Fuel reactor modelling in Chemical-Looping Combustion of coal:

2. Simulation and optimization

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Abstract

Chemical-Looping Combustion of coal (CLCC) is a promising process to carry out coal combustion with carbon capture. The process should be optimized in order to maximize the carbon capture and the combustion efficiency in the fuel reactor, which will depend on the reactor design and the operational conditions. In this work, a mathematical model of the fuel reactor is used to make predictions about the performance of the CLCC process and simulate the behaviour of the system over different operating conditions. The mathematical model considers the fluid dynamic characteristics of the fuel reactor, being a high-velocity fluidized bed reactor. It also considers the chemical processes happening inside the reactor, and the effect of a carbon separation system on the char conversion in the process. A sensitivity analysis of the effect of the efficiency of the carbon separation system, the solids inventory in the fuel reactor, the temperature in the fuel reactor, ratios of oxygen carrier to fuel, oxygen carrier reactivity, coal reactivity and coal particle on the carbon
capture and combustion efficiency is carried out. Also the relevance of the water–gas shift reaction (WGS) is evaluated. The most relevant parameters affecting the carbon capture are the fuel reactor temperature and the efficiency of the carbon separation system, $\eta_{\text{CSS}}$. A value for $\eta_{\text{CSS}}$ as high as 98% should be necessary to reach a carbon capture efficiency of 98.6%. Regarding the combustion efficiency, to use highly reactive oxygen carrier materials are desirable. In any case, additional actions or a modified design for the fuel reactor should be implemented to reach complete combustion of coal.

**Keywords:** Combustion, Fluidization, Mathematical modelling, Simulation, Chemical-Looping Combustion, Coal.
1. Introduction

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

\[
\text{Coal} \rightarrow \text{Volatiles} + \text{Char} \quad (1)
\]

\[
\text{Char} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{ash} \quad (2)
\]

\[
\text{Char} + \text{CO}_2 \rightarrow 2\text{CO} + \text{ash} \quad (3)
\]

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

\[
\text{H}_2 + \text{M}_x\text{O}_y \rightarrow \text{H}_2\text{O} + \text{M}_x\text{O}_{y-1} \quad (4)
\]

\[
\text{CO} + \text{M}_x\text{O}_y \rightarrow \text{CO}_2 + \text{M}_x\text{O}_{y-1} \quad (5)
\]

\[
\text{C}_x\text{H}_y + (2x+y/2)\text{M}_x\text{O}_y \rightarrow x\text{CO}_2 + y/2\text{H}_2\text{O} + (2x+y/2)\text{M}_x\text{O}_{y-1} \quad (6)
\]

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

\[
\text{H}_2 + \text{CO}_2 \leftrightarrow \text{H}_2\text{O} + \text{CO} \quad (7)
\]

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

Among the CLCC successfully operated, the fuel reactor was designed as a bubbling fluidized bed (Berguerand and Lyngfelt, 2008a, 2008b and 2009; Cuadrat et al., 2011, 2012a and 2012b), spouted bed (Gu et al., 2011) or high velocity fluidized bed (Markström et al., 2012). In all these cases, gasification of coal was an intermediate step happening in the fuel reactor. During the experiments, several operational conditions were used. This fact...
makes difficult to directly compare the different results obtained because of the inherent
differences in the units and in the experimental conditions chosen by every research group.
But in general, optimized conditions were not reached. The carbon capture efficiency was
rather low in most of cases, losses of solid carbon were found and complete combustion of
gases was not reached in the fuel reactor, making necessary to take additional actions. The
carbon capture can be improved by implementing a carbon separation system, which
separates char from oxygen carrier particles and return them to the fuel reactor (Cao et al.,
2006). A final gas polishing step with pure oxygen is proposed for the complete oxidation
of gas exiting the fuel reactor. Often the “oxygen demand” parameter, $\Omega_T$, is used to
describe the fraction of oxygen required in the oxygen polishing step.

