of oxygen consumed in the air reactor, [12, 20]. The oxygen needed for char combustion in the air reactor yields an O_2/C ratio of one. The oxygen needed for oxidation of the fuel yields a somewhat higher ratio, but because of the incomplete oxidation in the fuel reactor, $O_2/C \approx 1$. Thus, the definition used will give a good approximation of the ratio of carbon released as gas in the fuel reactor to total gaseous carbon released. The important advantage with this definition CO_2 capture efficiency is that only depends on the gas concentrations in the air reactor outlet, thus eliminating any uncertainty due to flows.

3. Results

The first phase of operation involved different fuels at different temperatures, [18, 19]. The periods of operation were constricted by the fuel feeding system. An overview of the results is given in Fig. 5. The results show that the oxygen demand is much lower for the low-volatile fuel, pet coke, as compared to the two bituminous coals. The lower oxygen demand, i.e. higher gas conversion is expected and consistent with observations in smaller pilots. It is also consistent with the observation that the oxygen demand is typically halved when fuel feeding is stopped, i.e. when the gas conversion of remaining char can be observed. Likewise a dramatic decrease in gas conversion has been observed when fluidizing steam is switched to nitrogen, thus stopping most of the syngas production from char gasification.

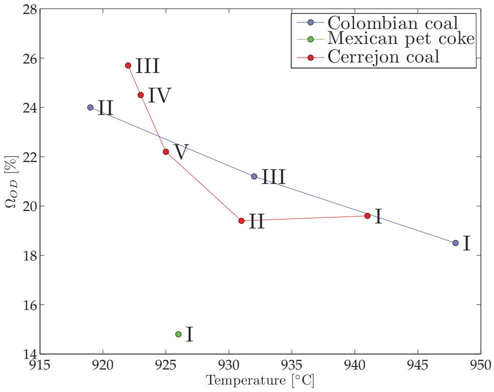


Fig. 5. Oxygen demand versus temperature in first phase of operation

The lower conversion of the volatiles can be explained firstly by by-pass of gas in the bubble phase, as compared to the syn-gas which may evolve in greater extent inside the particle phase, and secondly, by the lower reactivity of the ilmenite towards volatile hydrocarbons, as compared to syngas. The higher conversion at higher temperature can be explained firstly by more rapid char gasification increasing the fraction of syngas released relative to volatiles, and secondly by increasing reactivity of the oxygen carrier with temperature. An aspect of reactivity increasing with temperature is likely also increased rates of water-gas shift, converting CO to H_2, the latter known to be much more reactive towards ilmenite.

Besides the short periods of operation, which did not really give time for parameter variations, the first phase of operation did not reach fuel reactor temperatures above 950 C, as can be seen in Fig. 5.

3.1. Second phase of operation

In the second phase of operation, [20, 21], the fuel reactor temperatures were in the range 950-970ºC, with air reactor temperatures of around 1000ºC, and occasionally up to 1050ºC. The second phase also involved longer periods of operation, thanks to modified fuel feeding. The focus of these tests was the effect of fluidizing velocity in air reactor (AR), circulation riser (CR) and fuel reactor (FR). The effect of changes in such operational parameters is two-fold: Firstly the effect of operational behaviour of the system, e.g. solids circulation and solids inventory in the different parts. Secondly, the effect on performance such as gas conversion and CO_2 capture.

The fuel used in the second phase of operation was the same as in some of the tests in the first phase, i.e. a pulverized coal called El Cerrejon. The combination of this pulverized coal and higher operating temperatures in the second phase generally gave quite high carbon capture, thus the focus will be on the effect on gas conversion.

It should be said that there were no operational difficulties related to the process itself. Thus, operational difficulties encountered were always related with problems with external systems, i.e. steam production for fluidization, sampling of gas for analyzers, cooling of flue gases etc. With the exception of such external difficulties the operation was always stable. However, the effect of a parameter change such as increase in air reactor fluidizing velocity or start of fuel feeding always produced a response involving a period of time until process behaviour or performance reached steady-state. The coal used in the second series always showed quick response to parameter changes, typically within some minutes, but during operation under longer periods with no parameter changes no significant variations could be seen. Moreover, the quick responses made it possible to make a significant number of operational changes and see the effect.

