

1 Fuel reactor modelling in Chemical-Looping Combustion of coal:

2 2. Simulation and optimization

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10
11 **Abstract**

12 Chemical-Looping Combustion of coal (CLCC) is a promising process to carry out coal
13 combustion with carbon capture. The process should be optimized in order to maximize the
14 carbon capture and the combustion efficiency in the fuel reactor, which will depend on the
15 reactor design and the operational conditions. In this work, a mathematical model of the
16 fuel reactor is used to make predictions about the performance of the CLCC process and
17 simulate the behaviour of the system over different operating conditions. The mathematical
18 model considers the fluid dynamic characteristics of the fuel reactor, being a high-velocity
19 fluidized bed reactor. It also considers the chemical processes happening inside the reactor,
20 and the effect of a carbon separation system on the char conversion in the process.

21 A sensitivity analysis of the effect of the efficiency of the carbon separation system, the
22 solids inventory in the fuel reactor, the temperature in the fuel reactor, ratios of oxygen
23 carrier to fuel, oxygen carrier reactivity, coal reactivity and coal particle on the carbon

1 capture and combustion efficiency is carried out. Also the relevance of the water–gas shift
2 reaction (WGS) is evaluated. The most relevant parameters affecting the carbon capture are
3 the fuel reactor temperature and the efficiency of the carbon separation system, η_{CSS} . A
4 value for η_{CSS} as high as 98% should be necessary to reach a carbon capture efficiency of
5 98.6%. Regarding the combustion efficiency, to use highly reactive oxygen carrier
6 materials are desirable. In any case, additional actions or a modified design for the fuel
7 reactor should be implemented to reach complete combustion of coal.

8

9 **Keywords:** Combustion, Fluidization, Mathematical modelling, Simulation, Chemical-
10 Looping Combustion, Coal.

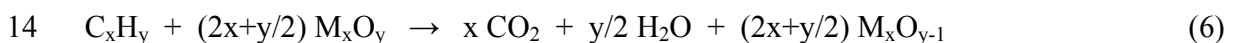
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1 **1. Introduction**

2 In the last years increasing interest is found about the application of Chemical-Looping
3 Combustion using coal as fuel (CLCC process), regarding the intensive use of this fuel
4 (Adanez et al., 2012). In this approach, coal is mixed with an oxygen carrier in the fuel
5 reactor. The coal is gasified by means of steam or CO₂ supplied to the reactor both as
6 fluidizing and gasifying agents.



10 The oxygen carrier particles subsequently react with the coal devolatilization/gasification
11 products, e.g. CO, H₂ or hydrocarbons, giving CO₂ and water:



15 Moreover, the model can assume, or not, that the reaction products (CO, H₂, CO₂ and H₂O)
16 reach instantaneously the water–gas shift (WGS) equilibrium –Eq. (7)– in all phases of the
17 reactor. Both assumptions are analyzed in this work.



19 Iron based materials have been extensively used as oxygen carriers in CLCC systems.

20 Among the CLCC successfully operated, the fuel reactor was designed as a bubbling
21 fluidized bed (Berguerand and Lyngfelt, 2008a, 2008b and 2009; Cuadrat et al., 2011,
22 2012a and 2012b), spouted bed (Gu et al., 2011) or high velocity fluidized bed (Markström
23 et al., 2012). In all these cases, gasification of coal was an intermediate step happening in
24 the fuel reactor. During the experiments, several operational conditions were used. This fact

1 makes difficult to directly compare the different results obtained because of the inherent
2 differences in the units and in the experimental conditions chosen by every research group.
3 But in general, optimized conditions were not reached. The carbon capture efficiency was
4 rather low in most of cases, losses of solid carbon were found and complete combustion of
5 gases was not reached in the fuel reactor, making necessary to take additional actions. The
6 carbon capture can be improved by implementing a carbon separation system, which
7 separates char from oxygen carrier particles and return them to the fuel reactor (Cao et al.,
8 2006). A final gas polishing step with pure oxygen is proposed for the complete oxidation
9 of gas exiting the fuel reactor. Often the “oxygen demand” parameter, Ω_T , is used to
10 describe the fraction of oxygen required in the oxygen polishing step.

11 Modelling and simulation of the CLCC system is a relevant tool to analyze the effect of
12 different operational conditions. Thus, the most relevant parameters affecting the process
13 can be determined, with the optimization of the CLCC system as the final objective. A
14 fundamental part of the reliability of a CLCC system is based on the behaviour of the fuel
15 reactor.

16 Some works have been presented in the literature for the modelling of specific aspects
17 involved in the fuel reactor of a CLCC system. In most cases, models are essentially based
18 on mass balances into the reactor considering the gasification reaction and oxidation of
19 volatile matter and gasification products by the oxygen carrier. Thus, Ströhle et al. (2009)
20 analyzed the effect of the solids inventory and the efficiency of a carbon separation system
21 on the carbon capture efficiency. Cuadrat et al. (2012c) predicted the carbon capture and
22 oxygen demand reached in the fuel reactor as a function of several operational parameters,
23 e.g. fuel reactor temperature, solids inventory, oxygen carrier to fuel ratio, steam to carbon

1 ratio or fluidizing gas composition. Also the presence of a carbon separation system was
2 considered. They determined that the fuel reactor temperature and the efficiency of the
3 carbon separation system are key parameters to improve the performance of the process. A
4 deeper analysis on the behaviour of a carbon stripper as carbon separation system and its
5 effect on the carbon capture of the CLCC process was done by Kramp et al. (2012). They
6 conclude that a carbon stripper can be designed in order to increase the residence time of
7 char particles in the fuel reactor, and thus to reach carbon capture efficiency values as high
8 as 98-99%. Other options, as to increase the solids inventory in the fuel reactor or to re-
9 design the fuel reactor as several stirred tank in series showed a lower effect on the carbon
10 capture.

