GHGT-9

Using chemical-looping with oxygen uncoupling (CLOU) for combustion of six different solid fuels

Henrik Leion[a]*, Tobias Mattisson[b],Anders Lyngfelt[b]

[a]*Department of Environmental Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden*
[b]*Department of Energy and Environment Chalmers University of Technology, S-412 96 Göteborg, Sweden*

Abstract

Chemical-looping with oxygen uncoupling (CLOU) is a novel method to burn solid fuels in gas-phase oxygen without the need for an energy intensive air separation unit. This paper presents batch laboratory fluidized bed CLOU tests where six different solid fuels are used with a Cu-based oxygen carrier. The results show that CLOU results in a factor 3 to 15 faster fuel conversions than conversional chemical-looping combustion.
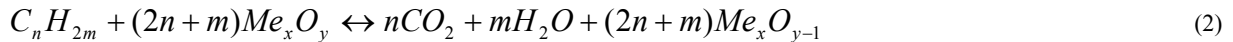ⓒ 2009 Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: CO_2-capture; Chemical-looping combustion; Chemical-looing with oxygen uncoupling; oxygen carrier; fluidized bed; kopper oxide;

1. Introduction

It is today believed that the increase in greenhouse gas concentrations has caused an increase in global temperature which in turn have caused changes in today's climate [1]. Chemical-looping combustion (CLC) has emerged as an attractive option for carbon dioxide capture. Since 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. The concept of CLC was proposed already in the 1980's [2] and the CLC-system consists of two reactors, a fuel and an air reactor. An oxygen carrier, usually a metal oxide, transports oxygen from the air reactor to the fuel reactor. The oxygen carrier is circulating between the reactors and is oxidized in the air reactor, according to the overall reaction (1), and reduced back to its initial state by the fuel, here assumed to be C, according to the overall reaction (2). The total amount of heat evolved from reaction (1) and (2) is equal to the heat released from conventional combustion, where the oxygen is in direct contact with the fuel.

$$O_2(g) + 2M_yO_{x-1} \leftrightarrow 2M_yO_x \qquad (1)$$

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

A majority of the publications concerning CLC have used gaseous fuel such as natural gas or methane [3]. When using solid fuel in CLC the fuel is fed directly into the fuel reactor. Here the gasification of the fuel and subsequent reactions of the gasification products, mainly CO and H_2, with the metal oxide particles will occur simultaneously in the same reactor. Successful attempts have been made to use solid fuels in CLC [4] but one of the main obstacles have been the slow gasification of the fuel and the large solid inventory of oxygen carrying material in such a system [5].

Another option of burning solid fuels is to use an oxygen carrier which releases O_2 in the fuel reactor and actually burns the fuel with gas-phase oxygen. This is referred to as chemical-looping with oxygen uncoupling (CLOU) and was first proposed by Mattisson et al. [6]. The advantage of CLOU, as compared to regular CLC, is that the slow gasification step is eliminated when employing solid fuels. The main advantage with this method is that less oxygen carrier material is needed in the system, which will also reduce the reactor size and associated costs. Although the focus in this paper is on solid fuels, the CLOU concept is highly relevant also for gaseous fuels such as natural gas and refinery gas and also liquid fuels, such as heavy residue oils.

This paper presents batch laboratory fluidized bed CLOU experiments where a number of different solid fuels are used with a Cu-based oxygen carrier. These results are compared with previously published CLC experiments [7] performed in the same setup, with the same fuels but with the Fe-based ilmenite as oxygen carrier.

2. Thermodynamics for CuO/Cu$_2$O

The CLOU-process needs oxygen carriers that have both the ability to release and capture oxygen at suitable temperatures and oxygen partial pressures. Three such metal oxide systems have been identified by Mattisson et al. [6]. This paper uses the CuO/Cu$_2$O system which can release oxygen in the gas phase through the following reversible reaction:

$4CuO \leftrightarrow 2Cu_2O + O_2(g)$ $\qquad \Delta H_{850} = 263.2$ kJ/mol O_2 $\qquad\qquad\qquad\qquad$ (3)

The equilibrium pressure of O2 over CuO gives a release of oxygen in air at temperatures above 1028°C and uptake of oxygen for Cu2O for lower temperatures in the same atmosphere. However, in the air reactor, the reduced metal oxide must be able to react with air to the oxidized form and hence lower the oxygen concentration to a reasonable level, given by the excess air. For instance, if the maximum outlet partial pressure of O2 from the air reactor should be 5% then Cu2O should be able to stay below this level at a temperature below 955°C.

