To be presented at First Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute
April 18-20, 2001, Göteborg, Sweden

Capture of CO_2 using chemical-looping combustion

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Abstract

Chemical-looping combustion (CLC) is a new 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 the combustion air to the fuel, and hence the direct contact between fuel and combustion air is avoided. Subsequently, the products from combustion, e.g. carbon dioxide and water, will be kept separate from the rest of the flue gases, e.g. nitrogen and any remaining oxygen. Two reactors in the form of interconnected fluidized beds are used in the process: *i)* a fuel reactor where the metal oxide is reduced by reaction with the fuel, and *ii)* an air reactor where the reduced metal oxide from the fuel reactor is oxidized with air. The outlet gas from the fuel reactor consists of CO_2 and H_2O while the outlet gas stream from the air reactor contains only N_2 and some unused O_2. The net chemical reaction over the two reactors is the same as normal combustion with the same amount of heat released, but with the important difference that carbon dioxide is inherently separated from nitrogen, and no extra energy is needed for this separation. This is in contrast to known techniques for separating carbon dioxide from flue gas, where large amounts of energy and expensive equipment are necessary for carrying out this separation. In this paper the thermodynamic feasibility of using several different metal oxides as oxygen carriers in CLC is discussed. Reactivity data for a few different types of iron oxide particles with methane and air is presented and discussed with respect to use in a CLC system based on interconnected fluidized beds. The rates of reaction obtained for all of the samples are sufficient to be used as oxygen carriers in a CLC system based on interconnected fluidized beds.

Chemical-looping combustion

A chemical-looping combustion (CLC) system is composed of two reactors, an air and a fuel reactor, as shown in Figure 1. The fuel is introduced to the fuel reactor in a gaseous form where it reacts with an oxygen carrier according to:

$$(2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m)M_yO_{x-1} + mH_2O + nCO_2 \quad (1)$$

The exit gas stream from the fuel reactor contains only CO_2 and H_2O, which means that pure CO_2 can be obtained when H_2O is condensed. The reduced metal oxide, M_yO_{x-1}, is then circulated to the air reactor where it is oxidized according to:

$$M_yO_{x-1} + ½O_2 \rightarrow M_yO_x \quad (2)$$

The flue gas from the air reactor will contain N_2 and any unreacted O_2. The extent of the reactions above may vary depending on the metal oxide and the reaction conditions. Reaction (1) is often endothermic while reaction (2) is exothermic with subsequent heat release. In all cases the total amount of heat evolved from reaction (1) plus (2) is the same as for normal combustion where the oxygen is in direct contact with the fuel. The advantage with this

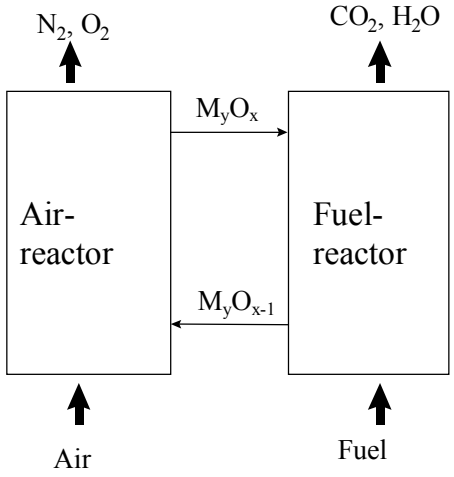

Figure 1: Chemical-looping combustion (CLC). M_yO_x and M_yO_{x-1} symbolizes oxidized and reduced oxygen carriers.

