

Oxygen Carriers for Chemical Looping Combustion - 4 000 h of Operational Experience

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Résumé — Transporteurs d'oxygène pour la combustion en boucle chimique : expérience accumulée pendant 4 000 h d'opération — La combustion en boucle chimique (CLC) est une nouvelle technique de combustion permettant la séparation intrinsèque du CO₂. Dans ce procédé, un oxyde métallique est utilisé comme transporteur d'oxygène pour véhiculer l'oxygène de l'air vers le combustible, ce qui permet d'éviter un contact direct entre le combustible et l'air. Deux lits fluidisés interconnectés sont utilisés, le réacteur air et le réacteur de combustion. Les fumées du réacteur de combustion contiennent le CO₂ et la vapeur d'eau qui peut être facilement éliminée par condensation. Des recherches considérables ont été menées dans ce domaine au cours des dernières années en matière de matériaux transporteurs d'oxygène, du dimensionnement des réacteurs, de l'étude de l'efficacité énergétique du procédé et pour tester le concept dans différents prototypes.

À ce jour, plus de 700 matériaux ont été évalués et la technologie a été testée avec succès dans des unités de puissances comprises entre 0.3 et 140 kW avec plusieurs matériaux à base d'oxydes métalliques de Ni, Co, Fe, Cu et Mn. Le temps cumulé d'opération dans ces diverses installations avoisine les 4 000 heures. Basé sur cette expérience, on peut conclure qu'il est possible d'atteindre des conversions quasi complètes du combustible et que le captage de la totalité (100 %) du CO₂ est possible. L'essentiel du travail réalisé jusqu'à présent s'est concentré sur les charges gazeuses, mais l'application aux combustibles solides est également étudiée. Une revue de l'expérience en opération acquise par combustion en boucle chimique avec différents matériaux transporteurs d'oxygène au cours de ces différentes études est présentée.

Abstract — Oxygen Carriers for Chemical Looping Combustion – 4 000 h of Operational Experience — Chemical Looping Combustion (CLC) is a new combustion technology with inherent separation of the greenhouse gas CO₂. The technology involves the use of a metal oxide as an oxygen carrier which transfers oxygen from combustion air to the fuel, and hence a direct contact between air and fuel is avoided. Two interconnected fluidized beds, a fuel reactor and an air reactor, are used in the process. The outlet gas from the fuel reactor consists of CO₂ and H₂O, and the latter is easily removed by condensation. Considerable research has been conducted on CLC in the last years with respect to oxygen carrier development, reactor design, system efficiencies and prototype testing. Today, more than 700 materials have been tested and the technology has been successfully demonstrated in chemical looping combustors in the size range 0.3-140 kW, using different types of oxygen carriers based on oxides of the metals Ni, Co, Fe, Cu and Mn. The total time of operational experience is more than 4 000 hours. From these tests, it can be established that almost complete conversion of the fuel can be obtained and 100% CO₂ capture is possible. Most work so far has been focused on gaseous fuels, but the direct application to solid fuels is also being studied. This paper presents an overview of operational experience with oxygen carriers in chemical looping combustors.

INTRODUCTION

Chemical Looping Combustion (CLC) has emerged as an attractive option for carbon dioxide capture because CO₂ is inherently separated from the other flue gas components, *i.e.* N₂ and unused O₂, and thus no energy is directly expended for the gas separation and no gas separation equipment is needed. A CLC system is composed of an air and a fuel reactor, and oxygen is transferred from air to fuel by the use of an oxygen-carrier. A number of metal oxides have been proposed and tested for use as oxygen carriers.

Chemical Looping Combustion was invented by Lewis and Gilliland [1] sixty years ago as a way to produce carbon dioxide, but long forgotten. Ishida *et al.* [2] proposed the use of Chemical Looping Combustion for climate mitigation and also started laboratory research on oxygen-carrier materials. Since 2000, the research in CLC has been steadily increasing.

The need to find suitable oxygen-carrier materials for the process, and comprehensive testing of these under realistic conditions is a cornerstone in the development of this technology. Another is to adapt the comprehensive experience from circulating fluidized bed boilers to this application, in the design of suitable reactor systems. Thus, the advancement of the technology is heavily dependent on achieving actual operational experience with oxygen carriers in well-working circulating fluidized reactor systems. For the building of experience and understanding of the process needed in the further up-scaling of the technology, it is not a disadvantage if these systems vary in design and size. This paper will report on such operational experiences.

1 CLC APPLICATIONS

When looking at the requirements for oxygen carriers, as well as for the process design, it needs to be pointed out that there are a number of possible applications of chemical looping technologies, using different fuels. For solid fuels, the use in large power plants is the expected application, even though there may be different ways of applying the technology. One is the partial oxidation to produce hydrogen: another is direct “combustion” of the solid fuel in the fuel reactor. In the EU project ENCAP a first design of a 455 MWe CLC solid fuel power plant was accomplished. This showed potential of a very low efficiency penalty, 2-3%, as well as a very low capture cost, around 10 €/ton of CO₂ [3].

For gaseous fuels, again power production would be an option. However, this should preferably involve a pressurized system, in order not to lose too much efficiency compared to presently used combined cycles. Another very attractive option, chemical looping reforming, is to convert the fuel, *e.g.* natural gas, to hydrogen, and thus provide a CO₂ free fuel. Chemical looping steam reforming was proposed by Rydén *et al.* [4]. This process is similar to commercial steam

reforming of natural gas, but uses Chemical Looping Combustion as heat source for the steam reforming and the off-gas from the hydrogen separation as fuel, thus capturing all carbon in the fuel. The process was investigated in EU-project Cachet as a way to produce hydrogen for power production. This hydrogen might not be competitive as fuel for base-load power production, as the cost, around 38 €/MWh, would be similar to crude oil, *i.e.* at 85 \$/barrel. However, it should be a useful fuel for many other applications and could emerge as a very important fuel in a CO₂-constrained future. Moreover, there should be a number of applications where Chemical Looping Combustion of gas could be used for steam or combined steam/power production, and where atmospheric operation would not be a major disadvantage with respect to efficiency. An additional application could be liquid fuels, *e.g.* heavy oils [5].

