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Carbon Capture via Chemical-Looping Combustion and Reforming

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Abstract

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of the greenhouse gas CO_2. The technique 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 inter-connected fluidized beds, a fuel reactor and an air reactor, are used in the process. In the fuel reactor, the metal oxide is reduced by the reaction with the fuel and in the air reactor; the reduced metal oxide is oxidized with air. The outlet gas from the fuel reactor consists of CO_2 and H_2O, and almost pure stream of CO_2 is obtained when water is condensed. Considerable research has been conducted on CLC in the last decade with respect to oxygen carrier development, reactor design, system efficiencies and prototype testing. The technique has been demonstrated successfully with both natural gas and syngas as fuel in continuous prototype reactors based on interconnected fluidized beds within the size range 0.3 – 50 kW, using different types of oxygen carriers based on the metals Ni, Co, Fe, Cu and Mn. From these tests it can be established that almost complete conversion of the fuel can be obtained and 100% CO_2 capture is possible. Further, two different types of chemical-looping reforming (CLR) have been presented in recent years. CLR is a technology to produce hydrogen with inherent CO_2 capture. This paper presents an overview of the research performed on CLC and CLR highlights the current status of the technology.

Introduction

CO_2 is the primary greenhouse gas and it is very likely that CO_2 formed by combustion of fossil fuels contributes to an increased global average temperature. [1] One way to achieve combustion without CO_2 emissions and still use fossil fuels is separation and sequestration of CO_2. This could be performed in several ways. Potential options which have been presented in the literature are i) absorbtion of the CO_2 from the flue gases in an amine solution, so called post-combustion capture, ii) burning the fuel in a stream of pure oxygen and carbon dioxide, i.e. oxy-fuel combustion or iii) de-carbonizing the fuel prior to combustion, i.e. pre-combustion. These techniques have rather high energy penalties, mostly associated with obtaining a pure stream of CO_2 from the rest of the combustion gases, mainly N_2. A way to avoid this energy penalty is to use unmixed combustion, as in Chemical-Looping Combustion.

Chemical-Looping Combustion

Chemical-looping combustion 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 separation and no new equipment is needed. The CLC system is composed of two reactors, an air and a fuel reactor, see Fig. 1. The fuel is introduced in the fuel reactor, which contains a metal oxide, Me_xO_y. The fuel and the metal oxide react according to:

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

The exit gas stream from the fuel reactor contains CO_2 and H_2O, and a stream of CO_2 is obtained when H_2O is condensed. The reduced metal oxide, Me_xO_{y-1}, is transferred to the air reactor where it is oxidized, reaction (2):

$$Me_xO_{y-1} + \tfrac{1}{2}O_2 \rightarrow Me_xO_y \quad (2)$$

The air which oxidizes the metal oxide produces a flue gas containing only N_2 and some unused O_2. Depending on the metal oxide and fuel used, reaction (1) is often endothermic, while reaction (2) is exothermic. The total amount of heat evolved from reaction (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The advantage of chemical-looping combustion compared to normal combustion is that CO_2 is not diluted with N_2 but obtained in a separate stream without any energy needed for separation. The concept of CLC was actually proposed already in the 1980's as an alternative to normal combustion. [2, 3] It was postulated that the use of certain oxygen carriers in such a system could result in higher efficiencies in comparison to normal combustion. At this stage the use of CLC for CO_2 capture was not considered, although the group of Ishida acknowledged the possibility in the middle 90's, [4] and today, almost all of the research conducted around CLC considers the capture of CO_2. The literature can be divided into three main areas of research: i) process studies, ii) reactor design and iii) oxygen carrier development. This paper will present an overview of the work which has been carried out within each of these categories and also highlight the status of the research.

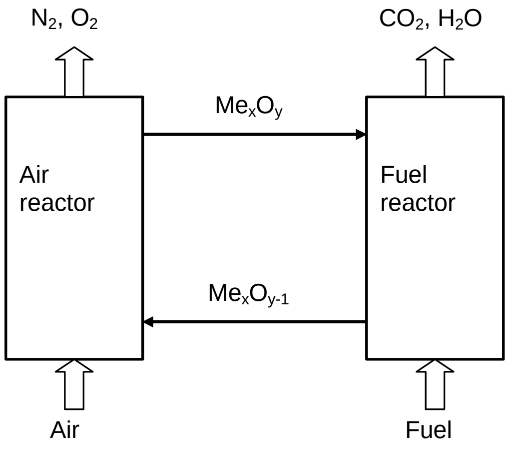


Figure 1. Chemical-looping combustion. Me_xO_y/Me_xO_{y-1} denotes recirculated oxygen carrier solid material.

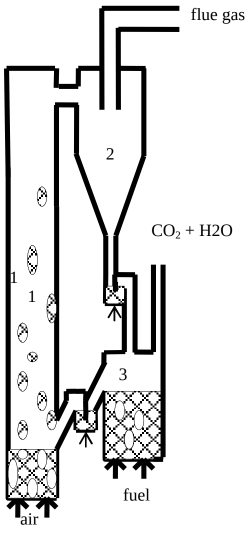


Figure 2. Layout of chemical-looping combustion process, with two interconnected fluidized beds. 1) air reactor, 2) cyclone, 3) fuel reactor.