When these oxidized particles are transferred to the fuel reactor where the partial pressure of O2 is low, they will release gaseous O2. The maximum concentration of oxygen is given by the temperature in the fuel reactor, which is determined by the temperature of the incoming particles, the circulation rate, as well as the heat of reaction in the fuel reactor. The reactions taking place in the fuel reactor are exothermic, thus it is possible to have a temperature increase in the fuel reactor, which results in a significantly higher partial pressure of O2. A higher partial pressure of oxygen will promote the overall conversion rate of the solid fuel. Further, it is also possible to use the temperature increase in the fuel reactor to choose a lower temperature in the air reactor.

3. Experimental

The oxygen carrier particle for the CLOU experiments was prepared by freeze granulation and was composed of 40wt% active material of CuO and 60wt% ZrO_2. The details of the freeze granulation procedure and particle characteristics can be found in earlier work [8]. The particles produced were spherical and the diameter of the particles was 90-125 μm. The fuels were the same as used by Leion et al. [7] and are presented in Table 1. All fuels were crushed and sieved to obtain particles in the size range 180-250 μm.

The experiments were conducted in a fluidized-bed reactor of quartz. In order to achieve good solids mixing in the bed, the reactor was conically shaped just above the distributor plate. The reactor had a total length of 870 mm with a porous quartz plate placed 370 mm from the bottom of the reactor. The porous plate and the reactor below the plate had an inner diameter of 10 mm. Above the distributor plate the inner diameter of the reactor increased to reach 30 mm at a height of 20 mm above the porous plate. The diameter was then constant for 250 mm after which the reactor diameter increased further to 45 mm for a length of 100 mm. This disengaging section was constructed in order to prevent smaller coal and metal oxide particles from leaving the reactor.

Table 1: Fuels use in this work

Fuels		Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
Volatiles	%	10	21.6	45.3	37	50.5	11
Moisture	%	8.0	8.3	8.5	3.3	10	3
Ash	%	0.5	15.9	1.4	5.2	5.0	3
HHV	MJ/kg	31.7	29.9	26.4	29.1	20.9	
C	%	81.3	62.5	66.1	74	69.9	83
H	%	2.9	3.5	4.7	5	5.4	
S	%	6.0	0.7	0.1	0.6	1.01	
N	%	0.9	1.4	0.7	1.4	0.63	
O	%	0.5	7.7	18.5	10.6	23.1	

A sample of 15 g of oxygen carrier particles was mixed with 15 g of quartz sand of the same size and placed on the porous plate before heated in 10% O_2 to the reaction temperature. When the bed was not fluidized the bed height was approximately 30 mm. The particles were then alternatingly exposed to an oxidizing gas of 10% O_2 in nitrogen followed by a reducing period where 0.1 g of fuel was introduced to the bed of oxygen carriers fluidized with pure nitrogen, thus simulating the cyclic conditions of a CLOU system burning solid fuel. The experiments were performed in this manner for 3-5 cycles for each test case using an inlet flow of 900 mL/min (at 1 bar, 0°C) for both

oxidation and reduction. The gas from the reactor was led to an electric cooler, where the water was removed, and then to a gas analyzer (Rosemount NGA-2000) where the concentrations of CO_2, CO, CH_4 and O_2 were measured in addition to the gas flow.

The temperature was measured 5 mm under and 10 mm above the porous quartz plate, i.e. inside the bed of oxygen carrier particles, using Pentronic CrAl/NiAl thermocouples with inconel-600 enclosed in quartz shells. The exothermic nature of both the oxidation and reduction means that the bed temperature varied throughout the cycle. The temperature given in the paper is the set-point temperature, i.e. the temperature at the beginning of the reduction. From high frequency measurements of the pressure drop it was possible to see that the bed was fluidized.

4. Data evaluation

The reaction of the fuel with the oxygen carrier was monitored by measuring the concentrations of CO, CO_2 and CH_4 as a function of time. The average conversion rate of the fuel was established by integration of these concentrations as a function of time and calculated from:

$$r_{av} = \frac{\int_{t_0}^{t_1} F_t(x_{CO_2} + x_{CO} + x_{CH_4})dt}{t_1 \int_{t_0}^{t_2} F_t(x_{CO_2} + x_{CO} + x_{CH_4})dt} \tag{4}$$

The first carbon containing gases reaches the analyzer at t_0, t_1 is the time elapsed since the start of the cycle and t_2 is the time when all added carbon has been converted. F_t is the flow of gas from the outlet of the reactor and x_i is the concentration of species i after condensation of steam. In this work the average rate was calculated for the period needed to reach 95% conversion of the carbon added to the bed.