In the following, one of the five operational periods will be covered in some detail to exemplify the results. Table 1 shows the parameter changes made, and each event of changing operation is given a number that is also used in the following figures.

Table 1. Parameter changing events from the seventh operational period with the Cerrejón coal

Event	0	1	2	3	4	5	6	7	8	9	10
AR flow (L_n/min)	1660	1660	2000	2250	2500	2500	2500	2500	2500	2500	Fuel stop
FR flow (kg/h)	15	15	15	15	15	5	5	5	5	15	
CR flow (kg/h)	5	5	5	5	5	5	5	10	5	5	
Fuel flow (kg/h)	6.3	12.6	12.6	12.60	12.6	12.6	12.6	12.6	12.6	12.6	
T_{AR} (°C)	1000	1000	1000	1000	1000	1000	1025	1025	1025	1025	

The increase in the set-point air reactor temperature in event 6, gives a rise in fuel reactor temperature of maximum 10 degrees as seen in Fig. 6. This maximum rise coincides with the maximum solids circulation, event 7, which is a result of high AR and CR flows, see Fig. 7. As can be seen in Fig. 7 the events 2, 3 and 4 of increasing AR flow results in increased circulation and pressure drop in the fuel reactor. The increase in CR flow, event 7, also gives raised circulation but lowered pressure drop. The effect of trebling the FR flow, events 9 and 5, is less significant, although a negative effect on FR temperature is noted.

The consequenses of these events and associated effects on circulation, solids inventory in FR and temperature, are seen in Fig. 8 showing gas concentrations and Fig. 9, showing performance. The effects of increased AR flow can be noted as higher CO_2 and lower concentrations of combustible gases, resulting in lower oxygen demand. The effect of raised CR flow on the other hand increases the oxygen demand. A small increase in the oxygen demand is seen as result of increased FR flow. The carbon capture is always high, although it is evident that increased circulation, as expected has a negative effect.

