Applications of chemical-looping combustion with capture of CO$_2$

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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 the combustion air to the fuel. 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$_2$O, 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 for 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. The parameters which are important for the design of a CLC system are discussed with respect to oxygen carrier reactivity and fluidization properties. The extension of the CLC concept for the combustion of solid fuels as well as for the production of hydrogen is presented.

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 the oxygen carrier, i.e., a metal oxide, M$_y$O$_x$:

$$(2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m)M_yO_{x-1} + mH_2O + nCO_2 \qquad (1)$$
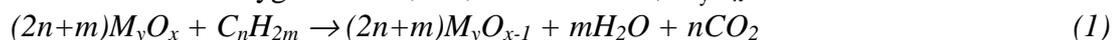
The exit gas from the fuel reactor contains CO$_2$ and H$_2$O, which means that pure CO$_2$ can be obtained when H$_2$O is condensed. The reduced metal oxide, M$_y$O$_{x-1}$, is then circulated to the air reactor where it is oxidized and thus regenerated:

$$M_yO_{x-1} + \tfrac{1}{2}O_2 \rightarrow M_yO_x \qquad (2)$$
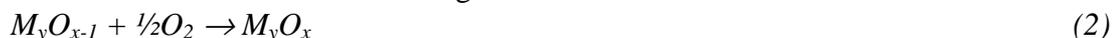
The flue gas from the air reactor will contain N$_2$ and any unreacted O$_2$. Reaction (1) is often endothermic while reaction (2) is exothermic. The total amount of heat evolved from reaction (1) plus (2) is the same as for normal combustion. The advantage with this system is that the CO$_2$ and H$_2$O are inherently separated from the rest of the flue gases, and no energy is expended for this separation. This should be compared to other technologies for CO$_2$ separation which, when used in a power process with natural gas as the fuel, have a relative reduction in the plant efficiency of 12-19%. [1]

A CLC system with interconnected fluidized beds

A chemical-looping combustion design which uses two interconnected fluidized beds has been presented by Lyngfelt et al. [2] In this design, shown in Figure 2, the air reactor (1) is a
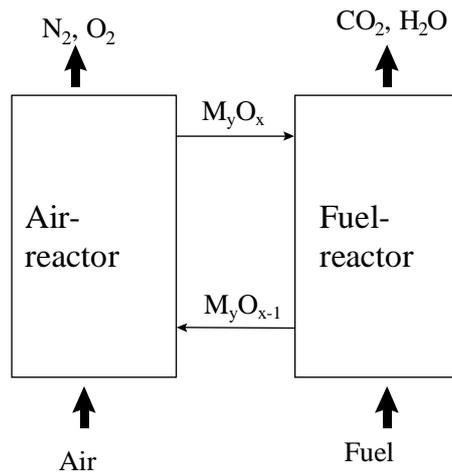
Figure 1: Chemical-looping combustion (CLC). M_yO_x and M_yO_{x-1} symbolizes oxidized and reduced oxygen carrier particles.
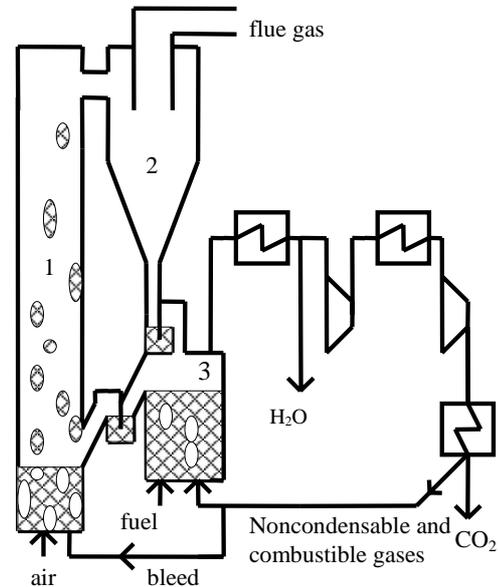
Figure 2: Chemical-looping combustion using two interconnected fluidized beds.

