

Prompt Considerations on the Design of Chemical-Looping Combustion of Coal from Experimental Tests

Ana Cuadrat, Alberto Abad*, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán,
Juan Adánez

Instituto de Carboquímica (C.S.I.C.), Department of Energy and Environment, Miguel
Luesma Castán 4, 50018, Zaragoza, Spain

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

Email address: abad@icb.csic.es (Alberto Abad).

Abstract

The Chemical-Looping Combustion of coal in the reactor system has been proposed as an interesting option to process a solid fuel in a CLC system. In this process, a solid fuel is directly fed to the fuel reactor in a CLC system. Solid fuel pyrolysis, char gasification and oxidation of gaseous products by reaction with the oxygen-carrier are the main chemical processes happening in the fuel reactor. The aim of this study is to analyze the performance of ilmenite as oxygen-carrier for CLC of coal regarding to the conversion of gaseous products from char gasification. Successive reduction-oxidation cycles were carried out in a fluidized bed using bituminous coal char as reducing agent. The changes on chemical and physical properties of ilmenite particles were determined. An activation process of ilmenite through the redox cycles was evidenced which was justified by an increase of porosity. The results showed that the activation for ilmenite reduction reaction was completed after 7 redox cycles. However, the oxidation reaction rate was increasing still after 16 redox cycles because the porosity was not fully developed. The gasification reaction rate and the ilmenite reactivity were analyzed. The effect of ilmenite itself and the influence of the gasification agent, i.e. H₂O, CO₂ or H₂O/CO₂ mixtures, and temperature on the gasification rate were evaluated. Limited use of CO₂ in the fluidizing gas was identified in order to maintain high gasification rates. Higher temperature improved the char gasification rate, mainly using steam as gasification agent, and the combustion efficiency of the gasification products. Nevertheless, the effect of temperature on the combustion efficiency was of lower relevance than that on the gasification rate. Finally, a theoretical approach was developed to easily evaluate the conversion of char in the fuel-reactor by gasification.

Keywords: CO₂ capture, Chemical-Looping Combustion, Oxygen-carrier, Ilmenite, Coal, Gasification

1. Introduction

According to the Intergovernmental Panel on Climate Change (IPCC) [1], “most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations”. There is therefore a broad acceptance by scientists of the link between greenhouse-gas emissions and global climate change. As the use of fossil fuels in energy generation represents about 65% of global anthropogenic greenhouse-gas emissions [2], actions geared to reduce emissions from fossil fuel combustion are necessary. The intensified use of coal would substantially increase the emissions of CO₂ unless there was very widespread deployment of carbon capture and storage [3]. Carbon dioxide capture is generally estimated to represent three-fourths of the total cost of a carbon capture, transport and sequestration system. Among the different capture concepts, Chemical-Looping Combustion (CLC) is one of the most promising technologies to carry out the CO₂ capture with low cost and small efficiency loss.

CLC is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen-carrier. CLC technology has been widely proven using two interconnected fluidized beds: the fuel reactor and the air reactor [4]. In the fuel reactor the fuel is oxidized through reduction of the oxygen-carrier. The oxygen-carrier is transported to the air reactor where it is regenerated by oxidation with air. The stream of combustion gases from the fuel reactor contains primarily CO₂ and H₂O. Water can be easily separated by condensation and a highly concentrated stream of CO₂ ready for compression, transport and sequestration is achieved. The gas stream from the air reactor is oxygen-depleted and consists only in N₂ and some unreacted O₂. Thus, N₂ in air is not mixed with the combustion gases and inherent separation of CO₂ from other gases is performed with no costs or energy penalty for gas separation.

Chemical Looping Combustion (CLC) with gaseous fuels has been developed in the last few years, but using CLC with solid fuels has shown to have recently a great interest [5]. The use of coal in CLC is very attractive in future sceneries with restriction in CO₂

emissions, since coal will keep on being a main energy source in the medium-term. One option for CLC with solid fuels is directly to introduce coal in the fuel-reactor, which is fluidized by a gasification agent [6-9]. The reactor scheme of Chemical-Looping Combustion of solid fuels is shown in Fig. 1. In this technology coal is physically mixed with the oxygen-carrier in the fuel reactor where H₂O and/or CO₂ are used as fluidizing gas and gasifying agent. Thus, different processes are happening simultaneously in the reactor: (i) the pyrolysis and gasification of coal, where CO and H₂ are the main product, proceed according reactions (1-3); and (ii) the reaction of volatiles and gasification products with the oxygen-carrier to give CO₂ and H₂O, according reaction (4). The oxygen-carrier reduced in the fuel reactor, Me_xO_{y-1}, is transferred to the air reactor where reaction (5) with oxygen from air takes place. Thus the oxygen-carrier is regenerated to start a new cycle. The net chemical reaction is the same as usual combustion with the same combustion enthalpy.



The gasification process is expected to be the slower step in the fuel reactor, thus the mean residence time for char particles in the fuel reactor should be higher than for oxygen-carrier particles. To increase the mean residence time of char and to avoid unreacted carbon entering the air reactor, the char particles can be separated from the oxygen-carrier in a so-called carbon stripper and re-introduced to the fuel reactor.

The possibility of using the CLC technology for solid fuels has been showed at laboratory scale using different oxygen-carrier materials –e.g. Cu- or Fe-based particles–, and different solid fuels –e.g. coal, biomass, solid wastes, pet-coke– [7-10]. After the encouraging results obtained at laboratory scale, the feasibility of the CLC process for solid fuels in a continuously operated prototype was proven by Berguerand and Lyngfelt [11-12] using ilmenite as oxygen-carrier. A carbon stripper was designed between the fuel reactor and the air reactor to increase the residence time of char particles in the fuel reactor. Due to the characteristics of this facility, the volatiles do not

get in contact with oxygen-carrier particles. Thus, only the conversion of gases from steam gasification (CO and H_2) was analyzed. The importance of using high temperatures in this process was acknowledged [13] in order to have high conversion of the solid fuel to gases into the reactor. Also the effect of the mean residence time of char particles –determined by the solids circulation flow-rate– on its conversion in the fuel reactor was analyzed [14]. A higher circulation of solids reduced the mean residence time in the reactor and thus a lower efficiency of gasification was obtained. In general, high carbon capture efficiencies can be reached (82-96%) [11]. However, some fraction of unconverted gases (CO and H_2) were obtained in the outlet stream, which demanded about 5-7% of the total oxygen necessary to burn coal to CO_2 and H_2O when the fuel reactor temperature was 1000°C [13]. Furthermore, Cuadrat et al. [15] investigated the effect of operating conditions such as temperature and coal particle size on the combustion efficiency as well as on the extent of gasification in a continuous CLC rig. In this case, volatiles were generated inside the bed. Values for the oxygen demand of gases from 5% to 15% were found in all the experimental work, mainly due to unconverted CO and H_2 coming from devolatilization process. Nevertheless, the char gasification and combustion reactions are faster and promoted at higher temperatures. They concluded that high carbon capture efficiencies are expected to be obtained, as well as high combustion efficiencies, especially at temperatures higher than 950°C .

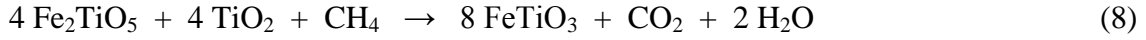
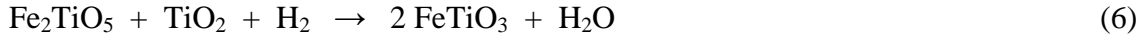
Most of the works involving CLC with solid fuels indicate that gasification is probably the rate-limiting step. Thus, in order to analyze the efficiency of carbon capture in a CLC system with solid fuels, the attention has been usually put on the reactivity of char gasification [10-19]. Some works have related the solids inventory in the fuel reactor to the reactivity of solid fuel. Thus, the residence time will be larger if a less reactive coal is used, and higher the needed solids inventory [20]. However, this fact is only true when the mean residence time of oxygen-carrier particles was the same order of magnitude than those for char particles. If a carbon stripper is used –as it was showed in Figure 1– the residence time of char particles in the fuel reactor can be increased without the need for increasing the oxygen-carrier inventory.

Nevertheless, to evaluate the performance of the fuel reactor in the CLC process with solid fuels, the reactivity of the oxygen-carrier must be also considered in addition to the gasification reactivity. Thus, the gasification kinetics and the reaction kinetics of

oxygen-carrier particles with reducing gases were considered by Brown et al. when they modelled the gasification and chemical-looping combustion of a lignite char in a fluidized bed of iron oxide particles [18]. The fraction of gases from coal gasification being converted to CO₂ and H₂O by the oxygen-carrier greatly depended on the oxygen-carrier reactivity. A more reactive oxygen-carrier gives higher conversion of gases to CO₂ and H₂O [21]. Nevertheless, unconverted CO, H₂, and CH₄ were found in the outlet gas even though highly reactive Ni-based materials were used. Unconverted gases come from both volatiles and gasification products [22,23]. Unconverted gases from gasification products are believed to be due to the characteristics of the char–oxygen-carrier mixing. Char gasification takes place throughout the fluidized-bed reactor. The gasification taking place in the upper part of the bed generates CO and H₂ which have not enough time to react with oxygen-carrier particles. So, some unconverted gases are expected to exit from the fuel reactor. This behaviour is fully different from the conversion of a fuel gas introduced at the bottom of the fluidized-bed reactor, where the fuel is gradually converted in the bed [24]. Thus, to evaluate the conversion of a solid fuel in a CLC system for solid fuels, both the reactivity of char gasification and oxygen-carrier material must be considered, in addition to the particular char–oxygen-carrier mixing pattern in the reactor.

A key factor for the CLC technology development is the oxygen-carrier material. Suitable oxygen-carriers for a CLC process must have high reactivity during reduction and oxidation, high attrition resistance and agglomeration absence. Low cost of the material is rather desirable for its use with coal, as it is predictable a partial loss together with the coal ashes when removing them from the reactor. Natural minerals are therefore very interesting materials for this purpose. In this context, ilmenite was identified by Leion et al. [25] as oxygen-carrier for solid fuels, proving to be an appropriate material for this scope. Ilmenite showed good fluidizing properties and only agglomeration problems were observed if ilmenite particles were reduced to a high extent, which is not expected at the CLC process. They also show a thermodynamic analysis showing that Fe³⁺ and Fe²⁺ can be involved during the redox cycles in a CLC system whereas the fuel gas can be fully oxidized into CO₂ and H₂O. Thus, Fe₂TiO₅ (i.e. Fe₂O₃·TiO₂) is the oxidized form, whereas FeTiO₃ (i.e. FeO·TiO₂) is the reduced form when ilmenite is used in CLC. Thus, the main reduction reactions, i.e. with H₂, CO or

CH₄ as reducing agents, proceed according reactions (6-8) and subsequent oxidation as reaction (9).



As for the reactivity, the reaction rate is quite high with syngas, and moderate with CH₄ [19,25,26]. Although ilmenite has initially a rather low reactivity to be used as oxygen-carrier, it undergoes an activation process after several redox cycles, being its reactivity remarkably increased for H₂, CO and CH₄ as reacting gases [26]. From a comparison among different iron oxide based minerals as well as oxide scale residues from the steel industry [27], ilmenite looks as a material highly reactive and adequate for its use as oxygen-carrier for CLC with solid fuels. In addition, natural ilmenite showed comparable reactivity with synthetic Fe₂O₃/MgAl₂O₄ particles with different solid fuels [17,21].

