The fate of Sulphur in the Cu-based Chemical Looping with Oxygen Uncoupling (CLOU) Process

Iñaki Adánez-Rubio, Pilar Gayán*, Alberto Abad, Francisco García-Labiano,
Luis F. de Diego, 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: pgayan@icb.csic.es

Abstract – Chemical Looping with Oxygen Uncoupling (CLOU) process is a Chemical Looping Combustion (CLC) technology that allows the combustion of solid fuels as in common combustion with air, by means of using oxygen-carriers that release gaseous oxygen in the fuel-reactor. The aim of this work is to study the behavior of the sulphur present in the fuel during CLOU combustion. Experiments using lignite as fuel were carried out in a continuously operated 1.5 kW_{th} CLOU unit during more than 15 h of operation. Particles prepared by spray drying containing 60 wt.% CuO on MgAl₂O₄ were used as oxygen-carrier in the CLOU process. The temperature in the fuel-reactor was varied between 900 and 935 °C. The CO₂ capture, the combustion efficiency and the sulphur split between fuel- and air-reactor streams in the process were analyzed. Complete combustion of the fuel to CO₂ and H₂O was found in all experiments. Most of the sulphur introduced with the fuel exits as SO₂ at the fuel-reactor outlet although a small SO₂ amount is measured at the air-reactor outlet. As the temperature in the fuel-reactor increases, the SO₂ concentration in the air-reactor exit flow decreases. At 935 °C, a carbon capture efficiency of 97.6% was reached with 87.9 wt.% of the total sulphur exiting as SO₂ in the fuel-reactor. Both, reactivity and oxygen transport capacity of the oxygen carrier were unaffected during operation with a high sulphur content fuel, and agglomeration problems did not occur. Predictions on the use of a

carbon separation system in the CLOU process in order to reduce the sulphur emission are calculated. Coals with high sulphur content, as lignite and anthracite, would need a carbon separation system to fulfill sulphur legislation limits. As a conclusion, coals with high sulphur content can be burnt in a CLOU process using a Cu-based material obtaining high carbon capture efficiencies.

Keywords: CO₂ capture, Cu-based oxygen carrier, CLOU, coal, sulphur.

1 Introduction

Chemical-Looping with Oxygen Uncoupling (CLOU) process is a Chemical-Looping Combustion (CLC) technology that allows the combustion of solid fuels with inherent CO₂ separation using oxygen-carriers. The CLOU technology may be especially suitable for solid fuels, such as coal, petroleum coke or biomass. The CLOU technology takes advantage of the property of some metal oxides which can generate gaseous oxygen at high temperatures. 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 have the ability to react both with oxygen in the air-reactor and then also to release this oxygen through decomposition in the fuel-reactor. Three such metal oxide systems have suitable properties to be used as oxygen-carriers in the CLOU process: CuO/Cu₂O, Mn₂O₃/Mn₃O₄, and Co₃O₄/CoO [1].

An analysis about the suitability of different Cu-based materials was carried out previously at ICB-CSIC, [2,3]. Particles prepared by several methods with different supporting materials and different metal oxide contents were tested. Particles of 60 wt.% CuO were tested in a 1.5 kW_{th} CLOU continuous unit [4], where the proof of the concept of the CLOU process was demonstrated using coal as fuel. The effect of the coal rank was also analyzed [5] in this plant using a lignite, two bituminous coals and an anthracite. Complete combustion to CO₂ and H₂O was reached with all of the different coals. However for low reactivity coals such as

anthracite, a carbon separation system would be needed in the system to reach high carbon capture efficiencies.

The design of an industrial CLC plant can be affected by the presence of the sulphur compounds in two ways. From the environmental point of view, the sulphur fed into the system can be released as SO_2 in the air-reactor gas outlet stream and must fulfil the legislation about gaseous emissions, or be emitted in the fuel-reactor gas stream affecting the quality of the CO_2 with important consequences for the compressing, transport and storage [6,7]. Pipitone and Bollard [8] give some examples of quality specifications for CO_2 , transport and storage of some industrial companies operating at the moment.

From the operational point of view, the sulphur compounds may react with the active metal oxide to form metal sulphides or sulphates that can be poisonous to the oxygen-carrier, decreasing its reactivity. Moreover, the low melting point of some sulphur compounds, e.g. 805°C for CuSO_4 or 1100°C for Cu_2S , could produce agglomerations and affect the solid circulation pattern between the interconnected fluidized-bed reactors.

Only few studies have been made in continuous units to analyze the effect of sulphur using CuO oxygen-carriers under different operating conditions. Forero et al. [9] studied the fate of sulphur in the combustion of natural gas in the CLC process using a Cu-based oxygen-carrier, with H_2S concentrations up to 1300 vppm. It was found that the majority of sulphur in the fuel was released as SO_2 in the fuel-reactor under normal operation conditions. The formation of Cu_2S or CuSO_4 was not detected when there was an excess of oxygen in the bed. Nevertheless, in favorable conditions for formations of Cu_2S , any agglomeration problems in the fluidized beds were never detected.