11 Schöny et al. (2011) built a more elaborated 3D model, which involves empirical equations
12 to consider the complex solids and gas flow in a high-velocity fluidized bed. They focused
13 their results on the combustion of gases evolved in the fuel reactor, and point out the
14 relevance of the coal particle size on the gas conversion.

15 In the previous work (Abad et al., 2012), a mathematical model describing the processes
16 happening in the fuel reactor of a CLCC process was presented. This model was mainly
17 based on semi-empirical equations to describe the fluid dynamics of a high-velocity
18 fluidized bed as fuel reactor (Pallarès and Johnsson, 2006). The fluid dynamic model has
19 been previously used to predict the performance of coal combustion in a 12 MW_{th} CFB unit
20 (Adánez et al., 2003). In addition, the model includes the reaction kinetics of the chemical
21 processes happening in the fuel reactor of a CLCC system. Also the effect of a carbon
22 separation system on the increase of the residence time of char particles in the fuel reactor
23 is considered. The model predicts the carbon capture efficiency and the oxygen demand of
24 the CLCC process depending on the operational conditions chosen for the fuel reactor. A

1 reference case for a 1 MW_{th} CLCC system was evaluated. The main dimensions and
2 operational conditions taken as reference were based on the 1 MW_{th} unit built at TU
3 Darmstadt (Abdulally et al., 2012; Ströhle et al., 2010). The developed model predicted
4 values for the oxygen demand, Ω_T , of 10.5% and for the carbon capture efficiency, η_{CC} , of
5 59% for the reference case. The mean residence time of solids in the fuel reactor was 100 s,
6 corresponding to a solids inventory of 260 kg. Thus, it is necessary to optimize the system
7 in order to improve the CLCC performance. The carbon capture efficiency could be
8 increased by increasing the carbon separation efficiency, η_{CCS} , but an extreme value of
9 $\eta_{CCS} = 99\%$ would be necessary to reach $\eta_{CC} = 95\%$.

10 In this work, the developed mathematical model is used to identify the most relevant
11 operational parameters in order to maximize the carbon capture efficiency and minimize the
12 oxygen demand of a CLCC system. To analyze the effect of several operational parameters,
13 i.e. fuel reactor temperature, solids inventory, oxygen carrier to fuel ratio, efficiency of the
14 carbon separation system, oxygen carrier reactivity, coal reactivity and coal particle size, a
15 sensitivity analysis is done. Finally, some conclusions are drawn in order to optimize the
16 CLCC system to obtain high coal conversion in the fuel reactor.

17

18 **2. Methodology**

19 In a previous work (Abad et al., 2012), an empirical model describing the fuel reactor in the
20 CLCC process was presented. The developed model is based on semi-empirical
21 correlations, and considers the reactor fluid dynamics, the coal conversion and the reaction
22 of the oxygen carrier with evolved gases from coal.

1 The model developed is focused on the fuel reactor behaviour, being a fluidised-bed
 2 reactor working at the high-velocity regime. The reactor is based on the design of a 1 MW_{th}
 3 CLCC unit at TU Darmstadt (Abdulally et al., 2012; Ströhle et al., 2010). A diagram of this
 4 reactor is presented in Fig. 1. More details about the connection of fuel reactor, cyclones
 5 and carbon stripper can be found elsewhere (Abdulally et al., 2012). The geometrical and
 6 the main process parameters of the fuel reactor are shown in Tables 1 and 2.

7 The performance of the fuel reactor was evaluated by analyzing the following parameters
 8 (Abad et al., 2012):

9 a) The oxygen demand of the flue gases. This value represents the extent that coal is burned
 10 to CO₂ and H₂O in the CLC system. The total oxygen demand, Ω_T , is the fraction of
 11 oxygen required to fully oxidize the unconverted gases exiting the fuel reactor to CO₂
 12 and H₂O with respect the total oxygen demand of the fuel, i.e. the stoichiometric amount
 13 of oxygen required in an oxy-fuel process.

$$14 \quad \Omega_T = \frac{M_O (F_{H_2} + F_{CO} + 4F_{CH_4})_{out}}{\Omega_{coal}} \quad (8)$$

15 The oxygen demanded by coal is defined as:

$$16 \quad \Omega_{coal} = M_O (2[C]_{coal} / M_C + 0.5[H]_{coal} / M_H - [O]_{coal} / M_O) \cdot F_{coal} \quad (9)$$

17 $[C]_{coal}$, $[H]_{coal}$ and $[O]_{coal}$ being the carbon, hydrogen and oxygen contents in the fuel,
 18 whose values are obtained from the ultimate analysis of the coal.