high velocity fluidized bed where the oxygen carrier particles are transported together with the air stream to the top of the air reactor, where they are then transferred to the fuel reactor (3) using a cyclone (2). The fuel reactor is a bubbling fluidized bed reactor, from which the reduced oxygen carriers are transported back to the air reactor by means of 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 to yield liquid CO_2, which can be disposed of in various ways. Three important design criteria are directly related to properties of the oxygen carrier: [2]

1. The amount of oxygen carrier necessary in the two reactors, i.e. the bed masses, is inversely proportional to the rate of conversion of the oxygen carrier, i.e. the rates of reactions (1) and (2).
2. The rate of circulation (flux) of the oxygen carrier between the air and fuel reactor is inversely proportional to the mass of oxygen that is released/captured by the oxygen carrier during a cycle.
3. The power expended for compression and liquefaction of CO_2 will increase if noncondensable combustible gas is present in the exit gas from the fuel reactor (see Fig. 2). Thus, a high yield of gaseous fuel to carbon dioxide and water is important.

Reactivity of oxygen carriers

The metals Cu, Co, Ni, Fe and Mn have oxides which could be used as oxygen carriers in a CLC system with natural gas as the fuel. [3] Reactivity investigations of oxygen carriers with methane have been conducted almost entirely with Fe_2O_3, although some data are available for large NiO particles. [4] Mattisson et al. [5] and Cho et al. [6] investigated the reactivity of iron oxide particles in fixed bed and fluidized bed reactors with methane and air. The amount of oxygen carrier was varied in a wide range and the samples were exposed to alternating periods of methane and air at 950°C. The product gases from the reactors were measured continuously, and the conversion of the metal oxide, X, defined as the ratio of the amount of oxygen in the particles to the amount of oxygen in the fully oxidized particles, was determined as a function of time. These experiments resulted in simultaneous data of *i)* the conversion rate of the oxygen carrier, *ii)* the amount of oxygen captured and released during each cycle and *iii)* the yield of methane to carbon dioxide and water. Thus the measured parameters relate directly to the three design criteria above. Figure 3 shows such a combination of data for an oxygen carrier composed of 60% Fe_2O_3 and 40% Al_2O_3, tested in a
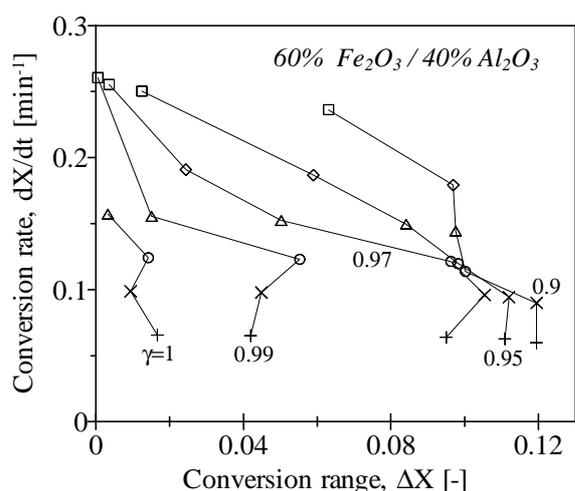
Figure 3: The rate of reduction, dX/dt, as a function of change in conversion, ΔX, for different gas yields of CH_4 to CO_2 and H_2O, γ. See [6] for details.
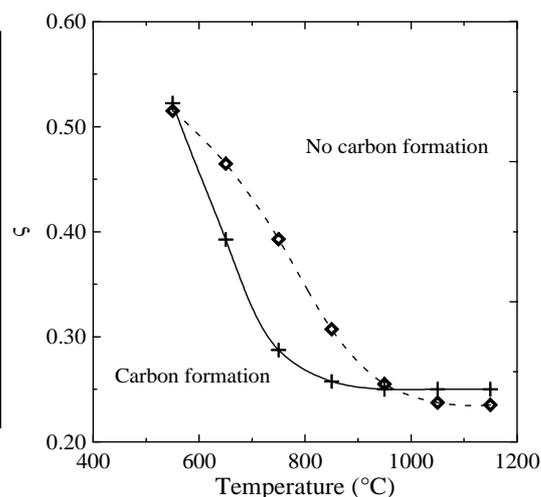
Figure 4: Thermodynamic evaluation of the region where carbon formation is possible in CLC. ς is defined in equation (4). P = 1 bar(+), 30 bar(◆).