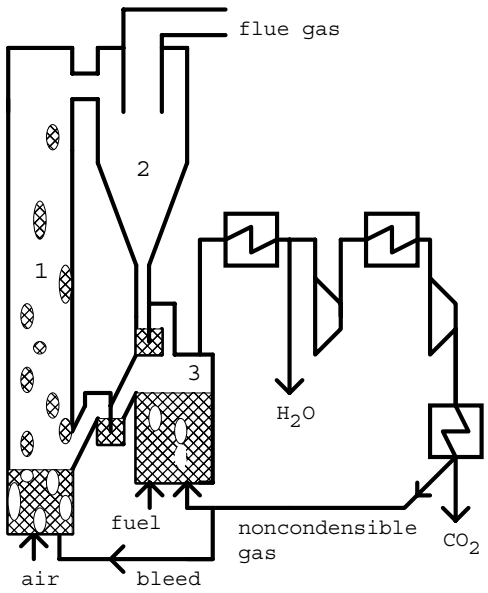

Figure 2: Chemical-looping combustion system using two interconnected fluidized beds.

system compared to normal combustion is that the CO_2 and H_2O is inherently separated from the rest of the flue gases, and no energy is expended for this separation. Chemical-looping combustion (CLC) was first presented as an alternative to normal combustion where the thermal efficiency of a power process may be increased because of the use of the fuel reactor as a heat sink.[1,2] However, this places a high demand on the reactivity of the oxygen carrier as well as the design of the reactor system, and this possibility is not considered here. Rather, the focus is on the inherent separation of carbon dioxide from the flue gas, where no energy or costly external devices are needed for this capture. This should be compared to other technologies for CO_2 separation which, when used in a power process, results in a drastic reduction in the plant efficiency.[3]

A chemical-looping combustion design based on two interconnected fluidized beds has earlier been presented by Lyngfelt et al.[4] In this design, shown in Figure 2, the air reactor (1) is a high velocity fluidized bed where the oxygen carrier particles are transported together with the air stream to the top of the air reactor, and then transferred to the fuel reactor (3) via a cyclone (2). The fuel reactor is a bubbling fluidized bed reactor, with the reduced oxygen carriers transported back to the air reactor by an overflow pipe. After condensation of the water in the exit gas from the fuel reactor, the remaining CO_2 gas is compressed and cooled in stages to yield liquid CO_2 which can be disposed of in various ways.[5] Three important design criteria are directly related to properties of the oxygen carrier [4]:

1. The amount of bed material necessary in the reactors is inversely proportional to the rate of reaction of the oxygen carrier, i.e. reactions (1) and (2).
2. The rate of circulation of the oxygen carriers between the air and fuel reactor is inversely proportional to the mass fraction of oxygen that is released/captured by the oxygen carrier during a cycle.
3. The amount of noncondensible gas that needs to be recirculated to the fuel reactor (see Fig. 2) is dependent on the yield of gaseous fuel to carbon dioxide and water. That is, any unconverted fuel needs to be recirculated back to the inlet of the fuel reactor.

Oxygen carriers - thermodynamics

It is important that the oxygen carrier used in a CLC system has an affinity for reaction with the fuel gas, i.e. reaction (1), and that the reduced oxygen carrier reacts rapidly with air. Metal oxides may be suitable to use as oxygen carriers, and below follows a thermodynamic

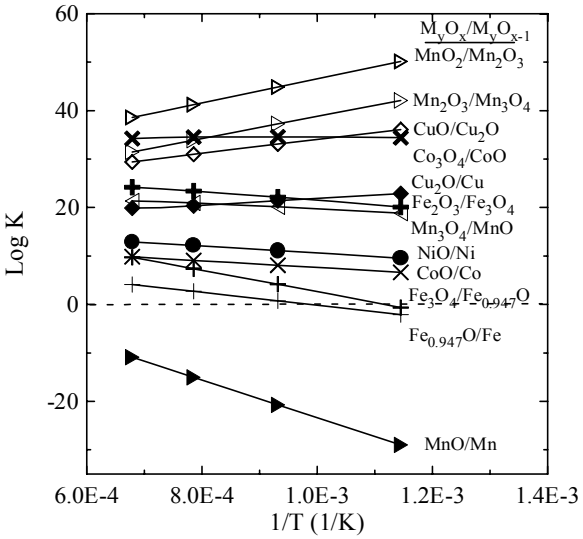

Figure 3: Log K as a function of 1/T in the temperature range 600 - 1200°C for different metal oxide systems.