19 To better evaluate the oxygen demand in the CLC system, the combustion efficiency in
 20 the fuel reactor is defined as the stoichiometric ratio of the oxygen transferred to the fuel
 21 in the fuel reactor versus the oxygen demand of the coal converted in the fuel reactor.

$$\eta_{c,FR} = \frac{(F_{H_2O} + 2F_{CO_2} + F_{CO})_{out} - (F_{H_2O} + 2F_{CO_2} + F_{CO})_{in}}{\Omega_{coal}/M_O - 2F_{CO_2,AR}} \quad (10)$$

b) The CO₂ capture efficiency: this parameter considers the physical removal of CO₂ that would be otherwise emitted into the atmosphere. It is defined as the fraction of the carbon introduced by the coal which is converted to gas in the fuel reactor.

$$\eta_{CC} = M_C \frac{(F_{CO_2} + F_{CO} + F_{CH_4})_{out} - (F_{CO_2})_{in}}{[C]_{coal} \cdot F_{coal}} \quad (11)$$

The carbon capture depends on the char conversion, X_{char} , in the fuel reactor, as all carbon present in volatile matter is evolved in the fuel reactor and it goes to the fuel reactor exit after reaction with the oxygen carrier. Therefore, the char conversion is also evaluated in this work.

$$\eta_{CC} = 1 - \frac{[C]_{fixed}}{[C]_{coal}} \cdot (1 - X_{char}) \quad (12)$$

By the analysis of these four parameters, the performance of the fuel reactor can be described at different operating conditions. From now on, these four parameters will be appointed as the “evaluating parameters”.

In the previous work (Abad et al., 2012), the effect of the presence of a carbon separation system on the evaluating parameters was evaluated. The carbon separation system includes a system of two cyclones and a carbon stripper, see Fig. 1. The carbon stripper is fluidized by steam, and therefore some char can be here gasified. Nevertheless, because of the effect of stripping char particles, the char concentration in the carbon stripper would be low. The amount of carbon gasified in this unit was neglected as a first approximation.

1 In this work, the effect of the following relevant operating variables and parameters of the
2 model on the CLCC system performance is assessed:

- 3 1. Temperature in the fuel reactor
- 4 2. Solids inventory in the fuel reactor
- 5 3. Oxygen carrier to fuel ratio
- 6 4. Oxygen carrier reactivity
- 7 5. Coal reactivity
- 8 6. Coal particle size

9 In addition, the relevance of the WGS reaction on the CLCC performance is weighed. The
10 reference case considers a fuel reactor temperature of 1000 °C, a pressure drop in the
11 reactor of 20 kPa, an oxygen carrier to fuel ratio of 1.2 and an efficiency of the carbon
12 separation system of 90%. Ilmenite is the oxygen carrier, whereas a high volatile
13 bituminous coal “El Cerrejón” from Colombia with a mean particle size of 120 µm is
14 considered as fuel.

15 Finally, a sensitivity analysis of the model results to these parameters, as well as the
16 efficiency of the carbon separation system is carried out.

17

18 **3. Simulation results of the 1 MW_{th} CLCC plant**

19 The developed model in a previous work (Abad et al., 2012) has been used to simulate the
20 behaviour of the fuel reactor in the 1 MW_{th} CLCC plant erected in TU Darmstadt (Ströhle
21 et al., 2010). The values obtained for the evaluating parameters at different operational
22 conditions will be evaluated and used in order to optimize the CLCC system.

23

1 *3.1. Temperature in the fuel reactor*

2 Experimental results in a 10 kW_{th} CLC unit showed the relevance of using high
3 temperature in the fuel reactor in order to increase the carbon capture efficiency
4 (Berguerand and Lyngfelt, 2009). So, the effect of temperature is first evaluated.
5 Fig. 2 shows the effect of the fuel reactor temperature on the evaluating parameters. It can
6 be seen that the temperature has a large effect on the gasification efficiencies. Indeed, the
7 carbon capture is as high as $\eta_{CC} = 89\%$ at 1200 °C. Although this temperature would be
8 extremely high for the 1 MW_{th} unit, this fact indicates the relevance of using high
9 temperature to facilitate high carbon capture efficiency in a CLCC system. As char
10 conversion is improved with the temperature, the char concentration in the bottom bed and
11 in the solids stream at the fuel reactor exit decreases when the temperature is increased. At
12 the bottom bed the char concentration in solids decreases from 1.3 wt.% to 0.4 wt.% when
13 temperature increased from 900 to 1200 °C. The corresponding values of char concentration
14 at the top, i.e. in the reactor exit stream, were 6.5 wt.% and 1.2 wt.%, respectively.
15 Nevertheless, the combustion efficiency and the oxygen demand are barely affected by the
16 temperature. CH₄ concentration, as indicative of volatile matter, at the reactor exit
17 decreases from 0.9 vol.% to 0.05 vol.% as the temperature increases from 900 to 1200 °C.
18 However, the concentration of gasification products, i.e. H₂ and CO, increases from 4.3 and
19 1.3 vol.% to 6.0 and 2.4 vol.%, respectively. Remember that CH₄ is uniquely generated in
20 the coal feeding point. This fact indicates that the combustion of volatile matter is increased
21 with the temperature, but it is compensated by the increase of gasification products, which
22 are continuously generated in the freeboard. Thus, the oxygen demand was approximately
23 constant.