The application of chemical looping will thus be decisive for the selection of oxygen carrier. Consequently, low cost oxygen carriers are investigated for solid fuels, whereas expensive and highly reactive materials have been in focus for gaseous fuels.

2 OXYGEN CARRIER DEVELOPMENT

For the fluidized bed systems outlined above, important criteria for a good oxygen-carrier are the following:

- high reactivity with fuel and oxygen, and ability to convert the fuel fully to CO₂ and H₂O;
- low fragmentation and attrition, as well as low tendency for agglomeration;
- low production cost and preferably being environmentally sound.

The ability of the oxygen carrier to convert a fuel gas fully to CO₂ and H₂O has been investigated thermodynamically and the metal oxide systems of NiO/Ni, Mn₃O₄/MnO, Fe₂O₃/Fe₃O₄, Cu₂O/Cu, CoO/Co were found to be feasible to use as oxygen carriers [6]. For CoO/Co the thermodynamics are not so favourable, with maximum 93.0% conversion at 1000°C, and moreover this oxygen carrier is expensive and involves health and safety aspects. Copper has the very interesting ability to release oxygen, which is utilized in the CLOU process (Chemical Looping with Oxygen Uncoupling) proposed for solid fuels, *e.g.* [7]. So far, most work has been focused on NiO/Ni being the most reactive oxygen carrier.

In addition to the previously mentioned simple monometallic oxides, also other oxides have potential for being transferring oxygen. These include for instance various sulphates, of which CaSO₄ is the most studied, as well as a number of bimetallic oxides. Among the latter the cheap natural mineral ilmenite, FeTiO₃, has received much attention for use with solid fuels. Very interesting is also the combination of manganese with a number of other oxides, which gives oxygen carriers with the ability to release minor amounts of oxygen [8-9].

Reviews show that there are clearly more than a hundred publications investigating oxygen carriers [10-12]. All of the early oxygen carrier development was made at Tokyo Institute of Technology. In the last decade important work has been made for instance at CSIC-ECB in Zaragoza and at Chalmers, where totally > 700 materials have been investigated by thermogravimetry or in laboratory fluidized bed. A number of materials have also been in actual operation as will be discussed below.

3 OPERATIONAL EXPERIENCE

The following overview summarizes the results from 41 scientific publications, relating more than 4 000 h of operational experience of 29 materials in 12 different units. Results from these units are presented in order of year of publication.

Lyngfelt *et al.* published results from a 10 kW prototype unit in 2004 [13-14]. The unit has a circulating Air Reactor (AR) and a bubbling Fuel Reactor (FR) with overflow (Fig. 1). Two loop seals separate AR and FR. Here, an oxygen-carrier based on nickel oxide was operated for 100 h with natural gas as fuel. A fuel conversion efficiency of 99.5% was achieved, and no carbon dioxide escaped to the Air Reactor, hence, all carbon dioxide was captured in the process. Moreover, the attrition of particles was found to be low, with loss of fines being around 0.002%/h. Later testing in the same unit involves additional nickel oxide material [15] and long term operation, > 1000 h, with a spray-dried material demonstrating the use of commercial material production [16].

Also in 2004, Ryu *et al.* presented results from a 50 kW combustor operating with methane as fuel; a nickel oxide oxygen-carrier was tested during 3.5 h and a cobalt oxide was tested during 25 h [17-18]. Also this unit used a circulating AR and a bubbling FR, and a loop seal after the AR (Fig. 2). However, outflow from the FR and thus the bed level was controlled by a slide valve, and particles were returned to the AR via a horizontal tube. Also in this unit high conversion of fuel, 98%, was noted. Moreover, it was also verified that no NO, NO₂ or N₂O is formed in the Air Reactor.

Later, Adanez *et al.* [19, 20] operated a 10 kW CLC unit for 120 h using a copper-oxide based oxygen carrier of two particle sizes. In this unit both AR and FR are bubbling beds with overflow exits leading to loop seals (Fig. 3). The particles from the FR are led to the AR, whereas the overflow from AR leads to a separate air-blown riser, blowing particles to an intermediate storage (7). Circulation of particles is controlled by a solids valve (5) controlling the flow from this storage to the FR. Operational temperature was lower, 800°C, compared to what is often used with other materials. Both particle sizes were in operation during 60 h with fuel. Complete methane conversion was achieved and no deactivation of the particles was noticed.