To date, there are not any available study on the performance of the CLOU process regarding the fate of the sulphur. A study of the effect of the sulphur present in the fuel on the oxygen-carrier behaviour and its distribution in the CLOU system is needed to know the real consequences in a CLOU process using coals with high sulphur content.

The aim of this work is to investigate the fate of sulphur in the CLOU process using a Cu-based oxygen-carrier. The experiments were carried out with a Spanish lignite with high sulphur contents in a continuous unit of 1.5 kW_{th}. The effect of fuel-reactor temperature on the combustion efficiency, carbon capture efficiency and sulphur distribution were investigated. The results obtained are analyzed and discussed in order to be useful for industrial operation of the CLOU process.

2 Experimental section

2.1 Materials

The material used was a Cu-based oxygen-carrier prepared by spray drying manufactured by VITO (Flemish Institute for Technological Research, Belgium). The CuO content of particles was 60 wt.% with a 40 wt.% of MgAl₂O₄. Particle size was +100-200 μm [10]. Table 1 shows the main properties of the oxygen-carrier.

A Spanish lignite with high S content was used for CLOU experiments. The coal particle size used for this study was +200–300 μm. Table 2 shows the proximate and ultimate analysis of this coal and its char. Also, it was done an analysis to determinate the amount of pyritic sulphur in the coal and the total sulphur in ashes recovered in the filters of the system.

2.2 Continous CLOU unit: ICB-CSIC-s1

A schematic view of the CLOU unit is shown in Fig. 1. The set-up is basically composed of two interconnected fluidized-bed reactors –the air- and fuel-reactors– joined by a loop seal, a riser for solids transport from the air-reactor to the fuel-reactor, a cyclone and a solids valve to control the solids circulation flow rate in the system. A diverting solids valve located below the cyclone allows for the measurement of the solids flow rates at any time. Therefore, this design allows us to control and measure the solids circulation flow rate between both reactors.

The fuel-reactor consists of a bubbling fluidized bed with 5 cm of inner diameter and 20 cm bed height. N_2 is used as fluidizing gas, the gas flow was 186 L_N/h , corresponding to a gas velocity of 0.11 m/s at 900 °C. The minimum fluidizing velocities of the oxygen carrier particles are 0.006 m/s for the smallest particle size and 0.023 m/s for the biggest one. Coal is fed by a screw feeder at the bottom of the bed right above the fuel-reactor distributor plate in order to maximize the time that the fuel and volatile matter are in contact with the bed material.

The oxidation of the carrier takes place in the air-reactor, consisting of a bubbling fluidized bed with 8 cm of inner diameter and 10 cm bed height, and followed by a riser, the air flow was 1740 L_N/h ($u_g = 0.40$ m/s). In addition, a secondary air flow (240 L_N/h) was introduced at the top of the bubbling bed to help particle entrainment through a riser. The total oxygen carrier inventory in the system was around 2.0 kg, being about 0.5–0.6 kg in the fuel reactor. The amount of solids in the fuel reactor was calculated from pressure drop measurements in the reactor for each test. Detailed information about the plant and the experimental conditions can be found in [4,5].

CO , CO_2 , H_2 , CH_4 , SO_2 , and O_2 were continuously analyzed in the outlet stream from fuel-reactor, whereas CO_2 , CO , SO_2 and O_2 were continuously analyzed from the flue gases of the air-reactor by means of an infrared, paramagnetic and conductivity analyzers. H_2S was analyzed by GC.

To determine the effect of S on the behavior of the oxygen-carrier, several tests under continuous operation were carried out. The fuel-reactor temperature was varied from 900 °C to 935 °C. The temperature in the air-reactor was maintained at around 900 °C in all experiments. The solids circulation rate was maintained at a mean value of 3 kg/h, whereas the coal feeding rate was 0.12 kg/h which corresponds to an oxygen-carrier to fuel ratio, ϕ , of 1.2.

To analyze the performance of the CLOU process, the combustion efficiency in the fuel reactor and the carbon capture efficiency are also calculated. Calculations are based on the

molar flow of every gas analyzed, F_i which is determined from the measured concentration. Mass balances are checked and a closing about 98% are found for the carbon balance in all cases.