Ilmenite has been tested with solid fuels in batch tests and in continuously operated prototypes. In a batch fluidized-bed reactor, Leion et al. [20] found that ilmenite enhances the gasification rate of coal because the presence of oxygen-carrier particles reduces the fraction of H₂ in the bed, which has an inhibitory effect on the gasification. This fact has been observed as much for steam gasification as for CO₂ gasification using different oxygen-carrier materials [10,18]. Thus, the char gasification rate is increased as the inhibitor gas (H₂ or CO) decreases its concentration in the reactor because of the reaction with the oxygen-carrier. The char conversion is related to the reactivity of solid fuel particles [28], being the nature of the oxygen-carrier of lower relevance [20,21]. In addition, the type of fluidizing gas –which acts also as gasifying agent– and reacting temperature have a great influence on the char gasification. Thus, the fuel conversion was reduced when H₂O was replaced by CO₂ [29], but it was increased with the temperature [12,19,20]. The ilmenite material was also tested in continuous CLC systems. The good conversion of syngas using ilmenite has been showed in dual fluidized bed CLC systems [19,30]. The performance of ilmenite in the 10 kW_{th} continuous CLC system was analyzed with various solid fuels [11-13]. They concluded

that the low tendency for attrition or agglomeration of this material and its low market price make it an interesting option for use in CLC with solid fuels.

H₂ and CO from char gasification can account for a relevant oxygen demand in unconverted gases. Moreover, non-gasified char can pass to the air reactor, so losing carbon capture efficiency. Thus, the char gasification process and subsequent oxidation of H₂ and CO by the oxygen-carrier is an important issue to be considered in the CLC process. This work investigated the performance of ilmenite as oxygen-carrier in CLC for solid fuels through the reduction-oxidation cycles when using coal as fuel. Specifically, the conversion of char particles and the subsequent oxidation of gasification products with ilmenite were analyzed. Coal char was used as reducing agent, thus avoiding complex interpretation of the results due to volatiles conversion when coal is fed to the reactor.

The activation process of ilmenite particles was investigated when repeated redox cycles using coal char as reducing agent were carried out. Ilmenite activation with a solid fuel was compared to previous activation carried out by gaseous fuels. In addition, the effect of operating conditions (temperature, gas composition) on the char conversion and combustion efficiency of gasification gases were analyzed. Results here obtained will be later used to describe the effect of the char–oxygen-carrier mixing on the combustion efficiency by using a simplified reactor model, and to propose a way to optimize the solids inventory in a CLC system for solid fuels.

2. Experimental

2.1. Oxygen-carrier: ilmenite

Ilmenite is a common mineral found in metamorphic and igneous rocks. The ilmenite used in this work is a concentrate from a natural ore from Norway with a purity of 94.3%. Ilmenite particles are mainly composed of FeTiO₃, TiO₂ and Fe₂O₃. This ilmenite has shown good reactivity and excellent properties from both TGA and batch fluidized bed testing [17,20,25,26]. It has also been tested with solid fuels in continuously operated facilities [11-15].

As starting material, pre-oxidized ilmenite particles were used in this work. They were obtained by exposing fresh particles to a thermal pre-treatment at 950°C in air during 24 hours. The pre-oxidation was considered in order to get ilmenite in its most oxidized state [25], to improve properties and initial reaction rates [26], and to avoid defluidization problems [30]. The main properties for pre-oxidized ilmenite are showed in Table 1. The composition of pre-oxidized ilmenite was 54.7 wt.% Fe₂TiO₅, 11.2 wt.% Fe₂O₃, 28.6% TiO₂ and 5.5 wt.% of other inert compounds, mainly MgSiO₃. Thus, the Fe:Ti molar ratio was around 1:1. In the fully oxidized ilmenite, the iron was found to be as Fe³⁺, either in the Fe₂TiO₅ compound or as free Fe₂O₃. However, in the CLC process pseudobrookite (Fe₂TiO₅) and hematite (Fe₂O₃) are reduced to ilmenite (FeTiO₃) and magnetite (Fe₃O₄), respectively. Rutile is considered to be an inert. Higher reduction prevents the complete conversion of the fuel to CO₂ and H₂O because thermodynamic constrictions (Leion et al., 2008b). Thus, the oxygen transport capacity of ilmenite, $R_{O,ilm}$, was defined as the oxygen transport capacity useful for CLC, being calculated as

$$R_{O,ilm} = \frac{m_o - m_r}{m_o} \quad (10)$$

being m_o the mass of the most oxidized form of the oxygen carrier, and m_r the mass in the reduced form, i.e. a mixture of FeTiO₃ and Fe₃O₄.

2.2 Solid fuel: coal char

The fuel used was char coming from a devolatilized South African coal, which is, as for the ASTM, classified as medium volatile bituminous coal. To produce the char, batch of 500 g of coal particles were devolatilized in a fluidized-bed reactor. The reactor was fluidized by N₂ and it was heated up from room temperature to 900°C with a temperature ramp of 20°C/min and afterwards cooled down. Since the gas velocity increases with the temperature, the N₂ flow was correspondingly reduced as the temperature increased to ensure bubbling bed conditions and to avoid elutriation of particles. The proximate and ultimate analysis of the obtained char is shown in Table 2. The particle size of char was in the range 100-200 μm, and the density of the particles was about 1000 kg/m³.

2.3 Experimental setup: fluidized-bed reactor

The experimental work has been carried out in a setup consisting of a system for gas feeding, a solid fuel feeding system, a fluidized-bed reactor and the gas analysis system. A schematic layout of the laboratory setup is presented in Fig. 2. The fluidized-bed reactor –55 mm D.I. and 700 mm height– is electrically heated by a furnace, and had a preheating zone just under the distributor plate. The temperature inside the bed was measured and used to control the reaction temperature. The reactor had pressure taps in order to measure the absolute pressure in the bed and pressure drop. Agglomeration and defluidization problems could be detected by a sharp decrease in the bed pressure drop during operation. The pressure tap was also useful to detect possible blocking in the downstream pipes due to elutriated particles or tar condensation in cold points.

The reactor was loaded with 400 g of ilmenite with a particle size of +150-300 μm . In some tests silica sand (200-400 μm) was used instead of ilmenite. The feeding of the solid fuel was done by means of a fuel chute which ends 3 cm above the distributor plate and about 5-6 cm below the upper level of the fluidizing particles. So, char particles are fed inside the fluidized bed. The upper part of the chute has a valve system that creates a reservoir in which the fuel is placed and later pressurized by nitrogen to ensure quick char feeding.

The gas feeding system had different mass flow controllers connected to an automatic three-way valve. In this way, it was possible to feed alternatively air, nitrogen or a mixture of steam/ CO_2 . The steam was obtained by evaporation with a resistance heater of a known water flow supplied by a peristaltic pump. Different gas analyzers continuously measured the gas composition at the reactor exit after water condensation. 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. As in most of cases gas is mainly composed by steam, a downstream N_2 flow of 90 $\text{L}_\text{N}/\text{h}$ is introduced to ensure a continuous dry gas flow feeding the analyzers. This nitrogen is also later used to calculate the total outlet gas flow by a nitrogen balance.

2.4. Experimental procedure

The experimental work has been carried out in the fluidized-bed reactor above described at temperatures between 900 and 1000°C. The reactor was loaded with 400 g of ilmenite particles and they were exposed sequentially to reducing and oxidizing conditions. During reduction periods, char was used as fuel whereas the reactor was fluidized with steam, CO₂ or steam/CO₂ mixtures, which also acted as gasification agent. After every reducing period, ilmenite particles were fully re-oxidized with air before starting a new cycle. Between the reducing and oxidizing periods a N₂ flow was also introduced during 2 min to purge the system. The total fluidizing flow was 200 L_N/h, which corresponds to a gas velocity of 0.1 m/s at 900°C in the reactor.

During the reducing periods, batch loads of South African coal char were fed to the reactor through the solids feeding system. Char particles were fed by valve v1 to a small reservoir placed in the upper part of the fuel chute, see Fig. 2. After that, the deposit was over-pressurized 1 bar with N₂ by valve v2. Once the reservoir was pressurized, valve v2 was closed and v3 was opened and quickly closed. Then, char particles fall to the fluidized bed through the fuel chute as the reservoir is unpressurized. Thus, it was ensured that char particles were forced to enter to the fluidized bed, whereas a continuous flow of nitrogen through the fuel chute is avoided.

Two series of experiments were performed. The first tests were done to evaluate the evolution of the reaction rate of ilmenite particles with the cycle number. In this case, the reducing periods consisted in introducing 2 loads of char –1.5 g each load– using steam as fluidization gas at 900°C. A previous series of tests were done introducing char loads with different weight of fuel. The loads of 1.5 g resulted to be the loads with highest char quantity that could be fed with no major fuel entrainment. Every load was left till char gasification was complete. Thus, the evolution in the ilmenite reactivity was evaluated in successive redox cycles. Reduction-oxidation cycles were made until it could be considered that ilmenite had reached a constant reaction rate. Once ilmenite was activated and for the second series of experiments, a load of 1.5 g of South African coal char was introduced in the reactor in every reduction period. The reduction periods were 1800 s. The oxidation periods necessary for complete oxidation varied between 600 and 1800 s. The effect of temperature and gas composition on the reaction rates of

gasification and subsequent combustion of gasification products was analyzed, as well as the role of ilmenite during char gasification. The oxygen carriers were exposed to a total number of 50 reduction/oxidation cycles.

SEM pictures of the different samples, XRD analysis, as well as Hg porosimetry were carried out to see the changes undergone in the physical properties of ilmenite after various cycles when using a solid fuel as reducing agent. In addition, the reactivity of ilmenite particles during the activation period was analyzed by TGA experiments using 5 vol.% H₂ at 900°C.

3. Data evaluation

To analyze the performance of ilmenite during char gasification and combustion of gasification products, a mass balance to carbon, hydrogen and oxygen was done from the concentration of CO₂, CO, H₂ and CH₄ analyzed in every experimental condition. The molar gas flow of each component exiting the fuel reactor, F_i , is calculated as:

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

y_i being the molar fraction of the component i (CO₂, CO, H₂ or CH₄) in the product gas. The total dry basis outlet flow, F_{out} , can be calculated by using the downstream introduced N₂ flow, F_{N_2} .

$$F_{out} = \frac{F_{N_2}}{(1 - \sum_i y_i)} \quad (12)$$

The rate of char conversion, $r_C(t)$, was calculated from a mass balance to carbon in gaseous form in the reactor.

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

Methane was not considered in the carbon balance because it was not detected in any case. The evolution of char conversion, X_{char} , with time can be calculated by integrating Eq. (13).

$$X_{char}(t) = \frac{1}{N_{C,char}} \int_0^t r_C(t) dt \quad (14)$$

$N_{C,char}$ being the mol number of carbon fed into the reactor.