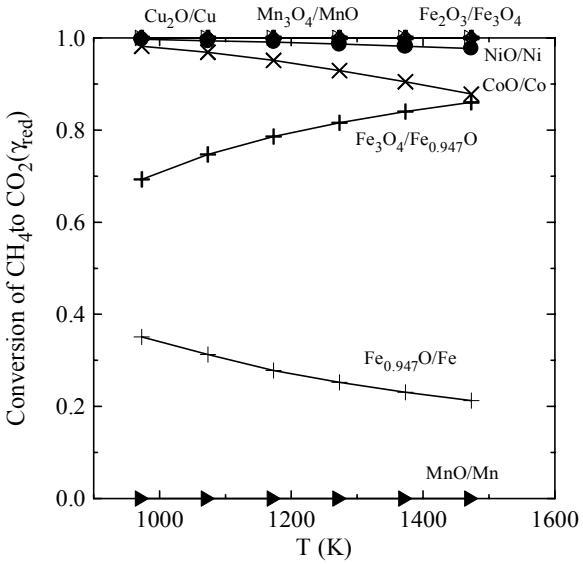

Figure 4: The conversion of CH_4 to CO_2 (γ_{red}) vs temperature for different metal oxide systems.

analysis of some common metal oxides. Though it is possible to use gas from coal as the fuel in CLC, natural gas is more likely for a first application, and in this paper methane is the fuel considered. In Figure 3 the equilibrium constant log K for reaction (1) using some different metal oxide/reduced metal species and CH_4 as the fuel gas is shown as a function of 1/T in the temperature range 600 - 1200°C. High log K values indicates high affinity for reaction with methane. As is evident from the figure the MnO_2/Mn_2O_3, Mn_2O_3/Mn_3O_4, Co_3O_4/CoO and CuO/Cu_2O systems have high affinities for methane. However, MnO_2, Mn_2O_3, Co_3O_4 and CuO decompose, with subsequent oxygen removal in air at temperatures above 460°C, 820°C, 890°C and 1030°C respectively. Thus, with the possible exception of CuO, these oxides are unsuitable for use as oxygen carriers in a CLC process at high temperatures.

The methane conversion to carbon dioxide and water must be high in the fuel reactor. This will reduce the amount of unreacted gas that is recirculated back to the fuel reactor and, more important, reduces the energy needed for compressing CO_2 to a liquid. The degree of methane conversion to carbon dioxide was calculated thermodynamically for the different oxide systems in Figure 3 using a method of minimization of Gibbs free energy.[6] The calculation was carried out with 100% CH_4 over the metal oxide (M_yO_x) at different temperatures in the range 700 - 1200°C at 1 bar total pressure. The gaseous species included in the calculation were CH_4, CO_2, CO, H_2O, H_2 and O_2 and the solid phases the metal oxide (M_yO_x) and the reduced metal oxide (M_yO_{x-1}). The degree of methane yield to carbon dioxide, defined as $\gamma_{red} = p_{CO_2}/(p_{CH_4} + p_{CO_2} + p_{CO})$ where p_i is the partial pressure of gaseous species i, is shown in Figure 4 as a function of the temperature. The conversion is complete for the Cu_2O/Cu, Mn_3O_4/MnO and Fe_2O_3/Fe_3O_4 systems, and above 97% for the NiO/Ni system in the temperature range considered. The conversion of methane for the three systems which are unstable at higher temperatures, i.e Mn_2O_3/Mn_3O_4, Co_3O_4/CoO and CuO/Cu_2O, was complete at temperatures below the decomposition temperature (not shown). The yield to CO_2 for the systems MnO/Mn and $Fe_{0.947}O/Fe$ is low in the entire temperature range and the yield for $Fe_3O_4/Fe_{0.947}O$ is insufficient. From the above analysis it can be concluded that the metal oxide systems which are feasible for use as oxygen carriers in a CLC system are Mn_3O_4/MnO, Fe_2O_3/Fe_3O_4, NiO/Ni, Cu_2O/Cu and CoO/Co. However, the yield of CO_2 for CoO/Co is somewhat low and the low melting point of Cu, 1089°C, may present difficulties at higher temperatures for Cu_2O/Cu.

