CHEMICAL-LOOPING COMBUSTION
-
STATUS OF DEVELOPMENT

A. Lyngfelt, M. Johansson, and T. Mattisson

Chalmers University of Technology, S-412 96 Göteborg, Sweden

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 years with respect to oxygen carrier development, reactor design, system efficiencies and prototype testing. In 2002 the process was a paper concept, albeit with some important but limited laboratory work on oxygen carrier particles. Today more than 600 materials have been tested and the technique has been successfully demonstrated in chemical-looping combustors in the size range 0.3 – 50 kW, using different types of oxygen carriers based on the metals Ni, Co, Fe, Cu and Mn. The total time of operational experience is more than a thousand hours. From these tests it can be established that almost complete conversion of the fuel can be obtained and 100% CO_2 capture is possible. Most work so far has been focused on gaseous fuels, but the direct application to solid fuels is also being studied. Moreover, the same principle of oxygen transfer is used in chemical-looping reforming (CLR), which involves technologies 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

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 gas separation and no gas separation 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:

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

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):

$$Me_xO_{y-1} + ½O_2 \rightarrow Me_xO_y \qquad (2)$$

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 the need of any active separation of gases. This paper will present an overview of the work which has been carried out with focus on experimental accomplishments. The metal oxides used for the oxygen transfer, are called oxygen carriers. Most of the work so far has been directed towards the application where the reactor system is made up by two interconnected fluidized beds, with the oxygen carrier in the form of particles being circulated between the two beds, Fig. 2. Clearly, the need to develop suitable

oxygen-carrier materials for the process, and comprehensive testing of these under realistic conditions is one of the cornerstones in the development of this technology. Another issue is of course to adapt the comprehensive experience from circulating fluidized bed boilers to this application.

The work on CLC so far has been mainly focused on the application to gaseous fuels, but liquid and solid fuels are other options. Moreover, the process can also be modified to be suitable for chemical-looping reforming, CLR, in order to capture CO_2 while producing a carbon-free fuel, H_2. For instance, the looping process can be used for the partial oxidation of fuel to produce a syngas suitable for reforming, i.e. autothermal chemical-looping reforming, CLR(a).

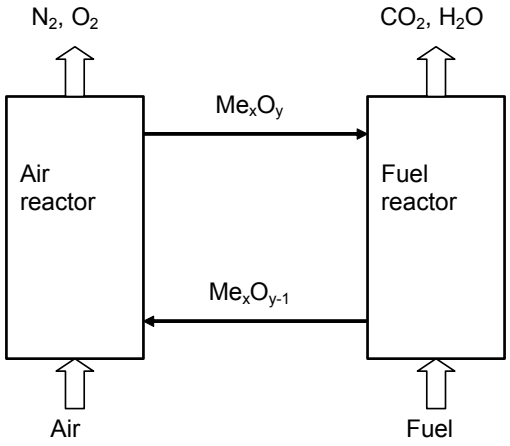

Fig. 1. Chemical-looping combustion. Me_xO_y/Me_xO_{y-1} denotes recirculating oxygen carrier material.

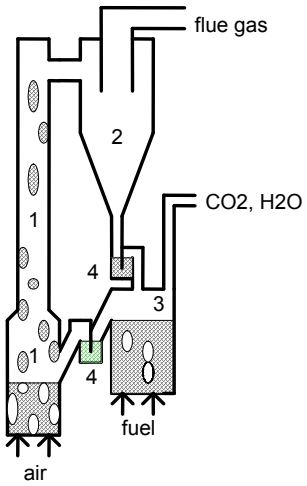

Fig. 2. CLC process, with two fluidized reactors. 1) air reactor, 2) cyclone, 3) fuel reactor, 4) particle locks

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 CO_2 and H_2O
- Low fragmentation and attrition, as well as low tendency for agglomeration
- Low production cost and preferably being environmentally sound.

Table 2 gives an overview of the development work on oxygen carrier particles. Major contributors are Tokyo Institute of Technology, Chalmers University of Technology in Sweden, CSIC-ECB in Spain and Korea Institute of Energy Research. All of the early oxygen carrier development was made by the Japanese group led by Professor Ishida. Totally, the table includes more than 600 tested materials, of which the majority was tested by CSIC, 50%, and Chalmers, 25%, while the contributions from Japan, S. Korea, North America and remaining Europe, are around 6-7% each. A large part of the CSIC/Chalmers work was financed by EU, e.g. the GRACE project. 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, [1] 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. [2-5] 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. [2]

The ability of the oxygen carrier to convert a fuel gas fully to CO_2 and H_2O, has been investigated thermodynamically and the metal oxide systems of NiO/Ni, Mn_3O_4/MnO, Fe_2O_3/Fe_3O_4, Cu_2O/Cu, CoO/Co were found to be feasible to use as oxygen carriers. [3] 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.

The four oxides of copper, iron, manganese and nickel have advantages and disadvantages, as can be seen in Table 1. Note for instance that most reactive particles are unfortunately also the most expensive. For NiO

there are also health aspects to be considered. Furthermore, NiO also differs from the other oxides by having a thermodynamic restriction; it cannot convert fuels fully to CO_2 and H_2O, with a maximum conversion of 99-99.5%. All the oxides have a more or less exothermic reaction in both reactors, if the fuel is H_2 or CO, but with methane the reaction is endothermic, for all the oxides except CuO. This is clearly an advantage for CuO, since it reduces the particle circulation needed to maintain fuel reactor temperature. On the other hand, Cu has the disadvantage of a low melting temperature.