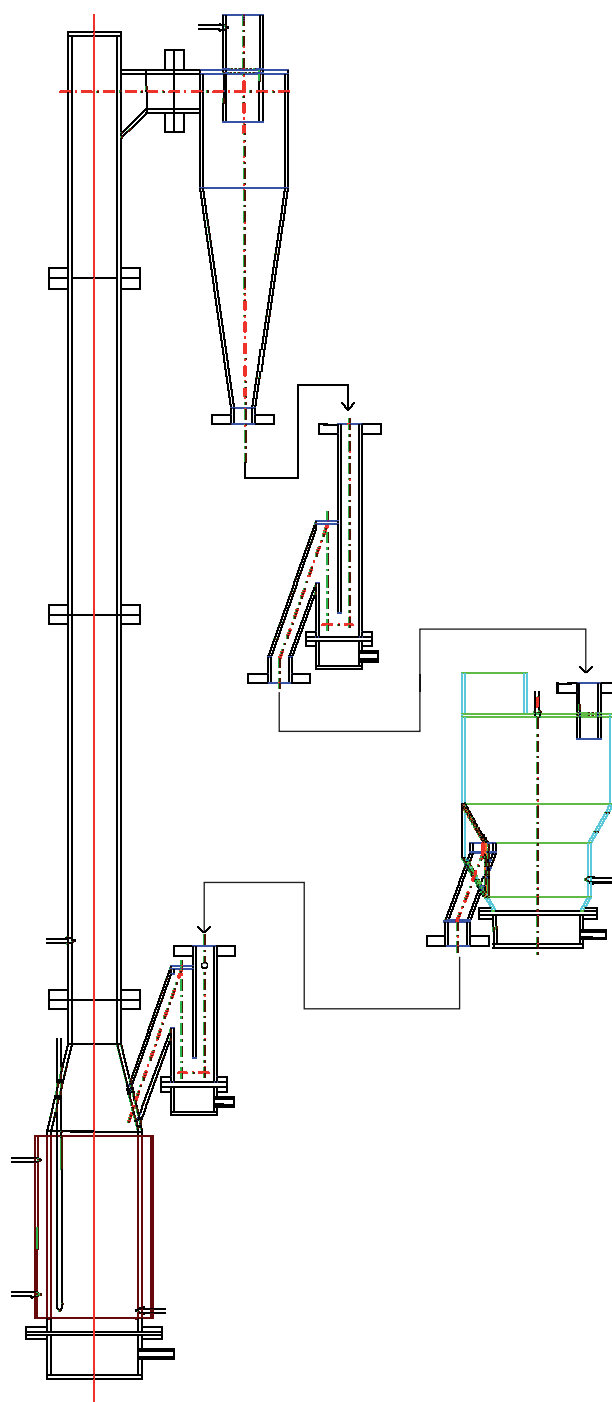


Figure 1

10 kW CLC at Chalmers University of Technology. To facilitate the overview of the unit, some components have been disconnected and rotated.

A number of oxygen carriers based on Ni, Mn and Fe have been used in a 300 W CLC reactor at Chalmers with both syngas and natural gas [21-30]. Here the FR is bubbling, and has an outflow to the AR via a fluidized slot (Fig. 4).

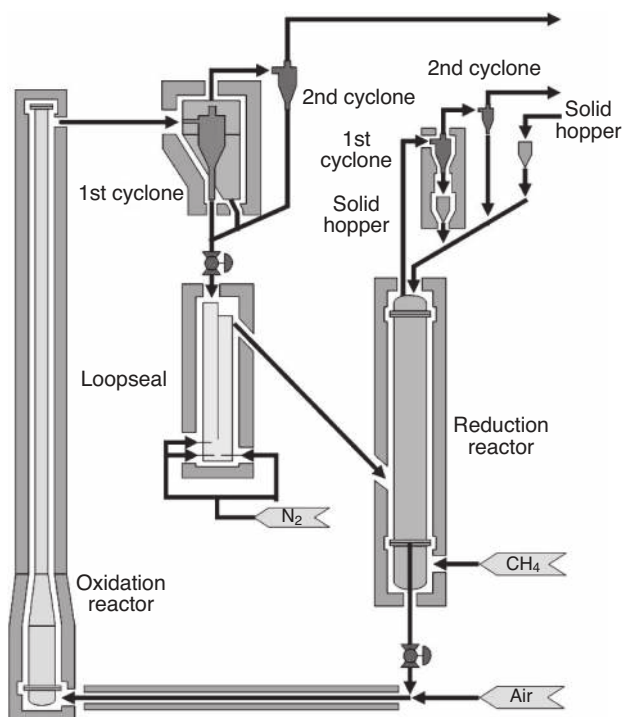


Figure 2

The 50 kW CLC at KIER in South Korea.

The AR has a higher velocity and particles thrown up from AR come to a widening section where they fall back. Part of this downflow is led through a downcomer leading directly into the bed of the FR. In design 2 there is a fluidized loop seal leading to the FR instead of the downcomer. Moreover the slot is improved to reduce leakage. In both designs there is some gas leakage between AR and FR.

The 300 W unit demonstrated the first successful use of Mn-based and Fe-based particles [22, 25]. Moreover, the unit has shown the use of combined oxides, *i.e.* calcium manganate [29]. Also the unit has demonstrated the option of partial oxidation of natural gas, giving a methane-free syn-gas [24, 26]. Total time of operation is more than 700 h.

Son and Kim used a mixed oxide system of NiO-Fe₂O₃/Bentonite in a reactor of about 1 kW [31]. Both AR and FR are bubbling beds in the form of concentric tubes with the AR is placed inside the FR (*Fig. 5*). Both reactors have outflows in the bottom leading to, and controlled by, loop seals and from these loop seals the particles are led to risers recycling the particles to FR/AR. The unit demonstrated operation of particles mixing two active oxides, NiO and Fe₂O₃, using various mixing ratios.

Berguerand used bituminous coal and pet coke in a 10 kW CLC combustor designed for solid fuels [32-35], thus demonstrating for the first time the use of solid fuels. The AR

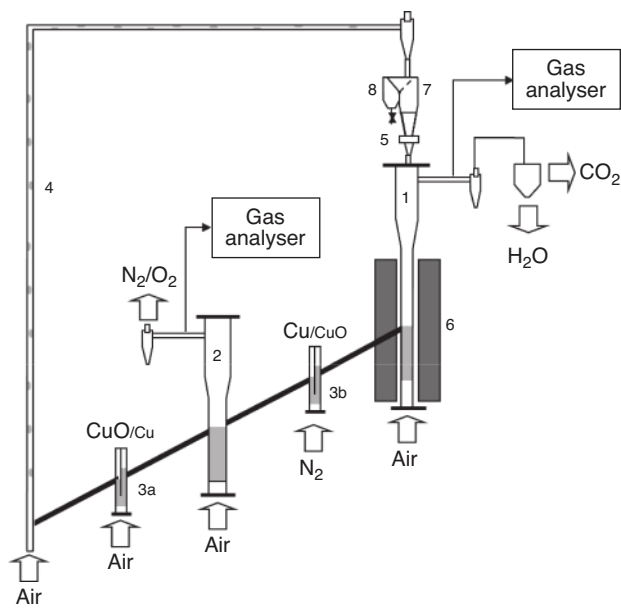


Figure 3

10 kW CLC at CSIC-ECB in Zaragoza.