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

Some works have been presented in the literature for the modelling of specific aspects
involved in the fuel reactor of a CLCC system. In most cases, models are essentially based
on mass balances into the reactor considering the gasification reaction and oxidation of
volatile matter and gasification products by the oxygen carrier. Thus, Ströhle et al. (2009)
analyzed the effect of the solids inventory and the efficiency of a carbon separation system
on the carbon capture efficiency. Cuadrat et al. (2012c) predicted the carbon capture and
oxygen demand reached in the fuel reactor as a function of several operational parameters,
e.g. fuel reactor temperature, solids inventory, oxygen carrier to fuel ratio, steam to carbon
ratio or fluidizing gas composition. Also the presence of a carbon separation system was considered. They determined that the fuel reactor temperature and the efficiency of the carbon separation system are key parameters to improve the performance of the process. A deeper analysis on the behaviour of a carbon stripper as carbon separation system and its effect on the carbon capture of the CLCC process was done by Kramp et al. (2012). They conclude that a carbon stripper can be designed in order to increase the residence time of char particles in the fuel reactor, and thus to reach carbon capture efficiency values as high as 98-99%. Other options, as to increase the solids inventory in the fuel reactor or to re-design the fuel reactor as several stirred tank in series showed a lower effect on the carbon capture.

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

In the previous work (Abad et al., 2012), a mathematical model describing the processes happening in the fuel reactor of a CLCC process was presented. This model was mainly based on semi-empirical equations to describe the fluid dynamics of a high-velocity fluidized bed as fuel reactor (Pallarès and Johnsson, 2006). The fluid dynamic model has been previously used to predict the performance of coal combustion in a 12 MW_th CFB unit (Adánez et al., 2003). In addition, the model includes the reaction kinetics of the chemical processes happening in the fuel reactor of a CLCC system. Also the effect of a carbon separation system on the increase of the residence time of char particles in the fuel reactor is considered. The model predicts the carbon capture efficiency and the oxygen demand of the CLCC process depending on the operational conditions chosen for the fuel reactor. A
reference case for a 1 MW\textsubscript{th} CLCC system was evaluated. The main dimensions and operational conditions taken as reference were based on the 1 MW\textsubscript{th} unit built at TU Darmstadt (Abdulally et al., 2012; Ströhle et al., 2010). The developed model predicted values for the oxygen demand, $\Omega_T$, of 10.5\% and for the carbon capture efficiency, $\eta_{CC}$, of 59\% for the reference case. The mean residence time of solids in the fuel reactor was 100 s, corresponding to a solids inventory of 260 kg. Thus, it is necessary to optimize the system in order to improve the CLCC performance. The carbon capture efficiency could be increased by increasing the carbon separation efficiency, $\eta_{CCS}$, but an extreme value of $\eta_{CCS} = 99\%$ would be necessary to reach $\eta_{CC} = 95\%$.

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

2. Methodology

In a previous work (Abad et al., 2012), an empirical model describing the fuel reactor in the CLCC process was presented. The developed model is based on semi-empirical correlations, and considers the reactor fluid dynamics, the coal conversion and the reaction of the oxygen carrier with evolved gases from coal.
The model developed is focused on the fuel reactor behaviour, being a fluidised-bed reactor working at the high-velocity regime. The reactor is based on the design of a 1 MWth CLCC unit at TU Darmstadt (Abdulally et al., 2012; Ströhle et al., 2010). A diagram of this reactor is presented in Fig. 1. More details about the connection of fuel reactor, cyclones and carbon stripper can be found elsewhere (Abdulally et al., 2012). The geometrical and the main process parameters of the fuel reactor are shown in Tables 1 and 2.

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

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

\[
\Omega_T = \frac{M_O (F_{H_2} + F_{CO} + 4F_{CH_4})_{out}}{\Omega_{coal}}
\]

(8)

The oxygen demanded by coal is defined as:

\[
\Omega_{coal} = M_O \left( 2[C]_{coal} / M_C + 0.5[H]_{coal} / M_H - [O]_{coal} / M_O \right) F_{coal}
\]

(9)

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

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

\[
\eta_{CC} = \frac{M_c \left(F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4}\right)_{\text{out}} - (F_{\text{CO}_2})_{\text{in}}}{[C]_{\text{coal}} \cdot F_{\text{coal}}}
\]  

(11)

The carbon capture depends on the char conversion, \(X_{\text{char}}\), 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.