5. Results

Figure 1 (left) shows the outlet gas concentrations after condensation of water as a function of time for a reducing period with lignite and the following oxidizing period. Figure 1 (right) gives a close-up of the same reduction. The set-point temperature, 950°C, is defined as the temperature as measured in the bed at the end of the oxidation prior to the reduction period when no reaction occurs. The fluidizing medium is pure nitrogen during the reduction and during oxidation the inlet oxygen concentration is 10% in nitrogen.
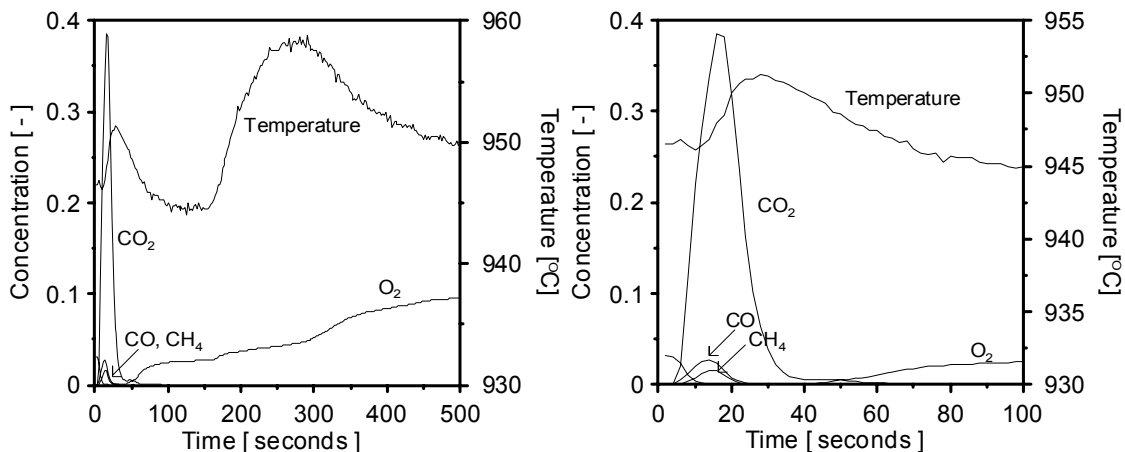

Figure 1: Concentration profile for the reduction and oxidation for a cycle with 0.1 g of lignite in 15 g CuO/ZrO$_2$ (left). Close-up of the reduction (right). The O₂ concentration during oxidation is 10%. The set-point temperature is 950°C and the fluidizing gas

Before the fuel is fed into the bed the oxygen concentration is 3%, somewhat lower than the equilibrium partial pressure for this temperature. The temperature has also dropt a few degrees due to the endothermic release of oxygen in reaction (3). As the fuel is added a small peak of CH_4 and CO is seen in the beginning of the reduction period. This is due the devolatilization of the fuel. At the same time the combustion starts and the CO_2 concentration and the temperature increases rapidly. The oxygen concentration falls to zero which indicates that the combustion of the fuel is faster that the release of oxygen from the particles. As the fuel burns out and the CO_2 concentration and the temperature drops, the O_2 increase to about the same level as before the reduction indicating that there is still CuO left in the bed that can release oxygen.

When no gaseous carbon species, i.e. CO_2, CO or CH_4, are detected in the outlet gas from the reactor, the burnout of the fuel is assumed to be complete and the oxidizing with 10% O_2 begins. The temperature rapidly increases due to the very exothermic oxidation. A large fraction of the particle oxidation takes place at an O_2 level fairly close to the equilibrium partial pressure for this temperature.

Figure 2 (left) shows the outlet gas concentrations after condensation for the same conditions as in Figure 1 but with petroleum coke as fuel. Figure 2 (right) gives a close-up of the reduction period. The main difference is the very low concentrations of CH_4 and CO, under 0.1% and therefore not visible in Figure 2, and the higher O_2 level during reduction. This means that more oxygen is released from CuO than is needed for the combustion. Thus, the release of oxygen from the oxygen carrier is in this case faster that the combustion of the fuel.