The combustion efficiency in the fuel-reactor is calculated through the ratio between the oxygen required to fully burn unconverted gases (CH_4 , CO and H_2) at the fuel reactor exit and the oxygen demanded by coal converted in the fuel-reactor. Thus, the oxygen demanded by the carbon bypassed to the air reactor, $F_{\text{CO}_2,\text{AR}}$, is subtracted from the oxygen demanded by coal in the denominator. Therefore, the combustion efficiency in the fuel-reactor is calculated as:

$$\eta_{\text{comb,FR}} = 1 - \frac{4F_{\text{CH}_4,\text{outFR}} + F_{\text{CO,outFR}} + F_{\text{H}_2,\text{outFR}}}{\frac{1}{M_{\text{O}}} \Omega_{\text{coal}} \dot{m}_{\text{coal}} - 2F_{\text{CO}_2,\text{outAR}}} \quad (1)$$

The carbon capture efficiency, η_{CC} , is defined as the fraction of carbon initially present in the coal fed in which is actually at the outlet of fuel-reactor. This is the actual CO_2 captured in the CLOU system; the rest is exiting together nitrogen in the air-reactor outlet.

$$\eta_{\text{CC}} = 1 - \frac{F_{\text{CO}_2,\text{outAR}}}{F_{\text{CO}_2,\text{outFR}} + F_{\text{CO,outFR}} + F_{\text{CH}_4,\text{outFR}} + F_{\text{CO}_2,\text{outAR}}} \quad (2)$$

A mass balance to sulphur can be done as:

$$f_S \cdot \dot{m}_{\text{coal}} = M_S (F_{\text{SO}_2,\text{outFR}} + F_{\text{SO}_2,\text{outAR}}) + S_{\text{ash}} \quad (3)$$

With the molar flow of SO_2 exiting from the air-reactor and the total volume gas flow, the concentration of SO_2 as mg/Nm^3 is calculated and normalized. In the EU legislation [11], the SO_2 concentration must be normalized using a 6 % of O_2 in the exit stream for power plants, which contains 15 % of CO_2 .

2.3 Batch fluidized-bed reactor

A batch fluidized bed reactor is used to deeply analyze the sulphur evolution with time during coal combustion. The experimental work is carried out in a setup consisting of a fluidized-bed

reactor, a system for gas feeding, a solid fuel feeding system, and the gas analysis system. The reactor –55 mm inner diameter and 700 mm height– is electrically heated by a furnace, and had a preheating zone just under the distributor plate [12].

A batch of 20 g of fuel was burnt in the batch fluidized bed reactor using a sand bed with a particle size of +200-300 μm . The total fluidizing flow was 200 L_N/h, which corresponds to a gas velocity of 0.1 m/s at the reactor temperature, which is 3 times the minimum fluidization velocity of largest sand particles. The bed was heated in N₂ until 925 °C. The volatile products were burnt in an after burner reactor using a 7 % of O₂ concentration. At 925 °C the char combustion was carried out using a 2.5% of O₂. Relatively low O₂ concentration was used to simulate fuel reactor conditions in the CLOU unit, where there is much lower O₂ concentration than a typical air-fired combustor. The SO₂, CO₂ and CO gas concentrations were continuously measured.

3 Results

3.1 Combustion behaviour

During 15 h of combustion operation no CH₄, CO, H₂S or H₂ were detected in the gases exiting from the fuel-reactor. The possible presence of tars or light hydrocarbons was also analyzed. For one experiment with conditions kept constant for more than two hours, tar measurements in the fuel-reactor were done using a tar protocol [13,14]. The results showed that there were not tars in the fuel-reactor outlet flow, that is, no hydrocarbons heavier than C₅. Thus, CO₂, H₂O, SO₂ and O₂ were the main gases, together the N₂ introduced as fluidizing gas, exiting the fuel-reactor. Therefore, volatiles were fully converted into CO₂ and H₂O in the fuel-reactor by reaction with the oxygen released from the CuO decomposition. In addition, the oxygen release rate was high enough to supply an excess of gaseous oxygen (O₂) exiting together with the combustion gases at equilibrium concentration at each temperature, being the oxygen concentration at equilibrium conditions 1.7% at 910 °C, 2.4% at 925 °C, 3.0% at 935 °C.

Fig. 2 shows the effect of the fuel-reactor temperature on the combustion and the carbon capture efficiencies. It can be seen that complete combustion to CO_2 and H_2O was always reached. The carbon capture efficiency increased when the fuel-reactor temperature increased, due to an increase of the char combustion rate. Thus, less char is transferred to the air-reactor.

3.2 Emissions of sulphur

Fig. 3 shows the distribution of S between both reactor exits as a function of the fuel-reactor temperature. It can be seen that the S exits mainly as SO_2 in the fuel-reactor stream and the amount increased with the temperature, decreasing the amount of SO_2 exiting from the air-reactor. This effect is due to the char conversion increases and therefore more sulphur is released in the fuel reactor and less sulphur is transferred with the char to the air-reactor. SO_2 concentration in the fuel reactor (dry basis) varies from 2400 ppmv at 910°C to 3000 ppmv at 935°C .