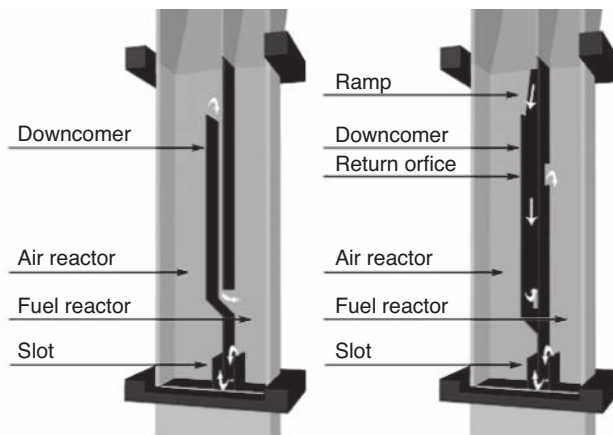


Figure 4

Chalmers' 300 W CLC unit, design 1/2 (left/right).

is circulating and similar to Chalmers' 10 kW unit for gaseous fuels. The FR (*Fig. 6*) is a bubbling bed divided in two sections by an underwear to create a more narrow residence time distribution in the FR, in order to reduce char loss to AR. There is also a small carbon stripper, 36 × 44 mm, after the FR. AR and FR are separated by loop seals. Solid fuel is fed on top of the Fuel Reactor by a fuel chute. The operational experience firstly indicates a significant loss of

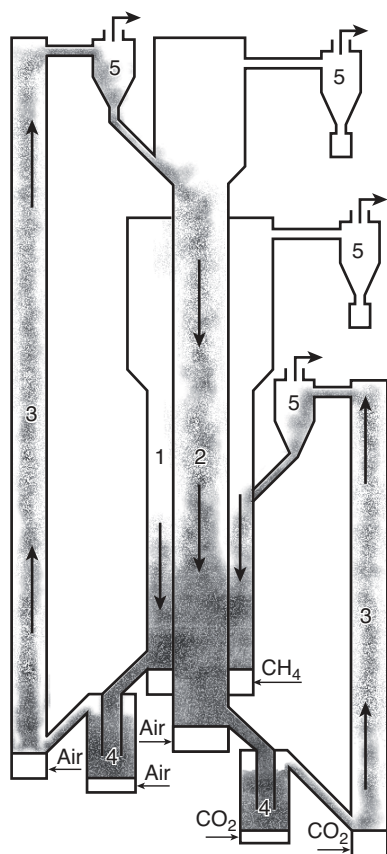


Figure 5
CLC unit at KAIST, South Korea, appr 1 kW.

unconverted char, explained by the very short residence time of fines in this system. Secondly, the fuel volatiles are released in the fuel chute and leave the system unconverted as they have essentially no contact with the oxygen carrier. The conversion of the syngas produced by the char on the other hand is around 90% or higher [35-36]. Lastly the CO₂ capture was not complete as some char leaks to the AR. The CO₂ capture could be modelled as function of char reactivity and circulation flow, using residence time distribution in FR [37].

Moreover significant testing of Ni and Cu materials have been performed in a 500 W unit by Adanez *et al.* [38-46]. The unit has a bubbling FR with overflow exit, leading through a loop seal to the AR (*Fig. 7*). The AR is also bubbling but has a narrow upper section through which particles are entrained by a narrow riser to a container. The container has a slide valve controlling the return flow to the FR. The unit has extended the operational experience of fuels by the study of ethane and propane, indicating that they have similar reactivities as methane [41, 44]. Moreover the negative effect of higher concentrations of sulphur on nickel-based material has been shown [40].

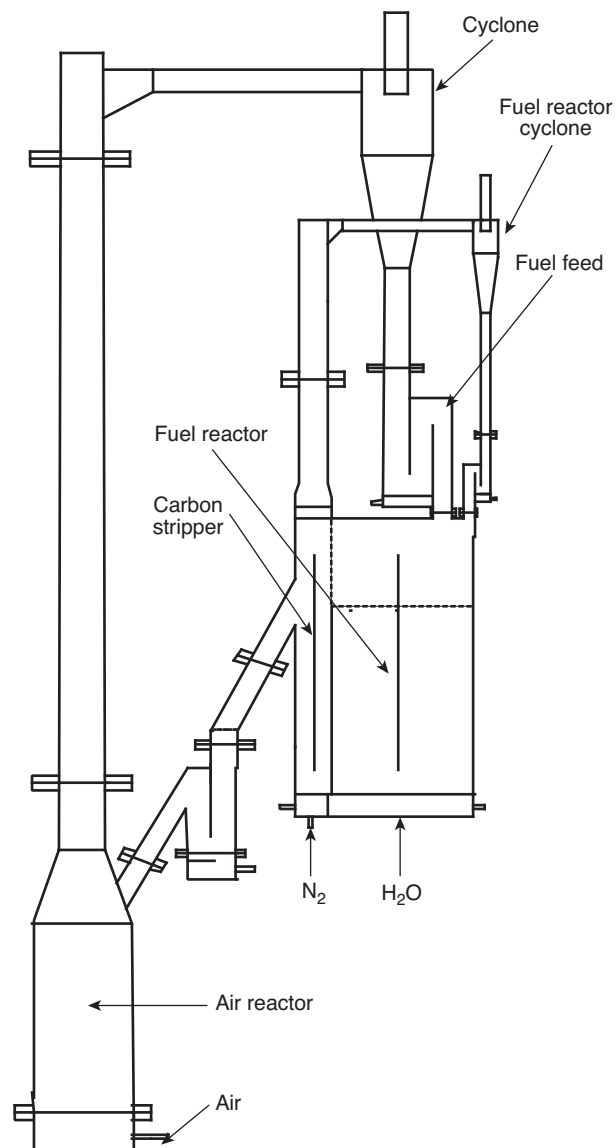


Figure 6
10 kW solid fuel CLC unit at Chalmers.