The instantaneous rate of conversion of the char, $r_{C,inst}$, is calculated as the rate of gasification per the amount of non-gasified carbon that is still in the reactor.

$$r_{C,inst}(t) = \frac{r_C(t)}{N_{C,char} - \int_0^t r_C(t) dt} \quad (15)$$

In addition, from the gas product distribution, it is possible to know the rate of oxygen transferred from ilmenite to the fuel gas, $r_O(t)$, which can be calculated by means of the following oxygen balance:

$$r_O(t) = F_{O_2,out} - F_{O_2,in} = [F_{out}(2y_{CO_2} + y_{CO}) - 2F_{CO_2,in}] + [F_{H_2O,out} - F_{H_2O,in}] \quad (16)$$

Note that in the experiments where CO_2 is fed to the reactor, the amount of CO_2 generated is represented and calculated by subtracting the inlet flow of CO_2 . Regarding the ultimate analysis it can be seen that the hydrogen and oxygen in the fuel used is negligible, and it was not considered in the mass balances, see Table 2. The flow of water at the reactor exit was calculated considering that the flow of hydrogen either in H_2 or H_2O comes only from introduced steam, $F_{H_2O,in}$. The hydrogen coming from char moisture was considered to be negligible.

$$F_{H_2O,out} = F_{H_2O,in} - F_{out} y_{H_2} \quad (17)$$

Thus, equation 13 can be reduced to:

$$r_O(t) = F_{out}(2y_{CO_2} + y_{CO} - y_{H_2}) - 2F_{CO_2,in} \quad (18)$$

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

$$X_{red}(t) = \frac{1}{N_{O,ilm}} \int_0^t r_O(t) dt \quad (19)$$

$N_{O,ilm}$ being the molar amount of oxygen in ilmenite active for CLC process, calculated as

$$N_{O,ilm} = \frac{m_o R_{O,ilm}}{M_o} \quad (20)$$

Finally, the conversion of gasification products, i.e. CO and H₂, to CO₂ and H₂O by reaction with ilmenite 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 fuel. Here, the combustion efficiency, η_c , is calculated with Eq. (21).

$$\eta_c(t) = \frac{r_o(t)}{2r_c(t)} \quad (21)$$

4. Results and discussion

In a previous work, an activation process of the ilmenite was observed when using gaseous fuels as reducing agents [26]. The activation process happened during ilmenite exposition to consecutive redox cycles. As activation proceeds, the reactivity increases but the oxygen transport capacity of ilmenite, $R_{O,ilm}$, decreases because of the appearance of free Fe₂O₃. After the activation period, reactivity of ilmenite was maintained roughly constant. Thus, prior to analyze the performance of ilmenite on gasification of char and subsequent combustion of gasification products, the activation

of ilmenite was carried out by doing consecutive redox cycles using char as fuel in the reduction period. After that, tests were carried out using the previously activated ilmenite varying the reaction temperature and the composition of the fluidizing gas.

4.1. Activation of ilmenite with coal char

In the first series of experiments, 16 consecutive redox cycles in batch fluidized bed were carried out using pre-oxidized ilmenite as starting material. Steam was used as fluidizing gas. Every reduction period consisted of two consecutive loads of 1.5 g of char. After the reduction period, the bed material was oxidized by air. The second load in the same period was fed to get further reduction of the oxygen carrier.

Figs. 3a), 3b) and 3c) show the evolution in the flow of CO₂, CO and H₂ corresponding to the initial 10 redox cycles. No CH₄ was observed during any test, since the volatile matter content in the fuel is negligible and no methane was generated at these conditions, e.g. by methanation of hydrogasification reactions. Just after introducing the char load, the concentration of CO₂, CO and H₂ had their maximum values and then decreased over time. This fact is evident as there was less remaining char in the reactor. In addition, the second loads showed similar profiles than the first ones. Differences can be attributed to experimental error. The final conversion of ilmenite after the reducing period was lower than 12 % in all cases, which are quite low and therefore no oxygen depletion effect in the ilmenite was seen. When the effect of consecutive redox cycles on the concentration of gases is analyzed, it can be seen that there is an increase in the production of CO₂ and a decrease in the gasification products (H₂ and CO) in the product gas with the cycles. After several redox cycles the CO₂ concentration achieves the highest value and no further substantial increase on CO₂ concentration or decrease on CO or H₂ concentration was observed. It seems that an activation process was happening, where the reactivity of ilmenite was increased, and the gas conversion of CO and H₂ to CO₂ and H₂O was increased during the initial 6 or 7 cycles. After that, ilmenite reactivity stabilizes and no further substantial increase in gas conversion was taking place.

To confirm the activation process, reactivity of ilmenite samples withdrawn from the reactor after 1, 3, 7, 10, 13 and 16 cycles was determined by thermogravimetric

analysis. The conversion vs. time curves obtained from TGA experiments are shown in Fig. 4. For comparison purposes, the conversion curves for pre-oxidized and fully activated ilmenite are also shown. The conversion curve for fully activated ilmenite was taken from activated ilmenite after 20 cycles using H₂ as reducing gas, as it was shown in a previous work [26]. The conversion during reduction reaction, X_{red} , and oxidation reaction, X_{ox} , were determined from the mass variation of solid samples in TGA by using Eqs (22) and (23), respectively.

$$X_{red} = \frac{m_o - m}{R_{O,ilm} m_o} \quad (22)$$

$$X_{ox} = \frac{m - m_r}{R_{O,ilm} m_o} \quad (23)$$

m being the instantaneous mass of the solid sample as the reaction proceeds.

For the reduction reaction, it can be seen in Fig. 4a) that the reaction rate mostly increases during the initial redox cycles. After one cycle, the reactivity increase is very important, and ilmenite can be considered activated after 7 cycles. On the contrary, for oxidation the activation process is slower than for reduction, see Fig. 4b). Indeed, ilmenite is not completely activated after 16 redox cycles for the oxidation reaction. In a previous work [31] it was determined that oxidation reaction proceeds in two consecutive steps: the first one controlled by chemical reaction and the second one controlled by diffusion of gases in the product layer. The second step is influenced by the porosity of the solid, and the conversion at which the product layer diffusion begins to control the reaction rate increases with the particle porosity. Thus, porosity of the ilmenite samples were determined by mercury porosimetry. Samples for ilmenite after 1, 3, 7, 10, 13 and 16 cycles have, respectively, porosities of 2, 3.8, 5.9, 8.5 and 12.6%. However, the porosity for a fully activated particle was 27.5%.

The two steps above described in the oxidation reaction can be clearly seen in Fig. 4b). The reactivity of the first step was maintained roughly constant in all cases, but the conversion at which the controlling mechanism is shifted increases with the cycle number, i.e. as the porosity of ilmenite particles increases.

To observe changes in the solid structure throughout consecutive redox cycles, a morphological characterization of several samples was performed by SEM. Fig. 5 shows SEM images of pre-oxidized particles and after 3 and 13 cycles. Pre-oxidized ilmenite shows a granular structure with little porosity development. There is a continuous development of porosity as well as the granulation is enhanced during redox cycles. The development of the granular structure and porosity leads to a reactivity increase with the cycle number. These observations follow the same pattern as when using gaseous fuels [26].

Furthermore, the possible variation in the oxygen transport capacity of ilmenite, $R_{O,ilm}$, with the cycle number has been analyzed. The oxygen transport capacity of several samples withdrawn from the reactor after 1, 3, 7, 10, 13 and 16 cycles was measured with TGA at 900°C using 5 vol.% H₂ and 40% H₂O in the reacting gases. At this condition, iron compounds in the fully reduced sample appear as FeTiO₃ or Fe₃O₄, i.e. the oxygen transport capacity useful for CLC is directly measured from the mass variation between the oxidized and reduced form. The oxygen transport capacity barely decreased with the cycle number. After 16 redox cycles with char there was only a very slight decrease in the measured $R_{O,ilm}$ value from 4 % to 3.9 %.

Previous work [26] showed that the oxygen transport capacity of ilmenite, $R_{O,ilm}$, got reduced gradually with the number of cycles. The reason for that was the migration of iron towards the outer surface of the particle creating an external shell of free Fe₂O₃. The initial $R_{O,ilm}$ value was 4%, and it decreased until 2.1% after 100 redox cycles because the Fe₂O₃ fraction increased with the cycle number at expenses of decreasing the fraction of Fe₂TiO₅.

SEM images show that in this work, the outer shell observed in the previous work is not formed. In addition, XRD analysis showed that the share of iron compounds between Fe₂TiO₅ and Fe₂O₃ was not affected by the cycle number in the fully oxidized samples. Thus, the composition described in Section 2.1 for pre-oxidized ilmenite was maintained roughly constant during the activation period. This fact confirms that the oxygen transport capacity –which depends on the share of iron– was barely affected by the number of cycles.

Thus, during the activation period showed in this work, the migration of iron was not observed as in previous work using gaseous fuels [26]. The difference between both cases can be found in the extent of ilmenite reduction happening in every redox cycle because the iron migration was enhanced as the reduction conversion increased [26]. In experiments showed in this work, ilmenite conversion was as low as 8 % in the first cycle and increased to 12 % after the activation period, i.e. 6th-7th cycle. These values were lower than the final conversion reached in previous tests with gaseous fuels. Thus, the migration of iron was not promoted at low ilmenite conversion values as in experiments carried out in this work, and it seemed not be affected by the fact that the initial fuel is gaseous or solid. Iron migration would be expected with higher conversion values or more redox cycles.

The effect of the activation process on the char gasification was analyzed by considering the rate of char conversion, $r_C(t)$, as the total flow of CO₂ and CO exiting from the reactor, as it is shown in Fig. 6. When the evolution of carbon in the gases is analyzed with the cycle number, it was observed a slight increase in the rate of char conversion during the initial 6-7 cycles and then it was maintained roughly constant. Thus, the char gasification is being affected in some mode by the increase of reactivity of ilmenite. Likely, the lower concentrations of H₂ and CO –which present an inhibitory effect on the char gasification– as ilmenite is being activated increased the gasification rate with the initial 6-7 cycles.

Regarding the differences in the density and particle size used for char and ilmenite particles, some char particles could be segregated to the top of the fluidized bed. Thus, some unconverted H₂ and CO could not have been in contact with the oxygen-carrier if they came from the gasification of segregated char particles. However, in that case the increase in ilmenite reactivity would have a lower effect on the H₂ and CO concentrations. Therefore, the effect of the possible segregation of the char particles on the gas distribution would be of low relevance.

All the following tests were performed with the so-called activated ilmenite, which has constant reactivity in the reducing reaction. Thus, the effect of the variation in ilmenite reactivity on the evaluation of the results can be ignored.

4.2. Role of ilmenite in char gasification

The effect of ilmenite as oxygen-carrier in the gasification process was evaluated by comparing the gas product distribution obtained using ilmenite or silica sand as bed material, see Fig. 7. Obviously, ilmenite has an effect on the gas distribution. It reacts with CO and H₂ and gives CO₂ and H₂O. Furthermore, the selectivity of ilmenite towards the reaction with H₂ or CO also can be observed. Thus, the ratio CO/H₂ in the product gas for sand is about 0.7, whereas is 2.8 for ilmenite because the reaction with H₂ is faster than with CO [31].

Fig. 8 shows the instantaneous rate of char conversion, $r_{C,ins}(t)$, when ilmenite or sand is used as bed material. The $r_{C,ins}$ values were higher for ilmenite than for sand. The positive effect of the oxygen-carrier in the gasification process has already been proven in several studies [10,18,20]. The use of ilmenite improves the gasification since the concentrations of H₂ and CO decreased, which are well known to be inhibitors for gasification. In both cases, a slight tendency towards the increase in the instantaneous rate of char gasification with char conversion is observed. Average values of char conversion rate of 10.9 %/min for ilmenite and of 6.5%/min for sand were obtained at 950°C using steam. Only average rates for char conversion between 0.35 and 0.75 were considered as representative of the process. So, it was avoided any possible effect of the back-mixing at the beginning or mathematical errors introduced at the end of the period when the concentrations or remaining char are too low.

Usually, the gasification process is explained by the homogeneous model or the random pore model [32]. If a random pore model was fulfilled the instantaneous rate goes through a maximum, which was not observed. If gasification followed a homogeneous model, the instantaneous rate of char conversion should be constant with the char conversion. From these batch tests and the resulting gas profiles (see Fig. 7), no conclusive statement about what the gasification model is for this fuel can be drawn up. However, a study made by TGA analysis on char gasification of this fuel showed that it follows a homogeneous model [33]. The slight increase in the rate of char gasification observed in these batch tests could be explained by an increase in the gasification rate because there was lower concentration of H₂ –which inhibits steam gasification–in the reacting gas as the char was being converted.