1 The predicted tendency of carbon capture and oxygen demand with temperature agrees to
2 experimental results previously obtained (Cuadrat et al., 2011 and 2012a).

3

4 *3.2. Solids inventory in the fuel reactor*

5 Previous predictions obtained from simplified models showed the relevance of the solids
6 inventory on the fuel reactor performance (Cuadrat et al., 2012c; Kramp et al., 2012;
7 Ströhle et al., 2009). An increase of solids inventory in the reactor mainly gives an increase
8 of the height of the bottom bed, and accordingly an increase of the pressure drop in the
9 reactor. Its main effect on the gasification reaction is the increase of the main residence
10 time of char particles in the reactor, thus affecting to the char conversion reached.

11 The effect of the solids inventory in the bed on the fuel reactor performance is evaluated by
12 changing the total pressure drop in the reactor. Fig. 3 shows the evaluating parameters as a
13 function of the pressure drop and the corresponding solids inventory. When the solids
14 hold-up increases from 190 to 2600 kg/MW_{th} the residence time of char particles in the
15 reactor increased from 75 to 1000 s. As a consequence, the carbon capture efficiency
16 increases because the amount of carbon gasified in the bottom bed increases. Besides, the
17 concentration of char particles in the bed decreases from 1.8 wt.% to 0.23 wt.% as char
18 particles are more converted and they are diluted in a higher amount of ilmenite particles.
19 At the reactor exit the char concentration decreases from 4.0 wt.% to 0.7 wt.%. The char
20 concentration in the solids should be taken into account for the design of the carbon
21 separation system (Kramp et al., 2012). As the gasification products generated in the
22 bottom bed are more efficiently converted to CO₂ and H₂O by the oxygen carrier than in the
23 freeboard, the combustion efficiency increases and, consequently, the oxygen demand
24 decreases.

1 The beneficial effect of increasing the solids inventory on the performance of the fuel
2 reactor is relatively important until increase the pressure drop to 70 kPa, corresponding to a
3 solids inventory of about 900 kg/MW_{th}. The calculated value of carbon capture efficiency
4 was $\eta_{CC} = 83\%$ and the oxygen demand $\Omega_T = 7.4\%$. Further increases on the solids
5 inventory causes lower increases in the combustion efficiency, although the oxygen
6 demand still shows a relevant decrease ($\Omega_T = 3.0\%$ at $\Delta P_{FR} = 200$ kPa or 2600 kg/MW_{th}).

8 3.3. Oxygen carrier to fuel ratio, ϕ

9 Fig. 4 shows the evaluating parameters as a function of the oxygen carrier to fuel ratio, ϕ .
10 This parameter was defined as the availability of oxygen in the flow of oxygen carrier
11 divided by the oxygen required to fully convert the fuel to CO₂ and H₂O:

$$12 \quad \phi = \frac{R_{OC} F_{OC}}{\Omega_{coal}} \quad (13)$$

13 So, $\phi = 1$ corresponds to the stoichiometric flow of oxygen carrier needed for a full
14 conversion of the fuel to CO₂ and H₂O. The ϕ ratio is a predefined parameter which is not
15 affected by the conversion of coal in the process

16 The ϕ ratio was changed by varying the oxygen carrier circulation flow–rate between the
17 air and fuel reactors, F_{OC} . For evaluation purposes, the variation of solids conversion,
18 ΔX_{OC} , also is shown in Fig. 4. ΔX_{OC} is affected by the ϕ ratio and also by the extension of
19 fuel conversion to CO₂ and H₂O in the fuel reactor (Adánez et al., 2009); so, the ΔX_{OC}
20 value decreases as the ϕ ratio increases or the char conversion and combustion efficiency
21 decreases. Increasing the oxygen carrier to fuel ratio, an increase in the combustion
22 efficiency and a decrease in the oxygen demand are observed. There is a difference in the

1 extent of the $\eta_{c,FR}$ and Ω_T variations for ϕ values below and above 1. For ϕ values below 1 a
2 sharp decrease in the combustion efficiency and an increase in the oxygen demand is
3 predicted. This fact is due to the lack of oxygen availability in the oxygen carrier flow from
4 the air reactor to fully convert coal to CO_2 and H_2O . Also, the decrease of the average
5 reactivity of ilmenite particles in the reactor as the particles are reduced in a higher amount
6 is relevant in this case. The decrease in the average reactivity of the oxygen carrier particles
7 is important as ΔX_{OC} increases above 0.5 (Abad et al., 2007), which is the case for $\phi < 1$,
8 see Fig. 4. However, the increase in the average reactivity is not relevant when ΔX_{OC} is
9 decreased below 0.5, thus the effect on the oxygen demand is less affected by increasing
10 the ratio of oxygen carrier to fuel above 1.

11 In Fig. 4, a continuous decrease in the carbon capture is observed when the oxygen carrier
12 to fuel ratio is increased. This fact is due to a decrease in the mean residence time of solids
13 in the fuel reactor as the solids circulation rate increases, with consequent decrease of the
14 char conversion. The mean residence time decreased from 130 to 40 s when the ϕ value
15 increased from 1 to 3.