Vienna University of Technology successfully operated a 140 kW dual circulating fluidized bed system, with natural gas, H₂, CO, using ilmenite and nickel oxides, [47-56]. The unit has a circulating AR leading the particles to the FR via a loop seal, and the FR reactor is also circulating, albeit with the return flow coming back to the FR (*Fig. 8*). The FR and the AR have a direct fluidized connection in the bottom. As material is circulated to the FR, the increased pressure drop causes a movement of particles through this connection back to AR. The operational experience include a wide range of operational conditions, loads of 20-145 kW, temperatures of

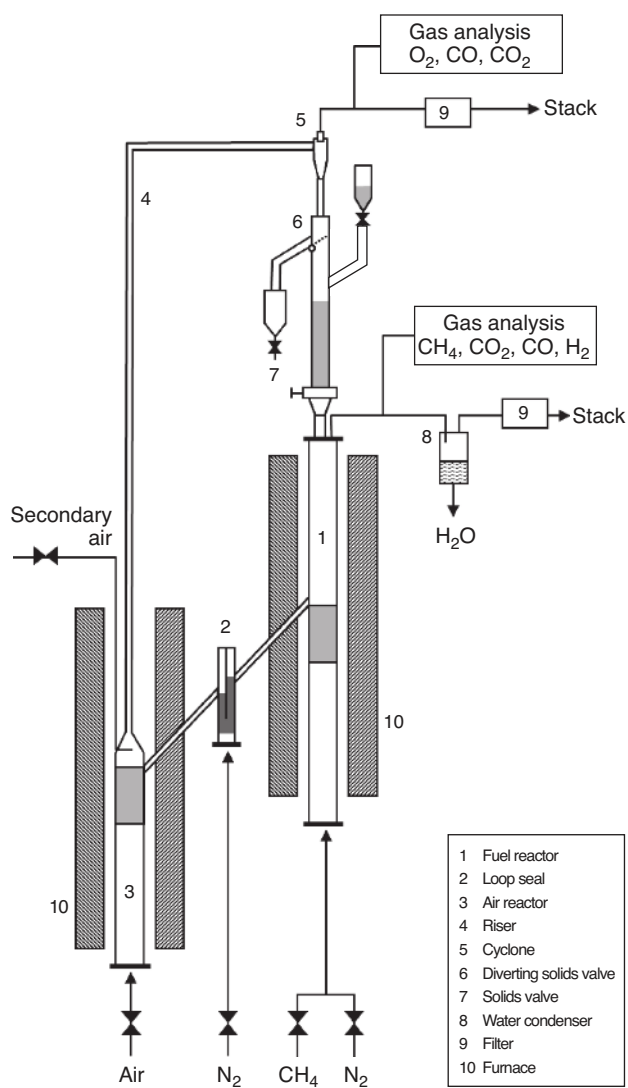


Figure 7

500 W CLC reactor at CSIC.

780-960°C and air ratios of 0.8-1.25. The lower air ratios were used for syngas production. The unit shows a fuel conversion up to 95% for CH₄ and 99% for H₂ and CO.

Shen *et al.* have operated with coal and biomass using nickel- and iron-based oxygen carriers in a 10 kW unit [57-60]. The unit has a circulating AR leading to a FR also acting as loop seal (Fig. 9). The FR is a spouted bed, and has an out-flow via a special direct connection to AR. Solid fuel is fed in the bottom of the FR together with fluidizing gas. The unit demonstrates the first use of biomass in CLC, using a nickel-based oxygen carrier under 100 h [58]. Similar testing with coal, however, showed deterioration of oxygen carriers, likely due to presence of sulphur [59]. Biomass was also operated with iron oxide [60].

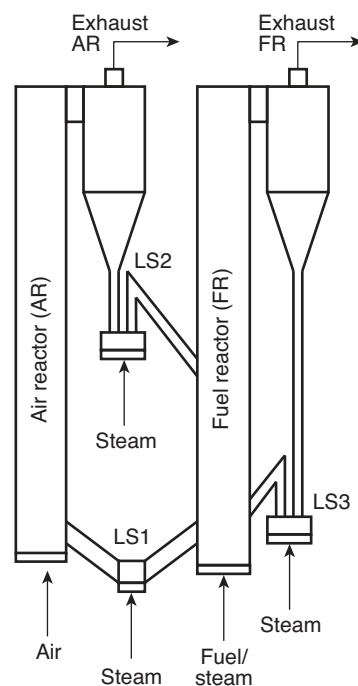


Figure 8

140 kW dual circulating fluidized-bed chemical looping combustor at Vienna University of Technology.

Alstom operated with natural gas and different nickel oxides in a compact highly integrated 15-kW design [61]. Both AR and FR are circulating and the material is in both cases led to seal-pots with double outlets, one flow is recycled and the other is led to the other reactor. Four nickel-based materials have been operated reaching conversions up to 99%.

Ryu *et al.* designed a new 50 kW chemical looping combustor which was operated with nickel and cobalt oxide particles [62]. Both AR and FR are bubbling beds, Figure 10, and fluidized by gas flows Q1 and Q2. Both AR and FR contain an internal riser into which bed material is transferred from the bubbling beds through holes. These risers are fluidized by the gas flows Q3 and Q4. The gas flow in each of these risers carries the particles up to the reactor outlet, where they are transported by the outlet flow to a cyclone which is placed over the other reactor. The particles then fall down in a downcomer leading down into the reactor bed. The downcomers are immersed in the beds which means that both beds also have the function of being loop seals. With a nickel-based oxygen carrier 99.2% CO₂ and 0.8% CO was attained in the exit from the Fuel Reactor. Thus, the CO concentration is a little higher than thermodynamic equilibrium for Ni/NiO system. The absence of H₂ in the exit gas is puzzling, as other

