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Use of Hopcalite derived Cu-Mn mixed oxide as Oxygen Carrier for Chemical Looping with Oxygen Uncoupling Process

Iñaki Adánez-Rubio, Alberto Abad*, Pilar Gayán, Imanol Adánez, Luis F. de Diego,

Francisco García-Labiano, Juan Adánez

Instituto de Carboquímica (ICB-CSIC), Dept. of Energy & Environment, Miguel

Luesma Castán, 4, Zaragoza, 50018, Spain

*Corresponding author. Tel.: +34 976 733977; fax: +34 976 733318

Email address: abad@icb.csic.es

ABSTRACT

Chemical-Looping with Oxygen Uncoupling (CLOU) is an alternative Chemical Looping process for the combustion of solid fuels with inherent CO₂ capture. The CLOU process needs a material as oxygen carrier with the ability to give gaseous O₂ at suitable temperatures for solid fuel combustion, e.g. copper oxide and manganese oxide. In this work, treated commercial Carulite 300[®] was evaluated as oxygen carrier for CLOU. Carulite 300[®] is a hopcalite material composed of 29.2 wt.% CuO and 67.4 wt.% Mn₂O₃. Oxygen release rate and the fluidization behavior, regarding agglomeration and attrition rate, were analyzed in a TGA and in a batch fluidized bed respectively. Experiments in a batch fluidized bed reactor were carried out at temperatures ranging from 800 to 930 °C with a medium volatile bituminous coal from South Africa and its char as fuels. The hopcalite derived oxygen carrier showed high O₂ release rate, no unburnt products at low oxygen carrier to fuel mass ratios and very high oxygen transference rate by gas-solid reaction. This material has the capacity to generate gaseous oxygen at lower temperatures than Cu-based oxygen carriers, which suggest this material is suitable to work at lower temperatures in the fuel reactor without the presence of unburnt products; however its low mechanical resistance after redox cycles makes necessary an improvement of its physical properties for being use as an oxygen carrier.

Keywords: CO₂ capture, combustion, coal, CLOU, mixed oxide, copper, manganese

1 INTRODUCTION

The Chemical Looping with Oxygen Uncoupling (CLOU) is a type of Chemical Looping Combustion (CLC) technology that allows the combustion of solid fuels with inherent CO₂ separation using oxygen carriers. CLOU technology takes advantage of the property of some metal oxides for generating gaseous oxygen at high temperatures, e.g. 800-1000 °C, and may be particularly suitable for solid fuels, such as coal and biomass. The oxygen generated by the oxygen carrier reacts directly with the solid fuel, which is mixed with the oxygen carrier in the fuel reactor. The oxygen carriers for CLOU must first to release oxygen through decomposition inside the fuel reactor and also have the ability to be regenerated by air inside the air reactor. Three metal oxide systems were found to have suitable properties for use as oxygen carriers in the CLOU process: CuO/Cu₂O, Mn₂O₃/Mn₃O₄, and Co₃O₄/CoO.¹ Combustion of solid fuels by CLOU process has better performance than *i*G-CLC process.² In the *i*G-CLC process the solid fuel must be gasified at the fuel reactor. The gasification reaction is slow and part of the unreacted char exits from the fuel reactor,^{3,4} thus requiring the use of a carbon stripper to re-circulate the unconverted char to the fuel reactor.⁵ Moreover, there are always unburnt products at the fuel reactor gas outlet.⁶

In CLOU process the char conversion is much faster than in *i*G-CLC, this fact was demonstrated by Mattisson et al.⁷ and Eyring et al.⁸ in experiments done in batch fluidized bed reactors with different solid fuels. This fact was also corroborated in a continuous CLOU unit with a Cu-based oxygen carrier burning different coals and biomass,⁹⁻¹¹ being the fast char conversion fundamental to obtain high CO₂ capture efficiencies. Moreover, complete combustion to CO₂ and H₂O, together with a slight

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excess of O₂ in the fuel reactor exit stream was observed in experiments done with different solid fuels in the continuous unit.⁹⁻¹¹

Operating conditions in the air reactor and fuel reactor would be determined by the thermodynamics of the oxygen release reaction with each specific oxygen carrier.

Figure 1 shows the partial pressure of oxygen as a function of the temperature for the systems CuO/Cu₂O, Mn₂O₃/Mn₃O₄, and Co₃O₄/CoO, calculated using HSC software.¹²

The O₂ concentration at equilibrium conditions must be low (4 vol.% or lower) at the air reactor temperature, in order to have a high use of the oxygen in air. On the other hand, the equilibrium concentration of oxygen in the fuel reactor will be given by the temperature in the reactor determined by the energy balance to the CLOU system. A high equilibrium partial pressure of oxygen together with a very reactive oxygen carrier will promote the overall conversion rate of the solid fuel in the fuel reactor. In addition, the combustion of the fuel will decrease the oxygen concentration in the reactor and can improve the decomposition reaction of the metal oxide particles. The temperature at which the air and fuel reactor will operate are determined by the temperature of the incoming particles, the circulation rate and the heat of reaction in both reactors, as it was analyzed by Eyring et al. for a CLOU process.⁸ The oxygen release reactions are endothermic for the three metal oxides, as it is shown in reactions (1), (2) and (3) for the three metal oxides.

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However, the global process can be exothermic in function of the metal oxide used as oxygen carrier. In the case of copper and manganese oxides, the overall reaction with carbon is exothermic in the fuel reactor, as it is showed in reactions (4) and (5).^{1, 13} Thus, it is possible to have a temperature increase in the fuel reactor, which results in a significantly higher partial pressure of O₂ at equilibrium conditions. However, the reaction of cobalt oxide with carbon is an endothermic reaction; see reaction (6). In addition to heat release, overall heat balances to include heat losses (or heat inputs) and heat withdrawals (either in oxygen carrier or fluidizing gas) are needed to obtain the temperatures in the reactors. Peltola et al.¹³ studied the mass and energy balance for CLOU process using a Cu-based oxygen carrier and predicted that low oxygen carrier inventory (400-680 kg/MW_{th}) will be necessary to complete combustion of the fuel with a temperature difference between fuel and air reactor about 50°C.

Mattisson¹⁴ reviewed the materials proposed to be used in CLOU, including oxygen carriers based on Cu,^{15, 16} and mixed oxides of Cu-Mn,^{17, 18} Mn-Fe and Mn-Si.¹⁹

Particles of 60 wt.% CuO prepared by spray drying were tested in a 1.5 kW_{th} CLOU continuous unit,⁹ where proof of the concept of the CLOU process was demonstrated using coal as fuel.⁹ The effect of the coal rank on the process performance was also analysed¹⁰ in this unit using a lignite, two bituminous coals and one anthracite.

Moreover, biomass combustion was tested with encouraging results.¹¹ The oxygen

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carrier did not show decrease in its reactivity, nor agglomeration problems. However, this oxygen carrier showed an important decrease in the crushing strength of the particles related with an increase in the porosity with the operation time. This fact indicates the need of an improvement in the lifetime of the particles.²⁰ So, nowadays the main effort to continue with the development of CLOU process is to find a suitable oxygen carrier for the process with high reactivity with solid fuels, high oxygen release rate and low attrition rate.