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

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

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

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

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

3. Simulation results of the 1 MW_th CLCC plant

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

Experimental results in a 10 kWth CLC unit showed the relevance of using high temperature in the fuel reactor in order to increase the carbon capture efficiency (Berguerand and Lyngfelt, 2009). So, the effect of temperature is first evaluated.

Fig. 2 shows the effect of the fuel reactor temperature on the evaluating parameters. It can be seen that the temperature has a large effect on the gasification efficiencies. Indeed, the carbon capture is as high as $\eta_{\text{CC}} = 89\%$ at 1200 °C. Although this temperature would be extremely high for the 1 MWth unit, this fact indicates the relevance of using high temperature to facilitate high carbon capture efficiency in a CLCC system. As char conversion is improved with the temperature, the char concentration in the bottom bed and in the solids stream at the fuel reactor exit decreases when the temperature is increased. At the bottom bed the char concentration in solids decreases from 1.3 wt.% to 0.4 wt.% when temperature increased from 900 to 1200 °C. The corresponding values of char concentration at the top, i.e. in the reactor exit stream, were 6.5 wt.% and 1.2 wt.%, respectively.

Nevertheless, the combustion efficiency and the oxygen demand are barely affected by the temperature. CH$_4$ concentration, as indicative of volatile matter, at the reactor exit decreases from 0.9 vol.% to 0.05 vol.% as the temperature increases from 900 to 1200 °C. However, the concentration of gasification products, i.e. H$_2$ and CO, increases from 4.3 and 1.3 vol.% to 6.0 and 2.4 vol.%, respectively. Remember that CH$_4$ is uniquely generated in the coal feeding point. This fact indicates that the combustion of volatile matter is increased with the temperature, but it is compensated by the increase of gasification products, which are continuously generated in the freeboard. Thus, the oxygen demand was approximately constant.
The predicted tendency of carbon capture and oxygen demand with temperature agrees to experimental results previously obtained (Cuadrat et al., 2011 and 2012a).

3.2. Solids inventory in the fuel reactor

Previous predictions obtained from simplified models showed the relevance of the solids inventory on the fuel reactor performance (Cuadrat et al., 2012c; Kramp et al., 2012; Ströhle et al., 2009). An increase of solids inventory in the reactor mainly gives an increase of the height of the bottom bed, and accordingly an increase of the pressure drop in the reactor. Its main effect on the gasification reaction is the increase of the main residence time of char particles in the reactor, thus affecting to the char conversion reached. The effect of the solids inventory in the bed on the fuel reactor performance is evaluated by changing the total pressure drop in the reactor. Fig. 3 shows the evaluating parameters as a function of the pressure drop and the corresponding solids inventory. When the solids hold–up increases from 190 to 2600 kg/MWth, the residence time of char particles in the reactor increased from 75 to 1000 s. As a consequence, the carbon capture efficiency increases because the amount of carbon gasified in the bottom bed increases. Besides, the concentration of char particles in the bed decreases from 1.8 wt.% to 0.23 wt.% as char particles are more converted and they are diluted in a higher amount of ilmenite particles. At the reactor exit the char concentration decreases from 4.0 wt.% to 0.7 wt.%. The char concentration in the solids should be taken into account for the design of the carbon separation system (Kramp et al., 2012). As the gasification products generated in the bottom bed are more efficiently converted to CO₂ and H₂O by the oxygen carrier than in the freeboard, the combustion efficiency increases and, consequently, the oxygen demand decreases.
The beneficial effect of increasing the solids inventory on the performance of the fuel reactor is relatively important until increase the pressure drop to 70 kPa, corresponding to a solids inventory of about 900 kg/MWth. The calculated value of carbon capture efficiency was $\eta_{CC} = 83\%$ and the oxygen demand $\Omega_T = 7.4\%$. Further increases on the solids inventory causes lower increases in the combustion efficiency, although the oxygen demand still shows a relevant decrease ($\Omega_T = 3.0\%$ at $\Delta P_{FR} = 200$ kPa or 2600 kg/MWth).