Table 1: Qualitative estimation of pros and cons for the active oxides

	Fe_2O_3/Fe_3O_4	Mn_3O_4/MnO	CuO/Cu	NiO/Ni	comments
R_0	0.03	0.07	0.20	0.21	Oxygen ratio
Reactivity	←decreasing		increasing→		
Cost	←decreasing		increasing→		
Health & Environm.				-	
Thermodynamics				-	<99.5% conv. for NiO
Reaction with CH4			+		CuO exothermic w. CH4
Melting point			-		1085°C for Cu

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, R_0, i.e. the ratio of free oxygen in the carrier, for some of the different systems can be seen in Table 1.

There are a few works by Adanez et al. [6] and Johansson et al. [7-9] which have compared a large number of different oxygen carriers. These generally indicate a large difference in reactivity between the different oxides following the ranking shown in Table 1. However, most the reactivity comparisons are focused on CH_4. In general, the reactivity is significantly higher using H_2 and CO compared to CH_4, and may be quite high for cheaper materials showing low reactivity with CH_4.

Reactivity may increase significantly with reaction temperature, especially in the case of low reactivity materials and CH_4. On the other hand the reactivity of iron and manganese materials with CO and H_2, may be high also at lower temperatures, the same applies to nickel materials with CH_4.

Thus, it is clear that there are advantages and disadvantages with the different oxide systems, and the choice of oxygen-carrier will be dependent on the application.

It should be pointed out that the potential for varying the properties of the materials are vast:

- there are several possible active oxygen carrier materials, and in addition to the oxides of copper, iron, manganese and nickel, there may also be a number of mixed oxides with suitable properties.
- there are a very large number of potential supporting materials
- the proportions of the active and supporting materials may be varied
- there are a many possible methods of particle production, and for each method a number of parameters by which the particle properties can be varied, e.g time and temperature of heat treatment
- the properties of the starting materials may vary depending on the source (supplier) for the materials. These properties include physical properties like particle size and porosity, oxidation state, chemical purity and contaminations etc. Moreover, starting materials can range from chemically pure (expensive) to natural minerals (highly contaminated but often inexpensive).

In short the large number of possibilities gives rise to an infinite number of possible materials with varying properties. To add some further complication to this, the optimal properties are not known per se, because the optimal properties vary depending on the application and will be a function of an optimization of the whole process for the given application. In addition some of the properties may be difficult to assess safely. Properties like particle production costs, lifetime, as well as possible health and environmental aspects may not easily be precisely quantified in simple tests or estimations, although indicative numbers or qualitative rankings can be achieved.

Table 2. Literature data on oxygen carriers for chemical-looping combustion. The literature given in Table 2 only includes primary sources, and excludes some papers which repeats information given in other published papers.