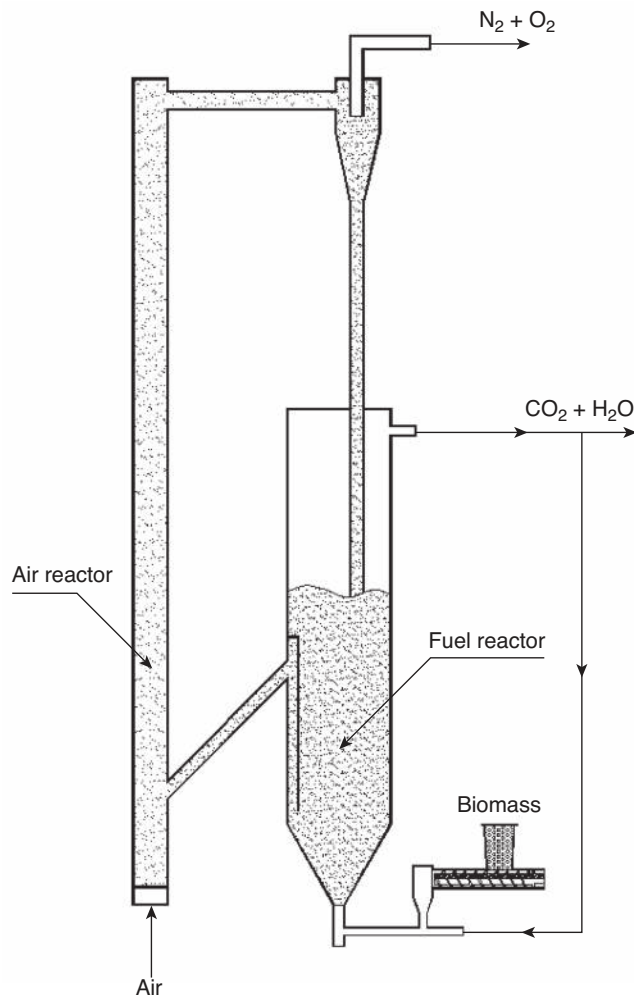


Figure 9

The 10 kW unit for solid fuels at South-East University in Nanjing.

testing with Ni/NiO system always show concentrations at or above equilibrium concentrations, *i.e.* above 1-1.5% depending on temperature.

Wu *et al.* have presented operational data from a smaller CLC unit for solid fuels operated with coal and an iron ore as bed material [63]. Except for the size, and the introduction of a loop seal in the passage from FR to AR, the unit, Figure 11, is similar to the 10 kW unit previously described in Figure 9. The ratio of carbon containing gases from the FR was typically 1% CH₄, 4% CO and 95% CO₂. The data indicate that reasonably high conversion of the gas from FR should be possible using bottom bed feeding of coal.

In addition to these units a number of units of various sizes are presently being planned or built, which will likely provide operational data from new designs.

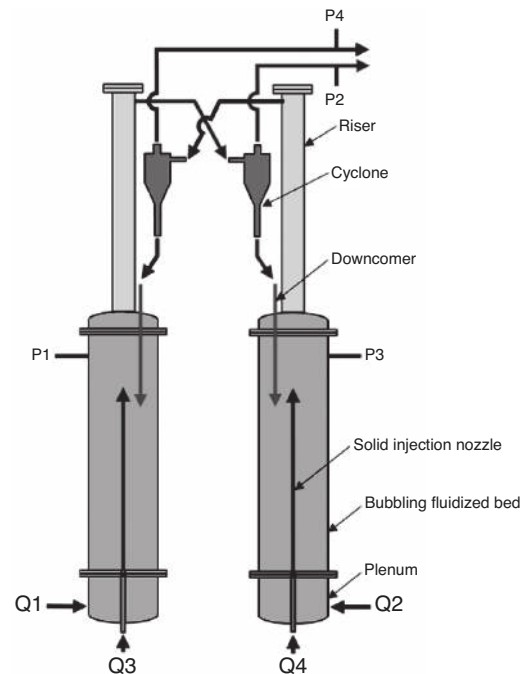


Figure 10

50 kW (new) CLC at KIER.

4 SUMMARY OF REACTOR TESTING

Thus, worldwide results from 12 chemical looping combustors, in size range 0.3 to 140 kW, have been reported in the last 6 years, Table 1. Total operational experience in these units exceeds 4 000 h.

TABLE 1
Overview of existing chemical looping combustors

Location	Unit	Oxides tested	Time	Fuel	Year ^a
Chalmers	10 kW	NiO, Fe ₂ O ₃	1 350	nat. gas	2004
KIER	50 kW	NiO, CoO	28	nat. gas	2004
CSIC	10 kW	CuO, NiO	140	nat. gas	2006
Chalmers	0.3 kW	NiO, Mn ₃ O ₄ , Fe ₂ O ₃ , ilmenite	730	nat. gas, syngas	2006
Chalmers	10 kW – SF	ilmenite	90	coal, petcoke	2008
CSIC	0.5 kW	CuO, NiO	660	nat. gas	2009
KAIST	1 kW	NiO + Fe ₂ O ₃	?	CH ₄	2009
Vienna U.T.	140 kW	ilmenite, NiO	390	nat. gas, CO, H ₂	2009
Alstom	15 kW	NiO	100	nat. gas	2009
Nanjing	10 kW – SF	NiO, Fe ₂ O ₃	230	coal, biom.	2009
KIER	50 kW	NiO, CoO	300	nat. gas, syngas	2010
Nanjing	1 kW – SF	Fe ₂ O ₃ (ore)	10	coal	2010

^a First published.

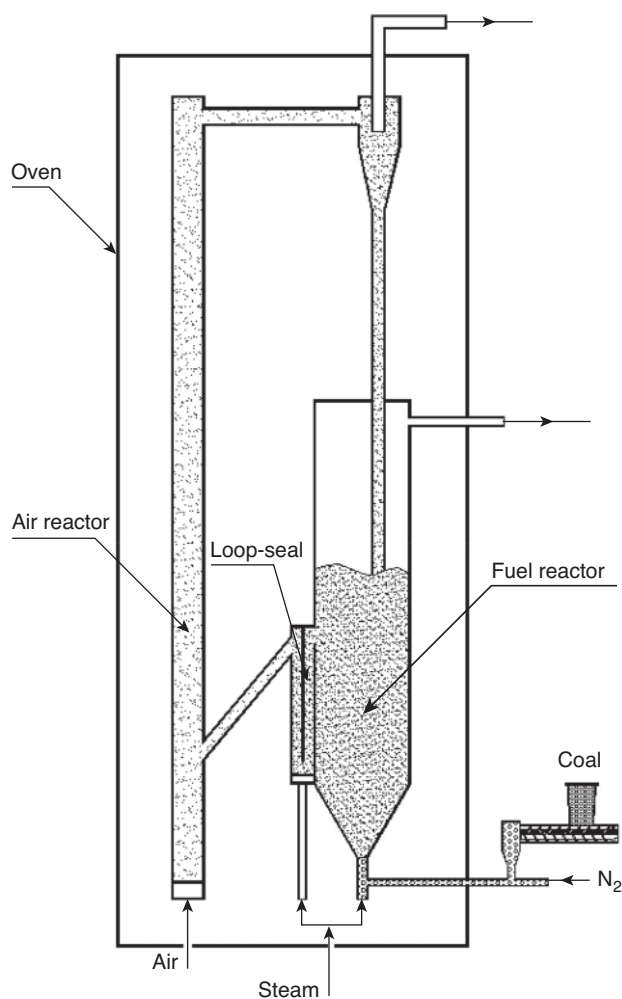


Figure 11

The 1 kW solid fuel CLC in Nanjing.