In addition, for comparison purposes tests were performed using N_2 as fluidizing gas and ilmenite or sand as bed material. Here, the rate of char gasification represents the flow of carbon species (CO_2 and CO) exiting in the gas stream. In this case, the evolution of carbon species to the gas stream was low when ilmenite was used, whereas no CO_2 or CO was detected when sand was used. Thus, fuel oxidation is exclusively performed by the solid-solid reaction among char and oxygen-carrier [34], which depends on the surface of contact between solids and the type of contact [35]. However, it can be observed a substantial increase in the rate of char gasification when a gasification agent (H_2O) is used as fluidizing gas. Therefore, the conversion of the solid fuel when is fluidized with H_2O is mainly happening through gasification as an intermediate step, with CO and H_2 as intermediate products, see Eqs. (1-4). In this case, solid-solid reaction between char and ilmenite particles would be negligible, which agreed to results previously obtained by other authors [10,18].

4.3. Effect of the fluidizing gas composition

As much H_2O as CO_2 has been proposed as fluidizing gas because both of them can act as gasifying agent. Indeed, several works have analyzed the gasification in the CLC process for solid fuels using either H_2O [10,20,25,27] or CO_2 [7,18,29]. CO_2 can be fed by recirculating a fraction of the product gas stream, as it was indicated in Fig. 1. Thus, the steam requirements for the gasification would be decreased in some extension if a mixture of CO_2 and H_2O was used, or even avoided if a pure stream of CO_2 was used as fluidizing gas.

Here, the effect of using a gas mixture of CO_2 and H_2O on the gasification of char particles from the South African bituminous coal was analyzed. Fig. 9 shows the instantaneous rate of char gasification, $r_{C,inst}(t)$, as a function of the char conversion when the reactor was fluidized by different $H_2O:CO_2$ mixtures, and Fig. 10 shows the char conversion reached throughout the time obtained from the gas distribution products by using Eq. (14). The instantaneous rate of char conversion increased significantly as higher was the H_2O percentage in the gasification gas. Thus, the average gasification rate of char from South African bituminous coal dropped from 10.9 %/min for steam to a value of 3.4 %/min for gasification with CO_2 . For 100% steam, most of the char is

gasified the first 30 minutes, whereas only 60% char conversion was reached after 30 minutes with CO₂.

To make comparisons about the use of H₂O:CO₂ mixtures as fluidizing gas it was considered the use of the half-life time, t_{50} , defined as the reacting time necessary to reach 50% of char conversion. In addition, the time to convert 95% char, t_{95} , which has been taken in other works [10,20] as a reference value to determine the residence time to mostly convert the char in the reactor, has been considered. Values of t_{50} and t_{95} were calculated from the following equations assuming the gasification reaction follows the homogeneous model.

$$\frac{1}{1 - X_{char}} \frac{dX_{char}}{dt} = r_{C,inst} \Rightarrow r_{C,inst} \cdot t = -\ln(1 - X_{char}) \quad (24)$$

Thus, the residence time to reach a conversion X_t , i.e. t_X , was obtained as:

$$t_X = -\frac{1}{r_{C,inst}} \ln(1 - X_t) \quad (25)$$

Table 3 shows the t_{50} values for different H₂O:CO₂ ratios, that is when $X_t = 0.5$. The half-life of char particles when fluidizing with 30% CO₂ is two times in comparison to 100% H₂O, whereas is three times when fluidizing with 100% CO₂. Furthermore, Table 3 also shows the t_{95} values for different H₂O:CO₂ ratios. Thus, the residence time of char particles in the fuel reactor should be 27.5 min when H₂O is used as gasifying agent, being increased up to 88.1 min if CO₂ was used. In addition, the introduction of 10 vol.% CO₂ in the fluidizing gases gives an increase of nearly 50% in the residence time necessary to convert char particles. From these results it can be concluded that steam seems to be the more adequate fluidizing gas for the South African coal used in this work. The case could be different for other type of coal, as lignite, which shows high reactivity for gasification with CO₂ [18,36].

In this technology, the gasification products, mainly composed of CO+H₂, must react with the oxygen-carrier getting oxidized. Thus, the reactivity of the oxygen-carrier with the gasification products will affect the combustion efficiency in the fuel reactor, and

also must be analyzed in order to fully understand the performance of the fuel reactor [18]. Fig. 11 shows the evolution of combustion efficiency, η_c , with the char conversion for different H₂O:CO₂ ratios. The combustion efficiency decreases as the CO₂ content in the fluidizing gas increases, in spite of the flow of gasification products which must react with a constant amount of ilmenite decreases as it was discussed above (see Fig. 9). Nevertheless, although the flow of reacting gases is lower, they are enriched in CO by reaction (3). That is, the outgoing H₂ flow decreases when using CO₂ as gasification agent, which leads to a worse combustion, since ilmenite reacts slower with CO than with H₂ [31]. Thus, not only the gasification step, but the oxidation is proven to be also influenced by the gasification agent.

Besides, when gasifying with 100% steam some H₂ was measured, but for the H₂O:CO₂ mixtures no H₂ was measured in the product gas. Here, the water-gas shift (WGS) reaction, see Eq. (26), it is believed to have low relevance in the CO generation because the gas composition is far away from WGS equilibrium. This is confirmed by the small amounts of H₂ obtained in the reactor outlet.



In addition, it can be seen in Fig. 11 that the combustion efficiency is maintained roughly constant with the char conversion, although the flow of gasification products, i.e. H₂ and CO, decreased as char is being converted. Thus, a constant amount of ilmenite (that existing in the reactor) is not able to better oxidize a lower flow of reacting gas (that is H₂ and CO). This means that the rate of oxygen transferred from ilmenite to the fuel, r_O , decreases as the amount of char remaining in the bed decreases. This decrease in the reaction rate of ilmenite is due to a lower concentration of H₂ and CO in the reacting gas mixture.

4.4. Effect of the reacting temperature

The effect of the reacting temperature on the gasification rate and the subsequent conversion of gasification products by reaction with ilmenite particles were studied in the batch fluidized bed. Fig. 13 shows the instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion when the reactor temperature was 900, 950

or 1000°C and fluidizing gas was steam or CO₂. It can be seen an important increase in the rate of char conversion with temperature when steam is used as gasifying agent. Thus, the average $r_{C,inst}$ value increases from 10.9 %/min at 900°C up to 37.3 %/min at 1000°C. The values here obtained are in concordance with the previous results and evidence the great influence of the temperature in the gasification process [10,20]. On the contrary, the gasification rate with CO₂ is not increased in the same proportion. Thus, the average $r_{C,inst}$ value increases from 3.4 %/min at 900°C up to 6.9 %/min at 1000°C. Table 4 resumes the average $r_{C,inst}$ values for the different temperatures. The apparent activation energy, E_a , can be calculated from these values assuming an Arrhenius type dependence with the temperature, thus calculating that $E_a = 162$ kJ/mol for steam gasification and $E_a = 88$ kJ/mol for gasification with CO₂.

Table 4 shows the t_{50} and t_{95} values for the different tests performed at various temperatures with steam and CO₂ as gasification agents. It can be seen that high temperature using steam as gasification agent is preferred in order to reduce the residence time of char particles to be gasified. So, the residence time to convert 95 % of char fed to the reactor is 7.8 min at 1000°C for char particles used (+100-200 μm) using steam, whereas 43.4 min should be necessary using CO₂.

Regarding the oxidation of gasification products by reaction with ilmenite, Fig. 14 shows the combustion efficiency, η_c , at different temperatures when the fluidization gas was steam or CO₂. For both gasification agents the combustion efficiencies are promoted with the temperature, as ilmenite reacts faster at higher temperatures. However, the dependence of η_c with temperature was of lower relevance that those showed for char gasification, see Fig. 13. The combustion efficiency for steam is very high and increases from about 89% at 900°C to 95% at 1000°C. For CO₂ η_c rises from about 59% at 900°C to 65% at 1000°C. H₂ is generated as a gasification product when H₂O is present in the fluidizing gas, whereas CO is the only gasification product when using CO₂. In a previous study on ilmenite kinetics, H₂ was proved to have higher reaction rate ilmenite than CO [31]. The differences seen in the combustion efficiencies when using H₂O or CO₂ as fluidizing agents lie in the generation of the more reactive gas H₂ when gasifying with H₂O.

4.5. Theoretical approach

The conversion of char in the fuel-reactor will determine the carbon capture efficiency of the CLC system with coal. A theoretical study in the fuel-reactor was done to get further valuable information about the char conversion in the CLC system. Considering the fuel-reactor as control volume, the simplified mass balance for carbon in char can be expressed with Eq. (27).

$$F_{C,in} + F_{C,r} = F_{C,out} + F_{C,g} \quad (27)$$

The carbon inlet flows to the fuel-reactor are: (1) the incoming carbon flow in char with the coal feed, $F_{C,in}$, and (2) the carbon flow that is separated by the carbon stripper and recirculated back to the fuel-reactor, $F_{C,r}$. The carbon outlet flows from the fuel-reactor are: (1) the remaining carbon in char exiting the fuel-reactor, $F_{C,out}$, and (2) the gasified carbon, exiting as part of the product gas, $F_{C,g}$. The following carbon balance was done to the carbon stripper:

$$F_{C,out} = F_{C,AR} + F_{C,r} = \frac{F_{C,AR}}{1 - \eta_{CS}} = \frac{F_{C,r}}{\eta_{CS}} \quad (28)$$

$F_{C,AR}$ being the carbon flow passing to the air-reactor and η_{CS} the efficiency of separation in the carbon stripper. The flow of gasified carbon was calculated as

$$F_{C,g} = r_{C,inst} \cdot m_C \quad (29)$$

$r_{C,inst}$ being the instantaneous char gasification rate, as defined in Eq. (15), and m_C the mass of carbon in the fuel-reactor. m_C was calculated assuming that a perfect mixing of solids in the fuel-reactor and a constant reaction rate for the char particles. Thus, the carbon concentration in the fuel-reactor, C_C , is equal to that in the outlet stream of solids.

$$C_C = \frac{F_{C,out}}{F_{ilm} + F_{C,out}} = \frac{m_C}{m_{ilm} + m_C} \quad (30)$$

F_{ilm} being the circulation flow of ilmenite and m_{ilm} the mass of ilmenite in the fuel-reactor. After some algebra arrangements with Eqs. (27-30), char conversion, X_C , is calculated as:

$$X_C = \frac{F_{C,in} - F_{C,AR}}{F_{C,in}} = 1 - \frac{F_{ilm}(1 - \eta_{CS})}{r_{C,inst} \cdot m_{ilm} + F_{ilm}(1 - \eta_{CS})} \quad (31)$$

Char conversion was defined as the fraction of carbon introduced with the char feed that exits as gaseous product from the fuel-reactor. Thus, char conversion can be easily calculated knowing the char gasification rate, $r_{C,inst}$, and giving some design and operational parameters, i.e. the circulation flow rate of ilmenite, F_{ilm} , the ilmenite inventory in the fuel-reactor, m_{ilm} , and the carbon stripper efficiency, η_{CS} .