Fig 4 shows the SO_2 emissions in the air-reactor in normalized mg/Nm^3 as a function of the fuel-reactor temperature. Moreover, the EU-legislated SO_2 emission limit for new coal power plants ($>300 \text{ MW}_{\text{th}}$) are also depicted [11]. It can be seen that SO_2 emissions in the air-reactor decreased with the temperature. This effect is due to more char is converted in the fuel-reactor as the temperature increases. Although, the SO_2 concentration exiting the air-reactor stream was lower than 10% of the total S fed at 935°C , the value of the SO_2 emission is still too high and exceeds the legislation limit of $200 \text{ mg}/\text{Nm}^3$. Note that direct combustion of this coal with air would give SO_2 emissions of $> 20000 \text{ mg}/\text{Nm}^3$.

From the char conversion values measured in the fuel reactor, the amount of char transferred to the air reactor can be determined, and therefore, assuming a S/C ratio constant and equal to the analysis of the nascent char, the S emitted as SO_2 in the air-reactor can be calculated. Fig. 4 shows the corresponding SO_2 emissions assuming a S/C ratio in char constant during the combustion time of the char in the fuel reactor. As it can be seen, this calculated SO_2 emissions are much lower than the measured ones. This fact could

be due to two different effects: S is transferred to the air-reactor in the oxygen-carrier particles by sulphur reaction with Cu or S is concentrated in the unburnt char transferred to the air-reactor.

To analyze whether sulphur is concentrated in the char, a detailed study of the S release during char combustion was carried out in the batch fluidized bed reactor installation. Fig 5 shows the profiles of C and SO₂ gas concentration at the outlet of the batch reactor, during the pyrolysis and followed by combustion of the generated char. The mass balance of the exiting gases indicates that the 43.1 wt.% of the sulphur exit from the devolatilization and the 56.9 wt.% during the char combustion. On one hand, it can be seen that during devolatilization, the sulphur and the carbon in volatiles are evolved at the same rate. However, S and C profiles are different during char combustion. During char combustion, the SO₂ generation rate is maximum when almost all the C in the char had been burnt. At this time, S/C ratio in char increases by a factor of 10 with respect to the S/C ratio measured in the char analysis. This behavior could be explained due to the high pyritic sulphur (2 wt.%) present in this lignite. At a low O₂ concentration environment, as it is the case in the CLOU process, there is a competition for oxygen between the carbon and the pyritic sulphur. As a consequence, carbon combustion is favored over pyrite oxidation [15]. These results show that the pyritic S present in the fuel can affect the S emissions of the air-reactor of a CLOU system. Thus S/C in char passing to the air reactor is higher than that in nascent char, and sulphur emissions from the air reactor are higher than expected. This S concentration in the fines recovered in the different filters of the plant has been taken into account in the global S balance. The analysis done to the fines recollected shows that the S/C ratio changes from 0.09 (nascent char) to 1 in the unburnt char exiting the fuel reactor, due to the presence of pyritic sulphur.

Fig. 6 shows the splitting of the total sulphur in the continuous plant between gas and solids streams. A major S emission comes from the fuel-reactor stream as SO₂. The S balance in the fuel- and air-reactor gas outlet closes at ~ 50-55 wt.%. It must be pointed out that fines recovered in filters from fuel-, and air-reactor were concentrated in S.

Fig 6 also shows the amount of sulphur in the ashes in form of pyritic sulphur in both solid reactor streams. Between 8 to 11 wt.% of the total sulphur fed was as unburned pyritic sulphur. Moreover, it is known that the presence of CaO in the lignite ashes allows the self-retention of sulfur during combustion by formation of CaSO_4 [16]. In this way, Fig. 6 also shows the amount of S in the ashes by self-retention, between 10 to 15 wt.% of the total sulphur fed in the system is retained by this way. Taking into account the sulphur in gas and solid phases, the sulphur balance closure is approximately 80 wt.%. A possible fate for the rest of sulphur could be accumulation in the oxygen carrier particles. If so, a sulphur content of 0.3 wt.% would be present in oxygen carrier particles, which is below the detection level for XRD or SEM-EDX measurements.

3.3 Oxygen-carrier behaviour

After 15 h of continuous operation at high temperatures and with a high sulphur-content fuel, the oxygen-carrier did not show any agglomeration problems.

Samples of oxygen carrier exposed to 15 hours of continuous operation were taken from the fuel reactor and analyzed by TGA and XRD to determine if there was sulphur retention in the oxygen-carrier. Fig 7 shows the reactivity of the fresh and used samples. It can be seen that both samples exhibited the same reactivity for reduction and oxidation. Also the oxygen transport capacity of the oxygen-carrier was not affected. The high sulphur concentration during 15 h did not affect the reactivity of the oxygen-carrier. Also XRD analysis, did not show any S compounds in the oxygen-carrier, although could be below the detection level.

