



Evaluation of the use of different coals in Chemical Looping Combustion using a bauxite waste as oxygen carrier

T. Mendiara*, F. García-Labiano, P. Gayán, A. Abad, L.F. de Diego, J. Adánez

Department of Energy and Environment, Instituto de Carboquímica (CSIC), Miguel Luesma Castán 4, 50018 Zaragoza, Spain

HIGHLIGHTS

- ▶ A bauxite waste (BW) was identified as a promising oxygen carrier for *i*G-CLC of coal.
- ▶ BW showed high combustion efficiencies of gasification products using different coals.
- ▶ The use of recycled CO₂ as gasifying agent should be limited except for lignite.
- ▶ In TGA, BW-char reaction extent was larger for chars from low rank coals.
- ▶ In fluidized bed, no significant evidence of BW-char reaction was observed.

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ABSTRACT

The interest in the use of solid fuels such as coal in Chemical Looping Combustion (CLC) is growing because of the benefits of the direct use of coal in this technology on the reduction of the costs linked to carbon dioxide capture. In CLC, the oxygen needed for the combustion is supplied by a solid oxygen carrier therefore avoiding the direct contact between fuel and air. Focusing on the use of solid fuels in the *in situ* Gasification Chemical Looping Combustion (*i*G-CLC), the oxygen carrier is mixed with the coal in the fuel reactor, where gasification of the coal and reaction of the gasification products with the oxygen carrier particles take place. In this process, the possible loss of oxygen carrier together with the ashes makes it interesting to find inexpensive materials to be used as carriers, such as natural minerals or industrial residues. In this work, an Fe-based bauxite waste is used as oxygen carrier in the combustion of different types of coal. Experiments were performed in a TGA and a batch fluidized bed (FB) using both coal and char from the corresponding coal. The influence of temperature as well as the gasifying agent composition on the performance of coal conversion in an *i*G-CLC process was evaluated. Tests in a thermogravimetric analyzer (TGA) revealed direct char combustion by oxygen in the bauxite waste material, but no evidences of such direct combustion were found in the experiments in the batch fluidized bed. In this case, gasification of char by H₂O or CO₂ was found as a necessary step in char conversion. Using steam as gasifying agent, higher char gasification rates were observed than using CO₂ and in all conditions lignite presented the highest char gasification rate. At 980 °C, the lignite char gasification rate in CO₂ doubled the value obtained with anthracite using steam, indicating that recirculated CO₂ can be fed to the fuel reactor of a CLC system if lignite is used as fuel. For the rest of the fuels, it was possible to use a mixture of H₂O and CO₂ as gasifying agent without decreasing the feasibility of the *i*G-CLC process. The bauxite waste was able to burn the gaseous products generated during the gasification of the different types of coal with high combustion efficiencies.

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1. Introduction

The increase in the atmospheric carbon dioxide concentration leads to an increased global temperature [1]. According to recent estimations, fossil fuels will continue contributing with an important share to fulfill the energy generation requirements, thus

increasing the anthropogenic CO₂ emitted to the atmosphere [2]. The use of coal is expected to remain in an important position in the energy mix in the foreseeable future as it is more abundant and less expensive than natural gas [3].

One of the possibilities to reduce CO₂ from fossil fuel combustion that is receiving increasing interest is Carbon Capture and Storage (CCS) which focuses on storing CO₂ at site, such as depleted oil/gas fields or deep saline aquifers, thus preventing that CO₂ from reaching the atmosphere. Among the CO₂ capture alternatives

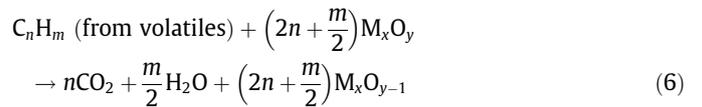
* Corresponding author. Tel.: +34 976 733 977; fax: +34 976 733 318.

E-mail address: tmendiara@icb.csic.es (T. Mendiara).

Nomenclature

C_c	carbon content of the char (ash free)	O/C	oxygen to carbon molar ratio
ε	decrease percentage of the average char conversion rates for steam and CO ₂ mixtures	$\Omega_g(t)$	oxygen demand of the gas products at time t (%)
$F_{CO_2,in}$	CO ₂ flow introduced in the fuel reactor (mol/s)	$\Omega_{g,av}(t)$	averaged oxygen demand of the gas products during the reducing period (%)
$F_{H_2O,in}$	H ₂ O flow introduced in the fuel reactor (mol/s)	R_{OC}	oxygen transport capacity
$F_{H_2O,out}$	H ₂ O flow in the product gas (mol/s)	$r_c(t)$	rate of fuel conversion (mol/s)
F_i	molar gas flow of each component i (CO ₂ , CO, H ₂ or CH ₄) in the product gas (mol/s)	$r_{c,inst}$	instantaneous rate of fuel conversion (s ⁻¹)
F_{N_2}	downstream introduced N ₂ flow (mol/s)	$r_{O(t)}$	rate of oxygen transferred from the bauxite waste to the fuel gas (mol/s)
$F_{O,in}$	oxygen flow introduced (mol O/s)	t	time (s)
$F_{O,out}$	oxygen flow at the reactor outlet (mol O/s)	t_{95}	time to convert 95% char (s)
F_{out}	dry outlet flow after nitrogen dilution (mol/s)	t_x	residence time to reach a conversion (s)
m	mass weight variation in the TGA experiments (Kg)	X_{char}	char conversion
M_O	oxygen molar weight (kg/mol)	X_{coal}	coal conversion
M_xO_y	oxidized form of the oxygen carrier	X_{red}	bauxite waste conversion for the reduction reaction being the molar fraction of the component i (CO ₂ , CO, H ₂ or CH ₄) in the product gas
M_xO_{y-1}	reduced form of the oxygen carrier	y_i	
m_o	mass of the oxidized form of the oxygen carrier (kg)	η_c	combustion efficiency of the gasification products
m_r	mass of the reduced form of the oxygen carrier (kg)		
m_{OC}	mass of the oxygen carrier (kg)		
$N_{O,bw}$	moles of oxygen in the bauxite waste active for CLC process (mol)		
$N_{C,char}$	moles of carbon from char fed into the reactor (mol)		
$N_{C,coal}$	moles of carbon from coal fed into the reactor (mol)		
$O_{2,demand,coal}$	oxygen needed for complete combustion of the coal fed		
		Acronyms	
		OC	oxygen carrier
		TGA	thermogravimetric analyzer
		A	anthracite
		HVB	bituminous with high volatile content
		MVB	bituminous with low volatile content
		L	lignite

currently in development, the Chemical Looping Combustion (CLC) technology has emerged as a promising option to capture CO₂ at low cost [4]. The main idea behind CLC is to avoid CO₂ dilution in the exhaust gases by providing the oxygen needed for combustion by means of an oxygen carrier, normally a metal oxide, so that a concentrated CO₂ stream is obtained. The preferred configuration for CLC is two interconnected fluidized bed reactors, fuel reactor and air reactor with the oxygen carrier circulating between them [5,6]. Different approaches for solid fuel combustion have been developed until now [6]. This work focuses on the *in situ* Gasification Chemical Looping Combustion (iG-CLC) technology for solid fuels. This technology was recently demonstrated during continuous operation in CLC units up to 10 kW_{th} [7–9]. The scheme of the process is shown in Fig. 1. In the iG-CLC process, the coal is introduced directly to the fuel reactor and mixed with the oxygen carrier, where it is devolatilized to produce volatile matter and solid char (reaction (1)). Char, which is mainly composed by carbon and ash, is gasified using steam or CO₂ continuously fed to the fuel reactor, following reactions (2) and (3). Several previous studies have pointed to char gasification as the rate limiting step [10–13]. After gasification, the gaseous products react with the oxygen carrier present in the fuel reactor to produce water and CO₂. These processes are summarized in reactions (4)–(6). Once water has been condensed, a highly-pure CO₂ stream is obtained ready for capture. The reduced oxygen carrier is then transferred to the air reactor where it is regenerated (reaction (7)) and sent back to the fuel reactor to start a new redox cycle.



In experiments performed in a continuous iG-CLC unit, unburnt gases (CH₄, CO and H₂) in the fuel reactor exit were measured using a bituminous coal as fuel and ilmenite as oxygen carrier [8]. Nevertheless, this study showed that these gases were volatile matter that had not been fully oxidized by ilmenite. Different alternatives have been proposed to deal with the unburnt gases, e.g. an oxygen polishing step downstream to complete gas combustion to CO₂ and H₂O, separation and recirculation of unburnt compounds or fuel reactor in series where exhaust gases were fed. It is expected that the use of little fraction of the total solids in the system in this second reactor had a high impact on the combustion efficiency increase [14].

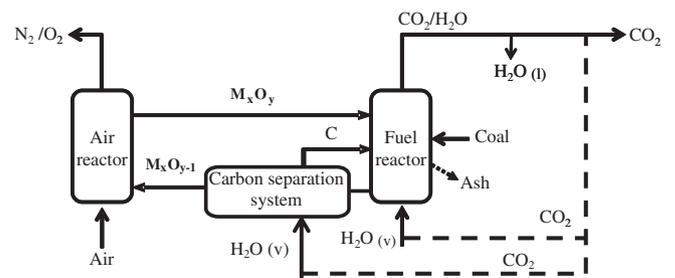


Fig. 1. *In situ* Gasification Chemical Looping Combustion process. (---) Optional streams to replace H₂O (v) by CO₂ in the fluidizing gas of fuel reactor and/or the carbon separation system.

Regarding the reactions taking place in the fuel reactor, several TGA studies have reported direct solid–solid reaction between coal/char and oxygen carriers based on Cu, Ni, Mn, Fe and Co in inert atmospheres [15–20]. In the case of the Cu-based carriers, Siriwardane et al. [18] determined that there is a fuel-induced oxygen release from the metal oxide if there is sufficient contact between CuO and carbon. The solid–solid contact may be achieved by having small particle sizes and can be enhanced by surface melting. The type of solid fuel in the vicinity of the oxygen carrier particles also determined the reaction temperature and the combustion rate. However, in studies carried out in fluidized bed, the solid–solid reaction was not found to be of significance [12,13,21,22].