Reference	Ref	Oxygen carrier (Me_xO_y/support)	# O.C. (new)	Reduction agent	T_{red} (°C)	D_p (mm)	Apparatus	Note
Nakano et al. 1986[a]	[10]	Fe_2O_3, Fe_2O_3-Ni, Fe_2O_3/Al_2O_3	3(3)	H_2, H_2O/H_2	700-900	0.007	TGA	a
Ishida and Jin 1994	[2]	NiO, NiO/YSZ, Fe_2O_3/YSZ	3(3)	H_2, H_2O/H_2	550 - 950	1.3 - 2.8	TGA	b, c
Ishida et al. 1996	[11]	NiO/YSZ	5(4)	H_2	600, 800, 1000	1.8, (1.0 - 3.2)[c]	TGA	c, u
Ishida and Jin 1996	[12]	NiO, NiO/YSZ	2(0)	H_2	600	2	TGA	d
Hatanaka et al. 1997	[13]	NiO	1(1)	CH_4	400 - 700	0.074	FxB	
Ishida and Jin 1997	[14]	NiO/YSZ, NiO/Al_2O_3, Fe_2O_3/YSZ,	3(1)	H_2, CH_4, H_2O/CH_4	600, 700, 750	2	TGA	e
Ishida et al. 1998	[15]	NiO and Fe_2O_3 on YSZ, Al_2O_3 and TiO_2	10(6)	H_2/N_2, CO/N_2, $CO/N_2/CO_2$, $CO/N_2/H_2O$	550- 900	1.6	TGA	e
Jin et al. 1998	[16]	NiO/YSZ, Fe_2O_3/YSZ, CoO/YSZ, CoO-NiO/YSZ	4(2)	H_2, CH_4	600	1.8	TGA	e
Ishida et al. 1999	[17]	$NiO/NiAl_2O_4$	1(1)	H_2	600, 900, 1100	0.097	CFzB	
Jin et al. 1999	[18]	NiO, CoO and Fe_2O_3 on Al_2O_3, TiO_2 and MgO; $NiO/NiAl_2O_4$, NiO/YSZ	11(5)	H_2, H_2O/CH_4	600, 700	1.8	TGA	e, f
Stobbe et al. 1999	[19]	Manganese Oxides	4(4)	CH_4/Ar, H_2/Ar	20-827	0.15-0.5	-	m, t
Copeland et al. 2000	[20]	CuO and Fe_2O_3 on alumina, aluminates and silicates	30(30)	$CO_2/H_2/CH_4$	800	Fine powder	TGA	
Mattisson et al. 2000	[21]	Fe_2O_3[j], Fe_2O_3/ Al_2O_3, Fe_3O_4	6(6)	CH_4	950	0.12-0.50	FxB	
Copeland et al. 2001	[22]	Fe_2O_3-based, NiO-based	?	H_2/CH_4, Syngas	720-1050	-[i]	TGA, FzB	
Jin and Ishida 2001	[23]	NiO, NiO/YSZ, $NiO/NiAl_2O_4$	3(0)	H_2, H_2/Ar	600	1.8, 2.1, 4.0×1.5[g]	TGA, FxB	m
Mattisson et al. 2001	[1]	Fe_2O_3[j]	1(0)	CH_4	950	0.18-0.25	FxB	
Ryu et al. 2001	[24]	NiO/bentonite[k], Ni/bentonite[l]	4(4)	CH_4/N_2	650 – 900	0.080	TGA	u
Cho et al. 2002	[25]	Fe_2O_3/Al_2O_3, Fe_2O_3/MgO	4(4)	CH_4	950	0.12-0.18, 0.18-0.25	FzB	
Copeland et al. 2002	[26]	Fe_2O_3-based, NiO-based	?	Syngas	780	-[i]	FzB	
Ishida et al. 2002	[27]	$NiO/NiAl_2O_4$	1(0)	H_2, H_2/Ar[h]	600 -1200	0.097	TGA, CFzB	h
Jin and Ishida 2002	[28]	NiO/YSZ, $NiO/NiAl_2O_4$, CoO-NiO/YSZ	3(0)	H_2O/CH_4	600, 700, 800[f]	4.0×1.5[g]	TGA, FxB	e, f
Ryu et al. 2002	[29]	NiO/bentonite	1(1)	CH_4/N_2	650 - 1000	0.091	TGA	e
Johansson M. 2002	[30]	NiO/TiO_2, Fe_2O_3/TiO_2, CuO/ TiO_2, MnO_2/ TiO_2	18(18)	CH_4, H_2O/CH_4	700- 900	1.5-2×2.5-3[g]	TGA	
Adánez et al. 2003	[31]	CuO/SiO_2	1(1)	CH_4	600-850	1	TGA	
Brandvoll et al. 003	[32]	$NiO/NiAl_2O_4$	3(3)	H_2	600-850	0.3-35	FxB/FzB	u
Jeong et al.[s] 2003	[33]	$NiAl_2O_4$, $CoAl_2O_4$, $CoO_x/CoAl_2O_4$, $NiO/NiAl_2O_4$	8(8)	H_2/Ar, CH_4/Ar/He	150-1000	-	TGA	s,m
Lee et al.[s] 2003	[34]	NiO/YSZ, CoO/YSZ, Fe_2O_3/YSZ, NiO-Fe_2O_3/YSZ	4(4)	-	-	-	TGA	s
Mattisson et al. 2003	[35]	NiO/Al_2O_3, CuO/Al_2O_3, CoO/Al_2O_3, Mn_3O_4/Al_2O_3	4(4)	H_2O/CO_2/ CH_4 /N_2	750, 850, 950	0.1-0.5	TGA	
Ryu et al. 2003	[36]	NiO/bentonite	1(0)	CH_4/N_2, H_2	500-1000, (ΔT=100)	0.091, 0.128, 0.4	TGA, FxB	e
Ryu et al. 2003[s]	[37]	NiO/bentonite, NiO/YSZ, $(NiO+Fe_2O_3)$/YSZ, $NiO/NiAl_2O_4$, $Co_xO_y/COAl_2O_4$	5(4)	H_2/N_2, CH_4/N_2	50-1000	-	TGA	m
Ryu et al. 2003	[38]	NiO/bentonite	1(0)	CH_4/N_2	650-1000 (ΔT=50)	0.091	TGA	e
Song et al. 2003	[39]	NiO/hexaaluminate	5(5)	H_2/Ar	25 – 1000	-	TGA	m
Villa et al. 2003	[40]	$NiO_x/NiAl_2O_4$, $Ni_{1-y}Mg_yAl_2O_4$	6(6)	H_2, CH_4/He, CH_4, CH_4/H_2O	800, 25 – 1000	-	TGA	e, m, v
Adánez et al. 2004	[6]	CuO, Fe_2O_3, MnO_2, NiO with Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2	240 (225)	CH_4/H_2O	800, 950	2×4[g]	TGA	
Adánez et al. 2004	[41]	CuO, Fe_2O_3, MnO_2, NiO with Al_2O_3, SiO_2, TiO_2, ZrO_2	26(2)	CH_4/N_2	800, 950	0.1-0.3	TGA, FzB	