An oxygen ratio for the metal oxide systems is defined as $R_o=(m_{ox} - m_{red})/m_{ox}$ where

m_{ox} and m_{red} are the masses of the oxidized (M_yO_x) and reduced (M_yO_{x-1}) form of the oxygen carrier, respectively. Table 1 shows the oxygen ratio for the oxide systems which are thermodynamically feasible according to the above discussion. The oxygen ratio shows the maximum amount of oxygen that can be transferred between the air and fuel reactor in CLC for a given mass flow of recirculating particles. The actual fraction of oxygen transported is the product of R_o and the change in the degree of fractional conversion between M_yO_x and M_yO_{x-1}, ΔX. A comparison to measured recirculating mass flows in a circulating fluidized bed boiler indicated that one realistic value of $R_o \cdot \Delta X$ was 0.006.[4]

Table 1. Oxygen ratios, R_o

M_yO_x/M_yO_{x-1}	R_o
Fe_2O_3/Fe_3O_4	0.03
Mn_3O_4/MnO	0.07
Cu_2O/Cu	0.11
NiO/Ni	0.21
CoO/Co	0.21

Oxygen carriers - reactivity

Experimental investigations of different oxygen carriers were reviewed by Lyngfelt et. al. [4]. A research group at Tokyo Institute of Technology has performed reactivity evaluations of NiO, Fe_2O_3 and CoO in a TGA using different types of binder material. Most of the reactivity data during reduction were obtained with hydrogen as the reducing gas, and only limited data are available for methane as the reducing gas. The particle sizes used were typically around 2 mm, which is larger than normally used in fluidized beds.

Mattisson et al.[7] presented reactivity data for cyclic reduction and oxidation of Fe_2O_3 with methane and air. The iron oxide particles used had a particle size of 0.25 mm and the experiments were carried out at a temperature of 950°C. The data obtained from these experiments were *i)* the conversion rate of Fe_2O_3 to Fe (in practice the iron oxide was never reduced all the way to Fe) *ii)* the conversion difference of the iron oxide/reduced iron oxide between the oxidation and reduction periods and *iii)* the gas yield of methane to carbon dioxide. The reduction rates measured were between 1-8%/min with carbon dioxide yields of 10 - 99% and conversion differences between 2-25%. When the gas yield was high, 90%, the rate was between 3-5%/min. The oxidation rate was considerably higher, >90%/min.

Experimental investigation of Fe_2O_3/Al_2O_3 as an oxygen carrier

Following the promising results from the investigation of natural hematite[7], synthetic iron oxide particles were prepared, with the reduction and oxidation rates measured with methane and air respectively. In order to obtain higher strength and reactivity, particles composed of 60% Fe_2O_3 and 40% Al_2O_3 were prepared. A description of the preparation method for the oxide sample can be found in [8] and the experimental set-up and procedure has been described in detail earlier [7] and will only be described briefly here: All of the experiments were carried out in a fixed-bed reactor of quartz. The reactor had a length of 860 mm, with a porous quartz filter of 30 mm in diameter about 450 mm from the top. The iron oxide was heated in the reactor to the desired temperature in a flow of nitrogen. After the temperature stabilized the experiment was initiated by exposing the iron oxide sample alternatingly to air and methane. Thus, the system simulates the cyclic exposure that the particles are subject to in a real system. In order to avoid the mixing of methane and air, nitrogen was introduced for two minutes after each oxidizing and reducing period. The cooled product gases from the reactor were led to a gas analyzer (Rosemount NGA-2000) where the concentrations of CH_4, CO, CO_2 and O_2 were measured. The degree of oxidation, or conversion, was defined as,