If the residence time for the char particles in the fuel reactor is not enough, some unconverted char may be transferred to the air reactor and burned there decreasing the efficiency of carbon capture. As it is shown in Fig. 1, the implementation of a carbon separation system after the fuel reactor could reduce this inefficiency [23]. In the carbon separation system, char particles are separated from the reduced oxygen carrier particles and conducted back to the fuel reactor. A theoretical approach of the *iG*-CLC system showed the relevance of the carbon separation system in order to achieve high carbon capture efficiencies [14].

Another aspect to take into account is coal ashes. In order to avoid accumulation in the reactors it will be necessary to drain the ash from the system. Nevertheless, some oxygen carrier particles can be swept away by the ashes. Therefore, as oxygen carrier losses are expected, low cost materials or materials which could be easily separated from the ashes are preferred for CLC with coal. Natural minerals and industrial wastes based on iron have been recently tested as oxygen carriers with different coals showing good performance [7,24–32]. Among them, ilmenite has been intensively tested. Ilmenite is a common mineral found in metamorphic and igneous rocks, mainly composed of FeTiO₃. Ilmenite has shown high reactivity to the main gases present in coal gasification, i.e. H₂ and CO. However, as it is the case of some other Fe-based oxygen carriers, the reactivity with methane was lower [24,34]. Besides, good mechanical properties were observed: low fragmentation/attrition and absence of agglomeration [7,8]. Ilmenite has shown good performance in CLC with coal. High CO₂ capture and combustion efficiencies were reached in a CLC unit [8,33,36]. Cuadrat et al. [36] also analyzed the effect of the coal rank on the performance of an *iG*-CLC system in a continuous unit. They found that the carbon capture in the fuel reactor was higher for the solid fuels with faster char gasification rates. The fuels with low volatile content presented high combustion efficiency. The combustion efficiency of the volatiles depended on the composition of the released volatiles of each type of fuel.

The reactivity of some Fe-based oxygen carriers to different types of coal and/or cokes has been evaluated in previous studies in a batch-fluidized bed reactor [24,28,35]. Leion et al. [24,28] used petroleum coke, charcoal, bituminous and sub-bituminous coals with ilmenite, iron ore and oxide scales with a high content in Fe₂O₃. More recently, Linderholm et al. [35] performed batch experiments using ilmenite and five different fuels (three devolatilized bituminous coals and two types of coke) in a 10 kW_{th} pilot. They found that the instantaneous rates of char conversion to gas increased with temperature. They observed in all the cases a slow gasification reaction compared to the reaction of CO and H₂ with the metal oxide. The gasification rate was similar for the bituminous coals analyzed and higher than the rate observed for pet coke. Lignite showed the highest gasification rate [28].

Regarding the use of different gasifying agents, it would be expected that sub-bituminous and lignite coal chars present dry gasification rates as high as for gasification in H₂O [37]. Therefore the use of these type of coals could be advantageous because recirculated CO₂ could be used as fluidizing agent. The gasification rate

observed for dry gasification of a lignite coal [38] was similar to the steam gasification rate of a bituminous Colombian coal [39] using in both cases Fe-based oxygen carriers. However, the Colombian coal char conversion rate was around five times slower during the dry gasification compared to steam gasification. Analogous results for dry and steam gasification were observed in batch fluidized bed experiments using a bituminous South African coal [13,21]. The decrease in the gasification rate when CO₂ was used as gasifying agent produced a decrease in the carbon capture efficiency [33]. In the case of using lignite, this decrease can be acceptable for an *iG*-CLC system. If the gasification rate is not high enough, the char concentration in the fuel reactor would increase. The carbon separation system should then also be optimized to separate high amount of char particles [13].

The present work is focused on the use as oxygen carrier of an Fe-based industrial residue generated in the production of alumina via the Bayer process. Previous studies in our research group have shown the good performance of this material both in gaseous and solid fuel combustion [21,40,41]. The bauxite waste was used in the combustion of syngas with good results [40]. The possibility of using this material in the combustion of coal was evaluated regarding two aspects, namely, the performance of the material in the combustion of volatiles and coal gasification products [41] and the gasification of the char in the oxygen carrier bed [21]. In both cases, the bauxite waste resulted more reactive than ilmenite, one of the more relevant oxygen carriers used for *iG*-CLC. The rate indices obtained in the TGA for activated bauxite waste in the reaction with H₂, CO and CH₄ were around 2–3 times higher than those obtained with activated ilmenite [41]. In experiments using char as fuel in a fluidized bed reactor, the bauxite waste displayed higher reactivity to the gasification products than ilmenite in the same conditions. Thus, higher combustion efficiencies were reached using steam or CO₂ as gasifying agents. The higher reactivity was expected to decrease the solids inventory when compared to ilmenite [21].

In the present work, the bauxite waste is further tested in batch fluidized bed experiments using different types of coal. In this work the char conversion rate and combustion efficiencies using different coals will be evaluated and compared at different temperatures in the range 900–980 °C using different fluidizing agents (H₂O, CO₂ and mixtures of both). The possible solid–solid interaction using the bauxite waste as oxygen carrier will be also analyzed.

2. Experimental

2.1. Materials used

The solid material used in this work was supplied by Alcoa Europe-Alúmina Española S.A. The material corresponds to the sand fraction (particles over 150 μm) separated from the suspension where the raw bauxite has been dissolved to extract the aluminum. The rest of the suspension (red mud) is kept in sedimentation tanks. This potential oxygen carrier will be named bauxite waste

Table 1
Characterization of calcined bauxite waste sample.

Fe ₂ O ₃ (wt.%)	71 ^a
XRD main phases	Fe ₂ O ₃ , β-Al ₂ O ₃
Crushing strength (N)	2.8
Oxygen transport capacity, R _{OC} (%)	2.4
Porosity (%)	3.7
Skeletal density (kg/m ³)	4500
Specific surface area, BET (m ² /g)	0.1

^a Determined by TGA.

hereafter. The bauxite waste sample was dried at room temperature for 72 h and then sieved to the desired size (150–300 μm). Prior to its use as oxygen carrier, the dried sample was calcined at 1200 °C during 18 h to ensure complete oxidation of the sample and to increase the resistance to attrition.

The main chemical and physical properties of the calcined material are shown in Table 1. Details about the oxygen carrier characterization have been presented before [21,41]. The oxygen transport capacity, R_{OC} , is defined as the mass fraction that can be used in the oxygen transfer.

$$R_{\text{OC}} = \frac{m_o - m_r}{m_o} \quad (8)$$

where m_o and m_r are the mass of fully oxidized and reduced bauxite waste sample, respectively.

The value of the oxygen transport capacity, R_{OC} , depends on the final oxidation state after reduction. Although iron compounds have different oxidation states (Fe_2O_3 – Fe_3O_4 – FeO – Fe), only the transformation from hematite (Fe_2O_3) to magnetite (Fe_3O_4) may be applicable for industrial CLC systems. Further reduction to FeO would decrease the CO_2 purity obtained in the fuel reactor due to the increase of CO and H_2 concentrations in the equilibrium [42]. Besides, it has been demonstrated that the reduction to FeO may lead to agglomeration in the subsequent oxidation process with air [43,44]. Therefore, the value of the oxygen transport capacity in this case, R_{OC} , corresponds to the transformation to Fe_3O_4 .

In previous works from our research group using this bauxite waste, an increase in the reactivity of the material with the number of redox cycles was observed. This increase was identified both working with gaseous fuels (CO , H_2 and CH_4) [41] and using char from a bituminous coal as fuel [21]. It was determined that the activation of the sample was an important fact to take into account when operating with this solid residue. Therefore, the bauxite waste used in this work was activated prior to the performing of the experiments presented in the following sections. The activation process took place in the fluidized bed detailed next and was described elsewhere [21].

A Spanish anthracite from “El Bierzo” (A), two bituminous coals, from Colombia (HVB) and South Africa (MVB), with high and medium volatile content, respectively, and a Spanish lignite (L) were used as fuel in the experiments. The bituminous Colombian coal showed strong swelling tendency which can lead to agglomeration of the fluidized bed. The coal was subjected to a thermal pre-treatment for pre-oxidation to avoid its swelling properties. Coal was heated at 180 °C in air atmosphere for 28 h. It was placed in trays with a maximum coal layer height of 3 mm.

For the analysis of the gasification rate, char from these coals was used. Char was produced when around 300 g of coal particles sized 200–300 μm were devolatilized in a fluidized bed reactor using N_2 as fluidizing agent. The bed operated in the bubbling bed regime through the whole experiment. Temperature was increased from room temperature to 900 °C using a heating rate of 20 K/min. This value is low compared to that in a real CLC plant, but it is the maximum that can be achieved in this setup. The characteristics of the char obtained may differ from those of the char in a fuel reactor, but this fact does not affect to the conclusions obtained regarding the influence of different variables, such as temperature and gasifying mixture composition. Once the temperature was reached, the heat supply was stopped and the sample was cooled down in nitrogen. Table 2 shows the proximate and ultimate analyses of both the coals and the corresponding chars obtained. The results corresponding to the experiments performed using char from South African coal were already presented in a previous paper [21]

but are included together with results obtained in the present work in order to compare.

2.2. Thermogravimetric apparatus (TGA)

The interaction of the bauxite waste sample with char was tested in a thermogravimetric apparatus (TGA) CI Electronics type operating at atmospheric pressure. A detailed description of this apparatus has been presented before [45]. The samples were placed in a quartz crucible. Preliminary tests showed that the reaction rate was not affected by the amount of sample used or the flow rate, neglecting external and interparticle diffusion control. Around 90 mg of well-mixed bauxite waste and char particles were loaded and introduced in the reacting chamber. The bauxite waste/char mass ratio was selected so that the stoichiometric oxygen was supplied. This corresponds to mass ratios among 75–125, depending on the type of char used.

Tests with the four different chars used in this work were performed. Nitrogen (25 $\text{L}_\text{N}/\text{h}$) was fed while the sample was heated from room temperature to 950 °C at 20 °C/min. Once this temperature was reached, the flow of nitrogen was maintained during 30 min and then the gaseous atmosphere was switched to water vapor (50% H_2O + 50% N_2) so that the remaining char could be gasified. The gasification was considered completed when the sample weight was stable. Nitrogen was introduced as a purge during 2 min before the oxidation period began. During the oxidation period, the particles were regenerated in air at the same temperature. To analyze the influence of the gases generated during char conversion on the char conversion rate some experiments were also performed. After ensuring the inert conditions, the nitrogen flow was stopped and no flow during the heating and the first 30 min of the experiment was provided. Then, the experiment continued as explained above: the remaining char was gasified using 50% steam in nitrogen and later the carrier was regenerated using air.

