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Effect of operating conditions in Chemical-Looping Combustion of coal in a 500 W_{th} unit

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Abstract

Chemical-Looping Combustion, CLC, is one of the most promising processes to capture CO_2 at a low cost. It is based on the transfer of the oxygen from air to the fuel by using a solid oxygen-carrier that circulates between two interconnected fluidized-bed reactors: the fuel- and the air-reactor. The CO_2 capture is inherent to this process, as the air does not get mixed with the fuel.

In this work, the CLC technology with coal was investigated in a continuous 500 W_{th} rig using ilmenite as oxygen-carrier. The plant was basically composed of two interconnected fluidized-bed reactors, a riser for solids transport from the air- to the fuel-reactor, a solid valve to control the flow rate of solids fed to the fuel-reactor and a cyclone. A Colombian bituminous coal is fed by a screw feeder at the bottom of the bed. In the fuel-reactor the oxygen-carrier is reduced by the volatile matter and gasification products of coal. Reduced oxygen-carrier particles were led to the air-reactor where they were re-oxidized and got ready to start a new cycle.

This work is focused on the study of the fuel-reactor within the process. The behaviour of the fuel-reactor has been evaluated for different operational conditions. The effect of operating conditions such as the solids circulation rate and the resulting oxygen-carrier and fuel residence times, the coal flow feed and the gasification agent flow were investigated on the combustion efficiency and the extent of gasification in the fuel-reactor. The fluidizing gas, which also acts as gasification agent, was steam. Besides, the influence of using CO_2 as gasification agent was assessed by doing experiments with different CO_2-H_2O mixtures. The experiments were carried out at about 900ºC in the fuel-reactor.

The results obtained are valid for the scale-up of a CLC process fuelled with coal. They indicate that it is feasible to decrease the gasification agent feeding flow to lower values than the corresponding stoichiometric flow for the fixed carbon gasification, and that some of the steam as gasification agent can be replaced by CO_2 recirculated from the outlet fuel-reactor flow. Low circulation rate of solids improved the coal conversion in the fuel-reactor.

1. Introduction

It is generally accepted that a reduction in the greenhouse gases emissions is necessary as soon as possible to restrain the effects of climate change. Up to now, the technological options for reducing net CO_2 emissions to the atmosphere have been focused on [1]: 1) reducing energy consumption, by increasing the efficiency of energy conversion and/or utilization; 2) switching to less carbon intensive fuels; 3) increasing the use of renewable energy sources (biofuel, wind power, etc.) or nuclear energy, and 4) sequestering CO_2. Carbon capture and sequestration or storage, CCS, has attracted interest as a measure for mitigating global climate change because large amounts of CO_2 emitted from fossil fuel use are potentially available to be captured and stored underground or prevented from reaching the atmosphere. Furthermore, large industrial sources of CO_2, such as electricity-generating plants, are likely initial candidates for CCS because they are predominantly stationary, single-point sources.

In this context, Chemical-Looping Combustion (CLC) is one of the most promising technologies to carry out CO_2 capture at a low cost [2]. CLC is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen-carrier that circulates between two interconnected fluidized beds: the fuel- and the air-reactor. In the fuel-reactor the oxygen-carrier is reduced through oxidation of the fuel, thus obtaining a gas stream composed by CO_2 and H_2O. The oxygen-carrier is afterwards directed to the air-reactor, where it is re-oxidized with air and regenerated to start a new cycle. The net chemical reaction is the same as at usual combustion with the same combustion heat released, but with the advantage of the intrinsic CO_2 separation in the process without an additional step.

Using CLC with solid fuels is very interesting, regarding the intensive use of solid fuels as energy source. One of the options for CLC with solid fuels is directly to introduce coal in the fuel-reactor, where it is mixed with the oxygen-carrier and being the fuel-reactor fluidized by a gasification agent, i.e. H_2O or CO_2 [3]. Thereby, the solid fuel gasification takes place as for

reactions (1-3), and simultaneously the oxidized oxygen-carrier, Me_xO_y, reacts with the gaseous products of coal devolatilization and gasification, with H_2 and CO as main components, according to reaction (4). The reduced oxygen-carrier from the fuel-reactor, Me_xO_{y-1}, is subsequently oxidized with air in the air-reactor following reaction (5).

$$\text{Coal} \rightarrow \text{Volatile matter} + \text{Char} \quad (1)$$

$$\text{Char} + H_2O \rightarrow H_2 + CO \quad (2)$$

$$\text{Char} + CO_2 \rightarrow 2\ CO \quad (3)$$

$$H_2, CO, \text{Volatile matter} + n\ Me_xO_y \rightarrow CO_2 + H_2O + n\ Me_xO_{y-1} \quad (4)$$

$$Me_xO_{y-1} + \tfrac{1}{2}\ O_2 \rightarrow Me_xO_y \quad (5)$$

Although ideally the CO_2 capture is inherent to this process, as the air does not get mixed with the fuel, the CO_2 capture efficiency when using solid fuels decreases if non-gasified char particles are by-passed to the air-reactor. The gasification process has been identified as the controlling step in this process [4,5]. Char gasification is usually a slow process, and the solids stream exiting from the fuel-reactor could contain some unconverted char together with the oxygen-carrier. Therefore, enough high residence time in the fuel-reactor is needed so that char particles are gasified.