laboratory reactor under fluidized conditions. [6] The figure shows the rate of conversion, dX/dt, as a function of the change in the degree of conversion between the oxidizing and reducing periods, ΔX, for various gas yields of methane to carbon dioxide and water, γ. The gas yield, γ, is defined as the molar ratio of CO_2 produced over the fuel carbon added. This type of diagram can be used to describe the relationship between the three parameters dX/dt, ΔX, and γ. For instance Fig. 3 shows that a complete yield of the gas, i.e. γ = 1, cannot be attained in combination with both high conversion rates, dX/dt, and conversion ranges, ΔX. For comparison, the rates and conversion ranges used in the process design by Lyngfelt et al. [2], can be used as target values for the reactivity. For the oxygen carrier used in Fig. 3, these targets are a dX/dt of 5%/min and a ΔX of 3.3%, with a γ of 95% in the fuel reactor. As is seen in Fig. 3, the targets are met with good margin. In the air reactor, a higher conversion rate, 15%/min, is targeted. Fortunately, the conversion rate under oxidizing conditions appears to be fast, up to 100%/min, as measured by Mattisson et al. [3,5]. It can be concluded that the reactivity of the particles studied should be sufficient.

Carbon deposition

If a hydrocarbon fuel, e.g. natural gas, is exposed to a high temperature, solid carbon may form through a number of reactions. Clearly, it is important that significant carbon formation be avoided in the fuel reactor of a CLC system. In the experiments conducted by Cho et al. [6] and Mattisson et al. [5] carbon was normally not formed during reduction of iron oxide with 100% CH_4. However, in experiments conducted by Ishida et al. on NiO as an oxygen carrier with CO as the reactant gas, carbon was formed under certain conditions. [7] One important difference is that the latter experiments were made under conditions where the conversion of the gas phase is small. The conditions, for which carbon formation is thermodynamically possible, depend on the amount of oxygen added as well as the temperature and pressure. The oxygen ratio, ς, is defined as the actual amount of O added with the metal oxide, $n_{O,added}$, over the stoichiometric amount needed for full conversion to CO_2 and H_2O, $n_{O,stoich}$:

Figure 5: A perspex model of a CLC system of interconnected fluidized beds. For details see [8].
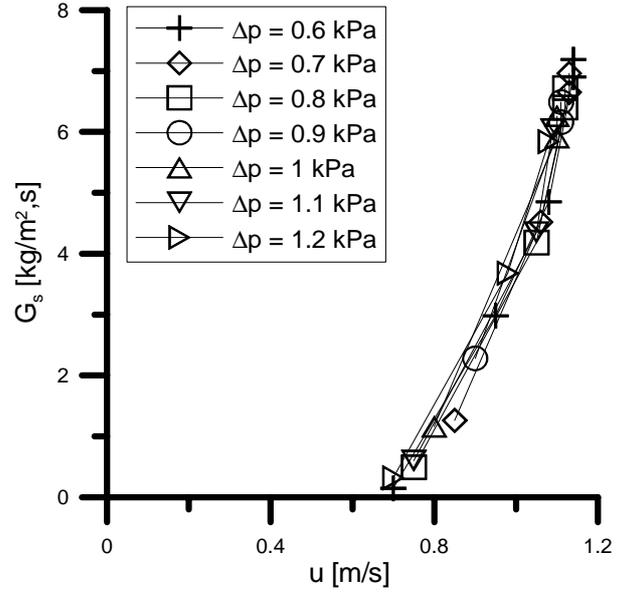
Figure 6: The recirculation rate of solid material from the air to fuel reactor as a function of fluidization velocity and pressure drop in the air reactor. Taken from [8].