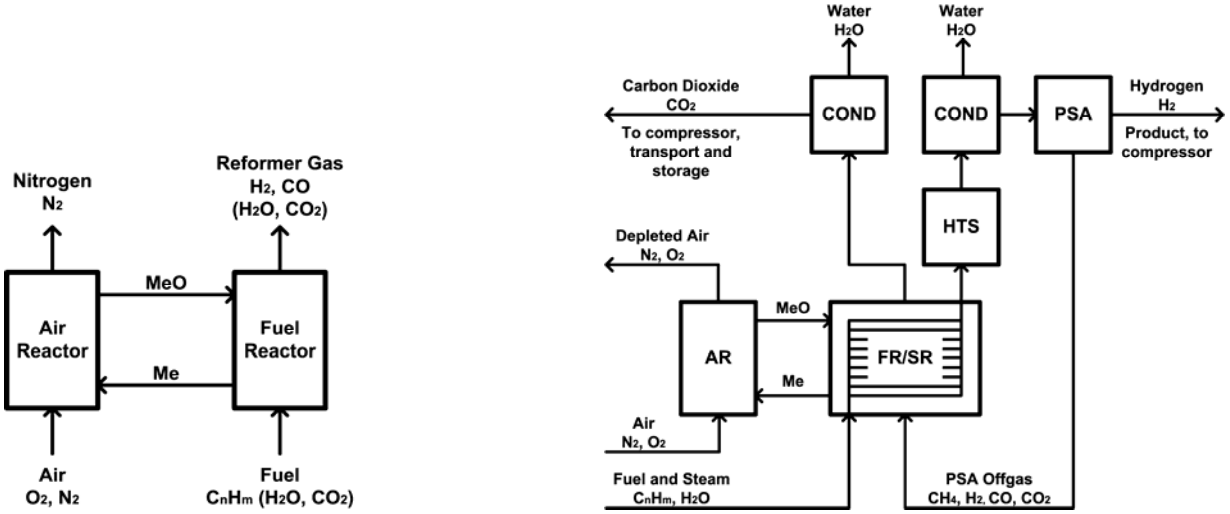
Chemical-Looping Reforming

The chemical-looping technique can also be adapted for the production of hydrogen with inherent CO_2 capture. Below, two processes by Rydén and Lyngfelt are outlined: i) Autothermal chemical-looping reforming, CLR(a) and ii) steam reforming using chemical-looping combustion, CLR (s). [5, 6]

CLR(a) is similar to CLC, but instead of burning the fuel, it is partially oxidized using a solid oxygen carrier and some steam to produce an undiluted stream of H_2, CO, H_2O and CO_2, see Fig. 3a. [6-8] The actual composition of this mixture depends upon the air ratio, i.e. the fraction of oxygen supplied to the fuel by the oxygen carriers in the fuel reactor to that needed for complete oxidation. This gas could then be converted to a mixture of pure H_2 and CO_2 in a low temperature shift-reactor. Depending upon the purity of H_2 required and the pressure, the CO_2 can be removed by either absorption or adsorption processes.

The second type of hydrogen production is called CLR(s) where the “s” denotes steam reforming. Here, natural gas is converted to syngas by conventional steam reforming, i.e. the natural gas reacts with steam at high pressures inside tubes containing suitable catalysts. However, the steam reforming tubes are here placed inside the fuel-reactor in a CLC unit. Hence, in contrast to the normal steam reforming process, the reformer tubes are not heated by direct firing but rather by the oxygen carrier particles in the normal CLC process. The syngas passes through a shift-reactor and a condenser before high purity H_2 is obtained through pressure swing adsorption (PSA). The offgas from the PSA unit, consisting of a mixture of CH_4, CO_2, CO and H_2, is then the feed gas to the fuel reactor. The proposed design of CLR(s) can be seen in figure 3b. [5]

Several other authors have explored the possibility of using oxygen storage materials for the production of syngas, e.g. [9-11]



a) b)

Figure 3. a) Chemical-looping reforming and b) steam reforming with CO_2 capture by chemical-looping combustion. [5, 6]

Current status of chemical-looping research

Since CLC on gaseous fuel has been the focus almost all research on chemical-looping technologies, the results given in the following sections are based upon, and deals with CLC unless otherwise stated.

Integration with power process and thermal efficiencies

It is important that the chemical-looping system in Fig. 1 can be integrated with a power process and achieve high efficiencies. There have been a number of process simulations performed in the literature using both natural gas and syngas and different types of oxygen carriers. A review of the literature around these process simulations can be found in doctoral theses of Anheden [12], Wolf [13] and Brandvoll. [14] As mentioned above chemical-looping combustion was first proposed as a combustion technique for increasing the thermal efficiency of combustion. It has been claimed that the exergy destruction in such a process is less in comparison to normal combustion. [2, 3, 15, 16] By performing the reactions in two steps, the inherent disorder of normal combustion is avoided and hence if the added exergy can be utilized in a good way, higher thermal efficiencies should be obtained. In the first set of systems analyzed the capture of CO_2 was not incorporated, and electrical efficiencies of between 50 – 67% based on the lower heating value of the fuel were reported, see [12]. Later, Anheden et al. found that it was theoretically possible to increase the efficiency using simple gas turbine systems incorporated with CLC, but that CLC together with a gas and steam turbine cycle did not have any efficiency improvement in comparison to normal combustion. [17-19] However, if CO_2 capture was added, the CLC combined cycle systems showed higher efficiencies compared to conventional systems with CO_2 capture. Later process studies have focused on CLC with CO_2 capture. Wolf et al. performed process studies on NGCC systems and found that the thermal efficiency could be increased by 5 percentage points by using CLC in comparison to conventional CO_2 capture technology. [20] The group of Bolland et al. has also performed several studies of natural gas fired cycles with different configurations, and in general the thermal efficiencies are high. [21-23] In conclusion, the process studies have shown that it is theoretically possible to achieve high thermal efficiencies using CLC integrated with CO_2 capture, almost always superior to alternative methods. This together with the added advantage that no new separation equipment is needed and hence, considerably smaller capital costs make CLC a highly interesting technology for further study. In the investigations presented above it is usually assumed that the reactions in the reactors are in equilibrium, which implicitly assumes that the oxygen carriers react at a rapid rate with the fuel and oxygen. Further, no aspects concerning oxygen carriers behaviour in the reactors are taken into account, i.e. deactivation, agglomeration and attrition. And as the temperatures employed in the process studies are usually in the excess of 1000°C in the air reactor, these aspects may be of critical importance. Finally, little or no information concerning reactor design is given. Thus, to reach the high efficiencies calculated above, it is crucial that reactor configurations and oxygen carrier particles are developed which can enable integration into a highly efficient power cycle. These aspects will be discussed in following sections.