3.3. Oxygen carrier to fuel ratio, $\phi$

Fig. 4 shows the evaluating parameters as a function of the oxygen carrier to fuel ratio, $\phi$. This parameter was defined as the availability of oxygen in the flow of oxygen carrier divided by the oxygen required to fully convert the fuel to CO$_2$ and H$_2$O:

$$\phi = \frac{R_{OC}F_{OC}}{\Omega_{coal}}$$  \hspace{1cm} (13)

So, $\phi = 1$ corresponds to the stoichiometric flow of oxygen carrier needed for a full conversion of the fuel to CO$_2$ and H$_2$O. The $\phi$ ratio is a predefined parameter which is not affected by the conversion of coal in the process. The $\phi$ ratio was changed by varying the oxygen carrier circulation flow-rate between the air and fuel reactors, $F_{OC}$. For evaluation purposes, the variation of solids conversion, $\Delta X_{OC}$, also is shown in Fig. 4. $\Delta X_{OC}$ is affected by the $\phi$ ratio and also by the extension of fuel conversion to CO$_2$ and H$_2$O in the fuel reactor (Adánez et al., 2009); so, the $\Delta X_{OC}$ value decreases as the $\phi$ ratio increases or the char conversion and combustion efficiency decreases. Increasing the oxygen carrier to fuel ratio, an increase in the combustion efficiency and a decrease in the oxygen demand are observed. There is a difference in the
extent of the $\eta_{c,FR}$ and $\Omega_T$ variations for $\phi$ values below and above 1. For $\phi$ values below 1 a sharp decrease in the combustion efficiency and an increase in the oxygen demand is predicted. This fact is due to the lack of oxygen availability in the oxygen carrier flow from the air reactor to fully convert coal to CO$_2$ and H$_2$O. Also, the decrease of the average reactivity of ilmenite particles in the reactor as the particles are reduced in a higher amount is relevant in this case. The decrease in the average reactivity of the oxygen carrier particles is important as $\Delta X_{OC}$ increases above 0.5 (Abad et al., 2007), which is the case for $\phi < 1$, see Fig. 4. However, the increase in the average reactivity is not relevant when $\Delta X_{OC}$ is decreased below 0.5, thus the effect on the oxygen demand is less affected by increasing the ratio of oxygen carrier to fuel above 1.

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

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

3.4. Oxygen carrier reactivity.

Several Fe-based materials have been used as oxygen carriers for the CLC process with coal. Thus, ilmenite (Berguerand and Lyngfelt, 2008a; Cuadrat et al., 2011), iron ore (Wu et al., 2010), or a bauxite waste material (Mendiara et al., 2012) have been used in
continuously operated units. In all cases, unburnt compounds were found. Besides, different
carbon capture efficiencies were obtained. However, from these works it is difficult to
evaluate the effect of the reactivity itself of every oxygen carrier on the process
performance because results were obtained in different conditions and in different CLC
units, which includes or not a carbon separation system. Only data reported for ilmenite
(Cuadrat et al., 2011 and 2012b) and bauxite waste (Mendiara et al., 2012a) can be
compared, showing that the use of a higher reactive material -i.e. the bauxite waste
compared to ilmenite (Mendiara et al., 2012b)- gave an increase of the combustion
efficiency, but barely the carbon capture was changed. With the developed model, the
effect of the oxygen carrier reactivity itself on the CLC performance can be evaluated. The
oxygen transport capacity and solids circulation flow rate was maintained at the same
values.

Fig. 5 shows the evaluating parameters as a function of the reactivity of the oxygen carrier.
This reactivity is expressed as a ratio with respect to the reactivity of the ilmenite, i.e. \((-r_{OC})/(-r_{ilm})\). As reference, the oxygen transference rate of a highly reactive iron ore in
hydrogen was about 1.5 times that showed by activated ilmenite (Mendiara et al., 2012b);
on contrary, the oxygen transference rate of activated ilmenite was about 5 times higher
than that showed by CaSO₄ (Shen et al., 2008).
The increase predicted in the combustion efficiency with the oxygen carrier reactivity is
very relevant, as well as the decrease in the oxygen demand. It was observed during the
simulation that the highest effect of oxygen carrier reactivity is to increase the combustion
of gases in the splash zone, because there is a higher solids concentration than in the
transport phase and a better gas-solid contact than in the bottom bed.
On the contrary, the carbon capture is less affected by the oxygen carrier reactivity because of its low effect on char gasification rate. Of course, the concentration of gasification inhibitors, i.e. H₂ and CO, decreases as the oxygen carrier is more reactive, and therefore the gasification rate increases to some extension. However, in any case the H₂ and CO concentration is low, and a further decrease in the concentration of these gases would have a marginal increase of the gasification rate.