Chahma et al. 2004	[42]	CuO, MgO, TiO_2, Al_2O_3, CuO/MgO, CuO/TiO_2, CuO/Al_2O_3	7(7)	CH_4	550, 650, 750	-	TGA	
Cho et al. 2004	[43]	Fe_2O_3/Al_2O_3, Fe_2O_3/Kaolin, NiO/$NiAl_2O_4$, CuO/$CuAl_2O_4$, Mn_3O_4 with $MnAl_2O_4$	7(7)	CH_4/H_2O	850, 950	0.125-0.18	FzB	k
de Diego et al. 2004	[4]	CuO with Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2	19(4)	CH_4, H_2, or CO/H_2 in H_2O	800	0.2-0.4	TGA	
García-Labiano et al. 2004	[44]	CuO/Al_2O_3	1(1)	$CH_4/CO_2/H_2O$, $H_2/CO_2/H_2O$ $CO/CO_2/H_2O$	500-800	0.1-0.3	TGA	u
Jin and Ishida 2004	[45]	NiO/$NiAl_2O_4$, CoO-NiO/YSZ	2(0)	$CO/H_2/H_2O/Ar/CO_2$, $CO/H_2/H_2O/Ar$, CH_4/H_2O	600, 700	4.0×1.5[g]	FxB	f
Johansson M et al. 2004	[46]	$Fe_2O_3/MgAl_2O_4$	15(11)	CH_4/H_2O	650-950	0.09- ..... -0.25	FzB	c
Lee et al. 2004	[47]	NiO with $AlPO_4$, ZrO_2, YSZ, $NiAl_2O_4$	7(6)	H_2	600	-	TGA	
Mattisson et al. 2004	[48]	Fe_2O_3 with Al_2O_3 (some with kaolin), ZrO_2, TiO_2, $MgAl_2O_4$	27(26)	CH_4/H_2O	950	0.125-0.18	FzB	
Mattisson et al. 2004	[49]	CuO/SiO_2	1(1)	CH_4/H_2O	800	0.18-0.25	FzB	t
Ryu et al., 2004 [s]	[50]	NiO/bentonite[k], Ni/bentonite[l]	5(0)	CH_4/N_2	25-1000	0.081, 0.091	TGA, FxB	s
Ryu et al. 2004	[51]	NiO/bentonite, $Co_xO_y/CoAl_2O_4$	2(1)	CH_4	750, 869	0.106-0.212	CFzB	h,o
Brandvoll 2005	[52]	NiO/$NiAl_2O_4$, Perovskite[n]	2(1)	H_2, CH_4, CH_4/H_2O	600, 700, 800	0.02- .... -2.6	FxB/FzB	
Cao et al, 2005	[53]	CuO	1(1)	Coal	50-900[m]	-	TGA	m,x
Cho et al. 2005	[54]	Fe_2O_3/Al_2O_3, NiO/$NiAl_2O_4$	2(0)	CH_4, CH_4/H_2O	750, 850, 950	0.125-0.18	FzB	e
Corbella et al. 2005	[55]	CuO, CuO/TiO_2	6(5)	H_2/Ar, CH_4	100-950[m] 800, 900	0.2-0.4	FxB	m
Corbella et al. 2005	[56]	NiO, NiO/TiO_2	5(5)	H_2/Ar, CH_4/Ar	100-1000[m], 900	0.2-0.5	FxB	e, m
de Diego et al.,2005	[57]	CuO/Al_2O_3	14(14)	CH_4/N_2, H_2	800, 950	0.1-0.32	TGA, FzB	p
De los Rios et a, 2005	[58]	Co_xTiO_y	2(2)	H_2/Ar	0-700[m], 700	-	TGA	m, t
Gupta et al, 2005	[59]	Fe_2O_3,Fe-Ti-O	2(2)	Coal, H_2/N_2	0-900[m]	-	TGA	m,x
Ishida et al, 2005	[60]	Fe_2O_3/Al_2O_3	7(7)	H_2	900	0.07	TGA	v
Lee et al. 2005	[5]	CoO/YSZ, Fe_2O_3/ YSZ, NiO, NiO w. ZrO_2, YSZ, $AlPO_4$, $NiAl_2O_4$	7(0)	H_2	600	2	TGA	
Lyngfelt and Thunman 2005	[61]	NiO based, Fe_2O_3 based	2(2)	Natural gas	560-900	-	CFzB	h,r
Readman et al., 2005	[62]	Perovskite[n]	1(1)	H_2/He	800	-	TGA	
Son and Kim 2005	[63]	NiO and Fe_2O_3 on TiO_2, Al_2O_3 and bentonite NiO-Fe_2O_3/bentonite	9(9)	$CH_4/H_2O/CO_2$	650-950	0.106-0.15	TGA	u
Zafar et al. 2005	[64]	NiO, CuO, Mn_2O_3, Fe_2O_3 with SiO_2	4(3)	CH_4/H_2O	700-950	0.18-0.25	FzB	t
Abad et al. 2006	[65]	Mn_3O_4/Mg-ZrO_2	1(0)	Natural gas, Syngas	800-1000	0.09-0.212	CFzB	h, q
Adánez et al 2006	[66]	NiO/Al_2O_3, CuO/Al_2O_3, NiO-CuO/Al_2O_3 some with K_2O or La_2O_3	22(22)	$CH_4/H_2O/N_2$ (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	[67]	CuO/Al_2O_3	1(1)	CH_4	700-800	0.1-0.3, 0.2-0.5	CFzB	r
Cao et al, 2006	[68]	CuO	1(0)	PRB Coal, Wood, Polyethene with N_2/CO_2	0-1000	0.050-0.150	TGA	x
Cho et al. 2006	[69]	Fe_2O_3/Al_2O_3, NiO/$NiAl_2O_4$, Mn_3O_4/Mg-ZrO_2	6(4)	CH_4	950	0.125-0.18	FzB	p
Corbella et al, 2006	[70]	NiO/TiO_2	2(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	[71]	CuO/SiO_2	3(3)	CH_4, CH_4/Ar[m], H_2/Ar[m]	800, 0-950[m]	0.2-0.4	FxB	m
Dennis et al. 2006	[72]	Fe_2O_3	1(1)	Lignite Char+ H_2O	900	0.30-0.42, 0.42-0.71	FzB	x
García-Labiano et al. 2006	[73]	Fe_2O_3/Al_2O_3, NiO/$NiAl_2O_4$, CuO/Al_2O_3	3(1)	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	[74]	NiO/$MgAl_2O_4$	1(0)	Natural gas	800 - 950	0.09-0.212	CFzB	h,q
Johansson E. et al. 2006	[75]	NiO/$MgAl_2O_4$, NiO based	2(0)	Natural gas, Syngas	800 - 950	0.09-0.212	CFzB	h,q
Johansson M. et al. 2006	[76]	Fe_2O_3, Mn_3O_4 and NiO on different inerts	50(19)	CH_4/H_2O	950	0.125-0.18	FzB	