As mentioned before, not much research has been performed on chemical-looping reforming. However, the two concepts have been compared in a process study, in which CO_2 capture has been considered. It is found that both alternatives have potential to achieve reforming efficiencies in the order of 80%, including CO_2 capture and compression. [7]

Reactor design of a chemical-looping combustor

Prior to the year 2001, most of the work surrounding CLC focused on system studies and also on the development of oxygen carrier particles, with limited information on how the reactors in Fig. 1 could be designed. Since then several cold-models and hot prototype units have been built and operated. In 2001 Lyngfelt et al. presented a design based on interconnected fluidized beds, see Figure 2. [24] A system based on interconnected fluidized beds has advantages over alternative designs, because the process requires a good contact between gas and solids as well as a significant flow of solid material between the two reactors. The gas velocity in the riser provides the driving force for the circulation of particles between the two beds. Thus, the particles carried away from the riser are recovered by a cyclone and led to the fuel reactor. From the fuel reactor the particles are returned to the air reactor by means of gravity; the fuel reactor bed is at a higher level than the bed of the air reactor. The gas streams of the two reactor systems are separated by fluidized particle locks. Thus, the system is very similar to circulating fluidized bed combustion of solid fuels, a well established technology which has been used commercially for decades. Lyngfelt et al. presented the critical design parameters of such a system as the solids inventory and recirculation rate of oxygen carriers between the reactors and identified the relationship between these and the oxygen carrier properties. [24] After condensation of the water, the remaining gas, containing mostly CO_2, is compressed and cooled in stages to yield liquid CO_2. If there is remaining non-condensable gas from this stream containing unreacted combustibles, one option would be to recover this gas and recycle it to the fuel reactor. Another option is to add some oxygen downstream of the fuel reactor. Johansson et al. constructed a cold-flow model with a design similar to that in Fig. 2 and explored suitable operating conditions for achieving a sufficient solids flux of particles between the reactors and solids inventory in the reactors. [25] Further, leakage between the reactors was low as long as proper pressure differences within the system were maintained. [26] Kronberger et al. conducted tests on a cold-flow model of a chemical-looping combustor with the principal layout shown in Figure 2. [27] Stable and suitable operating conditions were identified.

Several CLC prototypes have been presented in the literature, see Table 1. Lyngfelt et al. presented results from a 10 kW prototype unit in 2004.[28, 29] 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. Only small losses of fines were observed. [30] Ryu et al. have presented results from a 50 kW combustor operating with methane as fuel, and two types of oxygen-carriers. [31] A nickel oxide oxygen-carrier was tested during 3.5 h and a cobalt oxide was tested during 25 h. For the nickel oxide oxygen-carrier, the concentration based on dry flue gases of CO_2 leaving the fuel reactor was 98% and for cobalt oxide 97%. The two reactors have a similar design, but differ at the return from the fuel reactor. In the 10 kW unit at Chalmers the particles leave the fuel reactor through an overflow, i.e. the bed height in the fuel reactor is always constant, while in the 50 kW unit in South Korea the particles leave the fuel reactor from the bottom of the bed, and the particle flow i.e. the bed height of the fuel reactor, is controlled by a valve. Adanez et al. have also presented results from a 10 kW CLC unit which was operated for 120 h using a copper-oxide based oxygen carrier of two particle sizes. Complete methane conversion was achieved and no deactivation of the particles was noticed.[32] Recently Song and Kim presented results with the mixed oxide system of NiO-Fe_2O_3/Bentonite in a circulating fluidized bed reactor using methane at a thermal power of about 1 kW. Almost full conversion to CO_2 and H_2O was achieved; however no information was given of the endurance of the experiments. [33] Finally, oxygen carriers based on Ni, Mn and Fe have been used in a 300 W CLC reactor with both syngas and natural gas. [34-37] The same reactor was also used with nickel oxides in testing of CLR (a). [8] This reactor was designed specifically for testing smaller amounts of oxygen carrier material in a continuous fashion and was based on a cold-flow model tested by Kronberger et al. [38]

Table 1. Testing in chemical-looping combustors

	unit	particle	operation h (hot time^a)	Fuel^b	Reference
1	Chalmers 10 kW	$NiO/NiAl_2O_4$	105 (300^a)	n.g.	[28, 29]
2	Chalmers 10 kW	Fe_2O_3-based	17	n.g.	[29]
3	S Korea 50 kW	$Co_3O_4/CoAl_2O_4$	25	n.g.	[31]
4	S Korea 50 kW	NiO/bentonite	3^d	n.g.	[31]
5	Chalmers 300 W	$NiO/NiAl_2O_4$	8 (18^a)	n.g.	[34]
6	Chalmers 300 W	$NiO/MgAl_2O_4$	30 (150^a)	n.g./s.g.	[34, 35]
7	Chalmers 300 W	Mn_3O_4/ $ZrO_{2,\ Mg\text{-}stab.}$	70 (130^a)	n.g./s.g.	[36]
8	Chalmers 300 W	Fe_2O_3/Al_2O_3	40 (60^a)	n.g./s.g.	[37]
9	CSIC, 10 kW	CuO/Al_2O_3	2x60 (2x100^a)	n.g.	[32]
10	Chalmers 300 W	$NiO/MgAl_2O_4$	41 (CLR)^c	n.g.(CLR ^{c})	[8]
11	S Korea, 1 kW	NiO-Fe_2O_3/bentonite	?	CH_4	[33]

^{a} total time fluidized at high temperature, ^{b}n.g. = natural gas, s.g. = syngas, ^{c}chemical-looping reforming, ^{d}particles fragmentated

Oxygen carrier development

Most of the work on CLC has been focused on the development and testing of oxygen carriers in particle form. Initial ideas to suitable oxygen carrier material for CLC and CLR(a,s) are mainly taken from heterogeneous catalysis used for reforming of hydrocarbon fuel. However, it is important to point out that knowledge from research on catalysts for reforming is insufficient. The reason for this is that both CLC and CLR(a,s) are based on primary non-catalytic reactions and that the oxygen carriers act as a source of undiluted oxygen (i.e. without nitrogen). Even though the primary focus of CLC and CLR(a,s) differs, the exothermic oxidation of oxygen carriers with air in the air reactor is the driving force for the, most often, endothermic reactions in the fuel reactor. Because of the need to transfer large amounts of oxygen between the air and fuel reactor, the oxygen carriers for chemical-looping technologies have high ratios of active material to inert material (typically 20-80%), as compared to heterogeneous catalyst where the fraction of active material typically is less than 10%.