The weight variations registered during the different reaction steps described before can be attributed to several processes taking place simultaneously. When inert nitrogen atmosphere is surrounding the sample, the weight variation (Δw_1) can be attributed to the solid–solid reaction between the bauxite waste and the char and the subsequent reaction of the gaseous products formed with the oxygen carrier. During the step in which 50% steam is introduced, the weight variation (Δw_2) corresponds to the gasification of the char left in the solid mixture and the oxidation by the bauxite waste of the CO and H_2 produced. Finally, the weight gained by the sample during the oxidation step (Δw_3) indicates the total amount of oxygen transferred by the bauxite waste through all the processes mentioned. The amount of char reacted (ash free) can be estimated as:

$$(\Delta w_{\text{char}}) = |\Delta w_1| + |\Delta w_2| - |\Delta w_3| \quad (9)$$

The carbon content (C_c) for each of the chars tested (ash free) can be calculated from the char composition in Table 2 and therefore, the amount of carbon reacted can be estimated. Using this value and (Δw_3), the O/C mass ratio was calculated.

$$\frac{\text{O}}{\text{C}} = \frac{\Delta w_3}{\Delta w_{\text{char}} \cdot C_c} \quad (10)$$

The value of the O/C mass ratio obtained is used to estimate the proportion in which carbon is consumed by the oxygen carrier. For example, if the proportion were one mol of oxygen to one mol of carbon, the O/C mass ratio would be close to 1.3. Using the O/C mass ratio it can be estimated how much of the weight loss registered as (Δw_1) and (Δw_2) corresponds to the char reacted and how much to the oxygen consumed in each step, i.e. the step using N_2 and in the gasification step.

Table 2
Proximate and ultimate analysis of the different coals and chars used.

Proximate analysis	Anthracite (Spain)		Bituminous				Lignite (Spain)	
	Coal	Char	High vol. (HVB)		Medium vol. (MVB)		Coal	Char
Moisture	1.0	0.7	2.3	6.4	4.2	0.9	12.5	0.5
Ash	31.5	31.6	8.8	10.4	14.3	20.0	25.2	43.5
Volatile matter	7.5	0.9	33.0	3.0	25.5	1.1	28.6	1.2
Fixed carbon	59.9	66.7	55.9	80.1	56.0	78.0	33.6	54.8
<i>Ultimate analysis</i>								
Carbon	60.7	65.5	65.8	79.8	69.3	76.5	45.4	55.3
Hydrogen	2.2	0.6	3.6	0.7	4.0	0.2	3.9	0.4
Nitrogen	0.9	0.8	1.6	1.3	2.0	1.6	0.6	0.5
Sulfur	1.3	1.2	0.6	0.6	1.0	0.8	5.2	5.0
Oxygen	2.4	0	17.3	0.8	5.2	0	7.2	0

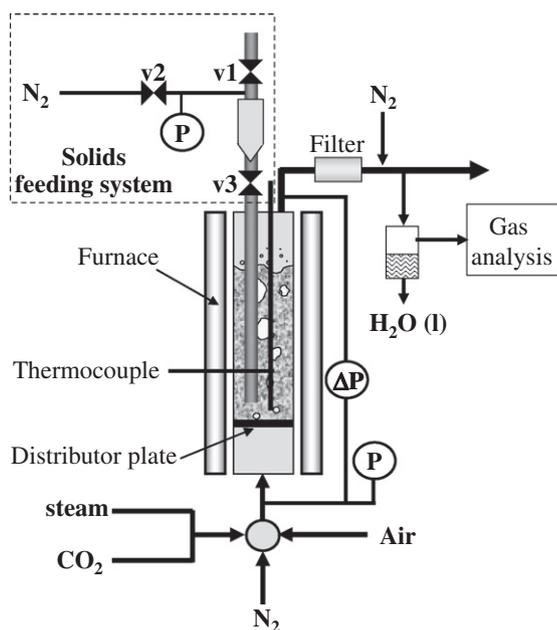


Fig. 2. Experimental setup: batch fluidized bed reactor.

2.3. Batch fluidized bed (FB)

Fig. 2 presents the scheme of the experimental setup which has also been used in previous works of our research group [21]. The bauxite waste sample was placed inside the fluidized bed reactor (FB). The FB reactor was 0.055 m I.D. and 0.7 m in length, with a pre-heating zone under the distributor, and was located inside an electrically-heated furnace. Both temperature and pressure drop in the bed were measured. The changes in the pressure drop help to detect possible agglomeration problems in the bed.

Gases were fed at the bottom of the reactor. By means of a three-way-valve, it was possible to switch between water vapor/ CO_2 , nitrogen and air so that the sample was sequentially exposed to reducing, purge and oxidation periods. Steam was produced by heating up in an evaporator the corresponding water flow supplied by a peristaltic pump.

Air was supplied as fluidizing agent while heating up to the desired temperature. Once the reaction temperature was reached, a nitrogen flow purged the system and the experiment started. During the reducing periods, coal or char was used as fuel whereas the reactor was fluidized with water vapor, CO_2 or water vapor/ CO_2 mixtures, which also acted as gasification agents. The fuel (coal or char) was fed at about 5–6 cm below the upper level of the

fluidizing particles using a fuel chute. The fuel particles were placed in a deposit in the upper part of the chute (v1) and overpressurized (0.1 MPa) with nitrogen (v2). At the beginning of the experiment, the valve connecting the deposit with the fuel chute (v3) was quickly opened and closed so that the fuel particles were introduced. This procedure ensures an efficient feeding inside the oxygen carrier bed, favouring the mixing between the fuel and bed material. After every reducing period, bauxite waste particles were fully re-oxidized with air before starting a new cycle. Between the reducing and oxidizing periods a nitrogen flow purged the system during 2 min. The total flow used was 200 $\text{L}_\text{N}/\text{h}$, which corresponds to a gas velocity of 0.1 m/s at 900 °C in the reactor.

The product gas leaving the reactor was conducted to a hot filter that retained the solids that may elutriate during reaction. Before entering the analyzers, the product gas flowed through a condenser to eliminate water prior to analysis and then, 90 $\text{L}_\text{N}/\text{h}$ nitrogen flow was introduced to ensure a continuous dry gas flow feeding the analyzers. This nitrogen flow was also used to estimate the total dry flow exiting from the reactor using the concentrations of the rest of the components, as will be described later. The dry gas concentration were continuously registered and collected with a data logger connected to a computer. CO , CO_2 and CH_4 dry basis concentrations were determined using non-dispersive infrared analysis (NDIR) and H_2 by thermal gas conductivity. The O_2 concentration was determined in a paramagnetic analyzer.

The effect of temperature and gasifying gas composition on the reaction rates of gasification and subsequent combustion of gasification products was analyzed. The temperature was varied in the 900–980 °C range. Different $\text{H}_2\text{O}:\text{CO}_2$ molar ratios were used (0:100, 10:90, 30:70; 100:0). The bauxite waste was exposed to a total number of 85 reduction/oxidation cycles (125 h).

2.3.1. Data evaluation

Mass balances of carbon, hydrogen and oxygen were done considering the CO , CO_2 , H_2 and CH_4 concentrations registered in every experiment. From the results obtained, the performance of bauxite waste during the fuel combustion was evaluated. The molar gas flow of each component exiting the reactor, F_i , is calculated as:

$$F_i = F_{\text{out}} \cdot y_i \quad (11)$$

where y_i is the molar fraction of the component i (CO_2 , CO , H_2 or CH_4) in the product gas.

The total dry basis outlet flow after nitrogen dilution, F_{out} , can be calculated using the N_2 flow introduced downstream, F_{N_2} :

$$F_{\text{out}} = \frac{F_{\text{N}_2}}{(1 - \sum_i y_i)} \quad (12)$$

The rate of fuel conversion, $r_c(t)$, was calculated from a carbon balance to gaseous species in the reactor.

$$r_c(t) = (y_{CO_2} + y_{CO} + y_{CH_4}) \cdot F_{out} - F_{CO_2,in} \quad (13)$$

Methane was not detected in experiments with char and therefore was not considered in those cases.

The evolution of the fuel conversion with time can be calculated by integrating Eq. (13). The resulting expressions for coal and char as fuels were:

$$X_{coal}(t) = \frac{\int_0^t r_c(t) \cdot dt}{N_{C,coal}} \quad (14)$$

$$X_{char}(t) = \frac{\int_0^t r_c(t) \cdot dt}{N_{C,char}} \quad (15)$$

where $N_{C,coal}$ and $N_{C,char}$ are the moles of carbon fed into the reactor with the coal or the char, respectively.

The instantaneous rate of fuel conversion, $r_{C,inst}$, is calculated as the mass flow of gaseous carbon per the amount of non-reacted carbon present in the batch fluidized bed reactor at a given time.

$$r_{C,inst}(t) = \frac{r_c(t)}{N_{C,i} - \int_0^t r_c(t) \cdot dt} = \frac{r_c(t)}{N_{C,i} \cdot (1 - X_i)} \quad (16)$$

where the subindex i corresponds to the fuel used, i.e. coal or char.

The rate of oxygen transferred from the oxygen carrier to the fuel gas, $r_o(t)$, can be calculated through the oxygen balance:

$$\begin{aligned} r_o(t) &= F_{O,out} - F_{O,in} \\ &= [F_{out} \cdot (2y_{CO_2} + y_{CO}) - 2F_{CO_2,in}] + [F_{H_2O,out} - F_{H_2O,in}] \end{aligned} \quad (17)$$

In Eq. (17) the amount of CO_2 fed to the reactor is subtracted in order to calculate the amount of CO_2 generated. According to the values presented in Table 2, the amount of hydrogen and oxygen introduced with the fuel is very low in most of the cases and therefore it was not considered in the mass balances. The flow of water at the reactor exit was calculated assuming that the flow of hydrogen either in H_2 or H_2O comes only from introduced steam, $F_{H_2O,in}$.

$$F_{H_2O,out} = F_{H_2O,in} - F_{out} \cdot y_{H_2} \quad (18)$$

Including all the previous assumptions in Eq. (17), it is reduced to:

$$r_o(t) = F_{out} \cdot (2y_{CO_2} + y_{CO} - y_{H_2}) - 2F_{CO_2,in} \quad (19)$$

The oxygen carrier conversion in the fluidized bed for reduction reaction, X_{red} , can be calculated from the integration of $r_o(t)$ with time:

$$X_{red}(t) = \frac{1}{N_{O,bw}} \int_0^t r_o(t) \cdot dt \quad (20)$$

where $N_{O,bw}$ are the moles of oxygen in bauxite waste active for CLC process:

$$N_{O,bw} = \frac{m_{OC} \cdot R_{OC}}{M_O} \quad (21)$$

where M_O is the oxygen molar weight, i.e. $M_O = 0.016$ kg/mol.