4 Discussion

With the results found in this work some considerations can be drawn. To fulfil the legislation limits in relation to the SO_2 emission from the air-reactor using high-sulphur content fuels different modifications in the system can be adopted. (1) Reduce the pyritic sulphur content in the fuel to reduce the amount of sulphur transferred with the char to the air-reactor, (2) increase the fuel-reactor temperature, (3) increase solids inventory to increase the char

conversion in the fuel-reactor or (4) use a carbon separation system to decrease the amount of char transferred to the air-reactor. Reducing the pyritic sulphur may not be achievable at industrial scale. Increasing the solids inventory would increase the cost of the process. Increasing the fuel-reactor temperature can increase the char conversion and the oxidation of the pyritic sulphur, but temperature restrictions up to 950 °C in the fuel-reactor can be assumed, to avoid high O₂ concentration at fuel reactor outlet.

In a previous work [5], an optimization of the CLOU process using a carbon separation system was carried out to maximize the CO₂ capture efficiency using the minimum solid inventory. A similar analysis can be now carried out to evaluate the effect of the use of a carbon separation system in the CLOU process regarding SO₂ emissions in the air-reactor.

The sulphur emissions in the air-reactor directly depend on the sulphur content in char particles to the air reactor. A carbon separation system can be used to improve the char conversion in the fuel reactor. This system allows the separation of char and oxygen-carrier particles by entrainment. In this way, the char is transported back to the fuel reactor to improve the char conversion, whereas the oxygen carrier particles are sent to the air reactor. So, at the same time that the carbon flow to the air reactor is reduced, also the SO₂ emissions in the air-reactor are reduced.

Considering a carbon separation system, char conversion can be calculated as a function of the carbon separation system efficiency as follows [17]:

$$X_{\text{char}} = 1 - \frac{\dot{m}_{\text{OC}}(1 - \eta_{\text{CSS}})}{(-r_c) \cdot m_{\text{OC,FR}} + \dot{m}_{\text{OC}}(1 - \eta_{\text{CSS}})} \quad (4)$$

where $\dot{m}_{\text{OC}}$ is the oxygen carrier flow rate, η_{CSS} is the carbon separation system efficiency, $(-r_c)$ the fractional conversion rate of char and $m_{\text{OC,FR}}$ the mass of oxygen carrier in the fuel reactor. The SO₂ emission from the air reactor is related to the char conversion in the fuel reactor with the following equation:

$$SO_{2,em} = \frac{\dot{m}_{\text{coal}} \cdot f_{\text{char}} \cdot f_{S, \text{char}} \cdot (1 - X_{\text{char}})}{V_{\text{air}}} \cdot 10^6 \quad (5)$$

Note that in the CLOU process, gas coming from the air reactor is the only stream emitted to the atmosphere. Where $\dot{m}_{\text{coal}}$ is the kg/s are needed to feed 1 MW_{th} of coal to the fuel-reactor, $f_{\text{S, char}}$ is the amount of sulphur present in the fix carbon and V_{air} the volume of air needed to burn 1 MW_{th} of coal. For preliminary estimation, it was assumed a uniform S release during char combustion, that is, a S/C ratio constant and equal to the nascent char.

Using Eq. 4 and 5, it is possible to analyse the effect of the oxygen carrier inventory and the efficiency of carbon separation system on SO₂ emissions in air-reactor, once the value of $(-r_c)$ is known. At 925 °C the char conversion rate was 4.4 %/s for Lignite. This value has been obtained by Adanez et al. in a study for the combustion of different types of coals in a CLOU process [5].

Figs. 8(a), (b) and (c) show the estimated SO₂ emissions as a function of the fuel reactor inventory using this lignite, when a carbon separation system with different carbon separation efficiencies ($\eta_{\text{CCS}} = 0, 50$ and 90%) are considered at 909 (a), 935 (b) and 950 °C (c). As can be seen in Fig. 8(a), if the carbon separation system efficiency (η_{CCS}) is given, the SO₂ emission decreases when the oxygen carrier inventory increases due to the increase of the residence time of solids in the fuel reactor. For the same reason, if η_{CCS} increases more char returns to the fuel reactor increasing its residence time. As a consequence, the SO₂ emission decreases with η_{CCS} . The effect of the carbon separation system is very high especially at the lowest temperatures and lowest oxygen carrier inventories in the fuel reactor.

Predictions considering different fuels have been done in a similar way. A medium volatile bituminous coal (MVB) with 0.9 wt.% of S and an anthracite with 1.3 wt.% of S were evaluated. In a previous work [5], the rates of char combustion of these coals were determined in the CLOU unit. At 925 °C the char conversion rate was 3.3 %/s for MVB and 0.4 %/s for the anthracite.

Fig. 9(a) and (b) show the SO₂ emission as a function of the fuel reactor inventory for these coals (lignite, anthracite and MVB) at 930 °C when a carbon separation system is considered (90%) or not (0%). In Fig 9(a) it can be seen that coals with high reactivity and low sulphur

content, e.g. MVB, would fulfil the legislation without a carbon separation system using low solid inventories. On the other hand, for coals with very high sulphur content (lignite) or low reactivity (Anthracite) a carbon separation system is necessary to fulfil the legislation limit with low inventories in the fuel-reactor.