The reactivity data showed in this work for char from a South African coal were used to calculate the char conversion at different operating conditions, see $r_{C,inst}$ in Tables 3 and 4. Table 5 shows the proximate and ultimate analysis of this coal. Taking 1 MW_{th} as reference value and considering $R_{O,ilm}=4.0$ wt%, the stoichiometric circulation flow rate of ilmenite to fully convert coal to CO₂ and H₂O was 2.1 kg/s, i.e. with an oxygen-carrier to fuel ratio $\phi = 1$. Abad et al. [24] showed that the optimum oxygen-carrier to fuel ratio was in the range 2.5 to 5. Thus, a ϕ value of 3 was here chosen for simulations. In addition, 200 kg/MW_{th} was considered as ilmenite inventory during first approach. In a previous work, it was estimated that 200 kg/MW_{th} would be enough to burn 95% of the gasification products [31].

Firstly, it was considered that the system had no carbon stripper, i.e. $\eta_{CS} = 0$. Fig. 15a) shows the effect of temperature in the calculated char conversion using steam or CO₂ as gasification agents. It can be seen that the char conversion reached a very low value even at 1000°C with steam as gasification agent, for which only 17% of char is gasified. Lower values were obtained at lower temperatures or using CO₂ as gasification agent because of the lower gasification reactivity. This fact evidences the need of a carbon stripper unit in order to separate a fraction of the non-gasified char and re-introduce it to the fuel-reactor. Thus, the residence time of char particles in the fuel-reactor will be

increased. Fig. 15b) shows the char conversion with steam at 1000°C as a function of the carbon stripper efficiency, η_{CS} . The char conversion is correspondingly increased with the carbon stripper efficiency. If 90% of char conversion is desired, the carbon stripper efficiency must be about 95%. Obviously, if the carbon separation efficiency is $\eta_{CS} = 1$, all carbon is gasified and no carbon is passing to the air-reactor. Fig. 15b) also shows the carbon concentration in the fuel-reactor. Thus, the carbon concentration increases with the carbon stripper efficiency. This fact will be relevant for the carbon stripper design.

Considering a reasonable carbon stripper efficiency of 90%, in order to ensure high char conversion efficiencies, higher ilmenite inventories are needed. Fig. 15c) displays the char conversion with steam at 1000°C calculated for increasing ilmenite inventory ($\eta_{CS} = 90\%$). The char conversion rapidly increases until a solids inventory about 500-1000 kg/MW_{th}. Thus, the char conversion increased from 67% with 200 kg/MW_{th} to 91% with 1000 kg/MW_{th}. Further increase in the solids inventory has a minor effect on the char conversion. To increase the solids inventory above 1000 kg/MW_{th} would not be therefore recommended.

These results show the reliability of the process using ilmenite as oxygen-carrier. High carbon capture efficiency can be obtained or by optimizing the carbon stripper design or by increasing the solids inventory. The following question is to know the fraction of gasification products that will be converted to CO₂ and H₂O by reaction with ilmenite particles. This task needs to consider simultaneously the reaction kinetics of the gaseous products with ilmenite and the gas flow throughout the reactor.

5. Conclusions

An analysis of the char gasification in presence of ilmenite particles –which act as oxygen-carrier– was carried out to determine key parameters in Chemical-Looping Combustion of coal. Both, char gasification and ilmenite reactivity were evaluated through consecutive redox cycles using char particles coming from devolatilization of South African bituminous coal. The activation process of ilmenite particles as well as the effects of the fluidization gas and temperature were studied.

For the reduction reaction, ilmenite increases its reactivity relatively fast during the initial redox cycles. Seven redox cycles are enough to fully activate ilmenite particles when coal char was used as fuel. However, ilmenite was not activated yet for the oxidation reaction even after 16 redox cycles, because of the low variation of the ilmenite conversion in every cycle. At this condition, porosity was not developed at enough extension to overcome diffusion restrictions in the oxidation reaction. Besides, the oxygen transport capacity of the ilmenite particles barely changed with the redox cycles.

Regarding the char conversion, lower concentration of H_2 and CO enhanced the gasification reaction. Thus, a relevant increase in the gasification rate was observed when ilmenite instead of an inert substance was used as bed material. Moreover, the gasification rate itself raises slightly by the increase of ilmenite reaction rate during activation period, and gasification is improved as the generated H_2 and CO decreases with the char conversion.

Steam is preferred as gasification agent as CO_2 , since gasification rate is higher. Even if low fraction of CO_2 was present in the feeding gas stream, the gasification rate was appreciably decreased. In addition, high temperature enhanced in high extent the steam gasification. Thus, the residence time to convert 95 % of char fed was decreased from 27.5 min at $900^\circ C$ to 7.8 min at $1000^\circ C$ using char from South African bituminous coal (+100-200 μm).

The later combustion of the gasification products with ilmenite is also influenced by the gasifying agent, as gasification with H_2O generates more H_2 that is more reactive with ilmenite and on the other hand gasification with CO_2 produces more CO . The resulting combustion efficiency is therefore higher when gasifying with increasing H_2O/CO_2 ratio. Moreover, the combustion efficiencies have turned out to be quite constant as char is further converted. A rise in the operation temperature also causes an increase in the combustion efficiencies, since ilmenite reaction rates are promoted.

A mass balance to the fuel-reactor and carbon stripper was done in order to know the conversion of char in the system. The use of a carbon stripper was found to be essential in order to reach high values of char conversion by gasification in the fuel-reactor. The

optimal range of solids inventory in the fuel-reactor that leads to high char conversions (around 90%) was found in the range 500-1000 kg/MW_{th}.

Notation

C_C = char concentration in the fuel reactor bed

$F_{CO_2,in}$ = CO₂ flow introduced in the fuel reactor (mol/s)

$F_{C,AR}$ = carbon flow in char that enters the air reactor (mol/s)

$F_{C,g}$ = gasified carbon flow exiting as part of the product gas (mol/s)

$F_{C,in}$ = carbon flow in char fed with the fuel flow (mol/s)

$F_{C,out}$ = carbon flow in char leaving the fuel reactor (mol/s)

$F_{C,r}$ = carbon flow in char recirculated back to the fuel reactor (mol/s)

$F_{H_2O,in}$ = H₂O flow introduced in the fuel reactor (mol/s)

$F_{H_2O,out}$ = molar gas flow of H₂O in the product gas (mol/s)

F_i = molar gas flow of each component i (CO₂, CO, H₂ or CH₄) in the product gas (mol/s)

F_{ilm} = ilmenite flow between reactors (mol/s)

F_{N_2} = downstream introduced N₂ flow (mol/s)

$F_{O_2,in}$ = total introduced oxygen flow in the fuel reactor (mol O₂/s)

$F_{O_2,out}$ = total oxygen flow exiting the fuel reactor (mol O₂/s)

F_{out} = total dry basis outlet gas flow (mol/s)

m = instantaneous mass of the ilmenite sample (kg)

m_C = mass of char in the fuel reactor bed (kg)

Me_xO_y = oxidized form of the oxygen carrier

Me_xO_{y-1} = reduced form of the oxygen carrier

m_{ilm} = ilmenite inventory in the fuel reactor (kg/MW_{th})

m_o = mass of the oxidized form of the oxygen carrier (kg)

m_r = mass of the reduced form of the oxygen carrier (kg)

$N_{o,ilm}$ = molar amount of oxygen in ilmenite active for CLC process (mol)

$N_{C,char}$ = mol number of carbon fed into the reactor (mol)

$R_{o,ilm}$ = oxygen transport capacity of ilmenite

$r_C(t)$ = rate of char conversion (mol/s)

$r_{C,inst}$ = instantaneous rate of char conversion (s^{-1})

$r_O(t)$ = rate of oxygen transferred from ilmenite to the fuel gas (mol/s)

t = time (s)

t_{50} = time to convert 50% char (s)

t_{95} = time to convert 95% char (s)

t_X = residence time to reach a conversion X_t

X_{char} = char conversion

X_{ox} = conversion of ilmenite for the oxidation reaction

X_{red} = conversion of ilmenite for the reduction reaction

X_t = char conversion reached with a residence time t_X

y_i = being the molar fraction of the component i (CO_2 , CO , H_2 or CH_4) in the product gas

η_{CS} = carbon stripper efficiency

η_C = combustion efficiency

Acknowledgments

This work was partially supported by the European Commission, under the RFCS program (ECLAIR Project, Contract RFCP-CT-2008-0008), from Alstom Power Boilers and by the Spanish Ministry of Science and Innovation (Project ENE2010-19550). A. Cuadrat thanks CSIC for the JAE Pre. fellowship. Alberto Abad thanks to the Ministerio de Ciencia e Innovación for the financial support in the course of the I3 Program.

References

- [1] IPCC Fourth Assessment Report – Climate Change 2007. Summary for Policymakers. Available at <http://www.ipcc.ch>.
- [2] IEA Statistics. CO₂ emissions from fuel combustion – Highlights. 2010 edition. Available at <http://www.iea.org/co2highlights/co2highlights.pdf>
- [3] Energy Technology Perspectives 2008: Scenarios and strategies to 2050. Executive Summary. IEA.
- [4] Lyngfelt A. Oxygen carriers for chemical-looping combustion – operational experience. Proceedings of the 1st International Conference on Chemical Looping, Lyon (France), 2010.
- [5] Fan L-S, Li F. Chemical Looping Technology and Its Fossil Energy Conversion Applications. *Ind Eng Chem Res* 2010; 49 (21):10200–10211.
- [6] Cao Y, Pan WP. Investigation of Chemical Looping Combustion by Solid Fuels. 1.Process Analysis. *Energy Fuels* 2006;20:1836-1844.
- [7] Cao Y, Casenas B, Pan WP. Investigation of Chemical Looping Combustion by Solid Fuels. 2. Redox Reaction Kinetics and Product Characterization with Coal, Biomass, and Solid Waste as Solid Fuels and CuO as an Oxygen Carrier. *Energy Fuels* 2006;20:1845-1854.
- [8] 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;79:187-190.
- [9] Scott SA, Dennis JS, Hayhurst AN, Brown T. In Situ Gasification of a Solid Fuel and CO₂ Separation using Chemical Looping. *AIChE J* 2006;52:3325-3328.
- [10] Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* 2007;86:1947-1958.
- [11] Berguerand N, Lyngfelt A. Design and operation of a 10 kWth chemical-looping combustor for solid fuels – Testing with South African coal. *Fuel* 2008;87:2713-2726.
- [12] Berguerand N, Lyngfelt A. The use of petroleum coke as fuel in a 10 kWth chemical-looping combustor. *Int J Greenhouse Gas Control* 2008;2:169-179.
- [13] Berguerand N, Lyngfelt A. Chemical-Looping Combustion of Petroleum Coke Using Ilmenite in a 10 kWth Unit – High-Temperature Operation. *Energy Fuels* 2009;23:5257-5268.