In the experiments with coal as fuel and as an indication of the performance of the combustion process, the instantaneous oxygen demand, $\Omega_g(t)$, was calculated as the fraction of oxygen lacking to achieve a complete combustion of the fuel reactor product gas in comparison to the oxygen demanded.

$$\begin{aligned} \Omega_g(t) &= \frac{0.5 \cdot F_{CO} + 2 \cdot F_{CH_4} + 0.5 \cdot F_{H_2}}{O_{2,demand,coal}} \\ &= \frac{0.5 \cdot F_{CO} + 2 \cdot F_{CH_4} + 0.5 \cdot F_{H_2}}{r_o(t) + 0.5 \cdot F_{CO} + 2 \cdot F_{CH_4} + 0.5 \cdot F_{H_2}} \end{aligned} \quad (22)$$

An average value for the whole reducing period can be calculated as:

$$\Omega_{g,av} = \frac{\int_0^t (0.5 \cdot F_{CO} + 2 \cdot F_{CH_4} + 0.5 \cdot F_{H_2}) \cdot dt}{O_{2,demand,coal}} \quad (23)$$

Finally, in the experiments using char as fuel, the conversion of gasification products, i.e. CO and H_2 to CO_2 and H_2O by reaction with the bauxite waste particles was evaluated using the combustion efficiency, η_c . The combustion efficiency is defined as the oxygen gained by the fuel for its oxidation divided per the oxygen needed to fully oxidize the gasification products.

$$\eta_c(t) = \frac{r_o(t)}{2r_c(t)} \quad (24)$$

3. Results and discussion

3.1. Fluidized bed experiments with coal

In a first step some experiments were performed using coal as feed. This gives a picture of what would be expected to happen in the fuel reactor of an iG-CLC system. The bituminous South African coal (MVB) and the lignite (L) were selected as fuels for this purpose. The amount of coal to be introduced to the batch fluidized bed reactor was optimized to be 0.45 g. This amount allowed to obtain representative results while avoiding excessive loss of coal particles dragged by the gases produced in the volatile release.

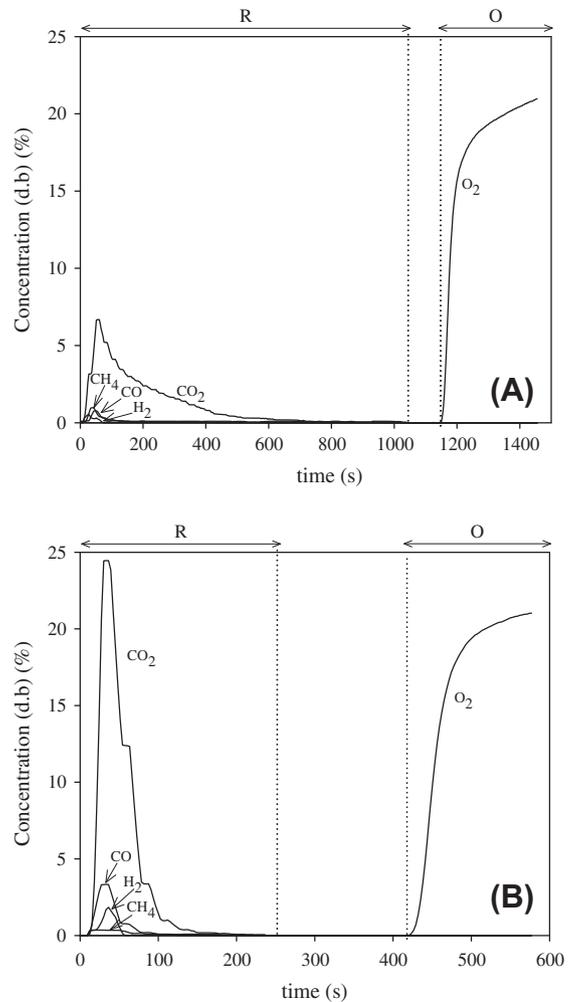


Fig. 3. Gas product distribution (dry basis) in a typical experiment with (A) South African coal (MVB) and (B) lignite (L) as fuel. Gasifying agent: H_2O ; Coal load: 0.45 g; $T = 900$ °C. R: reduction and O: Oxidation.

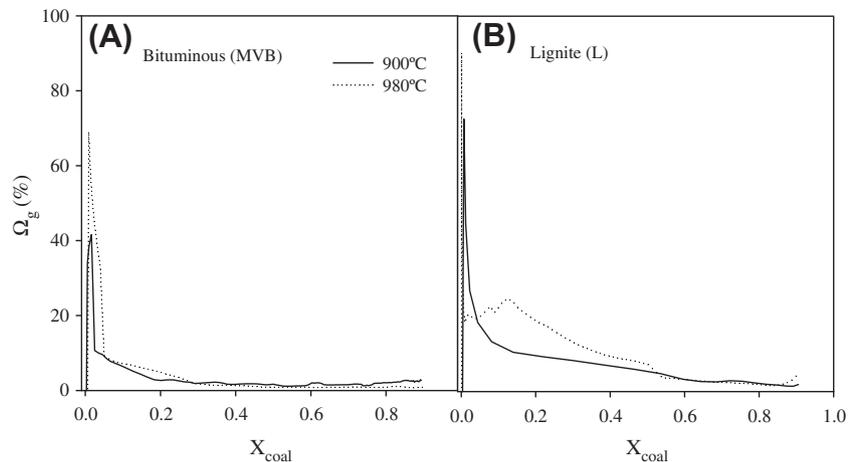


Fig. 4. Instantaneous oxygen demand, $\Omega_g(t)$, as a function of the fuel conversion at different temperatures for the (A) MVB: Bituminous coal with medium volatile content (South African) and (B) L: Lignite.

The experiments were conducted both at 900 °C and 980 °C using steam as fluidizing agent and 400 g of bauxite waste as solid bed. Fig. 3 shows the gas product distribution (dry basis) evolution in a typical experiment. Fig. 3A shows the results for the South African coal. At the beginning of the reducing period, certain amounts of CO, H₂ and CH₄ were detected. These gases may be released during coal pyrolysis and would escape from the bed without being combusted due to a not sufficient contact with the particles in the bed. For methane, the lower reactivity to the bauxite waste particles could be also a relevant issue [41]. During the rest of the experiment, the main product gas in the outlet of the reactor was CO₂. This indicates that the gasification of the char remaining in the bed is proceeding and that the CO and H₂ generated are completely burned by the bauxite waste particles. The oxygen carrier conversion during the whole period was low, around 4.5%. This value was calculated from Eq. (20), including in this case the amount of oxygen that was introduced with the coal, as it is not negligible like in the case of the char. Once the char gasification was considered completed, a nitrogen flow was fed to the fuel reactor to serve as purge before commencing the oxidation in air. Fig. 3B shows the corresponding results for lignite. Note the different time scale used in both Figures. Some of the volatiles released also appeared as unburnt in the product gas. In this case, CO and H₂ were observed in a higher amount than CH₄. The bauxite waste conversion was around 4.6%, but in this case the combustion process proceeded faster than with the South African coal. After the purge with nitrogen, the particles were regenerated in air. Similar experiments were performed at the highest temperature used in this work, 980 °C. Again some volatiles abandoned the bed without being converted to CO₂ and H₂O. The conversion values of the oxygen carrier observed in these experiments were 7.4% and 3.1% for the South African and the lignite coal, respectively. The values of the instantaneous rate of fuel conversion increased as the temperature increased for both coals, although the difference observed is larger in the case of the bituminous coal. Average values were calculated and resulted 33.0 and 94.3%/min for bituminous and 255.6% and 275.2%/min for lignite at 900 °C and 980 °C, respectively. These values are high compared to char conversion rates [12,13], but here the fast devolatilization of coal is being considered.

The instantaneous oxygen demand for the experiments was calculated, $\Omega_g(t)$. Fig. 4A and B plot the evolution of the oxygen demand with the coal combustion in the experiments with the bituminous South African coal and lignite calculated according to Eq. (22). For both coals and at both temperatures tested, the oxygen demand presents a maximum at the beginning of the

Table 3

Average oxygen demand, $\Omega_{g,av}$ (%), for the experiments with bituminous South African coal and lignite.

	Bituminous coal (MVB)	Lignite (L)
900 °C	4.2	6.0
980 °C	4.8	7.9

experiment. This maximum corresponds to the release of volatiles from the coal. Those volatile gases leave the fluidized bed without being combusted. The value of the maximum oxygen demand is higher, the higher the temperature, although the differences with temperature are larger in the case of the bituminous coal. After the maximum, the oxygen demand decreases to zero. As estimation for the whole reduction period, the global oxygen demand was calculated following Eq. (23) and is presented in Table 3. The values at the highest temperature tested (980 °C) for both coals are 4.8% for the bituminous coal and 7.9% for the lignite.

According to the results observed for these two coals, the configuration of the experimental system used facilitates that an important part of the volatiles released leave the fluidized bed without being converted. The inefficient contact between volatile matter and oxygen carrier particles has been proposed as the reason for the low conversion of volatiles [8,14] instead of the low reactivity of the oxygen carrier. The reactivity of the bauxite waste to the main volatiles from coal and gasification gases was evaluated in previous papers and was considered as sufficiently high [21,41]. Moreover, the gasification of the char from coal is considered the rate-limiting step in the char conversion occurring in the fuel reactor of an iG-CLC system. For this reason, the study explored the gasification of the char from different coals and the subsequent combustion of the gasification products.