Respect to the Mn-based oxygen carriers, these materials have some advantages respect to Cu-based material. Manganese materials are cheaper than copper ones and it could be possible to work at lower temperatures in the fuel reactor. Therefore, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ has a high potential for CLOU process with high O_2 partial pressure at temperatures of interest for coal combustion. However, according with thermodynamics, temperatures in the air reactor lower than 815°C are needed to oxidize Mn_3O_4 to Mn_2O_3 at 5 vol.% of O_2 , in order to have a high use of the oxygen in air. At these conditions, in practice, it has not been possible to carry out this oxidation.²¹⁻²³

Therefore, to overcome this problem, a high effort has been put in the development of mixed oxides with CLOU properties, such as Mn-Fe, Mn-Si, Mn-Mg.²⁴⁻³³ These materials have been tested in batch reactors and continuous units with good performance,²⁴⁻³² although their oxygen transport capacities for CLOU are low (always below 1.5%). Also, a perovskite material, $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$, was used as oxygen carrier in a 10 kW_{th} continuous CLC pilot plant with pet coke and wood char, fuels with low amount of volatiles, under iG-CLC or CLOU operation conditions.³³ This oxygen carrier was able to release gaseous oxygen, but the oxygen release rate was not enough

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to burn completely the fuel and they obtained worst result operating at CLOU than *iG*-

CLC operation conditions, contrary to what was found for Cu-based oxygen carriers.²

Mn-Cu mixed oxides has a higher potential for CLOU process due to the oxygen

originated by CuO can be regenerated at temperatures up to 900 °C.^{18, 34} Different Cu-

Mn material had been prepared in recent years. Xu et al.^{35, 36} prepared oxygen carriers

impregnating manganese ores with copper nitrate solution, obtaining oxygens carriers

with a amount of Cu between 0.5 wt.%³⁵ and 2 wt.%.³⁶ These oxygen carriers had been

tested in a batch fluidized bed reactor³⁵ and in a CLC continuous unit with gaseous

fuels.³⁶ They observed that the mixed oxide improve the results obtained using only the

manganese ore, improving the reactivity and the combustion efficiency. Azad et al.³⁴

also studied oxygen carriers of Cu-Mn mixed oxides, in this case with a 30.8 wt.% of

CuO and 69.2 wt.% of Mn₂O₃, prepared by extrusion. They observed that the oxygen

carrier had good reactivity with CH₄, but CO was present in the exit gases from the

batch fluidized bed reactor.

It is well known that a Cu-Mn mixed oxide called hopcalite is used as catalyst material,

which can be prepared by different methods at laboratory and industrial scale.³⁷⁻³⁹

Hopcalite is used to catalytically oxidize CO at ambient temperature³⁹⁻⁴¹ and ethylene at

low temperatures.⁴² The characteristics of this material make it very interesting for its

use in the CLOU process, since it can release free oxygen by means of reaction (7):

The aim of this work was to investigate the performance a Cu-Mn mixed oxide derived

from commercial catalyst Carulite 300[®] as oxygen carrier for the CLOU process. For

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that, the oxygen release rate and the fluidization behavior, regarding agglomeration and attrition rate, were analyzed in a TGA and in a batch fluidized bed. Then, the maximum oxygen generation rate of the material was determined in a batch fluidized bed reactor with fuel addition at different temperatures.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Oxygen carrier

Commercial particles of hopcalite (Carulite 300[®], Carus Corporation) were used as the precursor of the oxygen carrier particles. This commercial material is a mixed oxide of Mn (67.4 wt.% of Mn₂O₃), Cu (29.2 wt.% CuO) and an organic matrix to cement the material. The particle size of the commercial material is +0.8-1.7 mm. The commercial particles were developed for operation at atmospheric conditions (temperature and pressure); to use them at high temperature conditions it is necessary to stabilize the hopcalite particles by calcination. A study of how the calcination temperature affects to the physical properties of the particles was first carried out. It was found that a calcination period of 1h at 950°C was the optimum. For more information about the stabilization study see the supplementary material. Then, the particles were crushed and sieved to obtain the needed particle size diameter (+0.1-0.3 mm) for fluidization operation.

2.1.2 Oxygen carrier characterization

Physical and chemical characterization was carried out with these particles. The oxygen transport capacity, R_{OC} , was calculated as a function of the composition of the particles

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after the stabilization step. The crushing strength was determined by measuring the force needed to fracture a particle using a Shimpo FGN-5X crushing strength apparatus. The crushing strength was taken as the average value of at least 20 measurements of particles with size diameter between 0.1 to 0.3 mm. The real density was determined by He picnometry in a Micromeritics AccuPyc II 1340. The surface area of the oxygen carrier was determined by the Brunauer-Emmett-Teller (BET) method by adsorption/desorption of nitrogen at 77 K in a Micromeritics ASAP-2020 (Micromeritics Instruments Inc.), whereas the pore volumes were measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by X-ray diffraction (XRD) pattern collected by a Bruker D8 Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector. The diffraction pattern was obtained over the 2θ range of 10° to 80° with a step of 0.019° . The assignation of crystalline phases was performed on base of Joint Committee on Powder Diffraction Standards. DIFFRAC.EVA and TOPAS software were used for phase assignation and quantification. The oxygen carrier particles were also analyzed in a scanning electron microscope (SEM) ISI DS-130 coupled to an ultra thin window PGT Prism detector for energy-dispersive X-ray (EDX) analysis. Table 1 shows the main characteristics of the oxygen carrier particles.

The main phase determined by XRD is $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, so the mixed oxide was formed from the separate oxides during the oxygen carrier calcination step. Also, a small amount of free Mn_3O_4 remained in the stabilized particles; this fact can reduce the oxygen transport capacity for CLOU, because it is difficult to recover the O_2 release by oxygen carriers based exclusively on Mn oxide.^{22, 43, 44}

2.1.3 Solid fuels

The fuels used were a medium volatile bituminous South African coal and char prepared from this coal by pyrolysis.⁴⁵ The coal and char particle size used in this study was +200-300 µm. Elemental and proximate analyses of the coal and its char are shown in Table 2.

2.2 Experimental set ups

2.2.1 Thermogravimetric Analyzer

Multicycle tests to analyze the reactivity of the oxygen carriers during successive reduction-oxidation cycles were carried out in a TGA CI Electronics type described elsewhere.⁴⁶

Reactivity data were obtained in TGA tests from the weight variations during the reduction and oxidation cycles as a function of time. The oxygen carrier conversion was calculated as:

$$\text{For reduction: } X_{Red} = \frac{m_{Ox} - m}{m_{Ox} - m_{Red}} \quad (8)$$

$$\text{For oxidation: } X_{Ox} = 1 - \frac{m_{Ox} - m}{m_{Ox} - m_{Red}} \quad (9)$$

m being the mass of sample at each time; m_{Ox} is the mass of the sample fully oxidized and m_{Red} is the mass of the sample in the reduced form. Oxygen generation rates were calculated with Equation (10):

$$r_{O_2,Red} = R_{OC} \cdot \frac{dX_{Red}}{dt} \quad (10)$$

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R_{OC} is the oxygen transport capacity of the oxygen carrier particles for CLOU reaction, see equation (7), and was calculated as:

$$R_{OC} = \frac{m_{Ox} - m_{Red}}{m_{Ox}} \quad (11)$$

2.2.2 Batch Fluidized Bed Reactor for gaseous fuels (N_2 -air cycles)

Reduction-oxidation multi-cycles were carried out in a fluidized bed reactor to understand the oxygen release behaviour of the oxygen carrier under operating conditions similar to that existing in the CLOU process. A detailed description of the experimental apparatus can be found in the Supporting Information. The fluidization behaviour of the materials with respect to agglomeration phenomena and attrition rate could also be observed. The attrition rate is calculated with the following equation:

$$v_{attrition} = \frac{\frac{m_{elut}}{m_{OC}} * 100}{t} * 3600 [\%/h] \quad (12)$$

where $v_{attrition}$ is the attrition rate (%/h); m_{elut} is the oxygen carrier elutriated from the batch fluidized bed reactor (filters + pipes, with a size lower than 40 μm), m_{OC} is the total mass of the oxygen carrier in the bed and t the operation time. Deeper information of the batch fluidized bed reactor can be found in the supplementary material.