- [14] Markström P, Berguerand N, Lyngfelt A. The application of a multistage-bed model for residence-time analysis in chemical-looping combustion of solid fuel. *Chem Eng Sci* 2010;65:5055-66.
- [15] Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego LF, Adánez J. The use of ilmenite as oxygen-carrier in a 500 Wth Chemical Looping Coal Combustion unit. Submitted to publish.
- [16] Berguerand N, Lyngfelt A. Batch testing of solid fuels with ilmenite in a 10 kWth chemical-looping combustor. *Fuel* 2010;89:1749-62.
- [17] Azis MM, Jerndal E, Leion H, Mattisson T, Lyngfelt A. On the evaluation of synthetic and natural ilmenite using syngas as fuel in chemical-looping combustion (CLC). *Chem Eng Res Des* 2010; 88(11):1505-1514.
- [18] 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 Oxide. *Energy & Fuels* 2010;24:3034-48.
- [19] Bidwe AR, Mayer F, Hawthorne C, Charitos A, Schuster A, Scheffknecht G. Use of ilmenite as an oxygen carrier in Chemical Looping Combustion – Batch and continuous dual fluidized bed investigation. *Energy Procedia* 2010, in press.
- [20] Leion H, Mattisson T, Lyngfelt A. Solid fuels in chemical-looping combustion. *Int J Greenhouse Gas Control* 2008;2:180-193.
- [21] Leion H, Lyngfelt A, Mattisson T. Solid fuels in chemical-looping combustion using a NiO-based oxygen carrier. *Chem Eng Res Des* 2009;87:1543-1550.
- [22] Gao Z, Shen L, Xiao J, Qing C, Song Q. Use of Coal as Fuel for Chemical-Looping Combustion with Ni-Based Oxygen Carrier. *Ind Eng Chem Res* 2008;47:9279-9287.
- [23] Shen L, Wu J, Xiao J. Experiments on chemical looping combustion of coal with a NiO based oxygen carrier. *Combustion and Flame* 2009;156:721-728.
- [24] Abad A, Adánez J, García-Labiano F, de Diego LF, Gayán P, Celaya J. Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chem Eng Sci* 2007;62:533-549.
- [25] Leion H, Lyngfelt A, Johansson M, Jerndal E, Mattisson T. The use of ilmenite as an oxygen carrier in chemical-looping combustion. *Chem Eng Res Des* 2008;86:1017-26.

- [26] Adáñez J, Cuadrat A, Abad A, Gayán P, de Diego L.F, García-Labiano F. Ilmenite Activation during Consecutive Redox Cycles in Chemical-Looping Combustion. *Energy & Fuel* 2010;24:1402-1413.
- [27] Leion H, Jerndal E, Steenari B-M, Hermansson S, Israelsson M, Jansson E, Johnsson M, Thunberg R, Vadenbo A, Mattisson T, Lyngfelt A. Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers. *Fuel* 2009;88:1945-1954.
- [28] Linderholm C, Cuadrat A, Lyngfelt A. Chemical-looping combustion of solid fuels in a 10 kWth pilot – batch tests with five fuels. *Energy Procedia* 2010, in press.
- [29] Leion H, Mattisson T, Lyngfelt A. Effects of steam and CO₂ in the fluidizing gas when using bituminous coal in chemical-looping combustion. *Proceedings of the 20th International Conference on Fluidized Bed Combustion, Xian (China), 2009*, 608-611.
- [30] Pröll T, Mayer K, Bolhàr-Nordenkamp J, Kolbitsch P, Mattisson T, Lyngfelt A, Hofbauer H. Natural minerals as oxygen carrier for chemical looping combustion in a dual circulating fluidized bed system. *GHGT-9. Energy Procedia* 2009;1:27-34.
- [31] Abad A, Adáñez J, Cuadrat A, García-Labiano F, Gayán P, de Diego LF. Kinetics of redox reactions of ilmenite for Chemical-Looping Combustion. *Chem Eng Sci* 2011;66(4):689-702.
- [32] Johnson JL. Fundamentals of coal gasification. In: (2nd ed.) Elliot MA, editor. *Chemistry of Coal Utilization (second supplementary volume)*, New York: John Wiley and Sons; 1981. 1491-1598.
- [33] Cuadrat A, Abad A, Gayán P, de Diego LF, García-Labiano F, Adáñez J. Modeling and optimization of Chemical Looping Combustion for solid fuels with ilmenite as oxygen carrier. *International Conference on Coal Science & Technology (ICCS&T)*, October 2011.
- [34] 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.
- [35] Siriwardane R, Tian H, Miller D, Richards G, Simonyi T, Poston J. Investigation on Reaction Mechanism of Chemical-Looping Combustion of Coal Utilizing Oxygen Carriers. *Proceedings of the 1st International Conference on Chemical Looping, Lyon, 2010*.
- [36] Adáñez J, Miranda JL, Gavilán JM. Kinetics of a lignite-char gasification by CO₂. *Fuel* 1985;64:801-4.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Tables

Table 1. Chemical and physical properties of pre-oxidized ilmenite.

Table 2. Proximate and ultimate analysis (% weight) of char from devolatilizing South African coal.

Table 3. Average values of the instantaneous rate of char conversion, $r_{C,inst}(t)$, half-life time, t_{50} and residence time to convert 95% of char, t_{95} , at different H₂O:CO₂ ratios. $T = 900^{\circ}\text{C}$.

Table 4. Average values of the instantaneous rate of char conversion, $r_{C,inst}(t)$, half-life time, t_{50} and residence time to convert 95% of char, t_{95} , at different temperatures for H₂O or CO₂ as gasification agent.

Table 5. Proximate and ultimate analysis (% weight) of South African coal.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Table 1. Chemical and physical properties of pre-oxidized ilmenite.

XRD (main species)	Fe ₂ TiO ₅ , Fe ₂ O ₃ , TiO ₂
Oxygen transport capacity, $R_{O,ilm}$ (%)	4.0
Particle diameter (μm)	150-300
True density (kg/m ³)	4100
Porosity (%)	1.2
BET Surface (m ² /g)	0.8
Crushing strength (N)	2.2

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Table 2. Proximate and ultimate analysis (% weight) of char from devolatilizing South African coal.

Proximate analysis	
Water content	0.9
Ash	20.0
Volatile matter	1.1
Fixed carbon	78.0
Ultimate analysis	
Carbon	76.5
Hydrogen	0.2
Nitrogen	1.6
Sulfur	0.8

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Table 3. Average values of the instantaneous rate of char conversion, $r_{C,inst}(t)$, half-life time, t_{50} and residence time to convert 95% of char, t_{95} , at different H₂O:CO₂ ratios. $T = 900^{\circ}\text{C}$.

H ₂ O:CO ₂	100:0	90:10	70:30	50:50	0:100
$r_{C,inst}$ (%/min)	10.9	8.1	5.7	4.8	3.4
t_{50} (min)	6.4	8.6	12.2	14.4	20.4
t_{95} (min)	27.5	37.0	52.6	62.4	88.1

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Table 4. Average values of the instantaneous rate of char conversion, $r_{C,inst}(t)$, half-life time, t_{50} and residence time to convert 95% of char, t_{95} , at different temperatures for H₂O or CO₂ as gasification agent.

Gasification agent	H ₂ O			CO ₂		
	900	950	1000	900	950	1000
Temperature (°C)	900	950	1000	900	950	1000
$r_{C,inst}$ (%/min)	10.9	24.0	37.3	3.4	5.2	6.9
t_{50} (min)	6.4	2.9	1.8	20.4	13.3	10.0
t_{95} (min)	27.5	12.5	7.8	88.1	57.6	43.4

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Table 5. Proximate and ultimate analysis (% weight) of South African coal.

<hr/>	
Proximate analysis	
Water content	4.2
Ash	14.3
Volatile matter	25.5
Fixed carbon	56.0
<hr/>	
Ultimate analysis	
Carbon	69.3
Hydrogen	4.0
Nitrogen	2.0
Sulfur	1.0
LHV (kJ/kg)	25500
<hr/>	

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

Captions of figures

Fig. 1. Reactor scheme of Chemical-Looping Combustion using solid fuels (- - - optional stream).

Fig. 2. Schematic layout of the laboratory setup.

Fig. 3. Molar flow evolution with time of a) CO₂, b) CO and c) H₂ in the gas product during the initial 10 reduction cycles. The intervals between reducing periods have been removed. Every cycle consisted of 2 loads of char, 1.5 g each one. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Fig. 4. Conversion of (a) reduction, X_{red} , and (b) oxidation, X_{ox} , with time of ilmenite after 1, 3, 7, 10, 13 and 16 redox cycles using char as fuel and steam as fluidizing gas. The corresponding curves for pre-oxidized ilmenite and fully activated ilmenite are also showed. Reducing gas: 5% H₂ + 40% H₂O. Nitrogen to balance. Oxidation gas: air. $T = 900^{\circ}\text{C}$.

Fig. 5. SEM images of (a) detail of the external surface, (b) detail of the cross section inside the particles and (c) cross section of a particle for pre-oxidized ilmenite, after 3 cycles and after 13 cycles using coal char as fuel.

Fig. 6. Evolution of the rate of char conversion with time during the initial 10 reduction cycles. Every cycle consisted of 2 loads of char, 1.5 g each one. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Fig. 7. Gas flow evolution with char conversion of a) CO₂, b) CO and c) H₂ in the gas product during char conversion using activated ilmenite (—) or sand (- - -) as bed material. Loads of 1.5 g char. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Fig. 8. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion with activated ilmenite and sand as bed materials. Loads of 1.5 g char. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Fig. 9. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion with activated ilmenite as bed material when different $\text{H}_2\text{O}:\text{CO}_2$ ratios was used, corresponding to that showed in Table 3. Loads of 1.5 g char. $T = 900^{\circ}\text{C}$.

Fig. 10. Char conversion vs. time curves for different $\text{H}_2\text{O}:\text{CO}_2$ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^{\circ}\text{C}$.

Fig. 11. Combustion efficiency as a function of the char conversion for several $\text{H}_2\text{O}:\text{CO}_2$ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^{\circ}\text{C}$.

Fig. 12. Evolution with time of the flow of CO exiting from the reactor for different $\text{H}_2\text{O}:\text{CO}_2$ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^{\circ}\text{C}$.

Fig. 13. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion at 900, 950 and 1000°C . Fluidizing agent: (a) H_2O ; (b) CO_2 . Activated ilmenite as bed material. Loads of 1.5 g char.

Fig. 14. Combustion efficiency as a function of the char conversion at 900, 950 and 1000°C . Fluidizing gas: a) H_2O ; b) CO_2 . Activated ilmenite as bed material. Loads of 1.5 g char.

Fig. 15. Conversion of char by gasification in the fuel-reactor as a function of a) temperature with steam or CO_2 as gasification agents and without carbon stripper; b) carbon stripper efficiency; and c) ilmenite inventory in the fuel-reactor with a carbon stripper efficiency of $\eta_{CS} = 90\%$. In Figs. a) and b) the solids inventory was $200 \text{ kg/MW}_{\text{th}}$. In Figs. b) and c) steam was the gasification agent and the temperature 1000°C .

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

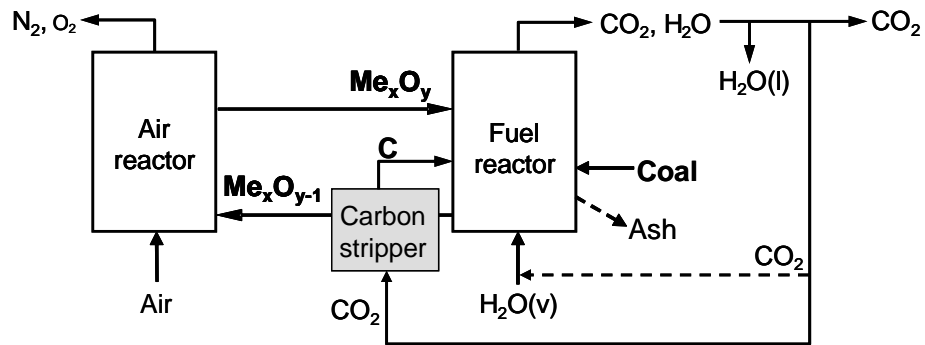


Fig. 1. Reactor scheme of Chemical-Looping Combustion using solid fuels (- - - optional stream).