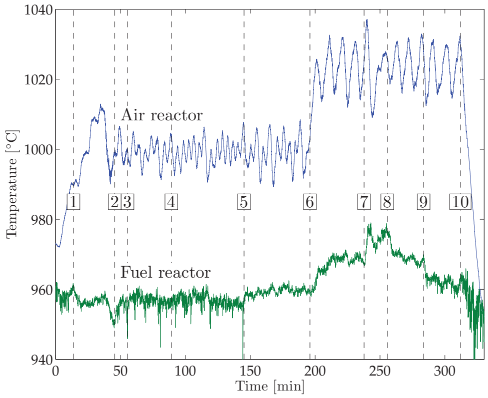


Fig. 6. AR and FR temperatures

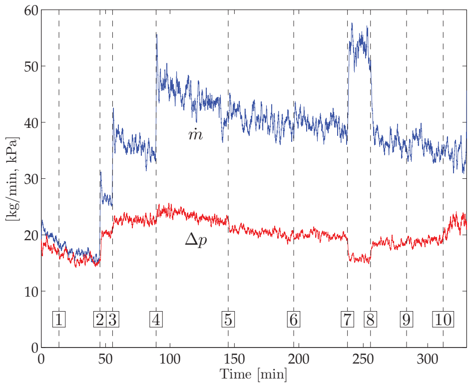


Fig. 7. Global circulation and pressure drop in Fuel reactor

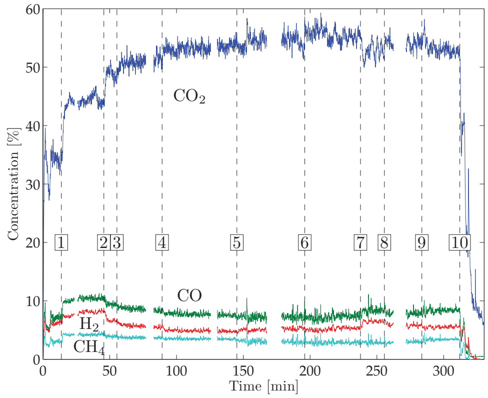


Fig. 8. Gas concentrations from fuel reactor

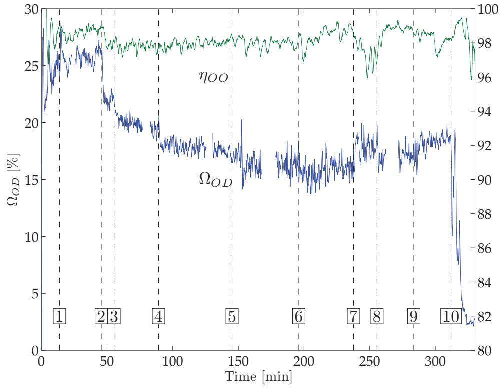
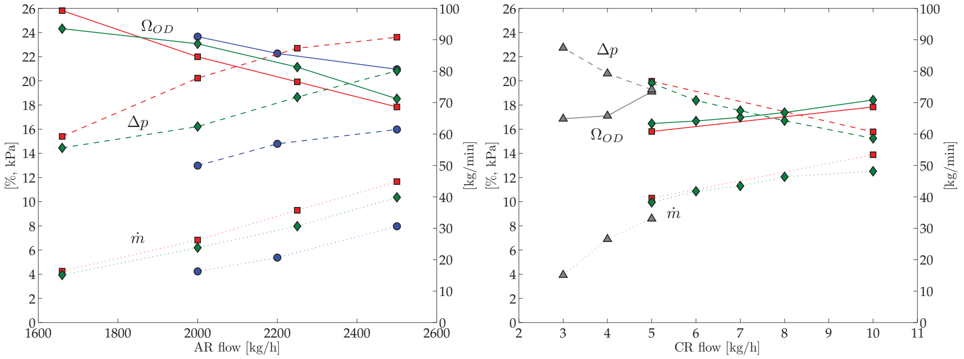


Fig. 9. CO_2 capture and oxygen demand

The data shown in Figs. 6-9 were from one five-hour period. Similar changes, as shown in Figs. 6-9, as well as some other specific tests, were made during the remainder of the 20 h of operation. The focus of the changes was on the AR, FR and CR flows, but the effect of FR flow was rather small so it will not be discussed further. Fig. 10 shows the effect of changes in AR flow on circulation, FR pressure drop and oxygen demand for three different series. All three series show a similar effect, i.e. increased circulation and pressure drop, and lowered oxygen demand. Similarly, Fig. 11 shows the effect of the CR flow. Here, the circulation rises whereas the pressure drop falls when CR flow is raised. The interesting point is that despite the increased circulation the oxygen demand increases. This indicates that the oxygen demand is much more strongly correlated to the pressure drop under the conditions in these tests.



Figs. 10 (left) and 11 (right). Oxygen demand, pressure drop and circulation versus AR flow and CR flow

In Fig. 12 the gas conversion for a number of different periods with different operating conditions is shown versus pressure drop. Data connected by lines are consecutive, and represent cases where only one operational parameter was varied to change the pressure drop, i.e. either AR or CR flow. A distinct correlation can be seen, albeit with some variation. A more detailed model analysis of all these data was made to see if the variation noted in Fig. 12 could be explained by any, or several, of the three variables: solids circulation, fuel reactor temperature, and total time of operation with fuel. The last variable was included to see if any positive or negative effect of operational time on the oxygen carrier material could be seen, i.e. if the material would increase or decrease in reactivity. The analysis showed a positive effect of circulation, which could explain about a third of the variation seen in Fig. 12. Also a positive effect of temperature and operating time could be noted, but as it could only explain a few percent of the variation it was judged to be insignificant. As previous operation generally shows a positive effect of temperature the small effect seen here is most likely explained by the limited temperature range of the tests. Further, it is not unlikely that the effect of temperature is more pronounced at lower temperatures, as in the first phase of operation. The absence of a significant effect of time of operation, indicates that no loss or gain in reactivity could be established during the 20 h of operation. It should be said that at the start of these 20 h, the ilmenite was likely activated as it was used for 4.5 h in the previous phase of operation.