Almost all research on oxygen carriers have been directed towards finding suitable materials for CLC. For CLR (a) only a limited amount of papers exist. [8, 10, 39, 40] . For CLR(s) the fuel feed mixture consists of reactive CH_4, CO and H_2 and unreactive CO_2. Earlier studies of oxygen carriers clearly indicate that methane is much more difficult to convert than CO and H_2. [41, 42] Therefore the development of oxygen carriers for burning methane-rich fuels in CLC is highly relevant for CLR(s).

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

- High reactivity with fuel and oxygen
- Low fragmentation and abrasion
- Low tendency for agglomeration
- Low production cost and preferably being environmentally sound.

For CLC and CLR(s) you have the additional requirement:

- Able to convert the fuel to CO_2 and H_2O to the highest degree possible (ideal 100%)

With respect to the ability of the oxygen carrier to convert a fuel gas fully to CO_2 and H_2O for CLC, Mattisson and Lyngfelt investigated the thermodynamics of a few possible oxygen carriers and concluded that the metal oxide/metal (or metal oxide of lower oxidation state) systems of NiO/Ni, Mn_3O_4/MnO, Fe_2O_3/Fe_3O_4, Cu_2O/Cu, CoO/Co were feasible to use as oxygen carriers. [43] Recently a comprehensive study was made by Jerndal et al where 27 different possible systems for CLC were investigated with respect to thermodynamics, melting points, oxygen ratio, fate of possible sulfur species in the fuel and carbon deposition. [44] Again, the same metal oxides were mentioned as suitable candidates. For the often studied NiO/Ni system there is one slight disadvantage, the conversion of fuel to CO_2 is not complete, although very high, 98.8 % at 1000 °C, and higher at lower temperatures. For CoO/Co the same problem exists, however with much less favorable thermodynamics, 93.0 % conversion at 1000 °C, and higher at lower temperatures. In practice it means that the CO_2 will contain combustible gases, i.e. CO and H_2, if these systems are used. As previously mentioned, these can either be separated and recycled or oxidized by adding oxygen downstream of the fuel reactor. However, since full conversion to CO_2 and H_2O is not desired in CLR(a), the thermodynamics of nickel and cobalt are not a disadvantage for this application.

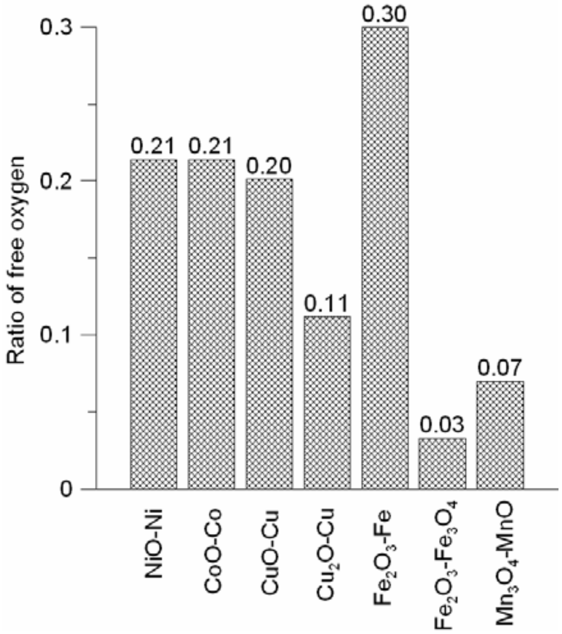


Figure 4. Amount of active material in different oxygen carrier material.

The oxygen carrier must also react at a sufficient rate. As the amount of oxygen carrier needed in the reactors is directly related to the reactivity of the oxygen carrier, a fast rate would mean less material and thus smaller reactor sizes and less material production costs. In relation to this, the oxygen carriers must also be able to transfer a sufficient amount of oxygen to the fuel to complete oxidation. This is directly related to the amount of active oxygen in the oxygen carrier and is dependent on the oxygen carrier used as well as the amount of inert material in the particle. The oxygen transfer capacity, i.e. the ratio of free oxygen in the carrier, for some of the different systems can be seen in Figure 4. Included in this figure is the amount of oxygen for Fe_2O_3/Fe, which is significantly higher than Fe_2O_3/Fe_3O_4. The reason why a transition to pure Fe^0 or FeO was not of interest in studies regarding CLC is the thermodynamical limitations for converting the fuel completely to CO_2 and H_2O, which limits its use for CLC and CLR(s). [44] The reason why Mattisson and Lyngfelt and Jerndal et al described Cu_2O/Cu as the proposed system for copper is that CuO can decompose to Cu_2O, depending on the reactor temperature and partial pressure of oxygen. As an example, if the partial pressure of oxygen in the air reactor is 4%, which is a valid assumption in the air reactor in CLC, a temperature of 944°C or higher means that CuO decomposes. Because of the low melting temperature of Cu, in practice a lower temperature may need to be used in a CLC system and thus the active system will be CuO/Cu, which naturally has a higher amount of available oxygen. [32]

During the last decade a lot of research on oxygen-carrier particles for chemical-looping combustion has been performed, see Table 2 for a review. The major contributors have been Tokyo Institute of Technology in Japan, Chalmers University of Technology in Göteborg, Sweden, CSIC in Zaragoza, Spain and Korea Institute of Energy Research. It should be acknowledged that all of the early research on oxygen carrier development in the 1990's has been performed by the former research group led by Professor Ishida. As can be seen from the table, most of the active metal oxides are combined with an inert material, such as Al_2O_3. There are some studies on non-supported materials, such as iron ore. [45] Although such material may have low costs, reactivity experiments simulating chemical-looping combustion performed on natural ores or unsupported metal oxides, have shown fast degeneration or low reactivity of these material. [4, 43, 46, 47] The use of inert material is believed to increase the porosity and reactivity of the particles, help to maintain the structure and possibly also increase the ionic conductivity of the particles. Even though the ratio of free oxygen in a particle decreases with the addition of inert material, the reactivity with the fuel and oxygen can still be higher due to the increased porosity. [4]