$$\varsigma = \frac{n_{O,added}}{n_{O,stoich}} \qquad (3)$$

Figure 4 shows the value of ς below which carbon formation is possible as a function of temperature at 1 bar and 30 bar total pressure. Thus, for a temperature of 950°C and 1 bar no carbon formation should be expected as long as more than one fourth of the oxygen needed for complete oxidation is supplied. Consequently, problems with carbon formation are very unlikely in a well-mixed fluidized fuel reactor where there is a high conversion of the fuel. However, carbon formation may have to be considered for applications where the local or total oxygen supply could be low, e.g for hydrogen production, see below.

Bed mass and recirculation rate of oxygen carriers

In a previous paper, the recirculation rates and bed masses suitable in a CLC system operating at atmospheric conditions were discussed. [2] Furthermore, the behavior of oxygen carrier particles has been investigated in a cold CLC model of perspex, see Fig. 5. [8] This cold model is based on a pressurized CLC of interconnected fluidized beds (the design is similar to the one shown in Fig. 2). Simplified scaling laws were used to establish the geometry and operating conditions of the cold model which simulates a boiler with a power of 30 MW$_{th}$ operating at 9 bars with iron oxide as the oxygen carrier. Figure 6 shows the solids recirculation rate, G_s, as a function of the gas velocity in the air reactor for different total pressure drops in the air reactor. The pressure drop correspond to different amounts of solid material in the air reactor. In the range studied, the increase in recirculation rate is reasonably independent of the pressure drops. From the scaling laws, which were used to establish the geometry and operating conditions of the cold model, the bed mass and recirculation rate measured can be related to actual values in the pressurized boiler. Consequently, the data obtained in the cold model can be directly related to oxygen carrier reactivity. Because of the lack of reactivity data for oxygen carriers at pressurized conditions, no safe prediction about the feasibility of using iron oxide as an oxygen carrier could be drawn. However, from reactivity data of iron oxide at atmospheric conditions, results were promising. [8]

Further applications of chemical-looping combustion

The CLC system described above is intended for the combustion of a gaseous fuel and could be integrated into a combined cycle power process. However the use of CLC with interconnected fluidized beds could be extended for use in other applications. Below the combustion of a solid fuel and production of hydrogen is discussed.

Combustion of solid fuels

The configuration shown in Fig. 2. could be adapted to the combustion of solid fuels by the introduction of a separate gasification process, where either oxygen or steam and oxygen are used to gasify the fuel to a gaseous fuel, which can be used directly in place of natural gas.

Figure 7: Production of H_2 from CH_4 using oxygen carriers and interconnected fluidized beds. . (1)= shift reactor, reaction (4).

However, because of the difficulties associated with gasification and the need for an energy intensive air separation unit, it would be an advantage if the solid fuel could be introduced directly to the fuel reactor. The fuel reactor, which would be fluidized with recirculated carbon dioxide or steam, would act both as a gasifier, where the char reacts with steam or CO_2, and as an oxidizer, where gaseous compounds are oxidized by the metal oxide. In order to obtain a high conversion of the gas phase, a two-stage fluid-bed system is probably needed, e.g. a lower bed where the fuel is gasified and partly oxidized and an upper bed to ensure sufficient conversion of the gas. A classifier would be needed between the fuel reactor and air reactor to separate fuel particles from the oxygen carriers. A small release of CO_2 from the air reactor is likely, since it would be difficult to completely eliminate the transfer of unburnt carbon to the air reactor. Possible interactions between fuel ash and oxygen carriers would need to be investigated.

Hydrogen production

By the conversion of hydrocarbon fuels to hydrogen with simultaneous CO_2 capture, a CO_2-free fuel is obtained. Today, the major route for production of hydrogen is through catalytic reforming of methane with steam. The heat necessary for this highly exothermic reaction is generated from external burners which produce and release CO_2 to the atmosphere. These carbon dioxide emissions can be eliminated by using a substantial part of the hydrogen as fuel for the reforming process, or by using air-blown partial oxidation. [9] In the latter case the CO_2 separation will be more costly because the CO_2 is diluted in nitrogen.