Several reduction-oxidation cycles using N_2 or CO_2 as fluidization media were carried out in this facility to determine the oxygen release behaviour as a function of the operating conditions. The conversion of the oxygen carrier as a function of time was calculated from the oxygen outlet concentration by the equations:

Reduction
$$X_{Red}(t) = \int_0^t \frac{F_{out}}{N_{O_2}} (y_{O_2,out}) dt \quad (13)$$

Oxidation
$$X_{Ox}(t) = \int_0^t \frac{1}{N_{O_2}} (F_{in} \times y_{O_2,in} - F_{out} \times y_{O_2,out}) dt \quad (14)$$

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X being the conversion of the oxygen carrier; F_{in} is the molar flow rate of the gas incoming to the reactor; F_{out} is the molar flow rate of the gas leaving the reactor; $y_{O_2,in}$ is the molar fraction of O_2 incoming to the reactor; $y_{O_2,out}$ is the molar fraction of O_2 exiting the reactor; N_{O_2} are the moles of molecular oxygen which can be released from fully oxidized oxygen carrier, and t is the time.

2.2.3 Batch Fluidized Bed Reactor for solid fuels (Fuel-air cycles)

Reduction-oxidation multi-cycles were carried out in a fluidized-bed reactor with solid fuel addition to measure the oxygen release rate when fuel combustion is happening at the same time as O_2 release. The experimental work was carried out in a set-up consisting of a fluidized bed reactor, a system for gas feeding, a solid fuel feeding system, and the gas analysis system. Further information about the batch fluidized bed reactor for solid fuels is presented in the Supporting Information.

The instantaneous rate of oxygen generation per amount of oxygen carrier (oxygen transference rate), $r_{O_2,Red}(t)$, was calculated from a mass balance to oxygen atoms in the reactor.

$$r_{O_2,Red}(t) = \frac{M_{O_2}}{m_{Ox}} \left[F_{O_2} + F_{CO_2} + 0.5(F_{CO} + F_{H_2O}) - 0.5F_{O,SF} \right] \quad (15)$$

Before starting a reducing period, the oxygen carrier particles were fully oxidized, i.e. the oxygen carrier conversion was $X_{Ox} = 1$. As the oxygen carrier particles were reacting during reduction period, the oxidation degree decreased. Thus, the oxygen carrier conversion was calculated from the integration of $r_{O_2,Red}$ with time:

$$X_{Ox}(t) = 1 - \frac{m_{Ox}}{M_{O_2} N_{O_2}} \int_{t_0}^t r_{O_2,Red}(t) dt \quad (16)$$

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Thus, the final conversion of the particles, X_{Ox} , was calculated by integrating Equation (16) for the time spent in reduction conditions.

In the same way, an oxygen balance was done to calculate the oxidation rate with air – Equation (17)– and the evolution with time of the oxygen carrier conversion, X_{Ox} – Equation (18)–. In some cases, char was not completely converted during the reduction period because the depletion of oxygen in the particles was reached. Thus, CO_2 and CO can appear during the oxidation period as the remaining char is burned with oxygen in air, being the oxygen for char combustion considered in Equation (18).

$$(-r_{O_2,Ox}(t)) = \frac{M_{O_2}}{m_{Ox}} \left[0.21F_{air} - F_{O_2} - (F_{CO_2} + 0.5F_{CO}) \right] \quad (17)$$

$$X_{Ox}(t) = X_f + \frac{m_{Ox}}{M_{O_2} N_{O_2}} \int_0^t (-r_{O_2,Ox}(t)) dt \quad (18)$$

3 RESULTS

3.1 Oxygen carrier reactivity in TGA

The oxygen carrier was first characterized using a TGA to analyze the oxygen release and regeneration rates. Ten redox cycles were carried out alternating air and nitrogen in the reacting atmosphere. Figure 2 shows the solids conversion vs. time curves for the oxygen carrier particles during the reduction with N_2 and oxidation with air at 950°C. The maximum reduction conversion of calcined hopcalite reached a value of 0.77, corresponding to an oxygen transport capability of 3.7 wt.%. This value is lower than the theoretical value of 4.7 wt.%, calculated assuming the mixed oxide was $Cu_{1.5}Mn_{1.5}O_4$. Both reduction and oxidation reaction rates, as well as the oxygen transport capability, were maintained during all the cycles done in the TGA with the calcined hopcalite. Moreover, it can be observed that the oxygen carrier was fully

regenerated ($X_{Ox}=0.77$) in less than 180 s, recovering all the oxygen released during the reduction, see Figure 2(b).

3.2 Oxygen carrier behaviour in batch fluidized bed for gaseous fuels

Reduction-oxidation multi-cycles were carried out in the batch fluidized-bed reactor to know the oxygen release and the behavior with respect to agglomeration and attrition phenomena during fluidization. A total of 30 h of fluidization to in the temperature range of 800-900 °C were carried out during 35 consecutive redox periods. As example, Figure 3 shows the oxygen concentration at the outlet of the reactor for 5 consecutive redox periods of the hopcalite derived oxygen carrier. It can be seen a constant reactivity both for reduction and oxidation reactions.

Figure 4 shows the solid conversion and oxygen concentration profile during a reduction and regeneration period in a typical cycle. The oxygen concentration and therefore the oxygen release rate, decreases slowly during the reduction cycle. Initially 2.5 vol.% O_2 was reached but decreased to 0.7 vol.% when the solid conversion reach the value of $X_{Ox} = 0.55$. This behaviour is similar to that found with mixed oxides oxygen carriers prepared with Cu and Mn for CLOU.^{17, 18, 34} Underline that the oxygen carrier gave oxygen concentration higher than the equilibrium condition for the CuO, but lower than the Mn_2O_3 equilibrium at each temperature.

The effect of the reaction temperature in the batch fluidized bed was analyzed in the 800-900°C interval. Figure 5 shows oxygen concentration profiles and the solid conversion during a reduction period with N_2 using different bed temperatures. These results are similar to those obtained by Azad et al.³⁴ with Cu-Mn oxygen carriers prepared by extrusion and tested in a batch fluidized bed reactor. Thus, at all temperatures, the oxygen release rate was limited by thermodynamic restrictions. At the

lowest temperature, the solid decomposition is highly limited and the oxygen concentration quickly decrease to values near 1%, but always higher than the O₂ equilibrium concentration corresponding for the CuO at this temperature (0.11 vol.%). At the highest temperature (900 °C), the solid reached a value of solid conversion of 0.5 in less than 30 minutes. Note that reduction rate was different of that found by TGA. In the fluidized bed, the O₂ concentration equilibrium limits the O₂ release rate since the gas flow has reached an O₂ concentration close to the equilibrium one at each temperature, whereas the reaction rate in TGA was not limited by the equilibrium concentrations. In all experiments the oxygen carrier was fully regenerated, recovering all the O₂ released, at all temperatures using a 10 vol.% of O₂ in the oxidation step. The effect of the oxygen concentration in the oxidation reaction was analyzed using 21 vol.%, 10 vol.% and 5 wt.% of oxygen during oxidation at the same temperature. Figure 6 shows the solid conversion in a typical oxidation period at 850 °C. An important effect of the oxygen concentration was found. The oxidation reaction rate was low when the oxygen concentration in the gas flow was 5 vol.% and thus the solid conversion after 20 minutes was low, although the material was totally regenerated in more than 1 hour. However, increasing the oxygen concentration to 21 vol.%, the regeneration of the oxygen carrier is almost completed in 10 min. Note that from TGA experiments, full conversion was reached in less than 180 seconds (see Figure 2) with air. These results confirmed those pointed out in previous works^{16, 20} about the important effect of the operating temperatures on the reduction and oxidation reactors for the successful development of the process.