Further the oxidation of the particle is much slower in Figure 2 compared to Figure 1. This is due to the high carbon and sulphur content in petroleum coke, making it a more reducing fuel. This can also be seen if the O_2 concentration in the end of the reduction in Figure 1 is closely compared to the same condition in Figure 2. In the case with the highly reducing petroleum coke the O_2 concentrations starts to fall whereas it is increasing or constant in the lignite case indicating that the bed is running short of CuO that can release oxygen.
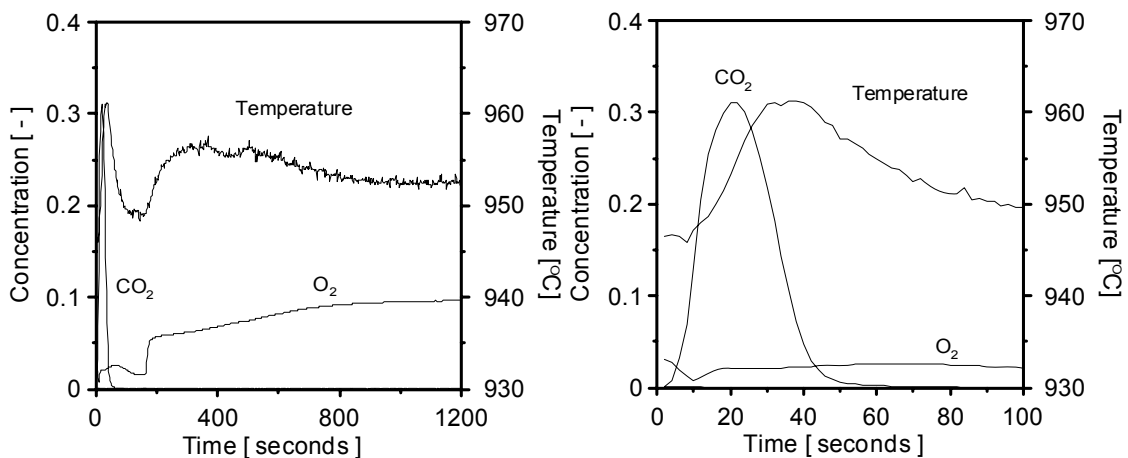

Figure 2: Concentration profile for the reduction and oxidation for a cycle with 0.1 g of petroleum coke in 15 g CuO/ZrO$_2$ (left). Close-up of the reduction (right). The O_2 concentration during oxidation is 10%. The set-point temperature is 950˚C and the fluidizing gas during reduction is pure nitrogen.

All the other fuel showed similar type of behavior as those shown in Figure 1 and 2 although the rate of reactions varied between that of lignite and petroleum coke. The outlet fraction of unburt volatiles was less or equal to that of the lignite. There was always some O_2 in the outgoing gases during the reduction, and the oxidation period was always shorter compared to that of the petroleum coke. The time for 95% conversion of all used fuel and the

corresponding reaction rates are shown in Table 2 and 3. For comparison, results from CLC experiments performed with the same fuels but with ilmenite as oxygen carrier are included in the tables. These experiments were performed at a temperature of 970˚C and 92% steam in N_2 in the fluidizing gas. These CLC experiments have previously been presented by Leion et al. [7].

Table 2: Conversion times in CLOU and CLC for different fuels

Time for 95% conversion (s)	Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
CLOU	41	40	30	51	25	28
CLC	648	612	282	606	84	378

Table 3: Conversion rates in CLOU and CLC for different fuels

Rate for 95% conversion (%/sek)	Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
CLOU	2.3	2.4	3.2	1.9	3.8	3.4
CLC	0.15	0.16	0.34	0.16	1.13	0.25

It is clear that CLOU gives much faster conversion rates than CLC. In the case of petroleum coke and South African coal the CLOU conversion is as much as 15 times faster. It is also important to keep in mind that the CLC experiments were done at a slightly higher temperature, 970˚C as compare to 950˚C in the CLOU experiments, and with a very high content of steam, 92%, in the fluidizing gas, both factors which would increase reaction rates using CLC.

The differences in reactivity between the fuels are more pronounced in CLC than in CLOU. For example the lignite, which in both cases had the fastest conversion rate, was a factor 8 faster than petroleum coke in CLC but only a factor 1.6 faster in CLOU. This can be explained by the difference in reaction paths between CLC and CLOU. In CLC, the limiting reaction is the slow gasification of the fuel, whereas in CLOU the burning of the fuel is limiting the reaction rate up until the level where all oxygen released from the oxygen carriers is consumed. At this point the release of oxygen from the oxygen carrying particle becomes rate limiting, thus which type of fuel that is used is no longer important.