Chemical-looping combustion could be adapted for the simultaneous production of hydrogen and power. Figure 7 shows how such a process could be designed. In the fuel reactor the methane reacts partially with the metal oxide to form a gas consisting of CO, CO_2, H_2 and H_2O. In a subsequent shift reactor the CO and H_2O in the gas react, yielding a gas composed mainly of H_2 and CO_2:

$$CO+H_2O \rightarrow CO_2+H_2 \qquad\qquad (4)$$

Figure 8 shows the equilibrium concentration of CO_2, CO, H_2O, H_2, CH_4 and C as a function of the amount of oxygen added (as metal oxide) to 1 kmol CH_4 at 950°C and 1 bar. If two kmoles of oxygen are added for each kmole of methane a 1:1 ratio of CO and H_2O is obtained, and ideally it would be possible to convert all of the fuel to CO_2 and H_2. In order to increase the yield of H_2 a minor part of the oxygen can be added in the form of steam. Thus, the overall reaction in the fuel reactor and the shift reactor(s) would be:
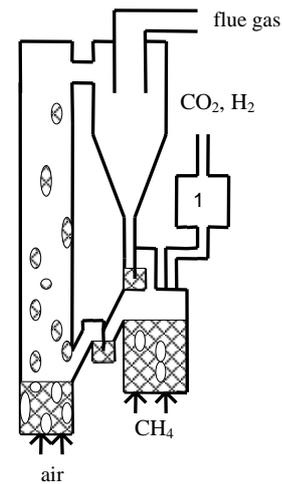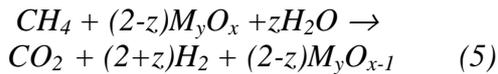
$$CH_4 + (2\text{-}z)M_yO_x + zH_2O \rightarrow$$
$$CO_2 + (2+z)H_2 + (2\text{-}z)M_yO_{x\text{-}1} \qquad (5)$$

The high concentration of the CO_2 in the resulting gas reduces the costs and energy spent in separation of CO_2 significantly. Depending on z, 60% or more of the heating value of the CH_4 is obtained as H_2 gas. In addition, substantial heat is released in the air reactor at high temperature, which can be used for power production.

Figure 8: Equilibrium amounts of chemical components when 1 kmol CH_4 reacts with different amounts of metal oxide, MO, at 1 bar and 950°C

Conclusions

Chemical-looping combustion using interconnected fluidized beds is a promising technique for the production of power with inherent separation of CO_2 from the flue gas. Results from reactivity tests of iron oxide as an oxygen carrier, as well as fluidization experiments in a cold model are promising when compared to criteria established from design modelling. The CLC concept could be extended to the combustion of solid fuel and CO_2 free hydrogen production.

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9. Audus, H., O. Kaarstad, and G. Skinner. *CO₂ capture by pre-combustion decarbonisation of natural gas*. In *4th International Conference on Greenhouse Gas Control Technologie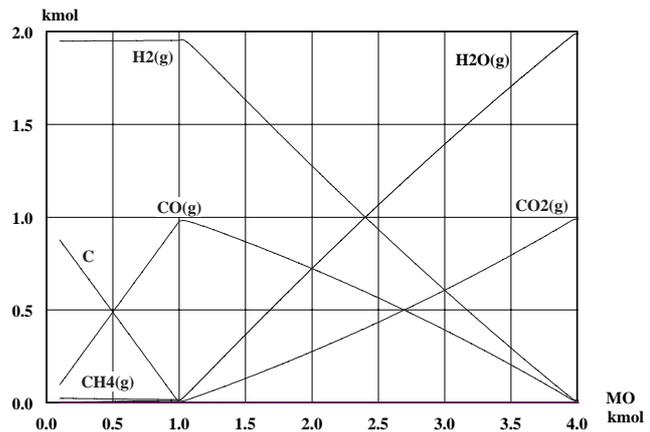s*. 1999. Interlaken, Switzerland: Pergamon.