Johansson M. et al. 2006	[9]	Fe_2O_3, Mn_3O_4, CuO and NiO on different inerts	58(15)	CH_4/H_2O	950	0.125-0.18	FzB	
Johansson M. et al. 2006	[77]	Mn_3O_4 on ZrO_2, Mg-ZrO_2, Ca-ZrO_2 and Ce- ZrO_2	15(14)	CH_4/H_2O	950	0.125-0.18	FzB	
Johansson M. et al. 2006	[78]	$NiO/NiAl_2O_4$	1(0)	CH_4/H_2O	950	0.09-0.125	FzB	
Johansson M. et al. 2006	[79]	$NiO/MgAl_2O_4$, $Fe_2O_3/MgAl_2O_4$	2(0)	CH_4/H_2O	650-950	0.125-0.18	FzB	
Liu et al. 2006	[80]	NiO-bentonite, NiO-barium-hexaalumunite	4(4)	$CO/CO_2/H_2$ in He	700-900	-	TGA	
Mattisson et al. 2006	[81]	NiO with $NiAl_2O_4$, $MgAl_2O_4$, TiO_2, ZrO_2	19(19)	CH_4/H_2O	950	0.125-0.18	FzB	k, w
Mattisson et al. 2006	[82]	$NiO/MgAl_2O_4$, Mn_3O_4/Mg-ZrO_2, Fe_2O_3/Al_2O_3	3(1)	Syngas, CH_4	650-950	0.18-0.25	FzB	
Readman et al. 2006	[83]	$NiO/NiAl_2O_4$	1(1)	H_2/Ar, CH_4/He	800	0.09-0.21	TGA	u
Roux et al. 2006	[84]	CaO, CuO, Fe_2O_3, MgO, MnO_2, NiO, TiO_2, Al_2O_3; Fe_2O_3 and NiO on Al_2O_3, TiO_2 and MgO; CuO on Al_2O_3, TiO_2 and MgO	19(13)	CH_4	550-950	0.0019-0.093	TGA	
Rydén et al 2006	[85]	$NiO/MgAl_2O_4$	1(0)	Natural gas (+steam)	820-930	0.09-0.212	CFzB	h,q,t
Scott et al 2006	[86]	Fe_2O_3	1(0)	Lignite + $H_2O/CO_2/N_2$	900	0.30-0.42, 0.42-0.71	FzB	x
Son and Kim 2006	[87]	NiO and Fe_2O_3 on TiO_2, Al_2O_3 and bentonite NiO-Fe_2O_3/bentonite	9(0)	$CH_4/H_2O/CO_2/N_2$ (TGA) CH_4 (CFzB)	650-950	0.106-0.15	TGA, CFzB	d,u,h
Song et al. 2006	[88]	$NiO/NiAl_2O_4$	9(9)	H_2	600	1-2	TGA	
Zafar et al. 2006	[89]	NiO, CuO, Mn_2O_3, Fe_2O_3 with SiO_2 and $MgAl_2O_4$	8(4)	$CH_4/H_2O/CO_2/N_2$	800-1000	0.18-0.25	TGA	t,y
Abad et al. 2007	[90]	Fe_2O_3/Al_2O_3	1(0)	Natural gas, Syngas, CH_4	800-950	0.09-0.212	FzB, CFzB	h,q
Corbella and Palacios, 2007	[91]	Fe_2O_3, Fe_2O_3/TiO_2	11(11)	CH_4, CH_4 in N_2	900, 0-1000[m]	0.2-0.4	FxB	m
de Diego et al.,2007	[92]	CuO/Al_2O_3	1(0)	CH_4, CH_4/H_2O^{TGA}	700-800	0.1-0.3, 0.2-0.5	CFzB, TGA	r
Leion et al. , 2007	[93]	$Fe_2O_3/MgAl_2O_4$	1(0)	Petcoke +H_2O/N_2 Syngas	850-1000	0.09-0.125	FzB	w, x
Mattisson et al. 2006	[94]	$NiO/NiAl_2O_4$	1(0)	CH_4/H_2O, $CH_4/H_2O/CO_2/N_2$ (TGA)	750-950	0.09- .... -0.25	TGA, FzB	c,e
Siriwardane et al., 2007	[95]	NiO/Bentonite, NiO, Bentonite	3(2)	CO_2/CO/He/H_2	700-900	0.074-0.840	TGA, press. FxB, TEOM	c, f
Zafar et al., 2007	[96]	$NiO/MgAl_2O_4$	1(0)	$CH_4/H_2O/N_2$	800-1000	90-250	TGA	c, u