$$X = \frac{m - m_{red}}{m_{ox} - m_{red}} \qquad (3)$$

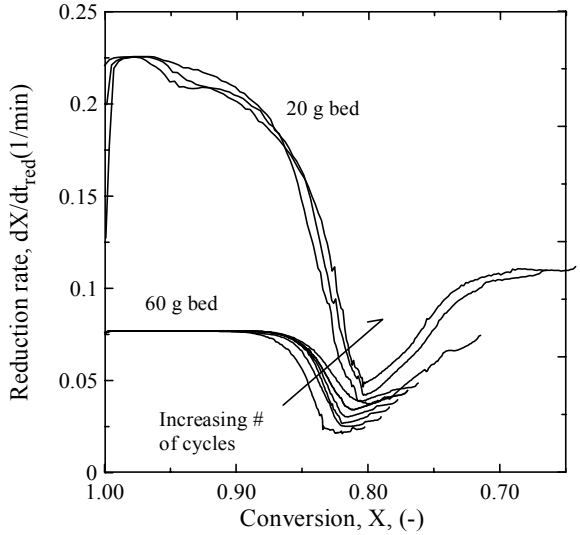

Figure 5: The rate of reduction as a function of the degree of conversion for an oxygen carrier composed of 60% Fe_2O_3 and 40% Al_2O_3 with 100% methane.

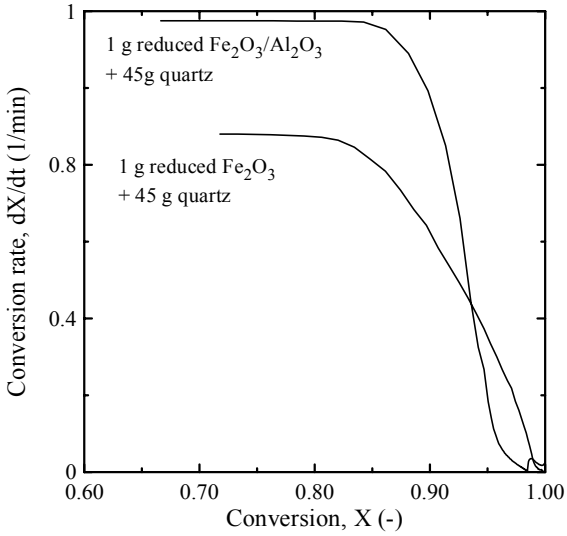

Figure 6: The rate of oxidation as a function of the degree of conversion for an oxygen carrier composed of i) 60% Fe_2O_3 and 40% Al_2O_3 and ii) natural Fe_2O_3.

where m is the actual mass of the iron oxide plus aluminum oxide in the sample, m_{red} the mass of the sample when all of the oxygen is removed, i.e. in the form Fe/Al_2O_3 and m_{ox} the mass of the iron oxide when fully oxidized, i.e. when in the form Fe_2O_3/Al_2O_3. Figure 5 shows the rate of reduction as a function of the degree of conversion for all cycles for experiments with 60 g and 20 g samples of bed material. For the larger sample it is clear that the reactivity is limited by the access to methane for conversions down to 85-90%. The reduction rate of the smaller sample is also initially limited by the access to methane, and the rate and yield fall rapidly at a conversion of about 90%. This corresponds closely to the level where all Fe_2O_3 has reacted to Fe_3O_4, 88%. It is likely that the Fe_2O_3 is initially reduced to Fe_3O_4 with a corresponding high yield of methane to carbon dioxide. Further reduction to FeO or $FeAl_2O_4$, correspond to a lower thermodynamic conversion of methane, c.f. Fig. 4, and this may explain the drop in the reaction rate below a conversion of about 0.9, i.e. a thermodynamically controlled reaction. The reason for the subsequent increase in reactivity at lower conversions is not entirely clear, but this phase of the reaction is of limited interest for CLC because of the low conversion of methane. The reactivity tends to increase as the number of cycles increases, which was also seen in an earlier study of natural hematite.[7]

In the experiments where the reduction rate was measured, i.e. with rather large amounts of bed material, it was not possible to simultaneously evaluate the oxidation rate during the oxidizing periods. The reason is that the oxidation is so rapid that all oxygen is consumed and thus the rate is limited by the availability of oxygen. Therefore, to investigate the rate of oxidation, experiments using smaller amounts of bed material were performed. In Figure 6 the rate of oxidation of *i)* a sample of 1 g reduced natural iron oxide and *ii)* a sample of 1 g reduced synthetic 60%/40% Fe_2O_3/Al_2O_3 are shown. The samples were diluted in 45 g quartz in order to avoid large temperature rises during the reaction. Even when using very small samples the rate is initially limited by the oxygen concentration with rates approaching 100%/min for the synthetic sample and about 80%/min for natural iron oxide sample.