3.2. Fluidized bed experiments with char

For a better analysis of the results, the bauxite waste was diluted in alumina (50:50 wt), so that the bauxite waste sample was not capable of burning all the gases generated during char gasification. At these conditions, a comparison between different oxygen carrier materials or types of coal can be done. Otherwise, the real effect of the operating conditions can be disguised by the full combustion of gasification products. A total amount of 400 g of the mixture bauxite waste-alumina was introduced in the fluidized bed reactor.

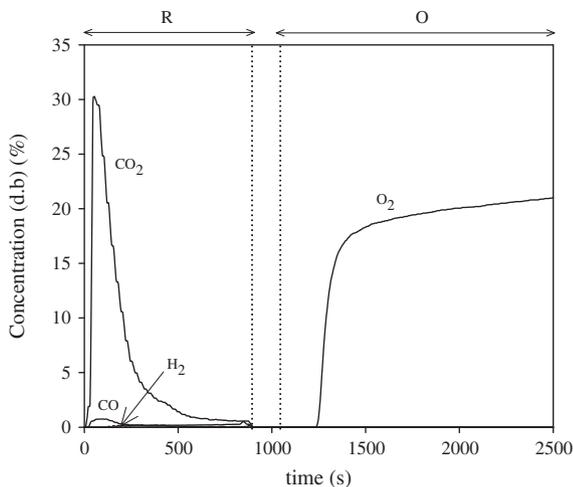


Fig. 5. Gas product distribution (dry basis) evolution in a typical experiment with char as fuel. Gasifying agent: H_2O ; char load (lignite): 1.5 g; bauxite waste in bed: 200 g. $T = 900^\circ\text{C}$. R: reduction and O: oxidation.

Fig. 5 shows the product concentration evolution of a typical experiment. As mentioned before, the char load was introduced at the beginning of the experiment directly into the fluidized bed. In the experiment presented in Fig. 5, the gasifying agent used was steam and lignite char was used as fuel. Most of the CO and H_2 produced during char gasification reacted with the bauxite waste particles in the bed to yield CO_2 and H_2O . As can be seen, the amounts of gasification products registered during the experiment were low, while CO_2 registered a maximum value of 30% (dry basis). The carbon dioxide concentration decreased with time as the char in the bed was consumed. The experiment was considered finished when all the char has been gasified. After the reduction period, nitrogen was introduced during 2 min as a purge and following this, the oxidation period in air began. As observed in the Figure, no CO_2 was registered indicating that all the char had been consumed during the reduction period. Besides, no oxygen was detected in the outlet of the reactor during the first stage of the oxidation. The reduced bauxite waste particles consumed all the oxygen introduced. Afterwards, the oxygen concentration increased up to 21%, indicating the complete regeneration of the particles in the bed.

3.2.1. Influence of the type of fuel

Experiments were performed using the chars from the different coals presented in Table 2. In every experiment, a load of around

1.5 g of the corresponding char was introduced into the fluidized bed. Fig. 6 presents the values of the instantaneous rate of char conversion, $r_{C,inst}(t)$, versus the char conversion for the different chars at 900°C . Fig. 6A shows the results using steam as fluidizing agent. The anthracite char (A) and the char from the bituminous coal with medium volatile content (MVB) presented similar values of the char conversion rate. The average value of this rate was calculated in a char conversion interval 0.2–0.8 and resulted 10.3 and 10.4%/min, respectively. The char conversion rate of the char from the bituminous coal with high volatile content (HVB) was higher. An average value of 17.4%/min was calculated. The highest char conversion rate was observed for lignite which showed an average char conversion rate in the abovementioned interval of 48.9%/min. These results were in accordance with what was expected considering the reactivity of these coals [36]. In Fig. 6B the evolution of the char conversion rate is plotted against the char conversion for the experiments using CO_2 as gasifying agent. In this case, the results corresponding to HVB coal are not available. In general, the average char conversion rates are lower than those observed gasifying with steam as the gasification reaction with CO_2 proceeds slower. The calculated averaged values were 2.2, 2.1 and 23%/min for the anthracite, MVB coal and lignite chars, respectively. It is especially interesting the high char conversion rate value observed for the experiment with lignite compared to the rest of the chars. This average value was higher than the observed at the same temperature for chars from bituminous coals gasifying with steam, as was found before in previous studies [39]. Therefore, the use of these types of coals could be advantageous because recirculated CO_2 could be used as a fluidizing agent in the iG-CLC process.

The gaseous products from char gasification, namely CO and H_2 , react with the oxygen carrier particles surrounding them. Fig. 7A present the evolution of the combustion efficiency with the bauxite waste conversion for the different chars used at 900°C and using steam as fluidizing agent. The observed values are higher than 0.95 in all the cases which demonstrates that the bauxite waste is capable of burning most of the gases generated during the gasification process in all the cases. Fig. 7B shows the corresponding results using CO_2 . In this case, the values of the combustion efficiency are in general lower than those registered with steam. The reactivity of the bauxite waste to CO, the main gasification product, is not as high as to hydrogen, as has been pointed before [21]. The combustion efficiencies for the chars from anthracite and the MVB coal are similar and are close to 0.8 in the solid conversion interval analyzed. For lignite, the values were higher, between 0.9–0.95 and decrease as the amount of oxygen in the bauxite waste decreases. However, they are still high enough to

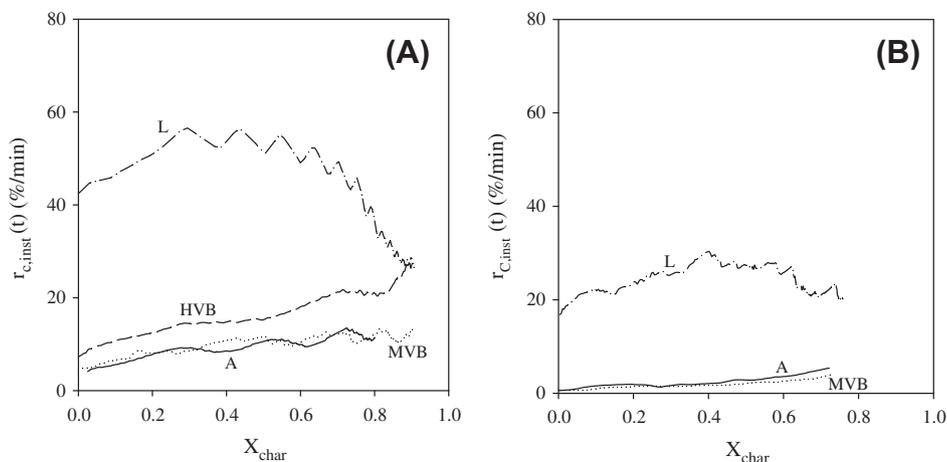


Fig. 6. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion at 900°C for the different coals used as fuels using (A) steam and (B) CO_2 as gasifying agents (A: anthracite; HVB: bituminous with high volatile content (Colombian); MVB: bituminous with medium volatile content (South African); L: lignite).

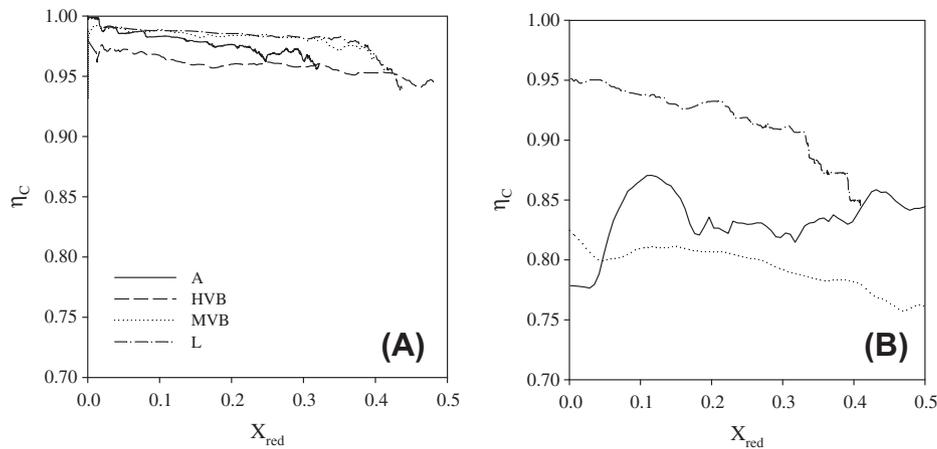


Fig. 7. Combustion efficiency, η_c , as a function of the bauxite waste conversion at 900 °C using (A) steam and (B) CO₂ as fluidizing agents (A: anthracite; HVB: bituminous with high volatile content (Colombian); MVB: bituminous with medium volatile content (South African); L: lignite).

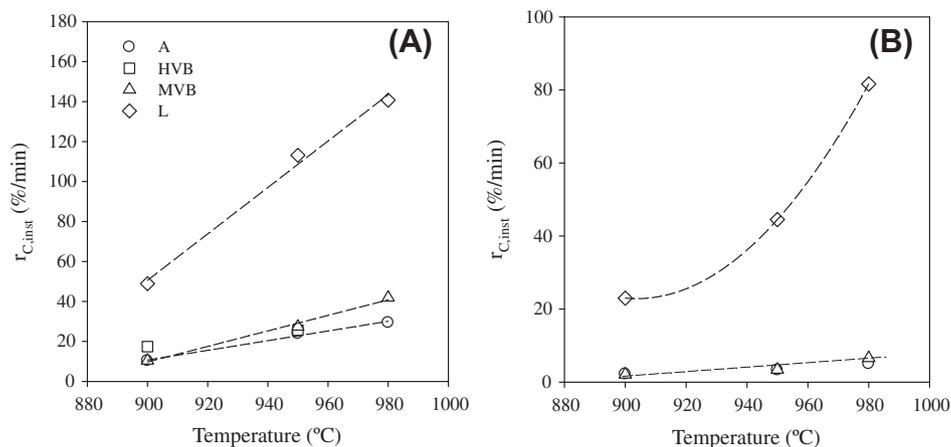


Fig. 8. Average instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the temperature for the different coals used as fuels using (A) steam and (B) CO₂ as fluidizing agents (A: anthracite; HVB: bituminous with high volatile content (Colombian); MVB: bituminous with medium volatile content (South African); L: lignite).

consider the use of CO₂ as gasifying agent in the iG-CLC processes using lignite. The real combustion efficiencies in the fuel reactor of an iG-CLC system would depend on the solids inventory in the fuel reactor.

