Chemical-looping combustion of solid fuels – status of development

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Abstract – Chemical-looping combustion (CLC) of solid fuels is a technology with the potential of reducing the costs and energy penalty dramatically for CO_2 capture. The potential for low costs is based on the similarity to coal combustion in fluidized beds. However, this assumes reaching high performance with respect to fuel and gas conversion, or that inadequate performance can be readily mitigated by downstream options. There are uncertainties with respect to the performance that can be reached in large-scale units, as well as with the extra costs needed to compensate for inadequate performance. Performance will be dependent on both reactor design and oxygen carrier properties. The status of chemical-looping combustion of solid fuels is discussed with respect to performance and experiences from pilot operation.

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], Fig. 1. Oxygen carriers in the form of metal oxide particles are used to transfer oxygen transfer between the two reactors.

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, e.g. [2-5]. First to study solid fuels for CLC was Lewis et al [6] using copper and iron oxides and fifty years later new studies emerged [7-9], involving the same oxides. Leion et al. investigated different fuels and oxygen carriers in a small laboratory fluidized bed, e.g. [10-12], and today there are a number of publications of laboratory work with solid fuels, as well as from actual operation in smaller pilots.

The direct use of solid fuel in CLC could use the circulating fluidized bed (CFB) concept outlined in Fig.1, 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. 2. This is determinant for the fuel reactor design and the following key targets have been identified in relation to 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, as well as 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 oxygen carriers 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.

An advantage for CLC with solid fuels is that most oxygen carriers, including low-cost materials, are highly reactive towards the syngas released from gasification. 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 able to release oxygen in the fuel reactor, see below.

1.1 Chemical-looping with oxygen un-coupling (CLOU)

Chemical-Looping with Oxygen Uncoupling (CLOU) is closely related to chemical-looping combustion but differs from CLC through the spontaneous release of oxygen in the fuel reactor. For instance the conversion $CuO \leftrightarrow Cu_2O$ has an equilibrium oxygen concentration of 2% at 913°C. This means that Cu_2O will be oxidized to CuO in the air reactor where oxygen concentration is higher, and release oxygen in the fuel reactor where oxygen concentration is essentially zero due to the presence of fuel. CLOU using CuO has been shown to work, first in laboratory batch fluidized-bed tests with solid fuel, [13, 14] and later in continuous operation with solid fuel [15]. This mechanism avoids the slow steam gasification of char as the char reacts directly with gas-phase oxygen. Moreover, the direct contact between reacting gas and oxygen carrier is not necessary as in CLC which should facilitate reaching full gas conversion

1.2 Oxygen carrier materials for solid fuels

Important criteria for oxygen-carriers are: *i)* High reactivity with fuel and oxygen, and ability to convert the fuel fully to CO_2 and H_2O *ii)* Low fragmentation and attrition, as well as low tendency for agglomeration *iii)* Low cost *iv)* Low risk for health and environment and *v)* Sufficient oxygen transfer capacity.

Oxygen carrier research has focussed mainly on oxides of Ni, Fe, Mn and Cu. Nickel oxide is less suitable for the solid fuels, being expensive and easily deactivated by sulphur. Iron and manganese oxides have the lowest cost and are available in the form of ores and waste materials. Copper oxide has a higher cost, but is on the other hand a CLOU material.

In addition to these monometallic oxides, metal oxides may also be combined forming new compounds with new properties. This includes Mn combined with Ca, Mg, Ni and Fe, [16],[17], having partial CLOU properties, i.e. with the ability to release some oxygen. Moreover, a combination of Mn and Fe was found to release large quantities of oxygen rapidly, [18]. With exception of $CaMn_{0.875}Ti_{0.125}O_3$, [19], these materials have not yet been tested successfully in operation. Another combined oxide is ilmenite, $FeTiO_3$, a low-cost naturally occurring mineral commonly used with solid fuels.

Contrary to combined oxides, the concept of mixed oxides does not involve the creation of new compounds: Instead it builds on synergies of mixing oxygen carrier materials with different properties. An example is addition of limestone to ilmenite in solid fuel CLC, [20, 21].