As seen above all units have different designs, some of which are suitable for testing in smaller scale and giving opportunities for careful circulation control. Also the sizes differ, with some units, *e.g.* Vienna's 140 kW, also having designs and sizes more close to what could be expected in future commercial designs. The dimensions of the units are summarized in Table 2. All these units are also quite simple and do not rely on any advanced or complex technology solutions. Nevertheless, all of the units seem to have worked well and, at least for the gas-fired units, produced highly concentrated CO₂ without losses to the stream coming from the AR. Also the results from the units fired by solid fuels suggest that high concentrations of CO₂ and high CO₂ capture should be possible given the proper design.

The operational experience also clearly indicates that a significant number of materials have shown very good

TABLE 2

Dimensions, diameter (D) in cm and height (H) in m. Rectangular cross-section is indicated by x and narrowing riser by /

Unit	D_{AR}	H_{AR}	D_{FR}	H_{FR}
Chalmers 10	15/8	2.2	15	0.34
KIER 50	10/8	5	14	2.5
CSIC 10	16	1.5	10	2
Chalmers 0.3	2.5 × 3.5/2.5 × 2.5	0.2	2.5 × 2.5	0.2
KAIST 1	2.3	1.5	5.5(-2.3)	0.9
Chalmers 10sf	15/8	2	9 × 19	0.5
CSIC 0.5	5/2		5	
Vienna 140	15	4.1	16	3
SEU 10sf	5	2	23 × 4	1.5
Alstom 15	?	?	?	?
KIER 50 new	?	?	?	?
SEU 1sf	2	1.6	5 × 3	1

performance. Moreover, the data highlight the availability of a range of different materials for different purposes, from highly reactive and expensive NiO materials to cheap natural minerals which could be a better option for ash-rich solid fuels. An overview of the materials tested is given in Table 3. If the number of materials tested in each unit is summarized the total is 47. However, some materials were tested in more than one unit, so the total number of different materials tested is 29. The active oxide in these 29 materials is based on nickel (13), iron (8), nickel plus iron (3), manganese (3) cobalt (1), and copper (1). Among the iron and manganese materials is also found two combined oxides, here meaning that the active oxide is actually a combined oxide, *e.g.* a bimetallic oxide. This is the case for the mineral ilmenite, FeTiO₃, and for CaMn_{0.875}Ti_{0.125}O₃. The majority of the materials are manufactured, but among the materials tested two natural ores and one industrial waste material are also found. Among the manufactured materials there are also a significant number of different production technologies.

Still the number of materials actually tested in operation is limited whereas there are many interesting materials still untested. Therefore, it is not unlikely that future results from operation will include interesting data from a number of new materials.

5 DISCUSSION

The work with gaseous fuels like natural gas, using nickel-based particles has been highly successful. The work has demonstrated that:

- nickel materials have very high reactivity, and, as it seems, rather independent on starting materials and production method;

TABLE 3
Materials tested

Chalmers 10 kW, 6 mtrls incl. 25 ^a	
1	NiO/NiAl ₂ O ₄ 40/60, freeze-granulated
2	Fe ₂ O ₃ /MgAl ₂ O ₄ 60/40, freeze-granulated
3	NiO/NiAl ₂ O ₄ 60/40, spin-flash drying
4	NiO/NiAl ₂ O ₄ 40/60, spray-dried
5	NiO/NiAl ₂ O ₄ /MgAl ₂ O ₄ 40/42/18, spray-dried
KIER 50 kW	
6	NiO/bentonite 60/40, mixing/drying/crushing/calcining
7	Co ₃ O ₄ /CoAl ₂ O ₄ 70/30, co-precipitation/impregnation
CSIC 10 kW	
8	CuO/Al ₂ O ₃ 14/86, wet impregnation, 2 sizes
Chalmers 300 W, 4 mtrls, incl. 1 ^a	
9	NiO/MgAl ₂ O ₄ 60/40, freeze-granulated
10	Mn ₃ O ₄ /Mg-ZrO ₂ 40/60, freeze-granulated
11	Fe ₂ O ₃ /Al ₂ O ₃ 60/40, freeze-granulated
Chalmers 300 W, design 2, 12 mtrls, incl 2, 4, 5, 23, 24, 25 ^a	
12	NiO/MgAl ₂ O ₄ 20/80, freeze-granulated
13	NiO/Mg-ZrO ₂ 40/60, freeze-granulated
14	Fe ₂ O ₃ /Mg-ZrO ₂ 60/40, freeze-granulated
15	Colomax, up-concentration of Mn minerals
16	Iron oxide shells, industrial waste material
17	CaMn _{0.875} Ti _{0.125} O ₃ , spray pyrolysis + freeze-granulation
KAIST 1 kW, 5 mtrls	
18	NiO/bentonite
19	NiO-Fe ₂ O ₃ /bentonite, NiO/Fe ₂ O ₃ 75/25
20	NiO-Fe ₂ O ₃ /bentonite, NiO/Fe ₂ O ₃ 50/25
21	NiO-Fe ₂ O ₃ /bentonite, NiO/Fe ₂ O ₃ 25/75
22	Fe ₂ O ₃ /bentonite
Chalmers 10 kW solid fuel, 1 mtrl	
23	Ilmenite, FeTiO ₃ natural ore
CSIC 500 W, 3 mtrls incl. 8 ^a	
24	NiO/γ-Al ₂ O ₃ 21/79, impregnation
25	NiO/α-Al ₂ O ₃ 18/82, impregnation
Vienna University 140 kW, 3 mtrls incl. 4, 5, 25 ^a	
South-East University 10 kW solid fuels	
26	Fe ₂ O ₃ , sintered iron oxide powder
27	NiO/NiAl ₂ O ₄ 33/67, impregnation
Alstom 15 kW, 4 mtrls incl. 1, 4, 5, 25 ^a	
KIER new 50 kW, 3 mtrls incl. 6, 7 ^a	
28	NiO/? 70/30, spray-drying
South-East University 1 kW solid fuel	
29	Iron ore

^a Refers to the number of material, *i.e.* for materials also tested in other units.