16 The results predicted of the effect of the solids circulation flow rate on the fuel reactor
17 performance are in line to the experimental results obtained in a continuously operated
18 CLC unit with coal (Cuadrat et al., 2012b).

19

20 *3.4. Oxygen carrier reactivity.*

21 Several Fe-based materials have been used as oxygen carriers for the CLC process with
22 coal. Thus, ilmenite (Berguerand and Lyngfelt, 2008a; Cuadrat et al., 2011), iron ore (Wu
23 et al., 2010), or a bauxite waste material (Mendiara et al., 2012) have been used in

1 continuously operated units. In all cases, unburnt compounds were found. Besides, different
2 carbon capture efficiencies were obtained. However, from these works it is difficult to
3 evaluate the effect of the reactivity itself of every oxygen carrier on the process
4 performance because results were obtained in different conditions and in different CLC
5 units, which includes or not a carbon separation system. Only data reported for ilmenite
6 (Cuadrat et al., 2011 and 2012b) and bauxite waste (Mendiara et al., 2012a) can be
7 compared, showing that the use of a higher reactive material -i.e. the bauxite waste
8 compared to ilmenite (Mendiara et al., 2012b)- gave an increase of the combustion
9 efficiency, but barely the carbon capture was changed. With the developed model, the
10 effect of the oxygen carrier reactivity itself on the CLC performance can be evaluated. The
11 oxygen transport capacity and solids circulation flow rate was maintained at the same
12 values.

13 Fig. 5 shows the evaluating parameters as a function of the reactivity of the oxygen carrier.
14 This reactivity is expressed as a ratio with respect to the reactivity of the ilmenite, i.e. ($-$
15 $r_{OC})/(-r_{ilm})$). As reference, the oxygen transference rate of a highly reactive iron ore in
16 hydrogen was about 1.5 times that showed by activated ilmenite (Mendiara et al., 2012b);
17 on contrary, the oxygen transference rate of activated ilmenite was about 5 times higher
18 than that showed by CaSO_4 (Shen et al., 2008).

19 The increase predicted in the combustion efficiency with the oxygen carrier reactivity is
20 very relevant, as well as the decrease in the oxygen demand. It was observed during the
21 simulation that the highest effect of oxygen carrier reactivity is to increase the combustion
22 of gases in the splash zone, because there is a higher solids concentration than in the
23 transport phase and a better gas-solid contact than in the bottom bed.

1 On the contrary, the carbon capture is less affected by the oxygen carrier reactivity because
2 of its low effect on char gasification rate. Of course, the concentration of gasification
3 inhibitors, i.e. H₂ and CO, decreases as the oxygen carrier is more reactive, and therefore
4 the gasification rate increases to some extension. However, in any case the H₂ and CO
5 concentration is low, and a further decrease in the concentration of these gases would have
6 a marginal increase of the gasification rate.

7

8 *3.5. Coal reactivity*

9 The type of coal has shown to have a high relevance on the performance of the CLCC
10 process (Cuadrat et al., 2012a). Apart from the effect of the volatile matter content
11 depending on the coal rank, the coal reactivity itself has a great influence on the carbon
12 capture efficiency. In this section, the effect of the coal reactivity on the evaluating
13 parameters was analyzed by the ratio between the global gasification rate of a determined
14 coal and the global gasification rate of the “El Cerrejón” coal, i.e. $(-r_{g,coal})/(-r_{g,Cerr})$. The
15 reactivity of coal can vary in two orders of magnitude between anthracite and lignite
16 (Johnson et al., 1981). In this case, the reactivity of “El Cerrejón” coal was found to be
17 between them. Also, the volatile matter content would affect the carbon capture as it was
18 experimentally proven (Cuadrat et al., 2012a) and predicted by theoretical considerations
19 (Ströhle et al., 2009). Nevertheless, this fact was not evaluated in this work.

20 As it can be seen in Fig. 6, the $(-r_{g,coal})/(-r_{g,Cerr})$ ratio was varied from 0.1 to 10. The lower
21 limit could correspond to the case of using anthracite as fuel, and the upper limit
22 corresponds to the use of a highly reactive lignite. The carbon capture increased with
23 increasing the coal reactivity as a consequence of a faster conversion of char in the fuel
24 reactor. However, as gasification is improved with increasing coal reactivity, the amount of

1 reacting gases in the fuel reactor increased, which produced a decrease in the combustion
2 efficiency in the fuel reactor and an increase in the oxygen demand. So, actions should be
3 taken in order to improve the combustion efficiency in the fuel reactor when very reactive
4 coals would be used.