Studies of low-cost materials for use with solid fuels, include iron ore [22-24], manganese ore [25], ilmenite, industrial waste materials [26, 27], as well as comparisons of materials of different sources, [28, 29]. Many studies have used ilmenite, e.g. [30-34], being cheap, having a reasonably high reactivity towards syngas and showing good fluidization behaviour.

2 Operational experiences

Operational experiences from twelve CLC units, most of them using gaseous fuels, have previously been reviewed, [4]. Below data from five solid fuel CLCs are presented, Table 1.

Table 4. Operational experiences in solid fuel chemical-looping combustors

Location	Size	Oxides tested, References	Time	Fuel	Year
Chalmers	10 kW	ilmenite, Mn ore, [20, 25, 31, 35-37]	90	coal, petcoke	2008
Nanjing	10 kW	NiO, Fe_2O_3, [38-41]	230	coal, biom.	2009
Nanjing	1 kW	Fe_2O_3 (ore) , [24, 42, 43]	>20	coal, biom.	2010
CSIC	0.5 kW	ilmenite, CuO, Fe_2O_3, [15, 32, 44, 45][46]	164	coal	2011
IFP	10 kW	natural ore [47]	52	coal	2012
Hamburg	25 kW	ilmenite [48]	21	coal	2012
Ohio	2.5 kW	Fe_2O_3 [49] [50]	300	solid fuels	2012
Ohio	25 kW	Fe_2O_3 [49] [50]	230	coal	2012
Chalmers	100 kW	ilmenite, [51] [52] [53]	23	coal	2012

Chalmers' 10 kW CLC combustor has been used in several studies using different solid fuels with ilmenite and manganese ore. Gas conversion was poor in the earlier studies, but significantly improved with a redesign giving in-bed feeding of fuel, to 77% for coal and around 80% for petcoke, [25]. Manganese ore was found to give significantly improved gas conversion, around 87% for petcoke, and a dramatic increase in the rate of steam gasification of char, [25]. Gas conversion was also improved by addition of limestone.

A 10 kW unit in Nanjing has been operated with coal and biomass using nickel- and iron-based oxygen carriers. Further work with iron ore has been done in a smaller 1 kW solid fuel unit in Nanjing. The ratio of carbon containing gases from the FR was typically 1% CH_4, 4% CO and 95% CO_2.

At CSIC a 0.5 kW solid fuel unit was used in comprehensive studies of the effect of operating conditions using coal and ilmenite. Gas conversion was in the range 70-95% with coal, and close to 100% using char. Furthermore, the unit demonstrated the first successful operation of CLOU with 100% gas conversion, [15].

At IFP a 10 kW pilot with three reactors, i.e. two air reactors in series, was operated with coal and a natural ore, [47]. Gas conversion was around 90%,

At Hamburg University of Technology, an Australian ilmenite was operated with lignite dust in a 25 kW unit, [48]. The fuel reactor was a two-stage reactor, and CO_2 concentrations above 90% were reached in the gas from the fuel reactor.

Two units of 2.5 and 25 kW using moving beds with supported iron oxides were operated with coals and other solid fuels at Ohio State University. CO_2 concentrations above 99% were reported, [49].

A 100 kW solid fuel unit at Chalmers was operated with bituminous coal and ilmenite, Fig. 3. With bituminous coal gas conversions up to 84% were reported, and the CO_2 capture was around to 98%, [52]. Gas conversion increased with bed height in fuel reactor, as well as with reduced volatiles content.

Totally, more than 1000 h of solid fuel operation in five 8 units of sizes 0.5 to 100 kW, using different oxygen-carriers and fuels has been accomplished. This demonstrates both that the process works, and that there are suitable oxygen-carriers for this new combustion technology.