3.5. Coal reactivity

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

As it can be seen in Fig. 6, the \((-r_{g,\text{coal}})/(-r_{g,\text{Cerr}})\) ratio was varied from 0.1 to 10. The lower limit could correspond to the case of using anthracite as fuel, and the upper limit corresponds to the use of a highly reactive lignite. The carbon capture increased with increasing the coal reactivity as a consequence of a faster conversion of char in the fuel reactor. However, as gasification is improved with increasing coal reactivity, the amount of
reacting gases in the fuel reactor increased, which produced a decrease in the combustion
efficiency in the fuel reactor and an increase in the oxygen demand. So, actions should be
taken in order to improve the combustion efficiency in the fuel reactor when very reactive
coals would be used.

3.6. Coal particle size

The effect of the coal particle size on the carbon capture efficiency is also analyzed. The
model predicts that a higher fraction of char is in the bottom bed as the coal particle size
increases, lowering the flow of char to the transport phase. This fact has relevant
consequences on the CLC performance. Fig. 7 shows the effect of the coal particle size on
the evaluating parameters. The char conversion, and correspondingly the carbon capture
efficiency, increases with the coal particle size. Basically, this fact is due to a decrease in
the char concentration in the reactor exit, which decreases from 4.9 wt.% to 2.2 wt.% when
the coal particle size increases from 50 to 500 μm. On the contrary, the char concentration
in the bottom bed and in the splash zone increases from 0.7 wt.% to 2.5 wt.%. Thus, a
lower flow of char goes to the carbon separation system and thereafter to the air reactor,
increasing the carbon capture. Also a higher fraction of char is gasified in the bottom bed
and in the splash phase. Of all carbon initially in char, only 11% is converted in the bottom
bed when coal particle size is 50 μm, increasing to 30% when the coal size increases to 500
μm. So, a higher flow of gasification products are generated in the bottom bed as well as in
the splash phase. The model predicts that the CH₄ flow -obtained solely from the volatile
matter- at the reactor exit was barely changed by the coal particle size; but CO and H₂
flows increases as more char is gasified when the coal size was increased. As a result, the combustion efficiency in the fuel reactor decreases and the oxygen demand increases. These results do not agree to experimental results showed by Cuadrat et al. (2011). These authors showed that a decrease in the particle size produced a decrease in the combustion efficiency of the fuel reactor. In this case, the fuel reactor was a bubbling fluidized bed. Small coal particles were more easily elutriated, increasing the relative relevance of the char gasification in the freeboard where gasification products had not the opportunity to react with the oxygen carrier. However, this is not the case for a high-velocity fluidized bed reactor, where gasification products can be oxidized by the oxygen carrier particles present in the dilute region. Schöny et al. (2011) modelled a circulating fluidized bed fuel reactor, and they predicted an increase in the combustion efficiency with increasing the coal particle size. They explained this result because a higher share of the char gasification products are released in the bottom bed where the highest oxygen carrier concentration is. However, they did not consider that the amount of char gasified in the fuel reactor increases with the coal particle size, as it was predicted in the present work. The higher amount of char gasified increases the load of gases to be burnt in the fuel reactor, and therefore the combustion efficiency predicted by the model falls with the coal particle size. Although the increase in the coal particle size is beneficial in terms of the carbon capture, it is necessary to point out that this result is obtained maintaining the same value for the carbon separation system ($\eta_{CCS} = 90\%$). However, a higher coal particle size may cause a drop in the carbon separation efficiency (Kramp et al., 2012), and therefore, it should be analyzed in more detail how the coal particle size affect jointly to the char distribution in the fuel reactor and to the performance of the carbon separation system.
3.7. Relevance of the WGS reaction in the gas phase