These results were obtained assuming that the ratio S/C ratio in the char was constant during all the combustion period. As it was shown in this work, the presence of pyritic sulphur in the char affected the SO₂ emissions in the air-reactor. Therefore, coals with high pyritic sulphur content must increase the oxygen-carrier inventories in the fuel-reactor with respect of those shown in Fig. 8 and 9, to increase the residence time in the fuel-reactor in order to fully burn the pyritic sulphur.

Conclusions

In this work, 15 h of continuous operation in a CLOU unit was carried out with a high sulphur lignite (5.2 wt.% S) using a Cu-based oxygen-carrier. Complete combustion to CO₂ and H₂O was obtained and high carbon capture efficiency (96% at 935 °C) was reached. The majority of sulphur present in the coal was released as SO₂ in the fuel-reactor. Only a small fraction is transferred to the air-reactor and emitted, although emissions higher than 200 mg/Nm³ were found. The emissions could be due to a not uniform S release during char combustion, due to the presence of pyritic sulphur in this coal (2 wt.%).

The oxygen-carrier particles never showed agglomeration problems. In addition, the oxygen-carrier reactivity remained constant.

The use of a carbon separation system to fulfill the SO₂ legislation limit was evaluated with different coals. It was found that the carbon separation system is not necessary with coals with high reactivity and low sulphur contents. The use of a high efficiency carbon separation system ($\eta_{\text{eff}} = 90\%$), would allow compliance with the SO₂ legislation requirements even for coal with high sulphur contents (lignite) or low reactivity (anthracite).

Acknowledgement

This work was conducted with financial support from the European Commission, under the RFCS program (ACCLAIM Project, Contract RFPCT-2012-406), the Spanish Ministry of Science and Innovation (PN, ENE2010-19550), and Government of Aragón and La Caixa (project 2012-GA-LC-076). I. Adánez-Rubio thanks CSIC for the JAE fellowship co-funded by the European Social Fund.

Nomenclature

Symbols

F_i	Molar flow of compound i (mol/s)
f_{char}	Mass fraction of char in coal (i.e. fix carbon) (-)
f_i	Mass fraction in coal of element or compound i (-)
$f_{\text{S, char}}$	Mass fraction in char of sulphur (-)
$\dot{m}_{\text{coal}}$	Mass-based flow of coal fed-in to the fuel-reactor (kg/s)
$M_{\text{OC, FR}}$	Mass of solids in the fuel-reactor (kg)
M_i	Molecular weight of i compound (kg/mol)
$(-r_c)$	Fractional conversion rate of the char (s^{-1})
$\text{SO}_{2, \text{em}}$	SO_2 concentration exiting from AR (mg/Nm^3)
S_{ash}	Sulphur in ashes (kg/s)
V_{air}	Air gas flow exit from the AR (Nm^3/h)
X_{char}	Carbon conversion in char particles (-)

366 **Greek letters**

367 η_{CC} Carbon capture efficiency (-)

368 η_{CSS} Carbon separation system efficiency (-)

369 $\eta_{comb,FR}$ Combustion efficiency (-)

370 ϕ Oxygen-carrier to fuel ratio (-)

371 Ω_{coal} Stoichiometric mass of O_2 to convert 1 kg of coal (kg/kg)