Table 2. Literature data on oxygen carriers for chemical-looping combustion

Reference	Ref #	Oxygen carrier (Me_xO_y/support)	Reduction agent	T_{red} (°C)	D_p (mm)	Apparatus	Notes
Nakano et al. 1986[a]	[48]	Fe_2O_3, Fe_2O_3-Ni, Fe_2O_3/Al_2O_3	H_2, H_2O/H_2	700-900	0.007	TGA	a
Ishida and Jin 1994	[4]	NiO, NiO/YSZ, Fe_2O_3/YSZ	H_2, H_2O/H_2	550, 600, 750, 950	1.3 - 2.8	TGA	b, c
Ishida et al. 1996	[49]	NiO/YSZ	H_2	600, 800, 1000	1.8, (1.0 - 3.2)[c]	TGA	c, u
Ishida and Jin 1996	[50]	NiO, NiO/YSZ	H_2	600	2	TGA	d
Hatanaka et al. 1997	[51]	NiO	CH_4	400, 500, 600, 700	0.074	FxB	
Ishida and Jin 1997	[52]	NiO/YSZ, NiO/Al_2O_3, Fe_2O_3/YSZ,	H_2, CH_4, H_2O/CH_4	600, 700, 750	2	TGA	e
Ishida et al. 1998	[53]	NiO/YSZ, NiO/Al_2O_3, NiO/TiO_2, Fe_2O_3/YSZ, Fe_2O_3/ Al_2O_3, Fe_2O_3/TiO_2	H_2/N_2, CO/N_2, $CO/N_2/CO_2$, $CO/N_2/H_2O$	550, 600, 700, 800, 900	1.6	TGA	e

Jin et al. 1998	[54]	NiO/YSZ, Fe_2O_3/YSZ, CoO/YSZ, CoO-NiO/YSZ	H_2, CH_4	600	1.8	TGA	e
Ishida et al. 1999	[55]	NiO/$NiAl_2O_4$	H_2	600, 900, 1100	0.097	CFzB	
Jin et al. 1999	[56]	NiO/Al_2O_3, NiO/TiO_2, NiO/MgO, CoO/Al_2O_3, CoO/TiO_2, CoO/MgO, Fe_2O_3/ Al_2O_3, Fe_2O_3/ TiO_2, Fe_2O_3/MgO	H_2, H_2O/CH_4	600, 700	1.8	TGA	e, f
Stobbe et al. 1999	[10]	Manganese Oxides	CH_4/Ar, H_2/Ar	20-827	0.15-0.5	-	m, t
Copeland et al. 2000	[57]	CuO-based, Fe_2O_3-based on alumina, aluminates and silicates	$CO_2/H_2/CH_4$	800	Fine powder	TGA	
Mattisson et al. 2000	[58]	$Fe_2O_3^j$, Fe_2O_3/ Al_2O_3, Fe_3O_4	CH_4	950	0.12-0.50	FxB	
Copeland et al. 2001	[59]	Fe_2O_3-based, NiO-based	H_2/CH_4, Syngas	720-1050	-^{i}	TGA, FzB	
Jin and Ishida 2001	[60]	NiO, NiO/YSZ, NiO/Al_2O_3	H_2, H_2/Ar	600	1.8, 2.1, 4.0×1.5^g	TGA, FxB	m
Mattisson et al. 2001	[45]	$Fe_2O_3^j$	CH_4	950	0.18-0.25	FxB	
Ryu et al. 2001	[61]	NiO/bentonite^k, Ni/bentonite^l	CH_4/N_2	650, 700, 750, 800, 850, 900	0.080	TGA	u
Cho et al. 2002	[62]	Fe_2O_3/Al_2O_3, Fe_2O_3/MgO	CH_4	950	0.125-0.18, 0.18-0.25	FzB	
Copeland et al. 2002	[63]	Fe_2O_3-based, NiO-based	Syngas	780	-^{i}	FzB	
Ishida et al. 2002	[64]	NiO/$NiAl_2O_4$	H_2, H_2/Ar^h	600, 900, 1100, 1200	0.097	TGA, CFzB	h
Jin and Ishida 2002	[65]	NiO/YSZ, NiO/Al_2O_3, CoO-NiO/YSZ	H_2O/CH_4	600, 700, 800^f	4.0×1.5^g	TGA, FxB	e, f
Ryu et al. 2002	[66]	NiO/bentonite	CH_4/N_2	650, 700, 750, 800, 850, 900, 950, 1000	0.091	TGA	e
Johansson M. 2002	[67]	NiO/TiO_2, Fe_2O_3/TiO_2, CuO/ TiO_2, MnO_2/ TiO_2	CH_4, H_2O/CH_4	700, 725, 750, 800, 850, 900	1.5-2×2.5-3^g	TGA	
Adánez et al. 2003	[68]	CuO/SiO_2	CH_4	600-850	1	TGA	
Brandvoll et al. 2003	[69]	NiO/$NiAl_2O_4$	H_2	600-850	0.3-0.5, 0.6-1.0, 1.2-1.7, 2.0-3,5	FxB/FzB	u
Jeong et al.^{s}, 2003	[70]	$CoO_x/CoAl_2O_4$, NiO/$NiAl_2O_4$	H_2/Ar, CH_4/Ar/He	150-1000	-	TGA	s,m
Lee et al.^{s} 2003	[71]	NiO/YSZ, CoO/YSZ, Fe_2O_3/YSZ, NiO-Fe_2O_3/YSZ	-	-	-	TGA	s