The multi-cycle test carried out in the fluidized bed also allowed determining the fluidization behavior of the oxygen carrier with respect to the attrition and

agglomeration phenomena. Figure 7 shows the attrition rate for hopcalite derived oxygen carrier as a function of the operation time. The attrition rate of this material was initially high (0.4 %/h) due to rounding of the particles. After 20 h of operation the value of the attrition rate seemed stable around of 0.04 %/h. However, this value was not stable after 30 h of hot fluidization. This sharp increase could be due to a reduction of the crushing strength of the particles and a reduction of the physical stability of the oxygen carrier particles; see Section 3.4. More hours of operation would be needed to determine the particle lifetime of the material.

3.3 Batch reactor experiments with coal and char: effect of the oxygen carrier to fuel ratio

In the fuel reactor of a CLOU process, two processes happen in series: oxygen generation and coal combustion with the oxygen generated. Moreover, the coal conversion process in the fuel reactor includes a first step of devolatilization, followed by the volatile matter and char combustion. Also, the gas-solid reaction between reacting gases, e.g. volatile compounds, and the solid oxygen carrier could be relevant. On the other hand, according to the CLOU scheme, the char combustion is the key variable to obtain high CO₂ capture efficiencies in the process.

To study the performance of the oxygen carrier for solid fuel combustion, tests in the batch fluidized bed reactor were made using coal and char as fuel. Differences using char or coal can be expected due to the presence of volatiles in coal. So, to evaluate the char conversion, independent of the volatile combustion, experiments using batches of char instead on coal were carried out. Following the experimental methodology proposed by Adánez-Rubio et al.,⁴⁵ several experiments were performed varying the oxygen carrier to fuel ratio to determine the maximum rate of oxygen transference by

the oxygen carrier and the rate of combustion of coal and char. Test series were carried out by using different bed materials: first, the bed material was hopcalite derived oxygen carrier particles; second, the bed material was only 2.5 wt.% of oxygen carrier diluted in alumina. All these tests were carried out with a total mass of particles in the reactor of 0.28 kg. The oxygen carrier was subjected to about 30 redox cycles which last during 30 h at different temperatures of 800 to 900 °C. It must be pointed out that the oxygen carrier never showed agglomeration problems, even when the oxygen carrier was highly reduced during the reduction period.

First, an analysis about the rate of char combustion and the oxygen released rate is done. Figure 8 shows the concentration of O₂, CO₂ and CO measured at the outlet of the reactor during a typical reduction and oxidation cycle at 900 °C with an oxygen carrier inventory in the reactor of 0.28 kg. The fluidizing medium was pure nitrogen during reduction and during oxidation the inlet oxygen concentration was 10 vol.%. The time $t = 0$ corresponds to the initial time of the reduction period, i.e. when the oxidizing gas mixture was replaced by nitrogen. At the beginning a rapid oxygen release occurred close to the oxygen concentration equilibrium for the measured bed temperature. After a short period, a batch of 2 g of char particles were fed to the reactor, and only CO₂ and O₂ were observed in the outlet gases, indicating full combustion of the char. The CO₂ concentration in this case was as high as 49 vol.% which was maintained constant during ~5 s, and eventually decreased to zero when the complete char combustion was reached. This result suggests a fast combustion of char.

In addition, the oxygen release rate was high enough to supply an excess of gaseous oxygen (O₂) exiting together the combustion gases. However, the oxygen concentration decreased from values around 3.5 vol.% to 0.6 vol.% O₂ during the char combustion.

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During the remaining reduction period the oxygen carrier continued releasing O_2 at this concentration. This decrease in the O_2 concentration as the oxygen carrier was being reduced was also observed in the experiments without char combustion, but the decrease was milder due to the slower reaction rate.

In Figure 8, the variation of oxygen carrier conversion, X_{Ox} , with reacting time is also shown. It can be seen that the oxygen carrier was slowly converted during the initial period before char addition. Likely the oxygen generation rate was limited by the fact that the equilibrium concentration is reached in absence of fuel. A sharp decrease in the oxygen carrier conversion was happening when char was fed to the reactor because the fast oxygen transference from oxygen carrier to fuel. After char was completely burnt, oxygen was still generated because the oxygen carrier was not completely reduced after char combustion. The variation in the solids conversion during the reducing period was 54%. Then, oxidation period starts at $t = 530$ s and a quick increase in the temperature occurred due to the highly exothermic reaction. The oxygen carrier was fully regenerated in 25 minutes.

Experiments varying the load of char from 0.5 to 2 g were carried out corresponding to oxygen carrier to char ratios between 510 and 125. As expected, the CO_2 concentration from fuel reactor increased with the char mass added because more fuel is burnt. Also, more oxygen is transferred to gases. Unburnt products, like CH_4 , CO or H_2 , were not observed in any case, indicating the full combustion of char in the bed. This fact contrasts with the results of Azad et al.³⁴ where they detected CO and CH_4 as unburnt product in the exit gases from the batch fluidized bed reactor burning CH_4 as fuel with a Cu-Mn-based oxygen carrier. The improved results obtained with the hopcalite derived

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oxygen carrier can be explained by the high O₂ release rate and oxygen transport capacity obtained in this work with this material.

At the CLOU conditions used in these experiments, the oxygen generated in the reactor was not limited by the reactivity of the oxygen carrier but for the demand of oxygen by coal; i.e. more oxygen is demanded, more oxygen is supplied. This fact suggests that a decrease in the oxygen carrier to coal ratio would allow increasing the oxygen transference rate provided by the hopcalite derived oxygen carrier. An attempt to determine the maximum oxygen transference rate of the hopcalite derived material was done in a two series of experiments. In these tests an additional dilution of the oxygen carrier material in alumina was done. So, the mass fraction of the hopcalite derived oxygen carrier was 2.5 wt.%, with a loads of coal were between 0.05 and 0.25 g, corresponding to oxygen carrier to char ratios from 175 to 24. In this second serie, it can be observed that with ratios lower than 45 the gaseous O₂ disappeared, nevertheless, CO, CH₄ or H₂ were not found in any case.

From the CO₂ and O₂ evolution in the gas phase, it was possible to calculate the instantaneous oxygen transference rate, $r_{O_2,Red}$, from Equation (15). Figure 9 shows the oxygen transference rate as a function of the oxygen carrier to char ratio. It can be observed a similar trend of the data obtained with different oxygen carrier dilutions at similar oxygen carrier to char ratios. When the oxygen carrier to char ratio decreased from high values until a value of 35, the oxygen transference rate increased. However, at lower oxygen carrier to char values it seemed that the oxygen transference rate reached a maximum, and no further incremental in the oxygen transference rate was obtained by decreasing the oxygen carrier to char ratio. Thus, for oxygen carrier to char ratio < 35 -where the maximum rate for oxygen transference was reached- the char

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conversion was limited by the oxygen transference rate from the oxygen carrier. The calculated value for the maximum oxygen transference rate was $0.3 \cdot 10^{-3}$ kg O₂/s per kg of oxygen carrier when the temperature during the reduction period increased up to $T_{max} = 880$ °C. Before adding the coal, the temperature of the bed was $T_0 = 850$ °C, but the bed temperature increase up around 30°C during the combustion, reaching a maximum value of $T_{max} = 880$ °C. Similar trend was found for the maximum oxygen transference rate at 900°C. Nevertheless, the maximum oxygen transference rate increased with the reacting temperature, as showed in Table 3.