5

6 *3.6. Coal particle size*

7 The effect of the coal particle size on the carbon capture efficiency is also analyzed. The
8 model predicts that a higher fraction of char is in the bottom bed as the coal particle size
9 increases, lowering the flow of char to the transport phase. This fact has relevant
10 consequences on the CLC performance. Fig. 7 shows the effect of the coal particle size on
11 the evaluating parameters. The char conversion, and correspondingly the carbon capture
12 efficiency, increases with the coal particle size. Basically, this fact is due to a decrease in
13 the char concentration in the reactor exit, which decreases from 4.9 wt.% to 2.2 wt.% when
14 the coal particle size increases from 50 to 500 μm . On the contrary, the char concentration
15 in the bottom bed and in the splash zone increases from 0.7 wt.% to 2.5 wt.%. Thus, a
16 lower flow of char goes to the carbon separation system and thereafter to the air reactor,
17 increasing the carbon capture. Also a higher fraction of char is gasified in the bottom bed
18 and in the splash phase. Of all carbon initially in char, only 11% is converted in the bottom
19 bed when coal particle size is 50 μm , increasing to 30% when the coal size increases to 500
20 μm . So, a higher flow of gasification products are generated in the bottom bed as well as in
21 the splash phase. The model predicts that the CH_4 flow -obtained solely from the volatile
22 matter- at the reactor exit was barely changed by the coal particle size; but CO and H_2

1 flows increases as more char is gasified when the coal size was increased. As a result, the
2 combustion efficiency in the fuel reactor decreases and the oxygen demand increases.
3 These results do not agree to experimental results showed by Cuadrat et al. (2011). These
4 authors showed that a decrease in the particle size produced a decrease in the combustion
5 efficiency of the fuel reactor. In this case, the fuel reactor was a bubbling fluidized bed.
6 Small coal particles were more easily elutriated, increasing the relative relevance of the
7 char gasification in the freeboard where gasification products had not the opportunity to
8 react with the oxygen carrier. However, this is not the case for a high-velocity fluidized bed
9 reactor, where gasification products can be oxidized by the oxygen carrier particles present
10 in the dilute region. Schöny et al. (2011) modelled a circulating fluidized bed fuel reactor,
11 and they predicted an increase in the combustion efficiency with increasing the coal particle
12 size. They explained this result because a higher share of the char gasification products are
13 released in the bottom bed where the highest oxygen carrier concentration is. However,
14 they did not consider that the amount of char gasified in the fuel reactor increases with the
15 coal particle size, as it was predicted in the present work. The higher amount of char
16 gasified increases the load of gases to be burnt in the fuel reactor, and therefore the
17 combustion efficiency predicted by the model falls with the coal particle size.
18 Although the increase in the coal particle size is beneficial in terms of the carbon capture, it
19 is necessary to point out that this result is obtained maintaining the same value for the
20 carbon separation system ($\eta_{\text{CCS}} = 90\%$). However, a higher coal particle size may cause a
21 drop in the carbon separation efficiency (Kramp et al., 2012), and therefore, it should be
22 analyzed in more detail how the coal particle size affect jointly to the char distribution in
23 the fuel reactor and to the performance of the carbon separation system.

1

2 *3.7. Relevance of the WGS reaction in the gas phase*

3 Results showed above were obtained assuming that the WGS reaction does not happen in
4 any extension in the reactor, and therefore the gas composition is not modified by the WGS
5 reaction. This assumption was adopted from experimental evidence of low relevance of
6 WGS reaction when ilmenite was used as oxygen carrier. Nevertheless, the WGS reaction
7 can be easily catalyzed at high temperatures, even by the gas contact with the reactor walls
8 depending on the material (Bustamante et al., 2004). Other Fe-based materials used in
9 CLCC have showed higher activity towards the WGS reaction (Mendiara et al., 2012c). Not
10 for nothing, Fe-based catalysts are used in WGS reactors. Therefore, it can be interesting to
11 analyse the effect on the fuel reactor performance when the WGS reaction was at
12 equilibrium conditions throughout the reactor.

13 Fig. 8(a) shows the oxygen demand and the carbon capture whereas Fig. 8(b) shows the gas
14 composition at the reactor exit considering or not the WGS reaction as a function of the
15 carbon separation efficiency. On the one hand, the oxygen demand slightly decreases when
16 the WGS reaction is considered due to some of CO is transformed into the highly reactive
17 H₂ by Eq. (7). As a consequence, the oxidation of gasification products is improved
18 because the change in gas distribution by the WGS reaction. The combustion of CH₄ was
19 barely affected by the WGS reaction, see Fig. 8(b). On the other hand, the carbon capture is
20 barely decreased when the WGS reaction is considered. This decrease is due to the
21 gasification rate is somewhat slower in the resulting gas mixture with a higher H₂ content.
22 Note that H₂ has an inhibitory effect on steam gasification.

23

1 **4. Sensitivity analysis and optimization**

2 In the above section it was described how different parameters affect to the carbon capture
3 efficiency and the oxygen demand of a CLCC system. In this section, a sensitivity analysis
4 is performed to assess the relative influence of different parameters on the evaluating
5 parameters. In similar way that as those used by Kolbitsch et al. (2009), the relative linear
6 sensitivity coefficient, χ , of the "*target variable*", v , towards the "*investigated model*
7 *parameter*", π , by the finite difference method is defined as follows

$$8 \quad \chi = \frac{\Delta v/v}{\Delta \pi/\pi} \quad (14)$$

9 The carbon capture efficiency and the oxygen demand are selected as "*target variables*",
10 whereas the "*investigated model parameters*" are the six parameters analyzed previously in
11 this work, besides the efficiency of the carbon separation system analyzed previously in
12 Abad et al. (2012). Thus, the relative relevance of the "*investigated model parameters*" on
13 the "*target variables*" is analyzed.