372

373 **Subscripts**

374 AR Air reactor

375 CLC Chemical-Looping Combustion

376 CLOU Chemical-Looping with Oxygen Uncoupling

377 FR Fuel reactor

378 LHV Low Heating Value

379 outFR Outlet stream from fuel-reactor

380 outAR Outlet stream from air-reactor

381 TGA Thermogravimetric analyser

382 XRD X-ray diffractometer

383

384

385
386

387 **References**

- 388 [1] Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for
389 combustion of solid fuels. *Int J Greenhouse Gas Control* (2009);3:11-9.
- 390 [2] Gayán P, Adánez-Rubio I, Abad A, de Diego LF, García-Labiano F, Adánez J.
391 Development of CuO-based oxygen-carrier materials suitable for Chemical-Looping
392 with Oxygen Uncoupling (CLOU) process. *Fuel* (2012);96:226-38.
- 393 [3] Adánez-Rubio I, Gayán P, García-Labiano F, de Diego LF., Adánez J, Abad A.
394 Development of CuO-based oxygen carrier materials suitable for chemical-looping with
395 oxygen uncoupling (CLOU). *Energy Procedia* (2011);4:417-24.
- 396 [4] Abad A, Adánez-Rubio I, Gayán P, García-Labiano F, de Diego LF, Adánez J.
397 Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5
398 kWth continuously operating unit using a Cu-based oxygen-carrier. *Int J Greenhouse*
399 *Gas Control* (2012);6:189-200.
- 400 [5] Adánez-Rubio I, Abad A, Gayán P, de Diego LF, García-Labiano F, Adánez J.
401 Performance of CLOU process in the combustion of different types of coal with CO₂
402 capture. *Int J Greenhouse Gas Control* (2012);12:430-40.
- 403 [6] Sass B, Monzyk B, Ricci S, Gupta A, Hindin B, Gupta N. Impact of SO_x and NO_x in
404 Flue Gas on CO₂ separation, compression, and pipeline transmission. In: Thomas DC,
405 Benson SM, editors. *Carbon dioxide capture for storage in deep geologic formations*
406 *results from the CO₂ capture project, vol. 2.* Oxford, UK: Elsevier; 2005 [chapter 17].
- 407 [7] Bryant S, Lake LW. Effect of impurities on subsurface CO₂ storage processes. In:
408 Thomas DC, Benson SM, editors. *Carbon dioxide capture for storage in deep geologic*
409 *formations e results from the CO₂ capture project, vol. 2.* Oxford, UK: Elsevier; 2005
410 [chapter 18].
- 411 [8] Pipitone G, Bolland O. Power generation with CO₂ capture: Technology for CO₂
412 purification. *Int J Greenhouse Gas Control* (2009);3:528-34.

- 413 [9] Forero CR, Gayán P, García-Labiano F, de Diego LF, Abad A, Adánez J. Effect of gas
414 composition in Chemical-Looping Combustion with copper-based oxygen carriers: Fate of
415 sulphur. *Int J Greenhouse Gas Control* (2010);4:762-70.
- 416 [10] Adánez-Rubio I, Gayán P, Abad A, de Diego LF, García-Labiano F, Adánez J.
417 Evaluation of a Spray-Dried CuO/MgAl₂O₄ Oxygen Carrier for the Chemical Looping
418 with Oxygen Uncoupling Process. *Energy Fuels* (2012);26:3069-81.
- 419 [11] On the limitation of emissions of certain pollutants into the air from large combustion
420 plants. European Council Directive 2001/80/EC. *Off. J. Eur. Commun.* L309, 1–21
421 (2001)
- 422 [12] Adánez-Rubio I, Gayán P, Abad A, de Diego LF, García-Labiano F, Adánez J.
423 Identification of Operational Regions in the Chemical-Looping with Oxygen Uncoupling
424 (CLOU) Process with a Cu-based Oxygen-Carrier. *Fuel* (2012);102:634-45.
- 425 [13] Simell P, Stahlberg P, Kurkela E, Albretch J, Deutch S, Sjoström K. Provisional
426 protocol for the sampling and analysis of tar and particulates in the gas from large-
427 scale biomass gasifiers. *Biomass and Bioenergy* (2000);18:19-38.
- 428 [14] Virginie M, Adánez J, Courson C, de Diego LF, García-Labiano F, Niznansky D,
429 Kiennemann A, Gayán P, Abad A. Effect of Fe–olivine on the tar content during biomass
430 gasification in a dual fluidized bed. *Applied Catalysis B: Environmental* (2012);121–
431 122:214–22.
- 432 [15] Benito RG and Dung NV. Emissions of SO₂ during batch fluidized bed combustion of
433 Rundle retorted shale. *Fuel* (1993);72:869-72.
- 434 [16] De Diego LF, Rufas A, García-Labiano F, de las Obras-Loscertales M, Abad A, Gayán
435 P, Adánez J. Optimum temperature for sulphur retention in fluidised beds working
436 under oxy-fuel combustion conditions. *Fuel* (2012),
437 <http://dx.doi.org/10.1016/j.fuel.2012.02.064>.
- 438 [17] Cuadrat A, Abad A, de Diego LF, García-Labiano F, Gayán P, Adánez J. b. Prompt
439 considerations on the design of Chemical-Looping Combustion of coal from
440 experimental tests. *Fuel* (2012);97:219-32.

Caption of figures

Fig 1. Schematic view of the ICB-CSIC-s1 unit for coal-fuelled CLOU (1.5 kW_{th}).

Fig 2. Effect of the fuel-reactor temperature in the combustion efficiency in the fuel-reactor (●) and carbon capture efficiency (▼).

Fig 3. Sulphur distribution in the continuous CLOU plant at the outlet of fuel-reactor (■) and air-reactor (●).

Fig 4. Effect of the fuel-reactor temperature in the SO₂ emissions normalized at 6% O₂ in the air-reactor: (▼) measures in CLOU unit and (■) calculated using a uniform S release during char conversion; SO₂ legislation emission limit (- - -)

Fig 5. Gas outlet concentrations of C(-) and SO₂ (···) from the batch fluidize bed reactor. Heating: N₂. Combustion: 2.5% O₂ in N₂.