Once the combustion of char was evaluated, and therefore the maximum oxygen generation rate obtained, the effect of the volatiles in the coal combustion was analyzed. To evaluate the coal conversion, experiments using batches of coal instead of char were carried out in the same fluidized bed reactor. The oxygen carrier to coal mass ratios varied from 175 to 3. Similar to experiments made with char, gaseous oxygen was in the gases for high oxygen carrier to coal ratios. But in this case, the oxygen concentration decreased for oxygen carrier to char mass ratio below 78, becoming zero at oxygen carrier to char ratios lower than 45. It was observed that for oxygen carrier to coal ratios lower than 47 the oxygen carrier was fully reduced after coal addition whereas char remained unburnt. Thus, some unconverted char was burnt in the subsequent oxidation period, which was evidenced by the presence of CO₂ in the gases when air was introduced to the bed. The value of oxygen carrier to coal of 47 was close to the stoichiometric oxygen available in the bed material to convert the coal to CO₂ and H₂O, which was an oxygen carrier to coal ratio of 43. This means that the oxygen carrier was able to transfer the available oxygen via oxygen uncoupling. In all the experiments carried out with coal, no CO was present in the outlet gases, even if oxygen was not

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present in the exhaust gases. This fact suggests that with this oxygen carrier all the volatiles present in the coal were burnt to CO₂ and H₂O in all conditions.

Figure 10 shows the oxygen generation rate as a function of oxygen carrier to fuel mass ratio when coal or char was burnt with 2.5 wt.% hopcalite derived oxygen carrier particles diluted in alumina. It can be observed that at oxygen carrier to fuel ratios higher than 150, oxygen transference rates were similar both for coal and char.

However, when the ratio decreased, oxygen transference rate with coal is more than 10 times higher than when char was used. At low ratios, oxygen was not present at the gas outlet. However, the maximum rate of oxygen transference was not reached for this condition. As it can be seen in Figure 10, the rate of oxygen transference when coal is burnt did not reach a maximum value decreasing the ratio OC to coal. It means the more coal was added to the bed, the faster was the transference of oxygen from the oxygen carrier to the fuel. This highest oxygen transference rate obtained when coal was used can be explained by the direct reduction of hopcalite (Cu_{1.5}Mn_{1.5}O₄) by the volatile matter by CLC reactions. The gas-solid CLC reaction between the mixed oxide and the volatiles can be observed in Equations (19) and (20). With oxygen carrier conversions for $CLOU \leq 1$, the equation (19) describes the reaction between the oxygen carrier and the volatiles. However, with oxygen carrier to coal ratios lower than 12, the mass balance of the reaction shows oxygen carrier conversions higher than 1. This is possible if the direct reduction would make that the mixed oxide decompose giving Cu⁰ and Mn oxide, see Equation (20). However, agglomeration problems were not detected in the bed material. In this case, gas-solid reaction between volatile matter and the oxygen carrier could be faster than oxygen generation rate. Note that during these tests no unburnt products were detected in the gas outlet flow, so all the volatile matter

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contained in the coal was burnt by the oxygen carrier, So, hopcalite derived oxygen carrier is able to burn completely the volatiles contained in the fuel at the same conditions that are used in a continuous CLOU unit. This fact makes that the use of this oxygen carrier for the combustion of fuels with a high content of volatiles is favoured.

Finally, it can be compared the contribution to the total oxygen transference rate by the different reactions (CLOU or CLC) that take place in the reactor, see Figure 10. It can be observed, that at ratios higher than 50, the contribution to the oxygen transference rate was similar for CLC (direct combustion of the volatiles with the oxygen carrier) and CLOU (combustion of the volatiles and char by the O₂ generated by the oxygen carrier) reactions. However, at lower rates, the transference of oxygen from the oxygen carrier to the volatiles by direct reaction is more important, from 4 times higher at ratios of 20 increasing to 16 times higher at ratios lower than 5.

3.4 Characterization of hopcalite derived oxygen carrier particles

Solids samples extracted from batch fluidized bed reactor for gaseous fuels after 30 h of fluidization were characterized by different techniques. Table 1 shows relevant properties for used particles compared to the fresh ones.

The XRD analysis of used particles revealed the presence of Cu_{1.4}Mn_{1.6}O₄ as major component. Thus, the unique change in chemical structure of the material was that the Mn₃O₄ free disappeared, integrating these manganese in the structure of the mixed oxide, modifying slightly the stoichiometry of the mixed oxide from Cu_{1.5}Mn_{1.5}O₄ to Cu_{1.4}Mn_{1.6}O₄. This fact would be related with the increase of the oxygen carrier oxygen transport capacity showed in TGA experiments, see Figure 2. The reactivity of samples

taken after 30 hours of operation in the batch fluidized bed reactor was determined by

TGA at 950 °C in N₂ for the decomposition reaction and in air for the re-oxidation;

Figure 2. It can be seen that the reactivity of the oxygen carrier particles remained

constant; however, the oxygen carrier capacity increased, from values of 3.7% to 4.2%.

This fact could be explained by the disappearance of the free Mn₂O₃ and integrating this Mn in the structure of the mixed oxide, being more reactive for the release of O₂.

Moreover, hopcalite derived oxygen carrier shows a different behaviour respect to the oxygen carrier prepared by Azad et al.³⁴ They observed that after experiments, a new spinel was formed Cu_{1.2}Mn_{1.8}O₄ and part of the Mn₃O₄ remained free, decreasing in this way its oxygen transport capacity.

On the other hand, the particles showed a decrease in their crushing strength after 30h of operation in the batch fluidized bed reactor for gaseous fuels, from values of 1.9 N to 0.8 N. This clearly indicates the need to improve the lifetime of this kind of materials for their use in a CLOU process of coal combustion.

SEM images of stabilized and used particles from the batch fluidized bed reactor after 30 h of operation are shown in Figure 11. It can be observed that after being used, the crystal size of the Cu_{1.5}Mn_{1.5}O₄ (cubic spinel structure with different planes⁴⁷) has increased. This increase in the crystal size can be observed both outside and inside of the particles; see Figures 11(c) and 11(d), respectively. This crystal growth changed the physical structure of the particles, from a sintered like surface to an individual and separately crystals appearance; see Figures 11(c) and 11(d), respectively. This change could affect to the decrease of the mechanical resistance detected during operation.

4 CONCLUSIONS

In this work, commercial hopcalite (67.4 wt.% Mn_2O_3 and 29.2 wt.% CuO) was evaluated as oxygen carrier for CLOU process. The oxygen release rate and the fluidization behavior, regarding agglomeration and attrition rate, were analyzed in a TGA and in a batch fluidized bed with gaseous and solid fuels. A medium volatile bituminous South African coal and char prepared with this coal were used as fuels. The capability of particles to evolve gaseous oxygen in the fuel reactor during fuel combustion was evaluated as a function of the oxygen carrier to fuel mass ratio and reactor temperatures from 800 to 900 °C. The oxygen carrier never showed agglomeration problems during all the experimental work.

With char, a decrease in the oxygen carrier to char mass ratio drives to a continuous increase in the oxygen generation rate of the hopcalite derived material until the maximum rate of oxygen generation was reached. The maximum generation rate obtained with char were $0.31 \cdot 10^{-3}$ at 880 °C to $0.62 \cdot 10^{-3}$ kg O_2 /s per kg of oxygen carrier at 930 °C.

The experiments done with coal showed that at oxygen carrier to coal ratios higher than 150, oxygen transference rates were similar both for coal and char. However, when the ratio decreased, oxygen transference rate with coal is more than 10 times higher than when char was used. At low ratios, oxygen was not present; moreover no unburnt products were detected. However, the maximum rate of oxygen transference was not reached for this condition. The more coal was fed to the bed, the faster was the oxygen transferred from the oxygen carrier to the fuel.

Results obtained with char were representative of the rate of evolution of gaseous oxygen from particles by CLOU, whereas experiments with coal also include a fast gas-

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solid reaction rate between volatile matter and solid particles with direct reduction of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$.

The results obtained in this work showed that the reactivity of the hopcalite derived oxygen carrier allows the complete conversion of the solid fuel in a CLOU process with high O_2 release at low temperatures, no unburnt products at low oxygen carrier to fuel ratios and very high oxygen transference rate by direct reaction. However, an important reduction in the crushing strength of the particles as the operation time increased was found, with values lower than 1 N after operation. This clearly indicates that the commercial material is not adequate for the CLOU process as it is, and makes necessary an improvement of its physical properties.