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] Particle size effect on reduction/oxidation
[d] No NO_x verified in experiments
[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
[y] In-situ XRD

REACTOR DESIGN AND OPERATIONAL EXPERIENCE IN CHEMICAL-LOOPING COMBUSTORS

The CLC was first introduced in 1954 as way to produce pure CO_2 from fossil fuels, using two interconnected fluidized beds [97]. In 1983 it was presented as a way of increasing the thermal efficiency of power plants [98], and in the nineties it was recognized as a possibility to capture CO_2 from fossil fuels in order to reduce climate impact [2]. In 2001 a design based on the circulating fluidized bed principle was presented, see Fig. 2, investigating the critical design parameters of a system such as the solids inventory and recirculation rate of oxygen carriers between the reactors and identifying the relationship between these and the oxygen carrier properties. [99] More detailed studies of reactor design have utilized cold-flow modelling, identifying stable and suitable operating conditions for various designs [100-103].

Although laboratory experiments give very valuable information, they cannot be used to prove the workability of the particles in the actual process. Therefore it is very important to test the particles in actual

chemical looping combustors under realistic conditions and sufficient time periods. Several CLC prototypes have been presented in the literature, see Table 3. Lyngfelt et al. presented results from a 10 kW prototype unit in 2004.[61, 104] 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. [78] 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. [105] Adanez et al. operated a 10 kW CLC unit 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.[67] 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. [87] Finally, oxygen carriers based on Ni, Mn and Fe have been used in a 300 W CLC reactor with both syngas and natural gas. [65, 74, 75, 90] The same reactor was also used with nickel oxides in testing of CLR. [85] Berguerand and Lyngfelt [106, 107] used bituminous coal and pet coke in a 10 kW CLC combustor designed for solid fuels. The operational experience with fuel in chemical-looping combustors worldwide, involving oxygen carriers based on oxides of Ni, Fe, Mn, Cu and Co, is presently more than 1000 h, with Chalmers >1000 h and CSIC > 300 h, if yet unpublished results are also included.

Table 3. Testing in chemical-looping combustors

	unit	particle	operation with fuel, h, (hot[a])	Fuel[b]	Reference
1	Chalmers 10 kW	$NiO/NiAl_2O_4$	105 (300[a])	n.g.	[61, 104]
2	Chalmers 10 kW	Fe_2O_3-based	17	n.g.	[61]
3	S Korea 50 kW	$Co_3O_4/CoAl_2O_4$	25	n.g.	[105]
4	S Korea 50 kW	NiO/bentonite	3[d]	n.g.	[105]
5	Chalmers 300 W	$NiO/NiAl_2O_4$	8 (18[a])[c]	n.g.	[75]
6	Chalmers 300 W	$NiO/MgAl_2O_4$	30 (150[a])	n.g./s.g.	[74, 75]
7	Chalmers 300 W	Mn_3O_4/ $ZrO_{2,\ Mg\text{-}stab.}$	70 (130[a])	n.g./s.g.	[65]
8	Chalmers 300 W	Fe_2O_3/Al_2O_3	40 (60[a])	n.g./s.g.	[90]
9	CSIC, 10 kW	CuO/Al_2O_3	2x60 (2x100)	n.g.	[67]
10	Chalmers 300 W	$NiO/MgAl_2O_4$	41 (CLR)[c]	n.g.(CLR [c])	[85]
11	S Korea, 1 kW	NiO-Fe_2O_3/bentonite	?	CH_4	[87]
12	Chalmers 10 kW	$NiO/NiAl_2O_4$	160	n.g.	[108]
13	Chalmers 10kW sf[e]	ilmenite	22 (140)	RSA coal	[106]
14	Chalmers 10kW sf[e]	ilmenite	11	pet coke	[107]

[a] total time fluidized at high temperature, [b]n.g. = natural gas, s.g. = syngas, [c]chemical-looping reforming, [d]particles fragmentated, [e]sf = unit designed for solid fuels

DESIGN CRITERIA

The reactivity of the particles will determine the minimum needed solids inventory, [99] and the rate index presented in Fig. 3 has been used for a first estimate of the minimum needed bed mass in the fuel reactor ($kg/MWCH_4$) using simplified and transparent assumptions, see [8] for calculation procedure. It should be pointed out that this estimation does not consider differences in gas-solids contact when fluidization conditions are varied, i.e. they assume that reactivities as measured in a small laboratory fluidized bed are applicable also for the larger scale. The estimate of bed mass is indicated on the right y-axis in Fig. 3. 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_{th} might be reasonable. [99] Based on this assumption, a majority out of the tested oxygen carriers would be appropriate for chemical-looping combustion. The solids inventory of the air-reactor is given less

attention in the literature; it is expected that a smaller inventory is needed compared to the fuel reactor, due to the faster oxidation reaction and no need to have complete conversion of the gas.