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

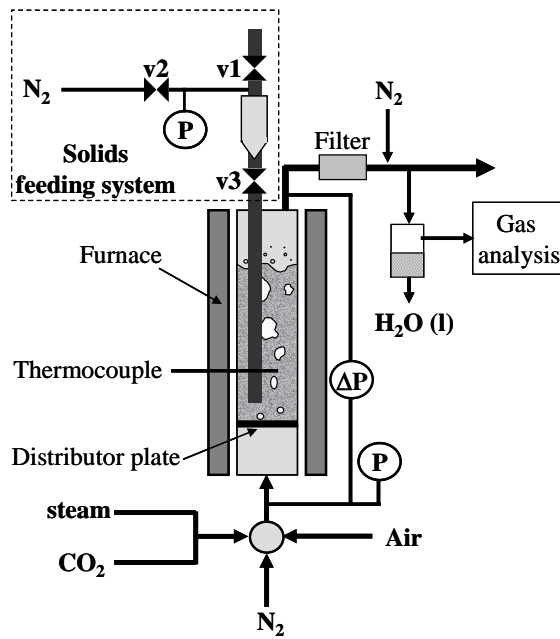


Fig. 2. Schematic layout of the laboratory setup.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

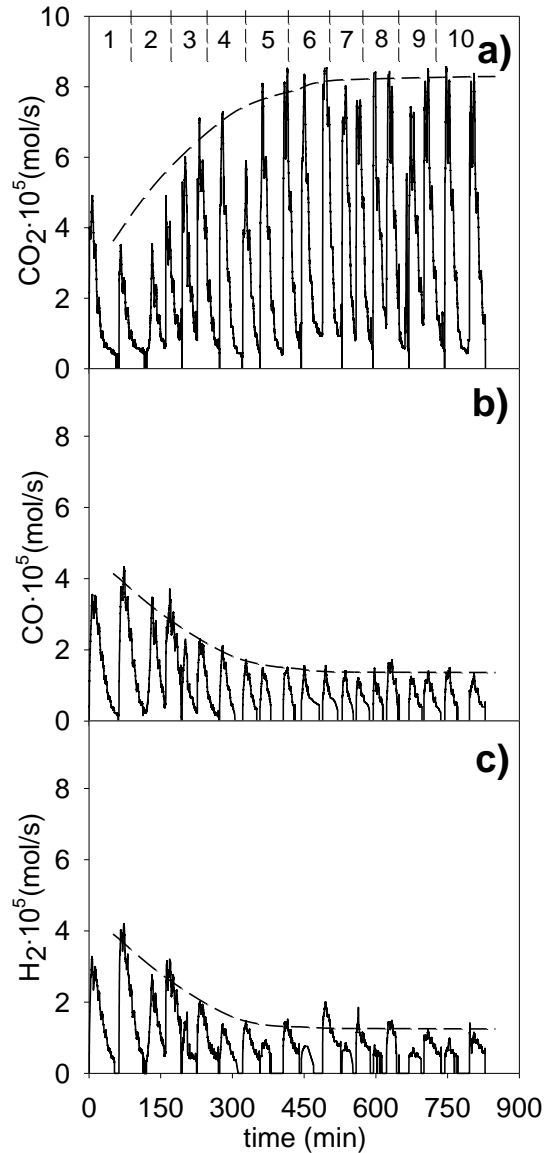


Fig. 3. Molar flow evolution with time of a) CO₂, b) CO and c) H₂ in the gas product during the initial 10 reduction cycles. The intervals between reducing periods have been removed. Every cycle consisted of 2 loads of char, 1.5 g each one. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

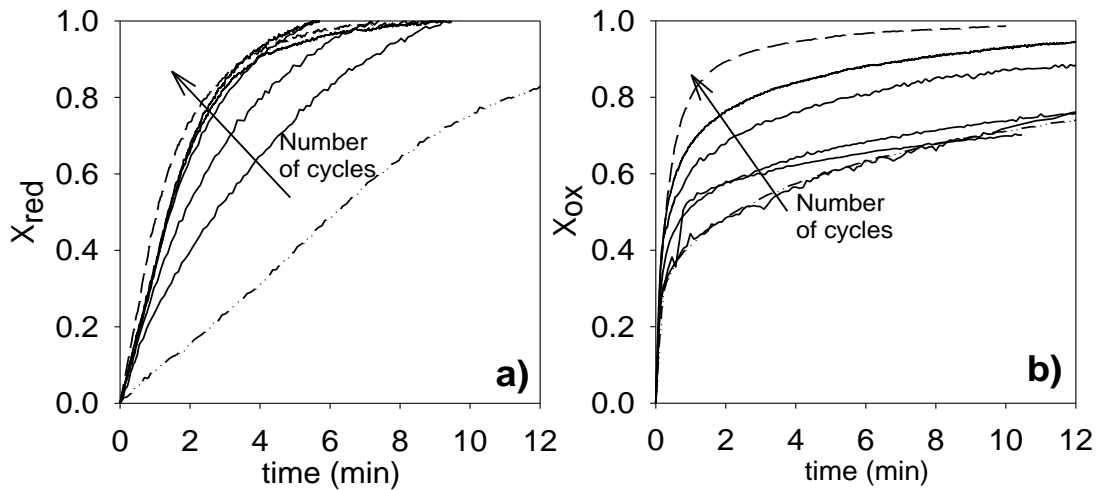


Fig. 4. Conversion of (a) reduction, X_{red} , and (b) oxidation, X_{ox} , with time of ilmenite after 1, 3, 7, 10, 13 and 16 redox cycles using char as fuel and steam as fluidizing gas. The corresponding curves for pre-oxidized ilmenite (---) and fully activated ilmenite (- - -) are also showed. Reducing gas: 5% H_2 + 40% H_2O . Nitrogen to balance. Oxidation gas: air. $T = 900^\circ C$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

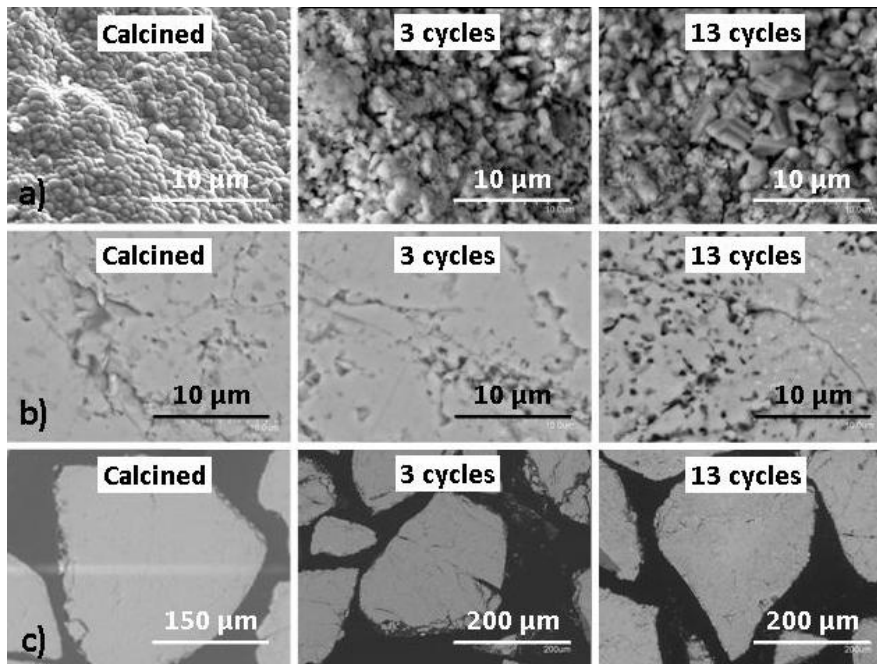


Fig. 5. SEM images of (a) detail of the external surface, (b) detail of the cross section inside the particles and (c) cross section of a particle for pre-oxidized ilmenite, after 3 cycles and after 13 cycles using coal char as fuel.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

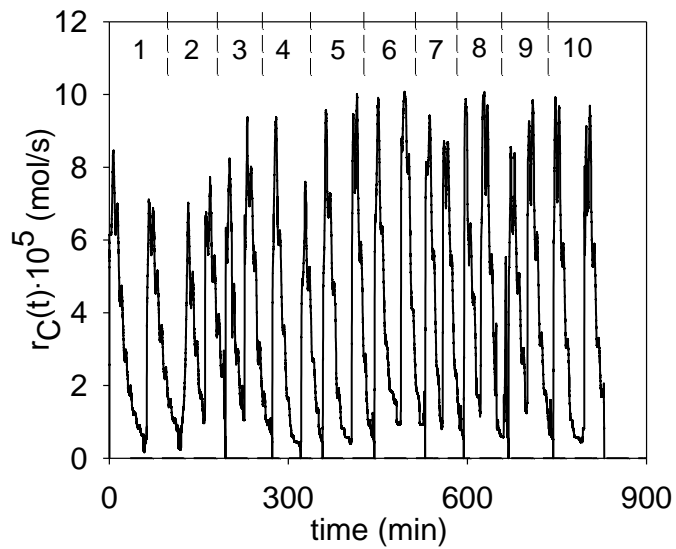


Fig. 6. Evolution of the rate of char conversion with time during the initial 10 reduction cycles. Every cycle consisted of 2 loads of char, 1.5 g each one. Gasification agent: steam. $T = 900^\circ\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

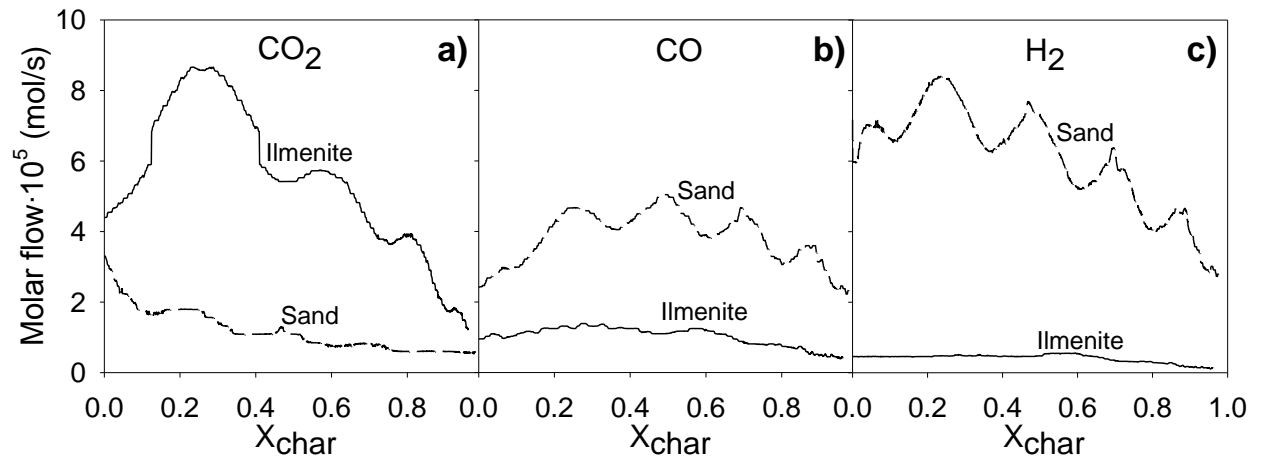


Fig. 7. Gas flow evolution with char conversion of a) CO_2 , b) CO and c) H_2 in the gas product during char conversion using activated ilmenite (—) or sand (---) as bed material. Loads of 1.5 g char. Gasification agent: steam. $T = 900^\circ\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