14 Fig. 9 shows the relative linear sensitivity coefficient, χ , calculated for every value of the
15 parameter π . To optimize the CLCC system high positive value of χ is desired for the
16 carbon capture, but negative value is desired for the oxygen demand.

17 From the sensitivity analysis, it can be said that the most important parameters to maximize
18 the carbon capture are the fuel reactor temperature and the carbon separation efficiency.

19 This result emphasizes the relevance in the use of a highly efficient carbon separation
20 system to reach high carbon capture values in a CLCC system. The solids inventory and the
21 reactivity of the coal have lower relevance. Although sensitivity analysis on the coal
22 reactivity is rather low, it is worth to note that the reactivity of coal can be increased one
23 order of magnitude if a highly reactive coal is used, e.g. lignite. In this case, a high increase

1 in the carbon capture efficiency is expected. Finally, very low relevance has the variation of
2 the oxygen carrier reactivity or coal particle size on the carbon capture, whereas the solids
3 circulation flow rate shows a negative influence.

4 The oxygen demand increases rapidly with the carbon separation efficiency, but it is less
5 affected by the temperature. In order to decrease the oxygen demand, higher solids
6 inventory or oxygen carrier to fuel ratio can be proposed, as well as to use a more reactive
7 oxygen carrier. However, the increase of the oxygen carrier to fuel ratio is not
8 recommended because the drop in the carbon capture efficiency linked to an increase of the
9 solids circulation flow rate. On the other hand, the reactivity of Fe-based oxygen carriers
10 tested for CLC processes, e.g. ilmenite, iron ores, industrial waste materials or synthetic
11 particles, varies in less than one order of magnitude (Mendiara et al., 2012b). As much the
12 reactivity is increased by a factor of 1.5, with which would not be large differences.

13 Therefore, other oxygen carrier materials should be considered if the beneficial effect of
14 increasing the reactivity of solids was desired.

15 In the reference case, a carbon capture efficiency of 59% was predicted, whereas the
16 oxygen demand was 10%. The efficiency of the carbon separation system was assumed to
17 be 90%. In the industrial application of a CLCC system, higher carbon capture and lower
18 oxygen demand values are desirables. From above considerations, a higher value for the
19 efficiency of the carbon separation system is highly recommended. Kramp et al. (2012)
20 simulated the carbon stripper by using a usual value for technical separation sharpness to
21 segregate char and oxygen carrier particles in a bubbling fluidized bed. It was calculated a
22 value for the carbon separation efficiency in the carbon stripper of ~98%. With this value,
23 they reported carbon capture efficiency values of 90% and 95% for bituminous coal and
24 lignite, respectively. Although low temperatures could be compensated by a highly efficient

1 carbon separation system, temperatures higher than 1000 °C are preferred. The solids
2 inventory is less relevant, especially when it was increased above 1000 kg/MW_{th}. This fact
3 indicates that it is not worthy to increase the solids inventory too much above this value.
4 A new simulation was performed with a technical feasible operational temperature of 1100
5 °C, a carbon separation efficiency of 98%, and a solids inventory of 1000 kg/MW_{th}. The
6 carbon capture efficiency predicted was 98.6 %, whereas the oxygen demand was 6.8 %.
7 The height of the bottom bed at these conditions was 4 m and the total pressure drop in the
8 fuel reactor was $\Delta P_{FR} = 80$ kPa, which seems unrealistic for the fuel reactor dimensions.
9 So, a new design of the bottom part of the fuel reactor should be considered to work in
10 these conditions, with a higher section in the bottom bed. If a maximum height of 1 m for
11 the bottom bed is considered, the section of the bottom bed should increase from 0.12
12 m²/MW_{th} to 0.5 m²/MW_{th} to maintain the same solids inventory of 1000 kg/MW_{th}. The
13 pressure drop at these conditions was $\Delta P_{FR} = 25$ kPa. The corresponding mean residence
14 time of solids in the fuel reactor is 390 s, being the residence time of char particles higher
15 by the presence of the carbon separation system.

16 Another option to improve the performance of the CLCC system is to maintain the reactor
17 design, but decreasing the input thermal power. For comparison purposes, the pressure drop
18 was maintained about 27 kPa, corresponding to a solids inventory of 350 kg in the reactor
19 and a deep of the bottom bed about 1 m. The efficiency of the carbon separation system
20 was kept to 90%. The solids circulation flow rate was decreased as the coal feeding rate
21 was decreased to maintain constant the oxygen carrier to fuel ratio $\phi = 1.2$. Fig. 10 shows
22 the evaluating parameters obtained when the input thermal power was decreased from 1
23 MW_{th} to 0.1 MW_{th}. Data are plotted as a function of the solids inventory per MW_{th}. The

1 carbon capture was improved with increasing the solids inventory per MW_{th} as result of a
2 decrease in the input thermal power. In this case, the residence time of particles in the
3 reactor was increased from 145 to 1450 s, and therefore the char conversion was improved.
4 The carbon capture was 95% with 2000 kg/MW_{th} , and reach the value of 97% with 3000
5 kg/MW_{th} . However, the oxygen demand was barely affected by the solids inventory. In
6 these simulations, the time of contact between gas and solids was not significantly varied
7 when the input thermal power was decreasing. This fact indicates that other factors, e.g. the
8 mass transfer diffusion from gas to solids or the lower concentration of volatile matter as
9 the thermal power decreased, are also of great relevance in oxidation of gaseous products.
10 To reduce the oxygen demand additional actions should be taken, which could include a re-
11 design of the fuel reactor. One option could be the use of internals in the freeboard, which
12 increases the presence of solids in this zone (Guío-Pérez et al., 2012). Other option could be
13 the use of a fluidized bed with oxygen carrier down stream to fully oxidize the gas from the
14 fuel reactor (Thon et al., 2012). This last option seems to be very effective due to a
15 relatively small solids inventory in the down stream reactor (Cuadrat et al., 2012c).