Mattisson et al. 2003	[72]	NiO/Al_2O_3, CuO/Al_2O_3, CoO/Al_2O_3, Mn_3O_4/Al_2O_3	$H_2O/CO_2/N_2/CH_4$	750, 850, 950	0.1-0.5	TGA	
Ryu et al. 2003	[73]	NiO/bentonite	CH_4/N_2, H_2	500, 600, 700, 800, 900, 1000	0.091, 0.128, 0.4	TGA, FxB	e
Ryu et al. 2003^s	[74]	NiO/Bentonite, NiO/YSZ, $(NiO+Fe_2O_3)$/YSZ, $NiO/NiAl_2O_4$, $Co_xO_y/COAl_2O_4$	H_2/N_2, CH_4/N_2	50-1000	-	TGA	m
Ryu et al. 2003	[75]	NiO/bentonite	CH_4/N_2	650, 700, 750, 800, 850, 900, 950, 1000	0.091	TGA	e
Song et al. 2003	[76]	NiO/hexaaluminate	H_2/Ar	25 – 1000	-	TGA	m
Villa et al. 2003	[77]	$NiO/NiAl_2O_4$, $Ni_{1-y}Mg_yAl_2O_4$	H_2, CH_4/He, CH_4, CH_4/H_2O	800, 25 – 1000	-	TGA	e, m, v
Adánez et al. 2004	[78]	CuO, Fe_2O_3, MnO_2, NiO with Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2	CH_4/H_2O	800, 950	2×4^g	TGA	
Adánez et al. 2004	[79]	CuO, Fe_2O_3, MnO_2, NiO with Al_2O_3, SiO_2, TiO_2, ZrO_2	CH_4/N_2	800, 950	0.1-0.3	TGA, FzB	
Cho et al. 2004	[80]	Fe_2O_3/Al_2O_3, Fe_2O_3/Kaolin, $NiO/NiAl_2O_4$, $CuO/CuAl_2O_4$, Mn_3O_4 with $MnAl_2O_4$	CH_4/H_2O	850, 950	0.125-0.18	FzB	k
de Diego et al. 2004	[46]	CuO with Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2	CH_4, H_2, or CO/H_2 in H_2O	800	0.2-0.4	TGA	
García-Labiano et al. 2004	[42]	CuO/Al_2O_3	$CH_4/CO_2/H_2O$, $H_2/CO_2/H_2O$ $CO/CO_2/H_2O$	500-800	0.1-0.3	TGA	u
Jin and Ishida 2004	[81]	$NiO/NiAl_2O_4$, CoO-NiO/YSZ	$CO/H_2/H_2O/Ar/CO_2$, $CO/H_2/H_2O/Ar$, CH_4/H_2O	600, 700	4.0×1.5^g	FxB	f
Johansson M et al. 2004	[82]	$Fe_2O_3/MgAl_2O_4$	CH_4/H_2O	650-950	0.09-0.125 0.125-0.18 0.18-0.25	FzB	c
Kim et al. 2004	[83]	NiO/ $NiAl_2O_4$	H_2	600	1-2	TGA	
Lee et al. 2004	[84]	NiO with $AlPO_4$, ZrO_2, YSZ, $NiAl_2O_4$	H_2	600	-	TGA	
Mattisson et al. 2004	[85]	Fe_2O_3 with Al_2O_3 (some with kaolin), ZrO_2, TiO_2, $MgAl_2O_4$	CH_4/H_2O	950	0.125-0.18	FzB	
Mattisson et al. 2004	[86]	CuO/SiO_2, NiO/SiO_2	CH_4/H_2O	800	0.18-0.25	FzB	t
Ryu et al. 2004 ^{s}	[87]	NiO-based Ni-based	CH_4/N_2	25-1000	0.081, 0.091	TGA, FxB	s
Ryu et al. 2004	[31]	NiO/bentonite, $Co_xO_y/CoAl_2O_4$	CH_4	750, 869	0.106-0.212	CFzB	h,o

Brandvoll 2005	[88]	$NiO/NiAl_2O_4$, Perovskite^n	H_2, CH_4, CH_4/H_2O	600, 700, 800	0.02-0.2, 0.09-0.2, 0.4-2.6	FxB/FzB	
Cao et al, 2005	[89]	CuO	Coal	50-900^m	-	TGA	m, x
Cho et al. 2005	[90]	Fe_2O_3/Al_2O_3, $NiO/NiAl_2O_4$	CH_4, CH_4/H_2O	750, 850, 950	0.125-0.18	FzB	e
Corbella et al. 2005	[91]	CuO/TiO_2	H_2/Ar, CH_4	100-950^m 800, 900	0.2-0.4	FxB	m
Corbella et al. 2005	[92]	NiO/TiO_2	H_2/Ar, CH_4/Ar	100-1000^m, 900	0.2-0.5	FxB	e, m
de Diego et al. 2005	[93]	CuO/Al_2O_3	CH_4/N_2, H_2	800, 950	0.1-0.32	TGA, FzB	p
De los Rios et a, 2005l	[94]	Co_xTiO_y	H_2/Ar	0-700^m, 700	-	TGA	m, t
Gupta et al, 2005	[95]	Fe_2O_3,Fe-Ti-O	Coal, H_2/N_2	0-900^m	-	TGA	m, x
Ishida et al, 2005	[96]	Fe_2O_3/Al_2O_3	H_2	900	0.07	TGA	v
Lee et al. 2005	[47]	CoO/YSZ, Fe_2O_3/ YSZ, NiO, NiO with ZrO_2, YSZ, $AlPO_4$, $NiAl_2O_4$	H_2	600	2	TGA	
Lyngfelt and Thunman 2005	[29]	NiO based, Fe_2O_3 based	Natural gas	560-900	-	CFzB	h,r
Readman et al, 2005	[97]	Perovskite^n	H_2/He	800	-	TGA	
Roux et al. 2005	[98]	CaO, CuO, Fe_2O_3, MgO, MnO_2, NiO, TiO_2, Al_2O_3	CH_4	550-950	0.0019-0.093	TGA	
Zafar et al. 2005	[39]	NiO, CuO, Mn_2O_3, Fe_2O_3 with SiO_2	CH_4/H_2O	700-950	0.18-0.25	FzB	t
Abad et al, 2006	[36]	Mn_3O_4/Mg-ZrO_2	Natural gas, Syngas	800-1000	0.09-0.212	CFzB	h, q
Abad et al, 2006	[37]	Fe_2O_3/Al_2O_3	Natural gas, Syngas, CH_4	800-950	0.09-0.212	FzB, CFzB	h,q
Adánez et al 2006	[99]	NiO/Al_2O_3, CuO/Al_2O_3, NiO-CuO/Al_2O_3 some with K_2O or La_2O_3	$CH_4/H_2O/N_2$ (TGA), CH_4 or CO or H_2 (FxB) , CH_4/N_2 (FzB)	950	0.1-0.3	TGA, FxB, FzB	
Adánez et al 2006	[32]	CuO/Al_2O_3	CH_4	700-800	0.1-0.3, 0.2-0.5	CFzB	r
Cao et al, 2006	[100]	CuO	PRB Coal, Wood, Polyethene with N_2 & CO_2	0-1000	0.050-0.150	TGA	x
Cho et al. 2006	[101]	Fe_2O_3/Al_2O_3, $NiO/NiAl_2O_4$, Mn_3O_4/Mg-ZrO_2	CH_4	950	0.125-0.18	FzB	p
Corbella et al, 2006	[102]	NiO/TiO_2	CH_4, CH_4/N_2, H_2/Ar^m	900, 0-950^m	0.2-0.4	FxB	m