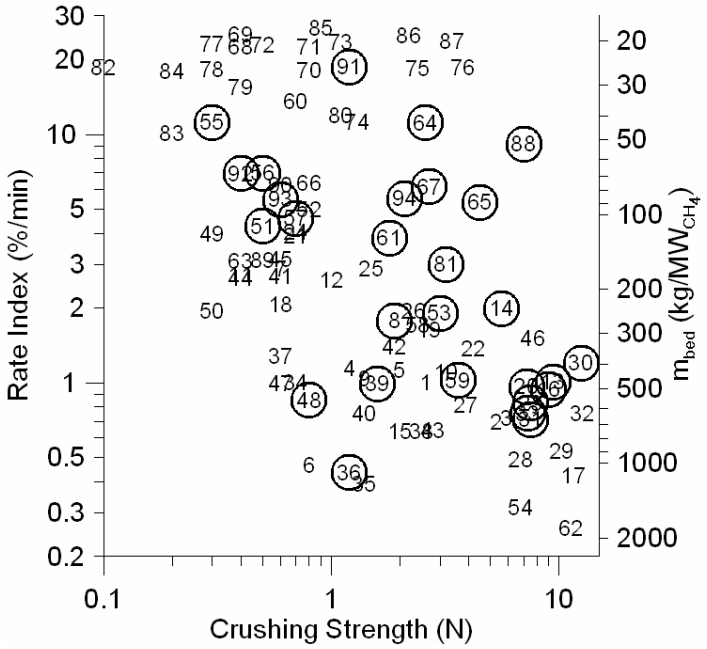

Fig. 3. Rate Index vs. crushing strength for freeze granulated particles. Circle around number indicates de-fluidization. For comparison corresponding solid mass inventory needed in the fuel reactor is included. Fe-based oxygen carriers: 1-39, Mn-based particles: 40-63, Cu-based: 64-67 and Ni-based oxygen carriers: 68-94. Data from Johansson et al [8, 9]

The group of Adanez calculated solids inventories based on kinetic data of Ni-, Fe- and Cu-based oxygen carriers using CH_4, CO and H_2 as fuel. [44, 109] 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 30 to 1000 kg/MW$_{th}$ for the three investigated carriers, using CH_4 as fuel. [109] For the more reactive CO and H_2 the range narrowed down to 25-90 kg/MW$_{th}$. Again these inventories do not consider mass transfer resistances related to the fluidization, as these are highly case dependent. Studies of the gas conversion in the fuel reactor utilizing a model considering both hydrodynamics and kinetics, was made by Adanez et al. [110]

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 has 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 [111], Wolf [112] Brandvoll [113] and Naqvi [114]. These process studies show that it is theoretically possible to achieve high thermal efficiencies using CLC integrated with CO_2 capture. It should be pointed out, however, that in order to reach very high efficiencies for gaseous fuels, combined cycle processes involving pressurized fluidized beds would need to be used. Moreover, the temperatures used in these combined cycles are higher than those for which oxygen carriers have normally been tested. Thus, the development of a gas-fired CLC power process for the highest thermal efficiencies, involves some efforts.

There is a different situation for the application of CLC to solid fuels, or chemical-looping reforming, where high efficiencies can be reached at atmospheric pressure and lower temperatures, see below.

CHEMICAL-LOOPING REFORMING

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

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 syn-gas of H_2, CO, H_2O and CO_2, see Fig. 4a. [85, 115, 116] The syn-gas composition depends on the fraction of oxygen supplied to the fuel by the oxygen carriers in the fuel reactor to that needed for complete oxidation. The syn-gas can then be shifted to contain undiluted CO_2 and H_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 absorbtion or adsorbtion processes.

The second type of hydrogen production is called CLR(s) where the "s" denotes steam reforming. The steam reforming part does not differ from ordinary steam reforming in the way that the reactions take place inside tubes using suitable catalysts and working at elevated pressure. However, the steam reforming tubes are here placed inside the fuel-reactor in a CLC unit. They may also be placed in a parallel fluidized-bed heat exchanger. Hence, the reformer tubes are not heated by direct firing but rather by the oxygen carrier particles in the normal CLC process. The feed gas to the fuel reactor is the offgas from the steam reforming which is a gas mixture of CH_4, CO_2, CO and H_2. The proposed design of CLR(s) can be seen in Fig. 4b. [117]

The two concepts have been compared in a process study, and it is found that both alternatives have potential to achieve reforming efficiencies in the order of 80%, including CO_2 capture and compression. [116]

Several other authors have explored the possibility of using oxygen storage materials for the production of syngas, e.g. [19, 118, 119], and a process for direct hydrogen production is also being studied. [120]