ASSOCIATED CONTENT

Supporting Information Available. Hopcalite pretreatment and description of the fluidized bed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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NOMENCLATURE

F_{air} molar flow of air (mol/s)

F_i molar flow of gas i (mol/s)

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F_{out}	molar flow at the reactor exit (mol/s)
$F_{O,SF}$	molar flow of oxygen from the existing oxygen in the solid fuel (mol/s)
m	Mass of the sample at each time (kg)
m_{char}	mass of char fed to the fuel reactor (kg)
m_{elut}	Oxygen carrier elutriated from the batch fluidized bed reactor (kg)
m_{FR}	mass of oxygen carrier in the fuel reactor (kg/MW _{th})
m_{Ox}	mass of fully oxydized oxygen carrier (kg)
m_{OC}	mass of oxygen carrier in the reactor (kg)
m_{red}	mass of reduced oxygen carrier, as Cu ₂ O (kg)
M_{O_2}	molecular weight of oxygen (=32·10 ⁻³ kg/mol)
N_{O_2}	amount of oxygen, expressed as O ₂ , in the bed material (mol)
$r_{O_2,Red}$	rate of oxygen generation in the reduction (kg O ₂ /s per kg of oxygen carrier)
$r_{O_2,Ox}$	rate of oxygen consumption in the oxidation (kg O ₂ /s per kg of oxygen carrier)
$r_{O_2,max}$	maximum rate of oxygen generation (kg O ₂ /s per kg of oxygen carrier)
R_{OC}	oxygen transport capability (-)
t	time (s)
T	temperature (°C)
T_0	initial temperature in the experiment (°C)
T_{max}	maximum temperature reached during experiment (°C)
X_{Ox}	Oxygen carrier oxidation conversion (-)
X_{Red}	Oxygen carrier reduction conversion (-)
X_f	oxygen carrier conversion at the end of the reducing period (-)
y_i	molar fraction of gas i (-)

Greek symbols

ΔH_r Enthalpy of reaction (kJ/mol)

$v_{\text{atrición}}$ Attrition rate (%/h)

Acronyms

BET Brunauer-Emmett-Teller

CLC Chemical Looping Combustion

CLOU Chemical Looping with Oxygen Uncoupling

OC Oxygen carrier

TGA Thermogravimetric analyser

XRD X-ray diffractometer

REFERENCES

1. Mattisson, T.; Lyngfelt, A.; Leion, H., Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int. J. Greenhouse Gas Control* **2009**, 3, (1), 11-19.
2. Adánez, J.; Gayán, P.; Adánez-Rubio, I.; Cuadrat, A.; Mendiara, T.; Abad, A.; García-Labiano, F.; de Diego, L. F. In *Use of Chemical-Looping processes for coal combustion with CO₂ capture*, Energy Procedia **2013**, 540-549.
3. Cuadrat, A.; Abad, A.; García-Labiano, F.; Gayán, P.; de Diego, L. F.; Adánez, J., The use of ilmenite as oxygen-carrier in a 500W_{th} Chemical-Looping Coal Combustion unit. *Int. J. Greenhouse Gas Control* **2011**, 5, (6), 1630-1642.
4. Cuadrat, A.; Abad, A.; García-Labiano, F.; Gayán, P.; de Diego, L. F.; Adánez, J., Relevance of the coal rank on the performance of the in situ gasification chemical-looping combustion. *Chem. Eng. J.* **2012**, 195-196, 91-102.
5. Markström, P.; Linderholm, C.; Lyngfelt, A., Chemical-looping combustion of solid fuels - Design and operation of a 100kW unit with bituminous coal. *Int. J. Greenhouse Gas Control* **2013**, 15, 150-162.
6. Gayán, P.; Abad, A.; de Diego, L. F.; García-Labiano, F.; Adánez, J., Assessment of technological solutions for improving chemical looping combustion of solid fuels with CO₂ capture. *Chem. Eng. J.* **2013**, 233, 56-69.
7. Mattisson, T.; Leion, H.; Lyngfelt, A., Chemical-looping with oxygen uncoupling using CuO/ZrO₂ with petroleum coke. *Fuel* **2009**, 88, (4), 683-690.

*Submitted, accepted and published by:
Energy & Fuels 30 (2016) 5953-5963*

8. Eyring, E. M.; Konya, G.; Lighty, J. S.; Sahir, A. H.; Sarofim, A. F.; Whitty, K., Chemical Looping with Copper Oxide as Carrier and Coal as Fuel. *Oil Gas Sci. Technol.* **2011**, 66, (2), 209-221.
9. Abad, A.; Adánez-Rubio, I.; Gayán, P.; García Labiano, F.; de Diego, L.; Adánez, J., Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operating unit using a Cu-based oxygen-carrier. *Int. J. Greenhouse Gas Control* **2012**, 6, 189-200.
10. Adánez-Rubio, I.; Abad, A.; Gayán, P.; de Diego, L. F.; García Labiano, F.; Adánez, J., Performance of CLOU process in the combustion of different types of coal with CO₂ capture. *Int. J. Greenhouse Gas Control* **2013**, 12, 430-440.
11. Adánez-Rubio, I.; Abad, A.; Gayán, P.; de Diego, L. F.; García-Labiano, F.; Adánez, J., Biomass combustion with CO₂ capture by chemical looping with oxygen uncoupling (CLOU). *Fuel Process. Technol.* **2014**, 124, 104-114.
12. Oy, O. R. *HSC Chemistry 6.1. Chemical reaction and equilibrium software with thermochemical database and simulation module*, **2008**.
13. Peltola, P.; Tynjälä, T.; Ritvanen, J.; Hyppänen, T., Mass, energy, and exergy balance analysis of chemical looping with oxygen uncoupling (CLOU) process. *Energ. Conver. Manage.* **2014**, 87, 483-494.
14. Mattisson, T., Materials for Chemical-Looping with Oxygen Uncoupling. *ISRN Chem. Eng.* **2013**, 2013, 19.

*Submitted, accepted and published by:
Energy & Fuels 30 (2016) 5953-5963*

15. Adánez-Rubio, I.; Gayán, P.; García-Labiano, F.; de Diego, L.; Adánez, J.; Abad, A., Development of CuO-based oxygen-carrier materials suitable for Chemical-Looping with Oxygen Uncoupling (CLOU) process. *Energy Procedia* **2011**, 4, 417-424.
16. Gayán, P.; Adánez-Rubio, I.; Abad, A.; de Diego, L.; García Labiano, F.; Adánez, J., Development of Cu-based oxygen carriers for Chemical-Looping with Oxygen Uncoupling (CLOU) process. *Fuel* **2012**, 96, 226-238.
17. Pour, N.; Leion, H.; Rydén, M.; Mattisson, T., Combined Cu/Mn oxides as an oxygen carrier in chemical looping with oxygen uncoupling (CLOU). *Energy Fuels* **2013**, 27, (10), 6031-6039.
18. Hosseini, D.; Imtiaz, Q.; Abdala, P. M.; Yoon, S.; Kierzkowska, A. M.; Weidenkaff, A.; Müller, C. R., CuO promoted Mn₂O₃-based materials for solid fuel combustion with inherent CO₂ capture. *J. Mater. Chem. A* **2015**, 3, (19), 10545-10550.
19. Ryden, M.; Rydén, M.; Lyngfelt, A.; Mattisson, T., Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system. *Energy Procedia* **2011**, 4, 341-348.
20. Adánez-Rubio, I.; Gayán, P.; Abad, A.; de Diego, L.; García Labiano, F.; Adánez, J., Evaluation of a Spray-Dried CuO/MgAl₂O₄Oxygen Carrier for the Chemical Looping with Oxygen Uncoupling Process. *Energy Fuels* **2012**, 26, (5), 3069-3081.
21. Shulman, A.; Cleverstam, E.; Mattisson, T.; Lyngfelt, A., Manganese/Iron, Manganese/Nickel, and Manganese/Silicon Oxides Used in Chemical-Looping With

Submitted, accepted and published by:

Energy & Fuels 30 (2016) 5953-5963

Oxygen Uncoupling (CLOU) for Combustion of Methane. *Energy Fuels* **2009**, 23, (10), 5269-5275.