- the nickel materials can be manufactured from materials commercially available in large quantities, at prices reasonably close to the world market price of nickel;
 - the nickel materials have sustained extended operation, 1 000 h, without losing reactivity and showing small loss of fines, clearly indicating a long lifetime.
- Obvious drawbacks with nickel materials are:
- the thermodynamic constraint, with maximum gas conversions around 99%;
 - the price. The expected long lifetime, however, suggests that low overall costs for nickel materials should be possible despite the fairly high price of nickel. It is also expected that spent material, *i.e.* elutriated fines, can be recycled for production of new particles;
 - the toxicity, which will add to costs for ensuring safety for health and environment.

As discussed before, nickel materials show high reactivity with methane-based fuels like natural gas. Based on measured kinetics and assuming perfect gas-solids contact, a very small solids inventory of around 10-20 kg/MW would be sufficient in the Fuel Reactor to reach full conversion, or, to be more precise, reaching the thermodynamic limit [64, 65]. However, in fluidized beds, the gas-solids contact is far from perfect, as there is a by-pass of gas induced by bubbles. Consequently, predictions based on kinetics and assuming perfect gas-solids contact will underpredict needed inventories, and much larger solids inventories would be needed in reality. This was already observed in pilot unit studies, using solids inventories of *e.g.* 133 and 500 kg/MW with conversions of 89% and 98% [64]. Two-phase modelling indeed indicates the need of significantly larger solids inventory to compensate for the imperfect contact between gas and solids [66]. Moreover, the actual contact will be highly dependent on fluidization conditions and reactor design, size, operating conditions and bed material properties.

Therefore, scale effects may alter performance. As a consequence, results from a pilot reactor of *e.g.* 100 kW cannot be transposed directly to predict safely performance in much larger units. A large unit could have a riser more than 10 times higher, thus a freeboard containing large amounts of solids which would be expected to give improved contact. Moreover, such a unit would also operate at higher gas velocities, which might also improve the mixing. On the other hand, the much larger cross-section area could have negative effect on the contact.

For other metal oxides the needed solids inventory would generally need to be higher. The reactivity towards methane is falling significantly in the order Ni > Cu > Mn > Fe. Here another approach could be to use so-called CLOU materials, *i.e.* oxygen carriers with the ability to release gaseous oxygen, as these provide a possibility to circumvent the gas-solids contact issue in fluidized beds. For oxygen carriers using the CLOU principle, the dependence on direct contact

between fuel gas and oxygen carrier particles is less crucial. For instance, oxygen released in dense regions with completely converted fuel, may mix with incompletely converted gas in the upper parts of the riser or in the cyclone.

It can be speculated that the advantages of the oxygen release of CLOU materials could compensate for a lower reactivity with CH_4 as compared to a nickel material, and that a good CLOU material could perhaps even need less material to reach full conversion. Experimental results give some support for this idea, thus the operation with CuO particles, known to have a CLOU effect, in the 10 kW unit at CSIC, achieved complete fuel conversion with a solids inventory corresponding to 290 kg/MW [19, 20].

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 this ash needs to be removed from the reactor system. Moreover, ash might directly affect the oxygen carrier. Consequently, low cost materials like ilmenite and iron ores have been studied;
- solid fuels, after having released volatiles that may react directly with the oxygen carrier, will form a char residue that cannot react directly with the oxygen carrier. This char residue is gasified, *e.g.* by steam, producing syngas. 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 particles.

An advantage for solid fuels is that most oxygen carriers, including low-cost iron-based materials, are highly reactive towards the syngas released from gasification. However, the syngas produced by the char particles is released inside the bed, 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. For this reason, complete conversion of the gas in the Fuel Reactor would be difficult to obtain. The gas conversion in the 1 kW unit in Nanjing reached approximately 95% [63], and batch testing with devolatilized fuels in the Chalmers 10 kW unit, show conversion of the syngas up to 95% [67]. However, there are several options to reach complete or very high conversion:

- the downstream introduction of pure oxygen to oxidize the remaining unconverted gases H_2 , CO and CH_4 , *i.e.* an “oxygen polishing” step;
- the separation of these unconverted gases from the liquid CO_2 by *e.g.* distillation and recirculation 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 CLOU oxygen-carriers, *i.e.* particles able to release oxygen in the Fuel Reactor – oxygen which can subsequently convert the remaining gases.

Although more development work is needed, it should be pointed out that the CLC technology provides unique advantages for avoiding the large costs and energy penalties inherent in gas separation. In the case of gaseous fuels, the technology should be ready to scale up to 1 or 10 MW size. For the solid fuel application, more work is likely needed to find the most optimal solution for the Fuel Reactor system.

The main obstacle in the development and commercialization of the CLC technology, as with all CO_2 capture technologies, is the lack of real incentives. Moreover, large efforts to scale up more established CO_2 capture technologies may divert the interest from a technology which is quite new, less well known and which may need a longer time period to reach commercial size. Nevertheless CLC is rapidly gaining recognition as a potential break-through technology with respect to cost and energy penalty, and intensified efforts to develop the technology can be expected.

CONCLUSIONS

Chemical Looping Combustion has successfully been operated in a number of units of varying designs in the size range 0.3 to 120 kW. This operation includes more than 4000 h, using close to thirty different oxygen-carriers. This is clearly an indication that the technology as such works, although further work is needed to find optimal scaled-up designs, especially for solid fuels. A number of suitable oxygen-carrier materials have been demonstrated, but on the other hand a vast number of potentially interesting materials have never been tested, so there should be a potential for finding improved materials, both with respect to costs and performance.

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