Fig 6. Sulphur splitting in the continuous CLOU plant. ▨: fuel-reactor gas outlet; ▩: air-reactor gas outlet; ▨▨: pyritic sulphur in ashes; ▨▨▨: self-retention by ashes.

Fig 7. Conversion vs. time curves for (a) reduction and (b) oxidation reactions for fresh and used 15 h CLOU unit particles. Reduction in N₂ and oxidation in air at 1000 °C in TGA.

Fig. 8. SO₂ emissions as a function of the fuel reactor inventory for lignite at three different efficiencies of the carbon separation system and three temperatures in the fuel reactor: (a) 909, (b) 935 and (c) 950 °C. η_{CSS} : 0(—), 50%(···), 90% (---). $\phi = 1.1$. $\dot{m}_{\text{OC}} : 1.35$ (kg/s per MW_{th}). SO₂ legislation emission limit (-·-·-·-).

Fig. 9. SO₂ emissions as a function of the fuel reactor inventory for three different fuels and two carbon separation system efficiencies: (a) $\eta_{\text{CSS}} = 0\%$, (b) $\eta_{\text{CSS}} = 90\%$. Fuels: Lignite (—), Anthracite (···), Medium volatile bituminous (---). $\phi = 1.1$. $\dot{m}_{\text{OC}} : 1.35$ (kg/s per MW_{th}). SO₂ legislation emission limit (-·-·-·-).

475

476 **Caption of tables**

477

478 **Table 1.** Properties of the oxygen-carrier Cu₆₀MgAl.

479

480 **Table 2.** Properties of lignite coal and its char.

481

482

Fig 1. Schematic view of the ICB-CSIC-s1 unit for coal-fuelled CLOU (1.5 kW_{th}).

488

489

490 **Fig 2.** Effect of the fuel-reactor temperature in the combustion efficiency in the fuel-reactor
491 (●) and carbon capture efficiency (▼).

492

Fig 3. Sulphur distribution in the continuous CLOU plant at the outlet of fuel-reactor (■) and air-reactor (●).

Fig 4. Effect of the fuel-reactor temperature in the SO₂ emissions normalized at 6% O₂ in the air-reactor: (▼) measures in CLOU unit and (■) calculated using a uniform S release during char conversion; SO₂ legislation emission limit (- - -)

502

503

504 **Fig 5.** Gas outlet concentrations of C(-) and SO₂ (···) from the batch fluidize bed reactor.

505 Heating: N₂. Combustion: 2.5% O₂ in N₂.

506

507

Fig 6. Sulphur splitting in the continuous CLOU plant. : fuel-reactor gas outlet; : air-reactor gas outlet; : pyritic sulphur in ashes; : self-retention by ashes.

513

514

515 **Fig 7.** Conversion vs. time curves for (a) reduction and (b) oxidation reactions for fresh and
516 used 15 h CLOU unit particles. Reduction in N_2 and oxidation in air at 1000 °C in TGA.

517

518

519

520 **Fig. 8.** SO₂ emissions as a function of the fuel reactor inventory for lignite at three different
521 efficiencies of the carbon separation system and three temperatures in the fuel reactor: (a)
522 909, (b) 935 and (c) 950 °C. η_{CSS} : 0 (—), 50% (····), 90% (---). $\phi = 1.1$. $\dot{m}_{OC} : 1.35$ (kg/s per
523 MW_{th}). SO₂ legislation emission limit (-·-·-·-).

524

525

526

527 **Fig. 9.** SO₂ emissions as a function of the fuel reactor inventory for three different fuels and
528 two carbon separation system efficiencies: (a) $\eta_{\text{CSS}} = 0\%$, (b) $\eta_{\text{CSS}} = 90\%$. Fuels: Lignite (—),
529 Anthracite (···), Medium volatile bituminous (---). $\phi = 1.1$. $\dot{m}_{\text{OC}}: 1.35$ (kg/s per MW_{th}). SO₂
530 legislation emission limit (-·-·-·-·-).

531

532

533 **Table 1.** Properties of the oxygen-carrier Cu₆₀MgAl.

Oxygen transport capacity, R _{OC} (wt.%)	6
Crushing strength (N)	2.4
Real density (g/cm ³)	4.6
Porosity (%)	16.1
Specific surface area, BET (m ² /g)	< 0.5
XRD main phases	CuOMgAl ₂ O ₄

534

535

536 **Table 2.** Properties of lignite coal and its char, as received basis.

	Lignite	Char
C	45.4 %	55.8 %
H	2.5 %	0.4 %
N	0.6 %	0.5 %
S	5.2 %	5.03 %
O ⁽¹⁾	8.5 %	----
Moisture	12.6 %	0.52 %
Volatile matter	28.6 %	1.17 %
Fixed carbon	33.6 %	54.8 %
Ash	25.2 %	43.5 %
LHV (kJ/kg)	16250	

537 ⁽¹⁾Oxygen to balance.

538

539