2.1   Performance optimisation and modelling

The performance targets previously given can be modelled separately:

i) *Solid fuel conversion* may be incomplete because of the loss of unconverted char from the fuel reactor by exiting gas. As steam gasification of char is slower compared to normal combustion, a fuel reactor can be expected to lose more unconverted char in comparison to a normal CFB boiler. Char conversion can be improved by increased reactor height, improved cyclone efficiency or use of an additional cyclone. The results available from small units are not really relevant and at present no modelling attempts have been made to predict solid fuel conversion in larger units.

ii) *Gas conversion* reflects the how well the gases released from the solid fuel, i.e. volatiles and syngas, have been oxidized to CO_2 and H_2O by the oxygen carrier. The operation in the CLC units presented above showed a gas conversion around 75-95%, depending on fuel, oxygen carrier and solids inventory. Fuels with no or low volatiles show higher gas conversion. For the volatiles, the modelling would be similar to that for gaseous fuels, assuming that the fuel is fed in such a way that the volatiles are released in the bottom bed. For the syngas produced by the char particles, a simple approach is to assume that the char is well-mixed with the oxygen carrier, i.e. that the syngas is evenly produced inside the dense phase. This approach gives a transparent analytical solution, [54]. Other approches include two-phase models [55] and CFC models, [56]. Modelling of conversion of syngas from char indicates higher conversion than is seen in actual operation, [54]. Both modelling, [55], and pilot plant testing indicate that full gas conversion is not possible, i.e. unless CLOU oxygen carriers are used.

iii) *CO_2 capture* may be incomplete as a result of char reaching the air reactor with the circulation flow. The minimum circulation flow is given by the need to transfer sufficient heat and oxygen to the fuel reactor. From the residence time distribution in the fuel reactor, and

the char conversion rate, the loss of char to the air reactor and thus the CO_2 capture can be predicted [55, 57, 58]. To reach adequate CO_2 capture a carbon stripper, both separating char particles from oxygen carrier and giving additional time for conversion, can be inserted between fuel reactor and air reactor.

2.2 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 MW_e. The air reactor would be very similar to a CFB, with some notable differences, such as the need for higher solids circulation, and a somewhat 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 MW_e CLC solid fuel power plant was made. A comparison to a similar fluidized bed combustion power plant indicated a very low efficiency penalty as well as a very low capture cost, 10 €/tonne of CO_2, [59]. The major additional costs were associated with the CO_2 compression. This work was likely optimistic with the CLC performance, as incomplete gas conversion will likely add more 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.

3 Conclusions

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 to reach high performance additional development is needed, either with regards to 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.

- The following options to have a complete conversion of the gas to CO_2/H_2O in the fuel reactor 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.

4   Acknowledgement

5   References

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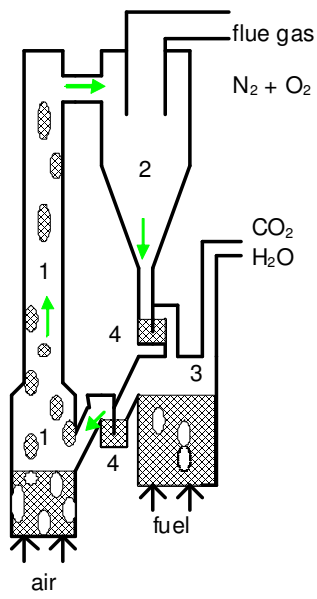
Fig. 1. Example of CLC reactor system for gas 1) air reactor and riser, 2) cyclone, 3) fuel reactor, 4) loop seals
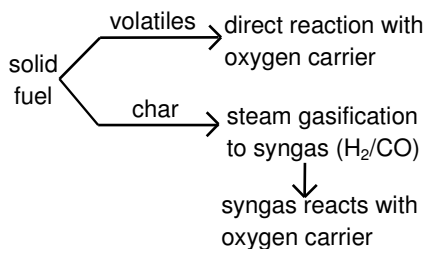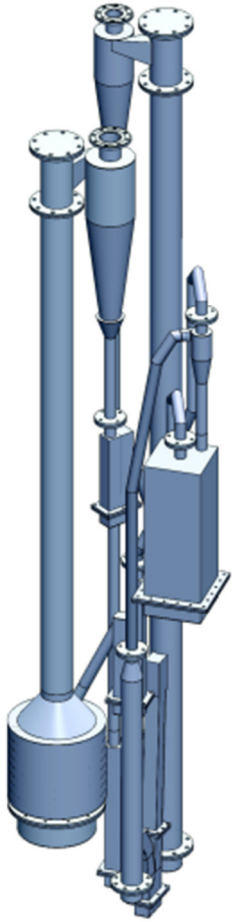

Fig. 2. Sold fuel reactions in CLC

Fig 3. Chalmers' 100 kW CLC