3.2.2. Influence of the temperature

The influence of the temperature on the gasification of different chars was analyzed in the interval 900–980 °C. In general, an increase in temperature produced an increase in the char conversion rate either using steam or CO₂ as gasifying agents. Fig. 8A shows the average char conversion rate values for experiments with steam at different temperatures. Again, the char from anthracite and from the MVB coal showed similar trend and values, although at the highest temperature the value for the MVB char was higher than for the anthracite (41.9 and 29.4%/min, respectively). The most significant influence of temperature was observed in the experiments with char from lignite. The char conversion rate increased from 48.9%/min at 900 °C to 140.7%/min at 980 °C. Fig. 8B shows the corresponding results for the experiments with CO₂. The anthracite and the MVB coal chars had similar values of char conversion rate, which reached a maximum around 5–6%/min at the highest temperature tested. However, the influence of temperature on the lignite char conversion rate was notably higher. The char conversion rate increased with temperature reaching a value at 980 °C of 81.6%/min, which doubles the value observed at

this temperature using steam with the char from bituminous coals. Assuming an Arrhenius type temperature dependence of the gasification rate constant, the value for the apparent activation energy could also be calculated, both for the experiments using steam or CO₂ as fluidizing/gasification agents. Table 4 summarizes the values obtained. Both the average char conversion rates and activation energy of the MVB coal are similar to those presented by Linderholm et al. [35] for a similar coal.

From the average values of the char conversion rate registered, an estimation of the residence time to mostly convert the char in the reactor was obtained. The residence time was estimated from the time to convert 95% of the char present in the bed, (t_{95}) [12,13,21,24]. For this purpose, it was assumed that the gasification reaction can be represented using the homogeneous model:

$$\frac{1}{1 - X_{char}} \frac{dX_{char}}{dt} = r_{C,inst} \quad (25)$$

Table 4

Apparent activation energy (kJ/mol) for char gasification from different types of coal in the interval 900–980 °C.

	Anthracite	Bituminous MVB	Lignite
Steam	161	210	173
CO ₂	130	178	171

Table 5

Values of the residence time to convert 95% of char in minutes, t_{95} , at different temperatures for H₂O or CO₂ as gasification agents.

	Temperature (°C)	Anthracite	Bituminous		Lignite
			HVB	MVB	
H ₂ O	900	29.1	17.2	28.8	6.1
	950	12.5	11.7	10.9	2.6
	980	10.2	–	7.1	2.1
CO ₂	900	136.2	–	142.7	13.0
	950	90.8	–	88.1	6.7
	980	59.9	–	45.4	3.7

From Eq. (25), the value for t_{95} can be calculated as:

$$t_x = -\frac{1}{r_{C,inst}} \ln(1 - X_t) \quad (26)$$

where t_x is the time to reach the conversion X_t .

A comparison of the values obtained for the different chars used is presented in Table 5. For the experiments with steam, the increase in the temperature from 900 to 980 °C implied a decrease in the residence time of the char in the fuel reactor from around 30 to 10 min for the chars from anthracite and bituminous coals. In the case of lignite, the residence time is always lower than 10 min, reaching a value of 2.1 min at 980 °C. If carbon dioxide is used as gasifying agent, it becomes necessary to increase the temperature to achieve more reasonable residence times of the char in the fuel reactor. Nevertheless, the values obtained for the chars from anthracite and MVB coal were at least 45 min. This is in contrast with the values for the lignite char, which were again much lower. At 980 °C, the residence time estimated for the lignite char gasifying with CO₂ was 3.7 min, also close to what was observed gasifying with steam. Cuadrat et al. [36] used the same coals as those presented here in a 500 W continuous unit operated with ilmenite as oxygen carrier and found similar values to those found in the conditions of the present work. Similar values were also found by Yang et al. [46] with an oxygen carrier prepared from Fe₂O₃ powder and a char from a bituminous coal with high volatile content (Baorixile coal).

The variation of the combustion efficiency with temperature was also analyzed in Fig. 9. Average values were calculated considered an interval for bauxite waste conversion of 0–0.5. As it can be seen in most of the experiments in Fig. 9A using steam as gasifying agent, the combustion efficiency is higher than 0.95 for all the fuels tested in this work and there is a trend to increase the efficiency value as the temperature increases. Fig. 9B shows the results for the experiments using CO₂. As expected, lower values are observed compared to the experiments using steam, although the average

values increase with temperature. The highest combustion efficiencies were registered for lignite, which showed values equal to or higher than 0.9 in all of the experiments performed. The lower combustion efficiency values using carbon dioxide indicates that CO, the only product of dry gasification of the char, reacts more slowly with the bauxite waste than hydrogen, main product of the char gasification with steam. Besides, the CO formed can be transformed to H₂ in the presence of steam through the WGS reaction, therefore increasing the combustion efficiency in the experiments with steam compared to those using CO₂:



3.2.3. Influence of the gasifying agent

As observed before, except in the case that lignite is used as fuel, the use of pure CO₂ as gasifying agent is not advantageous for the iG-CLC. Nevertheless, the use of steam-CO₂ gasifying mixtures could contribute to decrease the energy penalties associated with steam production without excessively decreasing the efficiency of the process. Experiments were conducted introducing steam-CO₂ mixtures to the fluidized bed reactor at two different temperatures (900 and 980 °C) in order to evaluate the performance of the process in these conditions. Fig. 10 shows the decrease percentage of the average char conversion rates (ε) for steam and CO₂ mixtures regarding the rate when pure steam was used, defined according to Eq. (28):

$$\varepsilon = \frac{r_{C,inst}|_{\text{H}_2\text{O}} - r_{C,inst}}{r_{C,inst}|_{\text{H}_2\text{O}}} \cdot 100 \quad (28)$$

Fig. 10A shows the results at 900 °C. In all the cases, when the CO₂ fraction increased, the gasification rate decreased. This decrease in the average char conversion rate gradually increases as the percentage of steam in the feeding is reduced. The decrease is proportional to the CO₂ fraction introduced for anthracite and MVB. However, for lignite the decrease is proportional to CO₂ concentration up to a H₂O:CO₂ molar fraction equal to 50:50. A further increase in the CO₂ concentration from 50% to 100% produces a lower decrease in the char gasification rate. Using a stream composed of 70% H₂O and 30% CO₂, a decrease in the char conversion rate around 30% is observed for all of them. When only CO₂ is used as gasifying agent, the differences between the chars are more significant. While there is approximately 80% decrease in the char gasification rate of anthracite and South African coal, the decrease is only around 50% for lignite. Similar trends were observed at 980 °C, as shown in Fig. 10B. In this case, the loss in the char gasification rate using lignite char as fuel and CO₂ as gasifying agent

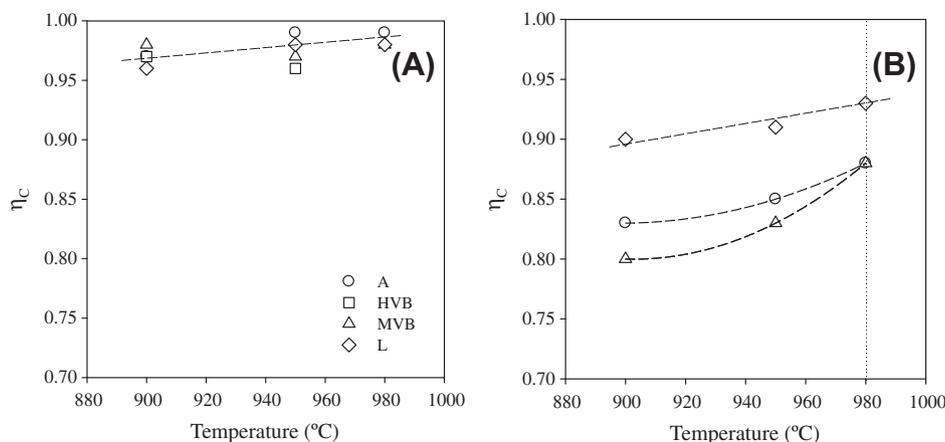


Fig. 9. Average combustion efficiency, η_c , as a function of the temperature using (A) steam and (B) CO₂ as fluidizing agents (A: anthracite; HVB: bituminous with high volatile content (Colombian); MVB: bituminous with medium volatile content (South African); L: lignite).

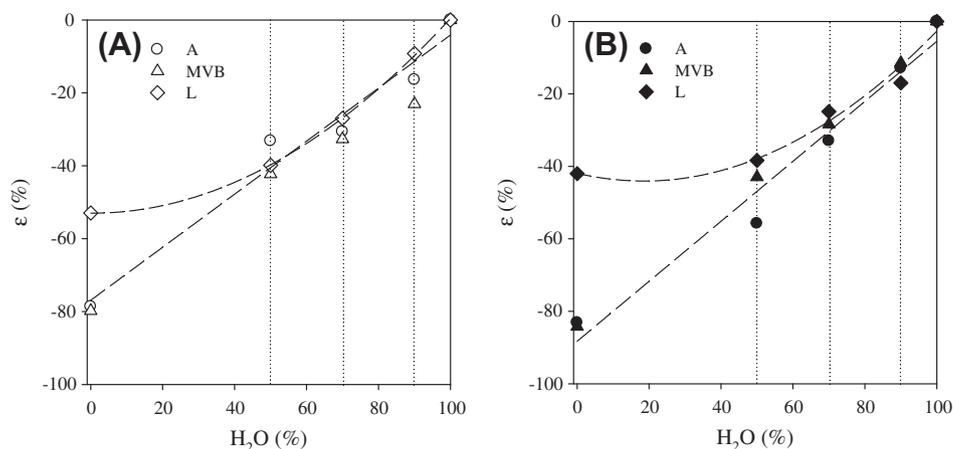


Fig. 10. Decrease percentage of the average instantaneous rate of char conversion, $r_{c,inst}(t)$ as a function of the steam percentage in the gasifying/fluidizing mixture for the different chars used as fuels (A: anthracite; MVB: bituminous with medium volatile content (South African); L: lignite) at (A) 900 °C (open symbols) and (B) 980 °C (closed symbols).

was even lower, around 40%. The combustion efficiencies of the gasification products when using steam- CO_2 mixtures notably increase with temperature. At 900 °C, they only exceed 0.95 for steam- CO_2 mixtures with 90% steam and 10% CO_2 . At 980 °C, the combustion efficiency values observed were higher than 0.95 using a more CO_2 enriched feed, i.e. 70% steam and 30% CO_2 .