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

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

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

$$\chi = \frac{\Delta \nu/\nu}{\Delta \pi/\pi}$$

The carbon capture efficiency and the oxygen demand are selected as "target variables", whereas the "investigated model parameters" are the six parameters analyzed previously in this work, besides the efficiency of the carbon separation system analyzed previously in Abad et al. (2012). Thus, the relative relevance of the "investigated model parameters" on the "target variables" is analyzed. Fig. 9 shows the relative linear sensitivity coefficient, $\chi$, calculated for every value of the parameter $\pi$. To optimize the CLCC system high positive value of $\chi$ is desired for the carbon capture, but negative value is desired for the oxygen demand.

From the sensitivity analysis, it can be said that the most important parameters to maximize the carbon capture are the fuel reactor temperature and the carbon separation efficiency. This result emphasizes the relevance in the use of a highly efficient carbon separation system to reach high carbon capture values in a CLCC system. The solids inventory and the reactivity of the coal have lower relevance. Although sensitivity analysis on the coal reactivity is rather low, it is worth to note that the reactivity of coal can be increased one order of magnitude if a highly reactive coal is used, e.g. lignite. In this case, a high increase
in the carbon capture efficiency is expected. Finally, very low relevance has the variation of
the oxygen carrier reactivity or coal particle size on the carbon capture, whereas the solids
circulation flow rate shows a negative influence.

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

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

In the reference case, a carbon capture efficiency of 59% was predicted, whereas the
oxygen demand was 10%. The efficiency of the carbon separation system was assumed to
be 90%. In the industrial application of a CLCC system, higher carbon capture and lower
oxygen demand values are desirables. From above considerations, a higher value for the
efficiency of the carbon separation system is highly recommended. Kramp et al. (2012)
simulated the carbon stripper by using a usual value for technical separation sharpness to
segregate char and oxygen carrier particles in a bubbling fluidized bed. It was calculated a
value for the carbon separation efficiency in the carbon stripper of ~98%. With this value,
they reported carbon capture efficiency values of 90% and 95% for bituminous coal and
lignite, respectively. Although low temperatures could be compensated by a highly efficient
carbon separation system, temperatures higher than 1000 °C are preferred. The solids
inventory is less relevant, especially when it was increased above 1000 kg/MW\text{th}. This fact
indicates that it is not worthy to increase the solids inventory too much above this value.

A new simulation was performed with a technical feasible operational temperature of 1100
°C, a carbon separation efficiency of 98%, and a solids inventory of 1000 kg/MW\text{th}. The
carbon capture efficiency predicted was 98.6 %, whereas the oxygen demand was 6.8 %.
The height of the bottom bed at these conditions was 4 m and the total pressure drop in the
fuel reactor was $\Delta P_{FR} = 80$ kPa, which seems unrealistic for the fuel reactor dimensions.

So, a new design of the bottom part of the fuel reactor should be considered to work in
these conditions, with a higher section in the bottom bed. If a maximum height of 1 m for
the bottom bed is considered, the section of the bottom bed should increase from 0.12
m$^2$/MW\text{th} to 0.5 m$^2$/MW\text{th} to maintain the same solids inventory of 1000 kg/MW\text{th}. The
pressure drop at these conditions was $\Delta P_{FR} = 25$ kPa. The corresponding mean residence
time of solids in the fuel reactor is 390 s, being the residence time of char particles higher
by the presence of the carbon separation system.