Discussion

A design calculation of the system in Fig. 2, using methane as the fuel, showed that a conversion rate of Fe_2O_3 to Fe of 9%/min would be needed in the air reactor for a bed height of 0.3 m and with a cross-sectional area typical of a circulating fluidized bed boiler, i.e. 0.25

m^2/MW. Similarly, rates of 3%/min would be necessary in the fuel reactor for a bed height of 1 m and a cross sectional area of the same size as the air reactor.[4] The average rate of conversion, dX/dt, as measured during the first reduction period, is shown as a function of the conversion difference, ΔX, in Fig. 7 for *i)* the synthetic Fe_2O_3/Al_2O_3 sample (SYN1) from Figure 5 and 6 above, *ii)* a similar synthetic sample of Fe_2O_3/Al_2O_3 (SYN2) prepared somewhat differently than SYN1 [8] and *iii)* two natural iron ore samples (NAT1 and NAT2).[7] The degree of gas yield of the methane to carbon dioxide, γ_{red}, is shown as well. The lowest rates are observed for the natural iron oxides, with rates below 3%/min. The synthetic sample (SYN1) show considerably higher rates of up to 23 %/min. For the same mass of oxygen carrier in the reactor, the conversion rates for the synthetic oxygen carriers need to be higher because of the inert Al_2O_3. Thus, the rate of 3%/min for pure Fe_2O_3 corresponds to 5%/min for the particles with 60% Fe_2O_3. As is evident from Fig. 6 and 7, the conversion rates of reduction and oxidation are sufficient for a CLC system.

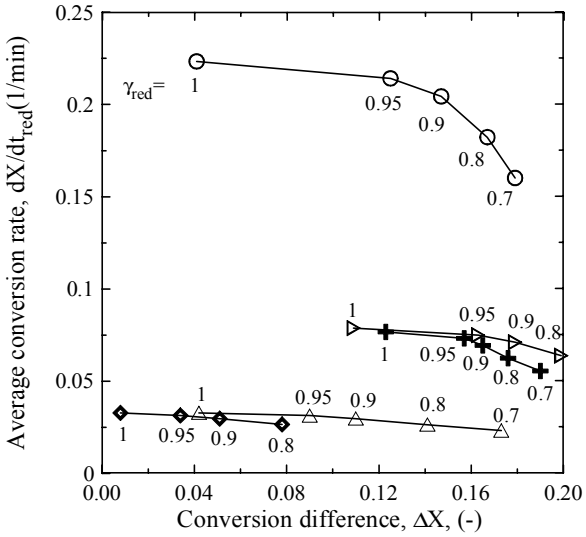

Figure 7: The conversion rate shown as a function of the conversion difference for different average gas yields for sample: NAT1 (◇), NAT2(△), SYN1 (✚), SYN1 (20 g bed sample)(○), SYN2(▷)

Conclusions

Chemical-looping combustion is a promising technique for the separation of CO_2 with small losses in energy. In this paper the thermodynamic feasibility of using several different metal oxides as oxygen carriers has been presented. The metals Ni, Cu, Co, Fe and Mn all have oxide phases which can substantially convert methane to carbon dioxide. The rates of reduction and oxidation of some iron oxide samples with methane and air were investigated in a cyclic manner using a fixed bed reactor at 950°C. The reduction rates were between 3-23 %/min with carbon dioxide yields of 70 - 100% and conversion differences between 0-20%, see Figure 7. The oxidation rates were considerably higher, up to 100%/min, see Figure 6. The rates of both reduction and oxidation found in the present paper should be sufficient to be employed in the CLC system in Fig. 2.

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