22. Mei, D.; Mendiara, T.; Abad, A.; De Diego, L. F.; García-Labiano, F.; Gayán, P.; Adánez, J.; Zhao, H., Evaluation of Manganese Minerals for Chemical Looping Combustion. *Energy Fuels* **2015**, 29, (10), 6605-6615.
23. Sundqvist, S.; Arjmand, M.; Mattisson, T.; Rydén, M.; Lyngfelt, A., Screening of different manganese ores for chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU). *Int. J. Greenhouse Gas Control* **2015**, 43, 179-188.
24. Källén, M.; Rydén, M.; Lyngfelt, A.; Mattisson, T., Chemical-looping combustion using combined iron/manganese/silicon oxygen carriers. *Appl. Energy* **2015**, 157, 330-337.
25. Arjmand, M.; Frick, V.; Rydén, M.; Leion, H.; Mattisson, T.; Lyngfelt, A., Screening of combined Mn-Fe-Si oxygen carriers for chemical looping with oxygen uncoupling (CLOU). *Energy Fuels* **2015**, 29, (3), 1868-1880.
26. Azimi, G.; Leion, H.; Mattisson, T.; Rydén, M.; Snijkers, F.; Lyngfelt, A., Mn-Fe oxides with support of MgAl₂O₄, CeO₂, ZrO₂ and Y₂O₃-ZrO₂ for chemical-looping combustion and chemical-looping with oxygen uncoupling. *Ind. Eng. Chem. Res.* **2014**, 53, (25), 10358-10365.
27. Arjmand, M.; Kooiman, R.; Rydén, M.; Leion, H.; Mattisson, T.; Lyngfelt, A., Sulfur Tolerance of CaxMn1-yMyO3-δ (M = Mg, Ti) Perovskite-Type Oxygen Carriers

Submitted, accepted and published by:

Energy & Fuels 30 (2016) 5953-5963

in Chemical-Looping with Oxygen Uncoupling (CLOU). *Energy Fuels* **2014**, 28, (2), 1312-1324.

28. Pour, N. M.; Azimi, G.; Leion, H.; Rydén, M.; Lyngfelt, A., Production and examination of oxygen-carrier materials based on manganese ores and Ca(OH)₂ in chemical looping with oxygen uncoupling. *AIChE J.* **2014**, 60, (2), 645-656.

29. Jing, D.; Arjmand, M.; Mattisson, T.; Rydén, M.; Snijkers, F.; Leion, H.; Lyngfelt, A., Examination of oxygen uncoupling behaviour and reactivity towards methane for manganese silicate oxygen carriers in chemical-looping combustion. *Int. J. Greenhouse Gas Control* **2014**, 29, 70-81.

30. Källén, M.; Hallberg, P.; Rydén, M.; Mattisson, T.; Lyngfelt, A., Combined oxides of iron, manganese and silica as oxygen carriers for chemical-looping combustion. *Fuel Process. Technol.* **2014**, 124, 87-96.

31. Rydén, M.; Leion, H.; Mattisson, T.; Lyngfelt, A., Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. *Appl. Energy* **2014**, 113, 1924-1932.

32. Sundqvist, S.; Arjmand, M.; Mattisson, T.; Leion, H.; Rydén, M.; Lyngfelt, A. In *Screening of different manganese ores for chemical-looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU)*, CFB-11: Proceedings of the 11th International Conference on Fluidized Bed Technology **2014**, 893-898.

33. Schmitz, M.; Linderholm, C.; Lyngfelt, A. In *Chemical Looping combustion of sulphurous solid fuels using spray-dried calcium manganate particles as oxygen carrier*, *Energy Procedia* **2014**, 140-152.

Submitted, accepted and published by:
Energy & Fuels 30 (2016) 5953-5963

34. Azad, A.-M.; Hedayati, A.; Rydén, M.; Leion, H.; Mattisson, T., Examining the Cu–Mn–O Spinel System as an Oxygen Carrier in Chemical Looping Combustion. *Energy Technology* **2013**, 1, (1), 59-69.
35. Xu, L.; Edland, R.; Li, Z.; Leion, H.; Zhao, D.; Cai, N., Cu-modified manganese ore as an oxygen carrier for chemical looping combustion. *Energy Fuels* **2014**, 28, (11), 7085-7092.
36. Xu, L.; Sun, H.; Li, Z.; Cai, N., Experimental study of copper modified manganese ores as oxygen carriers in a dual fluidized bed reactor. *Appl. Energy* **2016**, 162, 940-947.
37. Deraz, N. M., Synthesis and characterization of nano- crystalline bixbyite-hopcalite solids. *Int. J. Electrochem. Sci.* **2013**, 8, (7), 10112-10120.
38. Mele, A., Preparation-properties relation of Mn-Cu hopcalite catalyst. *Am. J. Appl. Sci.* **2012**, 9, (2), 265-270.
39. Krämer, M.; Schmidt, T.; Stöwe, K.; Maier, W. F., Structural and catalytic aspects of sol–gel derived copper manganese oxides as low-temperature CO oxidation catalyst. *Appl. Catal. A-Gen.* **2006**, 302, (2), 257-263.
40. Njagi, E. C.; Chen, C.-H.; Genuino, H.; Galindo, H.; Huang, H.; Suib, S. L., Total oxidation of CO at ambient temperature using copper manganese oxide catalysts prepared by a redox method. *Appl. Catal. B- Environ.* **2010**, 99, (1–2), 103-110.

Submitted, accepted and published by:
Energy & Fuels 30 (2016) 5953-5963

41. Luna, B.; Somi, G.; Winchester, J. P.; Grose, J.; Mulloth, L.; Perry, J. L. In *Evaluation of commercial off-the-shelf sorbents & catalysts for control of ammonia and carbon monoxide*, 40th International Conference on Environmental Systems, ICES **2010**.
42. Njagi, E.; Genuino, H.; Kingond, C.; Dharmarathna, S.; Suib, S., Catalytic oxidation of ethylene at low temperatures using porous copper manganese oxides. *Appl. Catal. A-Gen.* **2012**, 421-422, 154-160.
43. Zafar, Q.; Abad, A.; Mattisson, T.; Gevert, B.; Strand, M., Reduction and oxidation kinetics of Mn₃O₄/Mg-ZrO₂ oxygen carrier particles for chemical-looping combustion. *Chem. Eng. Sci.* **2007**, 62, (23), 6556-6567.
44. Driessens, F. C. M.; Rieck, G. D., Phase Equilibria in the System Cu-Mn-O. Z. *Anorg. Allg. Chem.* **1967**, 351.
45. Adánez-Rubio, I.; Abad, A.; Gayán, P.; de Diego, L.; García Labiano, F.; Adánez, J., Identification of operational regions in the Chemical-Looping with Oxygen Uncoupling (CLOU) process with a Cu-based oxygen carrier. *Fuel* **2012**, 102, 634-645.
46. Adánez, J.; De Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A.; Palacios, J. M., Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* **2004**, 18, (2), 371-377.
47. Deraz, N. M.; Abd-Elkader, O. H., Synthesis and characterization of nano-crystalline bixbyite- hopcalite solids. *Int. J. Electrochem. Sci.* **2013**, 8, (7), 10112-10120.

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Caption of Tables

Table 1. Properties of the hopcalite oxygen carrier particles, fresh and used 30h in the batch fluidized bed reactor.