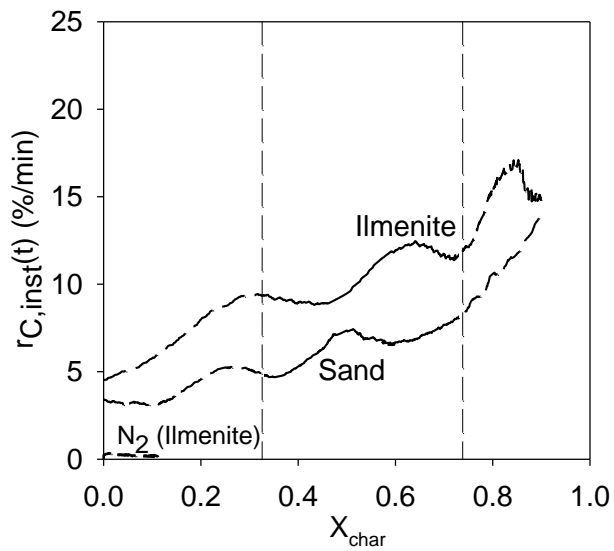


Fig. 8. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion with activated ilmenite and sand as bed materials. Loads of 1.5 g char. Gasification agent: steam. $T = 900^{\circ}\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

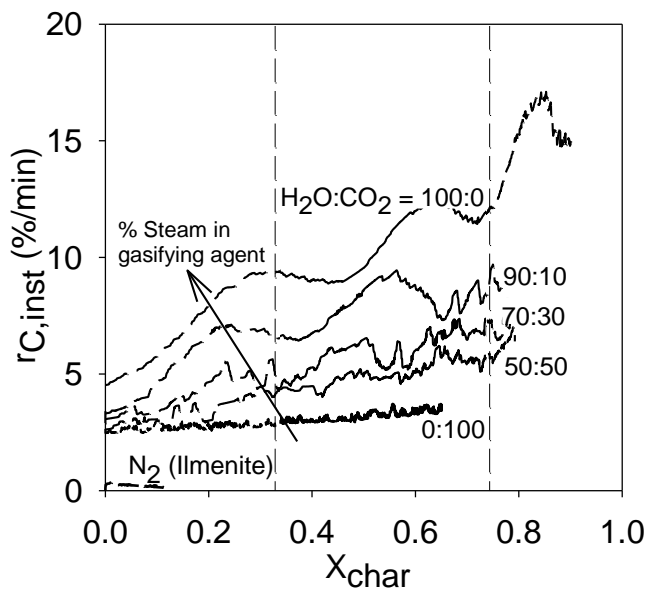


Fig. 9. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion with activated ilmenite as bed material when different $H_2O:CO_2$ ratios was used, corresponding to that showed in Table 3. Loads of 1.5 g char. $T = 900^\circ C$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

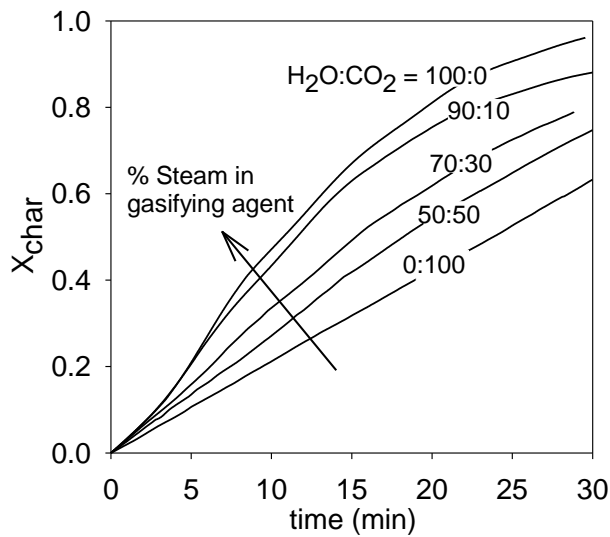


Fig. 10. Char conversion vs. time curves for different $H_2O:CO_2$ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^\circ C$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

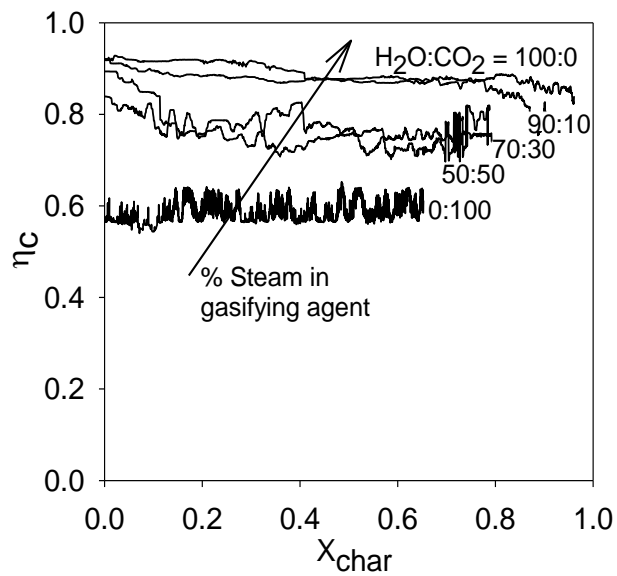


Fig. 11. Combustion efficiency as a function of the char conversion for several H₂O:CO₂ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^\circ\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

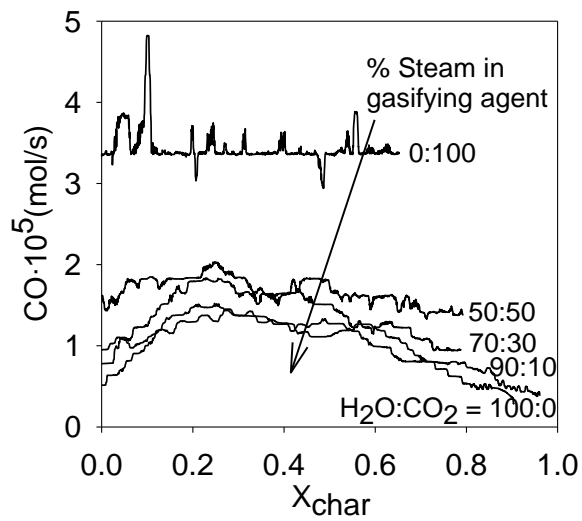


Fig. 12. Evolution with time of the flow of CO exiting from the reactor for different H₂O:CO₂ ratios. Activated ilmenite as bed material. Loads of 1.5 g char. $T = 900^{\circ}\text{C}$.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

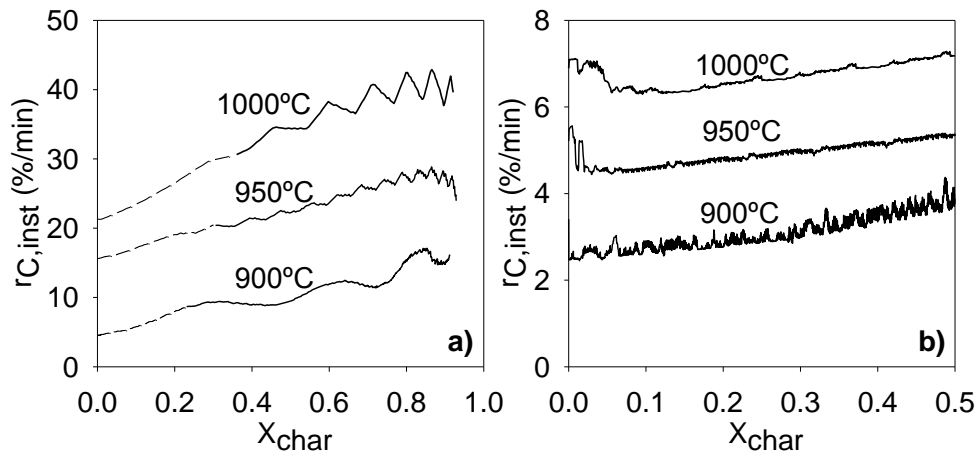


Fig. 13. Instantaneous rate of char conversion, $r_{C,inst}(t)$, as a function of the char conversion at 900, 950 and 1000°C. Fluidizing agent: (a) H_2O ; (b) CO_2 . Activated ilmenite as bed material. Loads of 1.5 g char.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

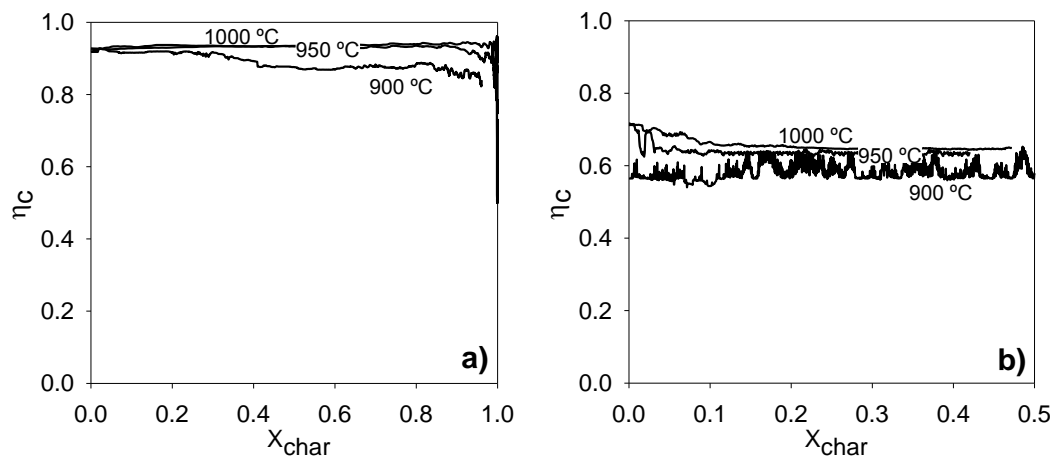


Fig. 14. Combustion efficiency as a function of the char conversion at 900, 950 and 1000°C. Fluidizing gas: a) H_2O ; b) CO_2 . Activated ilmenite as bed material. Loads of 1.5 g char.

Design Considerations for Chemical-Looping Combustion of coal – Part 1.
Experimental Tests.

Ana Cuadrat*, Alberto Abad, Juan Adánez, Luis F. de Diego, Francisco García-Labiano, Pilar Gayán.

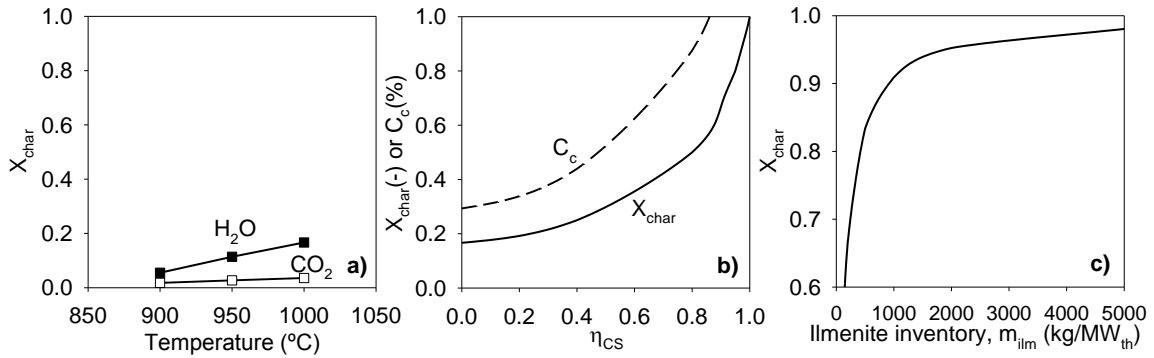


Fig. 15. Conversion of char by gasification in the fuel-reactor as a function of a) temperature with steam or CO_2 as gasification agents and without carbon stripper; b) carbon stripper efficiency; and c) ilmenite inventory in the fuel-reactor with a carbon stripper efficiency of $\eta_{CS} = 90\%$. In Figs. a) and b) the solids inventory was 200 kg/MW_{th}. In Figs. b) and c) steam was the gasification agent and the temperature 1000°C.