Therefore and as a conclusion, it can be said that the optimal conditions to operate in the fuel reactor in an iG-CLC system will depend on the fuel used. For highly reactive fuels like lignite, it is possible to use recycled CO_2 as gasifying agent, which is an interesting advantage from the cost-efficiency point of view. The char gasification rates and combustion efficiencies of the gasification products observed in the 900–980 °C were adequate. The amount of non-consumed char would be low and therefore, no very high efficiencies of the carbon separation system would be needed and high carbon capture could be expected, as the char transferred to the air reactor would be decreased. If less reactive fuels, such as anthracite, are fed, steam would be preferred as gasifying agent, which increases the cost of the process due to the energy needed to produce the steam. The use of recycled CO_2 in the gasifying stream in order to reduce this energy penalty would be limited to avoid significant drops in the char gasification rate. The use of steam- CO_2 mixtures could then be combined with a high-efficiency carbon separation system and high temperatures in the fuel reactor to achieve high carbon captures.

3.2.4. Solid–solid interaction

Some experiments were conducted loading 1.5 g of the corresponding char while nitrogen was fed to the fluidized bed at 900 °C to know the relevance of char conversion without a gasifying agent in the gas fed. The aim of these tests was to analyze the possible contribution of the direct solid–solid reaction between the oxygen carrier and the char. CO and CO_2 concentration at the reactor exit were monitored during 1 h and in any case it was observed that this interaction was taking place. Therefore, the contribution of the bauxite waste-char reaction to the global rate of the process was considered negligible in these conditions with all the coals tested in this work. Similar results have been reported before [12,13]. However, as it was mentioned before, several authors gave experimental results indicating the existence of direct solid–solid reaction between char and oxygen carriers based on Cu, Ni, Mn, Fe and Co. All of these studies were performed using either a TGA apparatus or a fixed-bed and bituminous coals [15–20].

Considering these results, TGA experiments were also performed using bauxite waste in order to analyze the possible so-

lid–solid interaction between this potential carrier and the solid fuel, as well as the dependence of this interaction on the dynamic conditions of the bauxite waste particles. Fig. 11 shows the experiments performed using a flow of N_2 as gaseous feed and according to the experimental procedure described in Section 2.2. The results for anthracite, MVB and lignite chars are shown.

In all the experiments presented, there is an initial weight loss during the heating and the first 30 min of experiment which is compared to the weight loss registered for a blank test in the same conditions using 90 mg of only bauxite waste sample. The difference among them is plotted in Fig. 11 and may be attributed to the char and oxygen consumption during the reaction between the bauxite waste and the char. As it can be seen in Fig. 11, the weight loss observed for the experiment with anthracite char was very low and close to that for the bituminous coal and both lower than the corresponding to lignite. Thus the net weight loss increases as the rank of the parent coal of the char used decreases. After the first 30 min, steam is fed and the weight variation observed corresponds to the reaction between the unreacted char and the steam and the subsequent reaction of the CO and H_2 released with the bauxite waste. The reaction proceeds until the sample weight does not vary significantly, which indicates that the gasification reaction is already finished. In the case of the experiment with lignite char in Fig. 11C, the gasification was very fast compared to the other two chars. Finally, after 2 min purge in nitrogen, the oxidation of the bauxite waste takes place in air. The weight increase corresponds to the oxygen gained by the sample and indicates the amount of oxygen consumed in the previous reactions. The results for the experiments presented in Fig. 11 are summarized in Table 6.

The values of the O/C mass ratio were calculated for the experiments performed. They were 0.8 for the experiment with anthracite, 1.2 for the experiments with MVB char, and 0.9 for the experiment with lignite char. Therefore, it was assumed that the proportion was one mol of oxygen consumed by each mol of carbon. With this assumption, it can be estimated the percentage of the char introduced that was consumed in the bauxite waste-char reaction. The percentage of reacted char increased from 8% for anthracite char, to 12.5% for the bituminous char to 37.5% in the case of the lignite char. Therefore, the amount of char consumed was larger the lower the rank of the coal used.

Nevertheless, the fact that there was a net weight loss in the experiments performed using bauxite waste and different chars in nitrogen atmosphere does not imply that it is due exclusively to a solid–solid reaction between the particles. The CO_2 generated

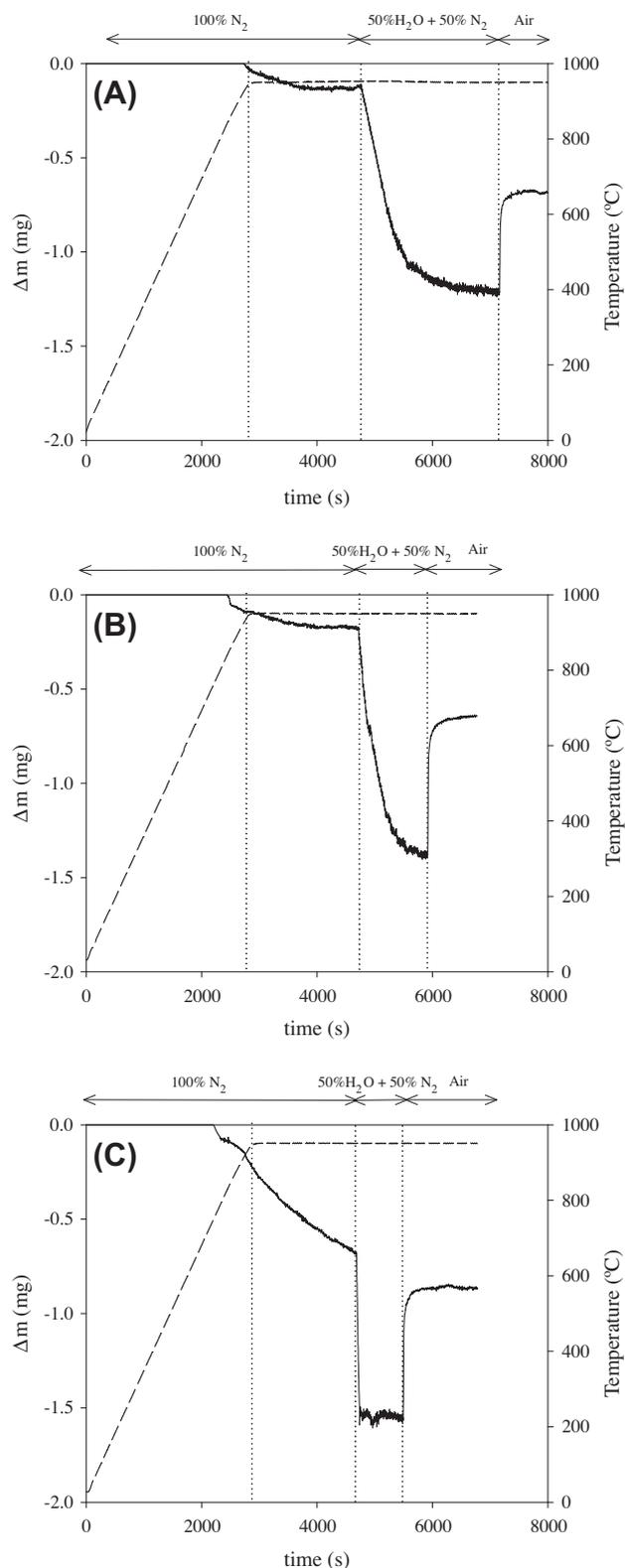


Fig. 11. Weight variation in the experiments performed in the TGA at 950 °C for the analysis of the solid–solid interaction between bauxite waste and (A) char from anthracite (B) char from bituminous South African coal (MVB) (C) char from lignite (L).

during the oxidation of char may play an important role as intermediate in the reaction mechanism. In order to test this hypothesis, the experiment presented in Fig. 11B using char from MVB coal was repeated in nitrogen atmosphere but with no nitrogen flow introduced during the heating step and the following 30 min. In

Table 6

Results from the TGA experiments to analyze the bauxite waste–char interaction ($T = 950$ °C).

	Anthracite	Bituminous MVB	Lignite
(OC + char)/char (wt)	125	98.5	75
Δw (mg) ^a			
100% N ₂	0.1237	0.1803	0.6816
50% H ₂ O + 50% N ₂	1.0905	1.1936	0.8748
21% O ₂ + 79% N ₂	0.52	0.7314	0.6929
O/C (wt.)	0.8	1.2	0.9
Char conversion solid–solid (%)	8	12.5	37.5

^a Net weight loss in different gaseous atmospheres.

this case, 60% of the char was consumed in the first step of the experiment compared to the 12.5% in the experiment with a nitrogen flow. If the gaseous products generated in bauxite waste–char interaction are not removed by the nitrogen flow, the reaction proceeds faster, reinforcing the idea of CO₂ as intermediate.

Besides, as mentioned before, no evidence of solid–solid interaction was observed in the fluidized bed experiments. The different results observed in fluidized bed and TGA may be attributed to the different conditions in these experiments. Solids in the batch fluidized bed are considered to be in a perfect mixture and the solid–solid contact is less favoured. In this case, the reaction between the char and the gaseous atmosphere surrounding the particles is more favoured. Therefore, if the fluidizing gas is H₂O or CO₂, the reaction mechanism will involve H₂ and CO from char gasification as intermediate products in the char conversion in a fluidized bed. This type of contact between reactants is similar to what would be expected in a real iG–CLC system. Thus, it is realistic to state that the solid–solid interaction between the oxygen carrier and the char particles is negligible in a real CLC combustion process where the fuel reactor is a fluidized bed reactor.

4. Conclusions

An industrial residue from the alumina production via de Bayer process has been tested as oxygen carrier for CLC using different types of coal at different operating conditions in a batch fluidized bed reactor. The coals tested were anthracite (A), two bituminous coals, Colombian (HVB) and South African (MVB), and lignite (L).

In experiments performed with coal, some volatiles were released as unburnt. The global oxygen demand in experiments with lignite and bituminous South African coal (MVB) were lower than 8% at the highest temperature tested, i.e. 980 °C.