In Table 4 the fraction of CO in the carbon containing flue gases is presented for the same experiments as in Table 2 and 3. It is obvious that CLOU gives much lower fractions of CO than CLC, in the case of petroleum coke the difference is as much as a factor 80. Also in CLOU, all CO was produced during the initial devolatilization of the fuel whereas in CLC the CO was produced throughout the whole cycle, even if the majority was formed during the devolatilization stage.

Table 4: Fraction of CO in flue gases in CLOU and CLC for different fuels

Fraction of CO (%)	Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
CLOU	0.1	1.7	3.7	3.3	4.8	0.6
CLC	8.0	25	37	26	62	21

Table 5 presents the fraction of CH_4 in the carbon containing flue gases for the CLOU experiments. The CH_4 fractions in CLC was not presented by Leion et al. [7] but in other experiments done by the same author with a slightly different setup [9] the CH_4 levels were 4% for petroleum coke and 8% for the Indonesian coal, thus, somewhat higher than in the performed CLOU experiments. Hence, CLOU gives somewhat better conversion of CH_4, but in both CLC and CLOU all CH_4 was detected during the initial devolatilization of the fuel.

Table 5: Fraction of CH_4 in flue gases in CLOU and CLC for different fuels

Fraction of CH_4 (%)	Mexican petroleum coke	South African coal	Indonesian coal	Colombian coal	German lignite	Swedish wood char
CLOU	0.1	1.0	2.6	3.3	2.3	0.6

When building a full scale CLOU-unit it is possible to arrange oxygen carrier load and fuel feeding in order to get good contact between oxygen carrier and fuel. With the right arrangement a complete conversion of carbon to CO_2 should be possible in a CLOU-unit. This is not possible in a CLC-unit since in a well mixed CLC-fuel reactor there will be fuel particles all the way up to the top of the bed. Thus, there will always be a fraction of the gasification products, i.e. CO and H_2, in a CLC-unit which will not have sufficient contact with the oxygen carrier even if the reactivity of the metal oxide particles is high.

6. Conclusions

The fuel conversion of six different solid fuels in CLOU was compared to the fuel conversion of the same fuels in CLC. CLOU gives between a factor 3 faster conversion, for high volatile lignite, up to a factor 15 faster for low volatile petroleum coke. There were also significantly lower fractions of unconverted flue gases in CLOU with at least a factor 10 less CO. In the case of petroleum coke the difference was a much as a factor 80. The amount of CH_4 was also lower in CLOU.

7. Acknowledgment

1. Rosenzweig, C., D. Karoly, M. Vicarelli, P. Neofotis, Q. Wu, G. Casassa, A. Menzel, T.L. Root, N. Estrella, B. Seguin, P. Tryjanowski, C. Liu, S. Rawlins, and A. Imeson, *Attributing physical and biological impacts to anthropogenic climate change.* Nature, 2008. 453(15): p. 353-357.
2. Ishida, M., D. Zheng, and T. Akehata, *Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis.* Energy (Oxford, United Kingdom), 1987. 12(2): p. 147-54.
3. Hossain, M.M. and H.I. de Lasa, *Chemical-looping combustion(CLC) for inherent CO2 separation – A review.* in press Chemical Engineering Science, 2008.
4. Berguerand, N. and A. Lyngfelt, *Design and Operation of a 10 kWth Chemical-Looping Combustor for Solid Fuels – Testing with South African Coal.* accepted for publication in Fuel, 2008.
5. Leion, H., T. Mattisson, and A. Lyngfelt, *The use of petroleum coke as fuel in chemical-looping combustion.* Fuel, 2007. 86(12-13): p. 1947-1958.
6. Mattisson, T., A. Lyngfelt, and H. Leion, *Chemical-looping with oxygen uncoupling for combustion of solid fuels.* Accepted for publication in International Journal of Greenhouse Gas Control, 2008.
7. Leion, H., T. Mattisson, and A. Lyngfelt, *CO2 capture from direct combustion of solid fuels with Chemical-Looping Combustion*, in *33rd International Technical Conference on Coal Utilization & Fuel Systems*. 2008: Clearwater Florida, USA.
8. Mattisson, T., H. Leion, and A. Lyngfelt, *Chemical-looping with oxygen uncoupling using CuO/ZrO2 with petroleum coke.* Accepted for publication in Fuel, 2008.
9. Leion, H., T. Mattisson, and A. Lyngfelt, *Solid Fuels in Chemical-Looping Combustion.* International Journal of Greenhouse Gas Control, 2008. 2: p. 180-193.