16

17 **4. Conclusions**

18 A model describing the behaviour of the fuel reactor of a Chemical–Looping Coal
19 Combustion (CLCC) process has been used to evaluate the effect of several operating
20 variables on the global performance of the process. From these results, the carbon capture
21 efficiency and the oxygen demand of the flue gases were determined.

22 In the reference case, assuming an efficiency of the carbon separation system of 90%, a
23 carbon capture efficiency of 59% and an oxygen demand of 10.5 % were predicted. The

1 oxygen demand decreased to 7.6%, whereas the carbon capture slightly decreased to 57.5%
2 when the water-gas shift equilibrium was considered.

3 After a sensitivity analysis the following conclusions were obtained:

4 ○ The carbon capture increased by increasing the efficiency of the carbon separation
5 system. This was the most important parameter in order to increase the carbon capture
6 efficiency in the process. However, the oxygen demand increased as the carbon
7 separation system was more efficient. It was estimated that a value for the carbon
8 separation system efficiency of 98% can be feasible.

9 ○ The temperature showed an important effect on the conversion of coal in the fuel
10 reactor. Temperatures higher than 1000 °C are desirables in the fuel reactor to improve
11 the char conversion, and thereafter the carbon capture. The temperature had a lower
12 effect on the oxygen demand.

13 ○ The carbon capture increased significantly when the solids inventory in the fuel reactor
14 was increased up to ~1000 kg/MW_{th}. Further increases in the solids inventory had lower
15 effect on the carbon capture. The oxygen demand decreased with the solids inventory,
16 but in a lower extent.

17 ○ The oxygen carrier to fuel ratio, oxygen carrier reactivity and coal particle size affected
18 the performance of the process, but their influence in carbon capture or oxygen demand
19 was low.

20 ○ Highly reactive fuels, e.g. lignite, are preferred in the CLCC process in order to reach
21 high carbon capture efficiency. In addition, with highly reactive fuels a very high value
22 for the efficiency of the carbon separation system is not required.

23 Finally, it was determined that a carbon capture efficiency of 98.6% and an oxygen demand
24 of 6.8% could be reached if the following conditions would be selected: a temperature of

1 1100 °C in the fuel reactor, a solids inventory of 1000 kg/MW_{th} and an efficiency of the
2 carbon separation system of 98%.

3

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7

8

1 **5. Nomenclature**

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3 $[C]_{\text{coal}}$ = mass fraction of carbon in coal

4 $[C]_{\text{fixed}}$ = mass fraction of carbon fixed in coal

5 $d_{\text{p,coal}}$ = average diameter of coal particles, m

6 d_{react} = inside diameter of the reactor, m

7 F_{coal} = rate of coal feeding, kg/s

8 F_i = molar flow of gas i , mol/s

9 F_{OC} = solids circulation rate, kg/s

10 H_{Coal} = height of the coal feeding, m

11 H_{CS} = height of the char feeding, m

12 H_r = height of the reactor, m

13 M_i = atomic mass of element i , kg/mol

14 P = pressure at the reactor outlet, Pa

15 $Q_{\text{g,in}}$ = inlet gas flow through the distributor plate at the bottom, Nm³/h

16 $Q_{\text{g,CS}}$ = gas flow from the carbon stripper, Nm³/h

17 $(-r_i)$ = reaction rate of an oxygen carrier i , mol m⁻³ s⁻¹

18 $(-r_{g,i})$ = gasification rate of coal i , mol m⁻³ s⁻¹

19 R_{OC} = oxygen transport capacity of the oxygen carrier

20 T_{FR} = temperature of the fuel reactor, °C

21 X_{char} = conversion of carbon in char

22 $\bar{X}_{\text{OC,in}}$ = average conversion of the oxygen carrier at the fuel reactor inlet

23

1 **Greek symbols:**

2 χ = relative linear sensitivity coefficient, defined by Eq. (X)

3 ΔP_{FR} = pressure drop in the reactor, Pa

4 ΔX_{OC} = variation of the conversion of oxygen carrier in the reactor

5 ϕ = ratio of oxygen carrier to fuel

6 $\eta_{c,FR}$ = combustion efficiency in the fuel reactor

7 η_{CC} = carbon capture efficiency

8 η_{CSS} = efficiency of the carbon separation system

9 v = target variable

10 π = investigated model parameter

11 Ω_{coal} = oxygen demand of coal, kg of oxygen per kg of coal

12 Ω_T = oxygen demand of flue gases from the fuel reactor

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