Some experiments were performed using char from these coals as fuel. Lignite char presented very high char gasification rates gasifying with steam in the temperature interval considered (900–980 °C), followed by the char from the bituminous Colombian coal (HVB). The chars from the bituminous South African (MVB) and the anthracite coals presented lower and similar gasification rates. High combustion efficiencies of the gasification products were observed in all the cases. The char conversion rates notably decreased when CO₂ was used as gasifying agent, except for the case of the lignite char. These results may encourage the use of recycled CO₂ from the flue gases if lignite is considered as fuel. Steam–CO₂ mixtures were also tested as gasifying agents. The use of a certain amount of CO₂ in the feeding was possible without decreasing the feasibility of the iG–CLC process with low reactive coals, especially at high temperatures.

The solid–solid interaction between the bauxite and char particles was analyzed both in the batch fluidized bed and in a TGA apparatus. In the TGA experiments, the amount of char converted by solid–solid reaction was larger, the lower the rank of the char

used was. However, it was concluded that the contribution of this reaction to the global char conversion rate is negligible in real CLC system because no significant evidence of this interaction was observed in the fluidized bed. If the fluidizing gas is H₂O or CO₂, the reaction mechanism will involve H₂ and CO from char gasification as intermediate products in the char conversion in a fluidized bed.

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References

- [1] Carbon capture and storage. IPCC report. New York: Cambridge University Press; 2005.
- [2] IEA World Energy Outlook 2010. Paris, France: OECD/IEA; 2010.
- [3] Buhre BJP. Oxy-fuel combustion technology for coal-fired power generation. *Prog Energy Combust Sci* 2005;31:283–307.
- [4] Eide LI, Anhedén M, Lyngfelt A, Abanades C, Younes M, Clodic D, et al. Novel capture processes. *Oil Gas Sci Technol* 2005;60:497–508.
- [5] Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chem Eng Sci* 2001;56:3101–13.
- [6] Adánez J, Abad A, García-Labiano F, Gayán P, de Diego LF. Progress in chemical-looping combustion and reforming technologies. *Prog Energy Combust* 2012;38:215–82.
- [7] Berguerand N, Lyngfelt A. Design and operation of a 10 kW_{th} chemical-looping combustor for solid fuels – testing with South African coal. *Fuel* 2008;87:2713–26.
- [8] Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego LF, Adánez J. The use of ilmenite as oxygen-carrier in a 500 W_{th} chemical-looping combustion unit. *Int J Greenhouse Gas Control* 2011;5:1630–42.
- [9] Shen L, Wu J, Gao Z, Xiao J. Characterization of chemical looping combustion of coal in a 1 kW_{th} reactor with a nickel-based oxygen carrier. *Combust Flame* 2010;157:934–42.
- [10] Dennis JS, Scott SA. *In situ* gasification of a lignite coal and CO₂ separation using chemical looping with a Cu-based oxygen carrier. *Fuel* 2010;89:1623–40.
- [11] Dennis JS, Scott SA, Hayhurst AN. *In situ* gasification of coal using steam with chemical looping: a technique for isolating CO₂ from burning a solid fuel. *J Energy Inst* 2006;79:187–90.
- [12] Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* 2007;86:1947–58.
- [13] Cuadrat A, Abad A, Adánez J, de Diego LF, García-Labiano F, Gayán P. Prompt considerations on the design of chemical-looping combustion of coal from experimental tests. *Fuel* 2012;97:219–32.
- [14] Cuadrat A, Abad A, Gayán P, de Diego LF, García-Labiano F, Adánez J. Theoretical approach on the CLC performance with solid fuels: optimizing the solids inventory. *Fuel* 2012;97:536–51.
- [15] Siriwardane R, Tian H, Richards G, Simonyi T, Poston J. Chemical-looping combustion of coal with metal oxide oxygen carriers. *Energy Fuels* 2009;23:3885–92.
- [16] Rubel A, Liu K, Neathery J, Taulbee D. Oxygen carriers for chemical looping combustion of solid fuels. *Fuel* 2009;88:876–84.
- [17] Zhao H, Liu L, Wang B, Xu D, Jiang L, Zheng C. Sol-gel derived NiO/NiAl₂O₄ oxygen carriers for chemical-looping combustion by coal char. *Energy Fuels* 2008;22:898–905.
- [18] Siriwardane R, Tian H, Miller D, Richards G, Simonyi T, Poston J. Evaluation of reaction mechanism of coal–metal oxide interactions in chemical-looping combustion. *Combust Flame* 2010;157:2198–208.
- [19] Saha C, Roy B, Bhattacharya S. Chemical looping combustion of Victorian brown coal using NiO oxygen carrier. *Int J Hydrogen Energy* 2011;36:3253–9.
- [20] Saha C, Bhattacharya S. Comparison of CuO and NiO as oxygen carrier in chemical looping combustion of a Victorian brown coal. *Int J Hydrogen Energy* 2011;36:12048–57.
- [21] Mendiara T, Gayán P, Abad A, de Diego LF, García-Labiano F, Adánez J. Performance of a bauxite waste as oxygen-carrier for chemical-looping combustion using coal as a fuel. *Fuel Process Technol*; 2012. <http://dx.doi.org/10.1016/j.fuproc.2012.09.038>.
- [22] Brown TA, Dennis JS, Scott SA, Davidson JF, Hayhurst AN. Gasification and chemical-looping combustion of a lignite char in a fluidized bed of iron ore. *Energy Fuels* 2010;24:3034–48.
- [23] Cao Y, Pan W-P. Investigation of chemical looping combustion by solid fuels. 1. Process analysis. *Energy Fuels* 2006;20:1836–44.
- [24] Leion H, Mattisson T, Lyngfelt A. Solid fuels in chemical-looping combustion. *Int J Greenhouse Gas Control* 2008;2:180–93.
- [25] Berguerand N, Lyngfelt A. The use of petroleum coke as fuel in a 10 kW_{th} chemical-looping combustor. *Int J Greenhouse Gas Control* 2008;2:169–79.
- [26] Berguerand N, Lyngfelt A. Chemical-looping combustion of petroleum coke using ilmenite in a 10 kW_{th} unit – high temperature operation. *Energy Fuels* 2009;23:5257–66.
- [27] Leion H, Mattisson T, Lyngfelt A. Use of ores and industrial products as oxygen carriers in chemical-looping combustion. *Energy Fuels* 2009;23:2307–15.
- [28] Leion H, Jerndal E, Steenari BM, Hermansson S, Israelsson M, Jansson E, et al. Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers. *Fuel* 2009;88:1945–54.
- [29] Xiao R, Song Q, Song M, Lu Z, Zhang S, Shen L. Pressurized chemical-looping combustion of coal with an iron ore based oxygen carrier. *Combust Flame* 2010;157:1140–53.
- [30] Xiao R, Song Q, Zhang S, Zheng W, Yang Y. Pressurized chemical-looping combustion of coal Chinese bituminous coal: cyclic performance and characterization of iron ore-based oxygen carrier. *Energy Fuels* 2010;24:1449–63.
- [31] Jerndal E, Leion H, Axelsson L, Ekvall T, Hedberg M, Johansson K, et al. Using low-cost iron-based materials as oxygen carriers for chemical looping combustion. *Oil Gas Sci Technol* 2011;66:235–88.
- [32] Leion H, Mattisson T, Lyngfelt A. Chemical looping combustion of solid fuels in a laboratory fluidized-bed reactor. *Oil Gas Sci Technol* 2011;66:201–8.
- [33] Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego LF, Adánez J. Effect of operating conditions in chemical-looping combustion of coal in a 500 W_{th} unit. *Int J Greenhouse Gas Control* 2012;6:153–63.
- [34] Adánez J, Cuadrat A, Abad A, Gayán P, de Diego LF, García-Labiano F. Ilmenite activation during consecutive redox cycles in chemical-looping combustion. *Energy Fuels* 2010;24:1402–13.
- [35] Linderholm C, Cuadrat A, Lyngfelt A. Chemical-looping combustion of solid fuels in a 10 kW_{th} pilot-batch tests with five fuels. *Energy Procedia* 2011;4:385–92.
- [36] Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego LF, Adánez J. Relevance of the coal rank on the performance of the *in situ* gasification chemical-looping combustion. *Chem Eng J* 2012;195:91–102.
- [37] Johnson JL. Fundamentals of coal gasification. In: Elliot MA, editor. *Chemistry of coal utilization*. New York: Wiley & Sons; 1981 [chapter 23].
- [38] Scott AA, Dennis JS, Hayhurst AN, Brown T. *In situ* gasification of a solid fuel and CO₂ separation using chemical looping. *AIChE J* 2006;52:3325–8.
- [39] Leion H, Lyngfelt A, Mattisson T. Effects of steam and CO₂ in the fluidizing gas when using bituminous coal in chemical-looping combustion. In: *Proc 20th int conf on fluidized bed combustion*, Xian, China; 2009. p. 608–11.
- [40] Ortiz M, Gayán P, de Diego LF, García-Labiano F, Abad A, Pans MA, et al. Hydrogen production with CO₂ capture by coupling steam reforming of methane and chemical-looping combustion: use of an iron-based waste product as oxygen carrier burning a PSA tail gas. *J Power Sources* 2011;196:4370–81.
- [41] Mendiara T, Abad A, de Diego LF, García-Labiano F, Gayán P, Adánez J. Use of an Fe-based residue from alumina production as oxygen carrier in chemical looping combustion. *Energy Fuels* 2012;26:1420–31.
- [42] Abad A, García-Labiano F, de Diego LF, Gayán P, Adánez J. Reduction kinetics of Cu-, Ni- and Fe-based oxygen carriers using syngas (CO + H₂) for chemical looping combustion. *Energy Fuels* 2007;21:1843–53.
- [43] Cho P, Mattisson T, Lyngfelt A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* 2004;83:1215–25.
- [44] Cuadrat A, Abad A, Adánez J, de Diego LF, García-Labiano F, Gayán P. Behavior of ilmenite as oxygen carrier in chemical-looping combustion. *Fuel Process Technol* 2012;94:101–12.
- [45] Adánez J, de Diego LF, García-Labiano F, Gayán P, Abad A, Palacios JM. Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* 2004;18:371–7.
- [46] Yang J, Cai N, Li Z. Reduction of iron oxide as an oxygen carrier by coal pyrolysis and steam char gasification intermediate products. *Energy Fuels* 2007;21:3360–8.