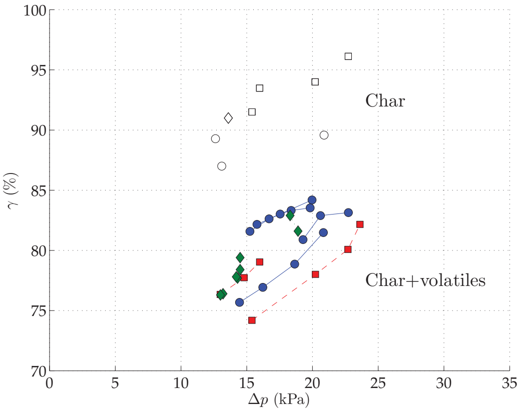


Fig. 12. Gas conversion versus pressure drop in fuel reactor

4. Summary of results and conclusions

A summary of results obtained in the first year is given below. For details see [18-21].

- An oxygen demand below 16% and a CO_2 capture up to 99% was reached.
- Tests replacing all nitrogen sources with CO_2 showed that the sum of measured gases was very close to 100%, indicating that only minute quantities of other species were released.
- Increasing the fuel reactor flow leads to a moderate decrease in gas conversion but the CO_2 capture seems largely unaffected.
- Raised air reactor gas flow increases global circulation. This leads to a transfer of bed material from the air reactor to the fuel reactor, provided that the circulation riser flow is constant.
- By raising the circulation riser flow, global solids circulation is drastically increased.
- The system allows for an independent control of global solids circulation and solids inventory in the fuel reactor by using the AR and CR flows.
- A careful analysis was made on the relation between the circulation riser flow, global solids circulation, fuel reactor bed inventory and gas conversion. The results show that it is the bed inventory in the fuel reactor, rather than the global solids circulation, which has the major impact on gas conversion.
- Despite several minutes without fluidisation in the many sections of the reactor system fluidised by steam, operation could be resumed without any harm having come to the oxygen carrier.
- The behaviour of the 100 kW unit corresponded well to that of the cold-flow model.

This work represents an important advance for the chemical-looping technology. Successful and extended operation with solid fuel was accomplished under stable and well controlled conditions, at a scale larger than previously demonstrated with solid fuels. A high performance with respect to gas conversion and CO_2 capture efficiency was achieved. The operational experience gives a strong confirmation of the viability of CLC with solid fuels. The following conclusions can be made:

- The technology is similar to established combustion of coal in circulating fluidized bed.
- There is a unique potential for dramatic reduction in cost and energy penalty for CO_2 capture.
- CLC operation with low-cost mineral ilmenite works well, but there is room for improving the gas conversion, either by improving the reactor system or the oxygen-carrier material used.
- Oxygen carrier materials other than ilmenite could provide significant improvement of performance, but it is not clear if are they available at reasonable costs.
- In order to reach a complete conversion of the gas coming from the fuel reactor to CO_2 and H_2O, the following options are available: i) oxygen polishing, ii) separation/recycling of unconverted gas iii) using two fuel reactors in series and iv) CLOU oxygen carriers
- For scale-up, a more detailed understanding of the processes in the fuel reactor is needed to design and optimize the fuel reactor system, in order to assess how the performance will be affected by the properties of the oxygen carrier and the reactor design.
- The optimization of the fuel reactor system will primarily need to consider three costs, i.e. costs for oxygen carrier, costs for the fuel reactor system, and costs downstream of the fuel reactor to accommodate for incomplete conversion, e.g. oxygen polishing. Consequently, a good understanding of these costs is needed to find the optimal solution, and realize the great potential of this technology.

5. Acknowledgement

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