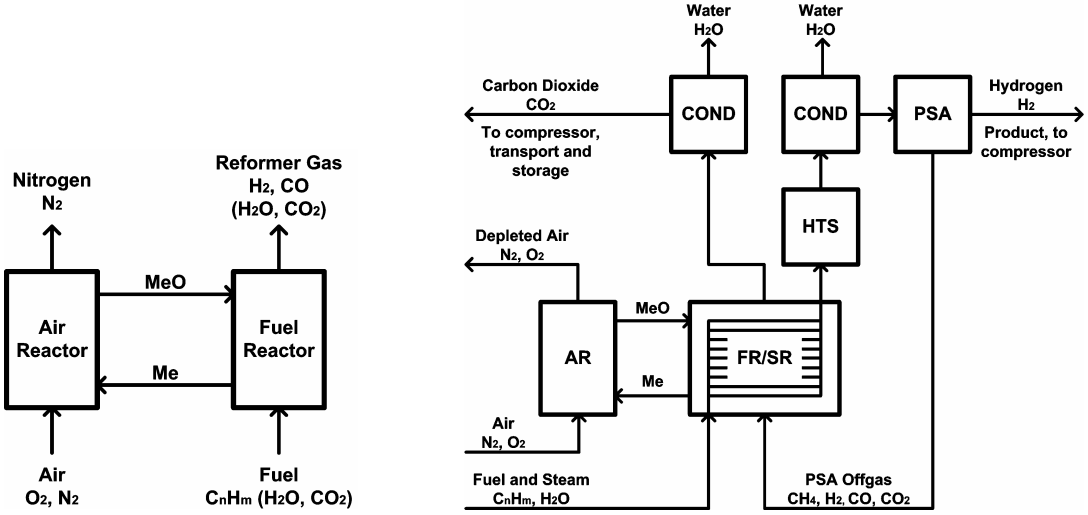

Fig. 4. a) Chemical-looping reforming and b) steam reforming with CO_2 capture by CLC. Air reactor (AR), fuel reactor / steam reformer (FR/SR), high temperature shift (HTS), condenser (COND), pressure swing adsorption (PSA). [115, 117]

CHEMICAL-LOOPING COMBUSTION OF SOLID FUELS

Most CLC research has been focused on gaseous fuels, but there is also a growing interest in using the process for solid fuels. [53, 68, 72, 86, 121] There are also more complex systems involving more cycles, e.g. lime calcination and carbonation, as well as hydrogen production [59, 122, 123]. However, the most straightforward option is to use the CLC - circulating fluidized bed concept outlined in Fig. 2, but adapting the fuel reactor system for direct addition of solid fuels, and testing in a 10 kW unit suggests the direct application to solid fuels should be feasible [106]. 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. This is determinant for the fuel reactor design, cf. [106], and the following key issues have been identified in relation to fuel reactor performance, *i.e.* solid fuel conversion, gas conversion and CO_2 capture:

- The ***solid fuel conversion*** is highly dependent on the capture efficiency of the cyclone system after the fuel reactor. The char gasification is slow, which means that a long residence time is needed to reach a high degree of conversion. However, a difference between of CLC and normal gasification is that the products of gasification H_2 and CO, known to inhibit the gasification reaction, are immediately oxidized in contact with oxygen carrier particles, which keeps the gasification reactants H_2O, CO_2 and SO_2, at high levels.

- The degree of ***gas conversion*** of the flue gas leaving the fuel reactor is dependent on the contact between fuel and oxygen-carrier particles. Good contact is essential to assure that the reducing gases, which are produced by volatiles release and gasification of the char particles, can react with the oxygen-carrier before

leaving the fuel reactor. The contact is a consequence of the reactor system design, but it is probably not possible to reach complete oxidation of the gas in practice. Incomplete gas conversion means that there is a need for downstream measures, for example oxygen polishing, i.e. oxygen injection at the fuel reactor outlet, to finalize the oxidation of gases.

- The ***CO_2 capture*** will be incomplete if there is loss of unconverted char particles to the air reactor. The loss of char to the air reactor will be determined by the design of the fuel reactor system, fuel reactivity, and solids circulation. The fuel needs a sufficient residence time in the fuel reactor, to minimize the loss of char in the stream leaving the fuel reactor, moreover char still contained in this stream can be stripped off in a so-called carbon stripper before the solids enter the air reactor. In conclusion, the key parameters determining the CO_2 capture are a well-functioning carbon stripper and a sufficient residence time in the fuel reactor in relation to the conversion rate of the solid fuel.

The above issues indicate that the fuel reactor system will be dependent on add-ons such as carbon stripper, oxygen polishing, and highly efficient particle separation, in order to reach high performance. Nonetheless the direct application to solid fuels has the potential to provide a process that could capture CO_2 with significantly lower energy penalty and cost, as compared to post-combustion, pre-combustion or oxy-fuel technologies. A major break-through in this development of solid fuel CLC, is the good results reached with low-cost naturally occurring oxygen-carriers such as ilmenite, [106].

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 2 and 3, there is extensive research currently being performed and the results with respect to oxygen carrier development and prototype testing are highly promising. Chemical-looping reforming processes, used for the production of hydrogen are also under investigation. Moreover, development of CLC for solid fuels is under way.

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