Another option to improve the performance of the CLCC system is to maintain the reactor
design, but decreasing the input thermal power. For comparison purposes, the pressure drop
was maintained about 27 kPa, corresponding to a solids inventory of 350 kg in the reactor
and a deep of the bottom bed about 1 m. The efficiency of the carbon separation system
was kept to 90%. The solids circulation flow rate was decreased as the coal feeding rate
was decreased to maintain constant the oxygen carrier to fuel ratio $\phi = 1.2$. Fig. 10 shows
the evaluating parameters obtained when the input thermal power was decreased from 1
MW\text{th} to 0.1 MW\text{th}. Data are plotted as a function of the solids inventory per MW\text{th}. The
carbon capture was improved with increasing the solids inventory per MW\textsubscript{th} as result of a
decrease in the input thermal power. In this case, the residence time of particles in the
reactor was increased from 145 to 1450 s, and therefore the char conversion was improved.
The carbon capture was 95% with 2000 kg/MW\textsubscript{th}, and reach the value of 97% with 3000
kg/MW\textsubscript{th}. However, the oxygen demand was barely affected by the solids inventory. In
these simulations, the time of contact between gas and solids was not significantly varied
when the input thermal power was decreasing. This fact indicates that other factors, e.g. the
mass transfer diffusion from gas to solids or the lower concentration of volatile matter as
the thermal power decreased, are also of great relevance in oxidation of gaseous products.
To reduce the oxygen demand additional actions should be taken, which could include a re-
design of the fuel reactor. One option could be the use of internals in the freeboard, which
increases the presence of solids in this zone (Guío-Pérez et al., 2012). Other option could be
the use of a fluidized bed with oxygen carrier down stream to fully oxidize the gas from the
fuel reactor (Thon et al., 2012). This last option seems to be very effective due to a
relatively small solids inventory in the down stream reactor (Cuadrat et al., 2012c).

4. Conclusions
A model describing the behaviour of the fuel reactor of a Chemical–Looping Coal
Combustion (CLCC) process has been used to evaluate the effect of several operating
variables on the global performance of the process. From these results, the carbon capture
efficiency and the oxygen demand of the flue gases were determined.
In the reference case, assuming an efficiency of the carbon separation system of 90%, a
carbon capture efficiency of 59% and an oxygen demand of 10.5 % were predicted. The
oxygen demand decreased to 7.6%, whereas the carbon capture slightly decreased to 57.5% when the water-gas shift equilibrium was considered. After a sensitivity analysis the following conclusions were obtained:

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

- The temperature showed an important effect on the conversion of coal in the fuel reactor. Temperatures higher than 1000 ºC are desirables in the fuel reactor to improve the char conversion, and thereafter the carbon capture. The temperature had a lower effect on the oxygen demand.

- The carbon capture increased significantly when the solids inventory in the fuel reactor was increased up to ~1000 kg/MWth. Further increases in the solids inventory had lower effect on the carbon capture. The oxygen demand decreased with the solids inventory, but in a lower extent.

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

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

Finally, it was determined that a carbon capture efficiency of 98.6% and an oxygen demand of 6.8% could be reached if the following conditions would be selected: a temperature of
1100 °C in the fuel reactor, a solids inventory of 1000 kg/MWth and an efficiency of the carbon separation system of 98%.

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5. Nomenclature

[C]_{coal} = mass fraction of carbon in coal

[C]_{fixed} = mass fraction of carbon fixed in coal

d_{p,coal} = average diameter of coal particles, m

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

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

F_i = molar flow of gas i, mol/s

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

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

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

H_r = height of the reactor, m

M_i = atomic mass of element i, kg/mol

P = pressure at the reactor outlet, Pa

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

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

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

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

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

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

X_{char} = conversion of carbon in char

\bar{X}_{OC,in} = average conversion of the oxygen carrier at the fuel reactor inlet
**Greek symbols:**

1. $\chi$ = relative linear sensitivity coefficient, defined by Eq. (X)
2. $\Delta P_{FR}$ = pressure drop in the reactor, Pa
3. $\Delta X_{OC}$ = variation of the conversion of oxygen carrier in the reactor
4. $\phi$ = ratio of oxygen carrier to fuel
5. $\eta_{c,FR}$ = combustion efficiency in the fuel reactor
6. $\eta_{CC}$ = carbon capture efficiency
7. $\eta_{CSS}$ = efficiency of the carbon separation system
8. $\nu$ = target variable
9. $\pi$ = investigated model parameter
10. $\Omega_{coal}$ = oxygen demand of coal, kg of oxygen per kg of coal
11. $\Omega_{T}$ = oxygen demand of flue gases from the fuel reactor
6. References