Corbella et al, 2006	[103]	CuO/SiO_2	CH_4, CH_4/Ar^m, H_2/Ar^m	800, 0-950^m	0.2-0.4	FxB	m
García-Labiano et al. 2006	[104]	Fe_2O_3/Al_2O_3, $NiO/NiAl_2O_4$, CuO/Al_2O_3	H_2/N_2, $CO/CO_2/N_2$, $CO/H_2O/CO_2$, $H_2/H_2O/CO_2$	800, 450-950	0.15-0.2	TGA	f,u
Johansson E. et al. 2006	[35]	$NiO/MgAl_2O_4$	Natural gas	800 - 950	0.09-0.212	CFzB	h,q
Johansson E. et al. 2006	[34]	$NiO/MgAl_2O_4$, NiO based	Natural gas, Syngas	800 - 950	0.09-0.212	CFzB	h,q
Johansson M. et al. 2006	[105]	Fe_2O_3, Mn_3O_4 and NiO on different inerts	CH_4/H_2O	950	0.125-0.18	FzB	
Johansson M. et al. 2006	[106]	Fe_2O_3, Mn_3O_4, CuO and NiO on different inerts	CH_4/H_2O	950	0.125-0.18	FzB	
Johansson M. et al. 2006	[107]	Mn_3O_4 on ZrO_2, Mg-ZrO_2, Ca-ZrO_2 and Ce- ZrO_2	CH_4/H_2O	950	0.125-0.18	FzB	
Johansson M. et al. 2006	[30]	$NiO/NiAl_2O_4$	CH_4/H_2O	950	0.09-0.125	FzB	
Johansson M. et al. 2006	[108]	$NiO/MgAl_2O_4$, $Fe_2O_3/MgAl_2O_4$	CH_4/H_2O	650-950	0.125-0.18	FzB	
Mattisson et al. 2006	[109]	NiO with $NiAl_2O_4$, $MgAl_2O_4$, TiO_2, ZrO_2	CH_4/H_2O	950	0.125-0.18	FzB	k, w
Mattisson et al. 2006	[41]	$NiO/MgAl_2O_4$, Mn_3O_4/Mg-ZrO_2, Fe_2O_3/Al_2O_3	Syngas, CH_4	650-950	0.18-0.25	FzB	
Mattisson et al. 2006	[110]	$NiO/NiAl_2O_4$	CH_4/H_2O, $CH_4/H_2O/CO_2/N_2$ (TGA)	750-950	0.09-0.125 0.125-0.18 0.18-0.25	TGA, FzB	c,e
Readman et al. 2006	[111]	$NiO/NiAl_2O_4$	H_2/Ar, CH_4/He	800	0.09-0.21	TGA	u
Rydén et al 2006	[8]	$NiO/MgAl_2O_4$	Natural gas (+steam)	820-930	0.09-0.212	CFzB	h,q,t
Scott et al 2006	[112]	Fe_2O_3	Lignite + $H_2O/CO_2/N_2$	900	0.300-0.425, 0.425-0.710	FzB	x
Son and Kim 2006	[33]	NiO and Fe_2O_3 on TiO_2, Al_2O_3 and bentonite, NiO-Fe_2O_3/bentonite	$CH_4/H_2O/CO_2/N_2$ (TGA) CH_4 (CFzB)	650-950	0.106-0.15	TGA, CFzB	d,u
Zafar et al. 2006	[40]	NiO, CuO, Mn_2O_3, Fe_2O_3 with SiO_2 and $MgAl_2O_4$	$CH_4/H_2O/CO_2/N_2$	800-1000	0.18-0.25	TGA	t

D_p = particle diameter
TGA = Thermogravimetric analyzer
FxB = Fixed bed
FzB = Fluidized bed
CFzB = Circulating fluidized beds, i.e. chemical-looping combustor
[a] In Japanese

[b] Effect of H_2O on reduction/oxidation
[c] Effect of particle size on reduction/oxidation
[d] No NO_x formation at 1200°C
[e] Study of carbon deposition
[f] Effect of pressure
[g] Cylindrical form, diameter×height
[h] Data from continuous CLC reactor
[i] Spray dried particles.
[j] Natural iron ore.
[k] Study of reduction
[l] Study of oxidation
[m] Temperature programmed reduction
[n] $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$
[o] 50 kW Chemical-Looping Combustor
[p] Study of de-fluidization
[q] 300 W Chemical-Looping Combustor
[r] 10 kW Chemical-Looping Combustor
[s] In Korean
[t] Chemical Looping reforming
[u] Study on kinetics
[v] Pulse experiment
[w] Study on sulfur
[x] Study on solid fuel

The literature given in Table 2 only includes primary sources, and excludes some papers which repeat information given in other published papers.