Table 2. Properties of South African coal and the char prepared.

Table 3. Maximum value of the oxygen generation rate, $r_{O_2, \max}$, for the hopcalite derived oxygen carrier as a function of the temperature.

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Table 1. Properties of the hopcalite oxygen carrier particles, fresh and used 30h in the batch fluidized bed reactor.

	Stabilized	Used
Composition (wt.%)	21.6% Cu 43.4% Mn 0.7% Ca 1.0% K 0.9 % Na	22.6% Cu 46.2% Mn 0.7% Ca 0.3% K 1.2 % Na
Oxygen transport capacity for CLOU, R_{OC} (wt.%)	3.7	4.2
Crushing strength (N)	1.9	0.8
Skeletal density of particles (kg/m ³)	4129	4100
Porosity (%)	56.5	43.5
Specific surface area, BET (m ² /g)	<0.5	<0.5
XRD main phases	Cu _{1.5} Mn _{1.5} O ₄ , Mn ₂ O ₃	Cu _{1.4} Mn _{1.6} O ₄

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Table 2. Properties of South African coal and the char prepared.

	Medium Volatile Bituminous	Char coal
Proximate Analysis (wt.%)		
C	69.3	76.5
H	4.0	0.2
N	2.0	1.6
S	1.0	0.8
O ⁽¹⁾	5.2	0.0
Ultimate Analysis (wt.%)		
Moisture	4.2	0.9
Volatile matter	25.5	1.1
Fixed carbon	56.0	78.0
Ash	14.3	20.0

(1) to balance

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Table 3. Maximum value of the oxygen generation rate, $r_{O_2, \max}$, for the hopcalite derived oxygen carrier as a function of the temperature.

T_0 (°C)	$T_{\max}$ (°C)	$r_{O_2, \max} \cdot 10^3$ (kg O ₂ /s per kg OC)
850	980	0.3
900	930	0.61

Caption of Figures

Figure 1. O₂ concentration at equilibrium as a function of the temperature for the systems (—)CuO/Cu₂O, (-·-·-)Mn₂O₃/Mn₃O₄ and (---)Co₃O₄/CoO.

Figure 2. TGA Conversion vs. time curves for (a) reduction and (b) oxidation reactions for fresh and used 30 h in the batch fluidized bed reactor for gaseous fuels. Reduction: N₂; Oxidation: air, at 950 °C in TGA.

Figure 3. O₂ concentration as a function of time for 5 consecutive cycles of reduction-oxidation in the batch fluidized bed reactor for gaseous fuels at 800 °C. Reduction: N₂. Oxidation: 10 vol.% O₂ in N₂.

Figure 4. Solid conversion and oxygen concentration profile during a reduction and regeneration period in the batch fluidized bed reactor for gaseous fuels at 850 °C. Reduction: N₂. Oxidation: 10 vol.% O₂ in N₂. (···) O₂ equilibrium concentration for CuO and Mn₂O₃.

Figure 5. Oxygen concentration and solid conversion profiles during a reduction period using different bed temperatures in the batch fluidized bed reactor for gaseous fuels.

Figure 6. Solids conversions during an oxidation period in the batch fluidized bed reactor for gaseous fuels using different oxygen concentrations: 5, 10 and 21 vol.% at T= 850 °C.

Figure 7. Attrition rate of hopcalite derived oxygen carrier during multi-cycle operation in the batch fluidized bed for gaseous fuels.

Figure 8. Concentration of O₂, CO₂, CO, H₂ and CH₄ during a typical reduction and oxidation cycle in the batch fluidized bed reactor for solid fuels. The variation in the oxygen carrier conversion, X_{Ox} , during the reduction and oxidation periods is also

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shown. $T_0 = 900\text{ }^{\circ}\text{C}$; reduction in N_2 and oxidation with 10 vol.% O_2 in N_2 ; mass

fraction of oxygen carrier: 100 wt.%; Char batch: 2 g. OC/char ratio = 124.

Figure 9. Instantaneous oxygen generation rate, $r_{\text{O}_2, \text{red}}$, for the hopcalite derived oxygen carrier as a function of the oxygen carrier to char mass ratio. $T_0 = 850\text{ }^{\circ}\text{C}$. Mass fraction of hopcalite derived oxygen carrier in the reactor: (●) 100 wt.%; (▲) 2.5 wt.%.

Figure 10. Instantaneous oxygen transference rate, $r_{\text{O}_2, \text{red}}$, for the hopcalite derived oxygen carrier as a function of the oxygen carrier to fuel mass ratio. $T_0 = 850\text{ }^{\circ}\text{C}$. Mass fraction of hopcalite derived oxygen carrier in the reactor: 2.5 wt.%. Fuel: (Δ) coal; (▲) char.

Figure 11. SEM images of calcined (left) and used (right) particles after 30 h in the batch fluidized bed reactor: (a, c) image of the particles; (b, d) cross section of a particle.

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Figure 1. O₂ concentration at equilibrium as a function of the temperature for the systems (—)CuO/Cu₂O, (-·-·-)Mn₂O₃/Mn₃O₄ and (---)Co₃O₄/CoO.

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Figure 2. TGA Conversion vs. time curves for (a) reduction and (b) oxidation reactions for fresh and used 30 h in the batch fluidized bed reactor for gaseous fuels. Reduction: N_2 ; Oxidation: air, at 950°C in TGA.

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Figure 3. O₂ concentration as a function of time for 5 consecutive cycles of reduction-oxidation in the batch fluidized bed reactor for gaseous fuels at 800 °C. Reduction: N₂. Oxidation: 10 vol.% O₂ in N₂.

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Figure 4. Solid conversion and oxygen concentration profile during a reduction and regeneration period in the batch fluidized bed reactor for gaseous fuels at 850 °C.

Reduction: N₂. Oxidation: 10 vol.% O₂ in N₂. (···) O₂ equilibrium concentration for CuO and Mn₂O₃.

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Figure 5. Oxygen concentration and solid conversion profiles during a reduction period using different bed temperatures in the batch fluidized bed reactor for gaseous fuels.

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Figure 6. Solids conversions during an oxidation period in the batch fluidized bed reactor for gaseous fuels using different oxygen concentrations: 5, 10 and 21 vol.% at $T = 850\text{ }^{\circ}\text{C}$.

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Figure 7. Attrition rate of hopcalite derived oxygen carrier during multi-cycle operation in the batch fluidized bed for gaseous fuels.

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Figure 8. Concentration of O_2 , CO_2 , CO , H_2 and CH_4 during a typical reduction and oxidation cycle in the batch fluidized bed reactor for solid fuels. The variation in the oxygen carrier conversion, X_{Ox} , during the reduction and oxidation periods is also shown. $T_0 = 900\text{ }^\circ\text{C}$; reduction in N_2 and oxidation with 10 vol.% O_2 in N_2 ; mass fraction of oxygen carrier: 100 wt.%; Char batch: 2 g. OC/char ratio = 124.

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Figure 9. Instantaneous oxygen generation rate, $r_{O_2,red}$, for the hopcalite derived oxygen carrier as a function of the oxygen carrier to char mass ratio. $T_0 = 850$ °C. Mass fraction of hopcalite derived oxygen carrier in the reactor: (●) 100 wt.%; (▲) 2.5 wt.%.

Figure 10. Instantaneous oxygen transference rate, $r_{O_2,red}$, for the hopcalite derived oxygen carrier as a function of the oxygen carrier to fuel mass ratio. $T_0 = 850$ °C. Mass fraction of hopcalite derived oxygen carrier in the reactor: 2.5 wt.%. Fuel: (Δ) coal; (▲) char.

Figure 11. SEM images of fresh (left) and used (right) particles after 30 h in the batch fluidized bed reactor: (a, c) image of the particles; (b, d) cross section of a particle.