It is difficult to give a detailed review of the results from these studies, because reactivity data is very dependent upon oxygen carrier system, preparation method, particle size, fuel gas as well as reactor type. However, some general conclusions can be made from all these studies regarding oxygen carriers for CLC ;

- Nickel oxides and copper oxides are by far the most reactive oxygen carrier materials
- Copper oxides have a disadvantage of being apt to de-fluidize and agglomerate, although some researchers have prepared well suited particles based on copper [32, 93]
- Nickel oxides can not totally convert the fuel gases to CO_2 and H_2O. Besides, reduced Ni^o catalyzes steam reforming and carbon formation
- The reduction reactivity is faster with H_2 and CO as a fuel than with CH_4
- Reactivity generally increases with reaction temperature, although high reactivity has also been seen at rather low temperatures in many cases
- No real correlation between particle size and reactivity has been established

There are a few works by Adanez et al. [78] and Johansson et al. [105, 106, 113] which have compared a large number of different oxygen carriers. Johansson compared the reactivity with methane of a large number of particles using a rate index. The rate index is a rate of reaction normalized to an average concentration of methane in a certain interval of conversion of the particles. As only one number is obtained per oxygen carrier, it gives a good basis for comparison of different oxygen carriers. Figure 5 shows this rate index as a function of the crushing strength of a large number of particles based on Ni, Mn and Fe prepared by freeze granulation. The rate index is generally highest for the particles of low crushing strength, which can be explained by the higher porosity of these particles. Clearly the nickel based oxygen carriers have the highest reactivity.

Design criteria

The reactivity will determine the minimum needed solids inventory, [24] and the rate index presented in Fig. 5 has been correlated to the needed bed mass in the fuel reactor (kg/MW_{CH4}) using an estimation with simplified and transparent assumptions. This mass is indicated on the right y-axis in the figure, see [105] for calculation procedure. No similar calculations on the mass inventory of the air-reactor have been performed; however, its is expected that a smaller mass inventory is needed compared to that in the fuel reactor, due to the faster oxidation reaction. It is clearly seen that there is a large difference in needed mass inventory for the most reactive nickel oxygen carriers compared to the ones based on iron and manganese. A low solid mass inventory would result in a smaller reactor needed, which lowers the capital costs of a combustor. The upper limit for the amount of bed material needed, with respect to technical and economical feasibility, will depend on a number of circumstances and cannot easily be set. Lyngfelt et al suggested that solid mass inventories of less than 500 kg/MW_{fuel} might be acceptable. [24] Based on this assumption, a majority out of the tested oxygen carriers would be appropriate for chemical-looping combustion.

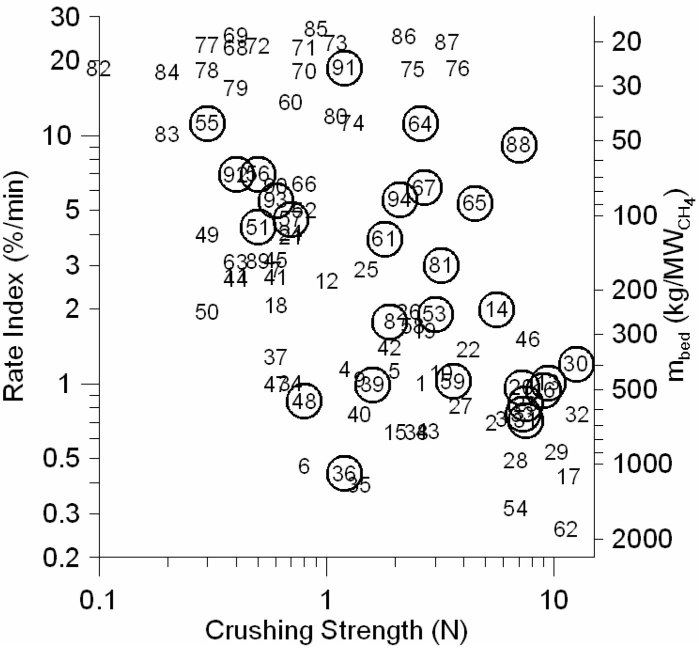


Figure 5. Rate Index vs. crushing strength for freeze granulated particles. Circle around number indicates de-fluidization. For comparison corresponding solid mass inventory needed in the fuel reactor is included. Fe-based oxygen carriers: 1-39, Mn-based particles: 40-63, Cu-based: 64-67 and Ni-based oxygen carriers: 68-94. Data from Johansson et al [105, 106]

The group of Adanez has calculated recirculation rates and solids inventories based on kinetic data of Ni-, Fe- and Cu-based oxygen carriers using CH_4, CO and H_2 as fuel. [42, 114] The recirculation rate of oxygen carrier is related to the conversion variation obtained in the oxygen carrier in the fuel and air reactors. At a reasonable conversion difference, the recirculation rates were ~12 kg/s,MW, ~15 kg/s,MW, and ~3 kg/s,MW for the Cu-, Fe- and Ni-based oxygen carriers tested. The minimum solids inventories depended on the fuel gas used, and followed the order CH_4>CO>H_2. The minimum solids inventories ranged from 40 to 170 kg/MW_f for the three investigated carriers. [114]

Conclusions

Chemical-looping combustion is an unmixed combustion technology which captures CO_2 by completely avoiding any gas separation. Thus, it is fundamentally different from the major paths for CO_2 capture studied, which all involve a major step of gas separation. Not surprisingly, the process studies performed have shown high efficiencies in comparison to other capture techniques. As seen in Table 1 and 2, there is extensive research currently being performed and the results with respect to oxygen carrier development and prototype testing is highly promising. Two types of chemical-looping reforming used for the production of hydrogen are also under investigation. The research of these is quite new and very little is published so far. Nevertheless, the first studies display promising results, theoretical as well as experimental.

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