To increase the residence time of char particles in the fuel-reactor, without excessive increase of the reactor size, an option is to separate the char exiting the fuel-reactor from the oxygen-carrier particles and recirculate the char to the fuel-reactor. Thereby, the amount of carbon transferred from the fuel- to the air-reactor is reduced. Based on the different fluidizing properties of remaining char and oxygen-carrier particles, a carbon stripper has been proposed as a feasible equipment to carry out the separation of char [3,6]. In previous CLC experiments with solid fuels performed to date, full oxidation of the outlet fuel-reactor stream could not be achieved [7-12]. Therefore, in order to oxidize completely unburnt compounds to CO_2 and H_2O, an "oxygen polishing" step downstream was proposed, that is, injection of pure oxygen to the gas flow after the fuel-reactor cyclone [7,8], which is usually called oxygen demand.

To use an oxygen-carrier with adequate behaviour and properties is fundamental to reach high performance of the CLC process. As for this option of CLC with solid fuels, the fuel is physically mixed with the oxygen-carrier, being predictable a partial loss of oxygen-carrier particles together with the draining stream of coal ashes to avoid their accumulation in the

system. In this context, the use of low cost materials such as natural minerals or industrial waste products as oxygen-carriers turns out to be very interesting. Ilmenite is a low cost natural mineral which is promising for its large scale industrial use as oxygen-carrier with solid fuels. Performance of ilmenite has been proven to be acceptable as oxygen-carrier for CLC in recent studies made at different scales [13,14]. Comparing the performance of several natural iron ores and industrial products, Norwegian ilmenite was ranged among the materials which showed higher reactivity as for gaseous fuel as for solid fuels [15,16]. Although ilmenite particles have initially a rather low reactivity, it undergoes an activation process after several redox cycles, being its reactivity remarkably increased for H_2, CO and CH_4 as reacting gases [13]. The gas conversion showed by activated ilmenite was even similar to one synthetic $Fe_2O_3/MgAl_2O_4$ material selected from previous works [17]. Ilmenite has high conversion of CO and H_2 for syngas applications, but moderate conversion of CH_4 for the use of natural gas as fuel [13]. On the whole, ilmenite has adequate values of reactivity and oxygen transport capacity for its use in the CLC technology with solid fuels, which is confirmed by the results from the continuous CLC experiments done to date. Additionally, ilmenite showed good mechanical stability and good fluidizing properties [18].

The feasibility of the process has been proven during continuous operation in CLC units ranging from 500 W_{th} to 10 kW_{th}. As mentioned, ilmenite was the most common oxygen-carrier used. Continuous operation using solid fuels showed that the concentration of CO and H_2 in the flue gases due to unconverted gasification products are in the range 0.7-1.5 vol%, corresponding to an oxygen demand of 5-9% [9]. Besides, unconverted gases from volatiles in the fuel-reactor outlet were detected when using ilmenite [10]. The extent of unburt volatiles was the same as if a highly Ni-based oxygen-carrier was used [11,12]. Indeed, the unconverted gases from volatiles were higher than those originated in char gasification. Experiments in a 500 W_{th} CLC unit showed that unburnt tars or hydrocarbons were not present in the fuel-reactor outlet, except CH_4 which was found at low concentration [10]. Gasification products were near fully converted to CO_2 and H_2O but unconverted CO and H_2 proceeding from coal devolatilization were outgoing from the fuel-reactor. In the bigger scale and with other type of fuels, ilmenite was also successfully tested in a 10 kW_{th} chemical-looping combustor using South African coal and petroleum coke as solid fuels by Berguerand et al. [7,8]. They analyzed the combustion process focusing on char conversion. From results showed in these studies the temperature is the main parameter of influence in the performance of the system, being higher efficiencies reached at high temperatures. Temperatures above

1000 ºC were tested in some cases [9]. Combustion efficiencies from 85 to 95 % and average carbon capture efficiencies of 80% were obtained in all the experimental works at high temperatures in CLC with solids fuels using ilmenite.

The combustion efficiency in the fuel-reactor, the efficiency of char separation in the carbon stripper, and the separation of ashes from the oxygen-carrier are key factors for the development of this process. The coal combustion efficiency depends on the char conversion in the reactor and on the reactivity of the oxygen-carrier with the volatiles and gasification gases.

Biomass as solid fuel was evaluated by Shen et al. [19] in a continuous 10 kW_{th} CLC combustor using an oxygen-carrier prepared from iron oxide and CO_2 as gasification medium. The CO concentration of the fuel-reactor flue gas increased with the fuel-reactor temperature, since biomass gasification with CO_2 was more temperature dependent than CO oxidation with iron oxide.

The effect of the gasification agent has been assessed in batch experiments. Previous research using bituminous Colombian coal show that the conversion rate of char using CO_2 as fluidizing agent is about 5 times lower than using H_2O instead [4]. The CO_2 concentration in the fluidizing gas would be limited to 20% in order to maintain a high gasification rate with that bituminous coal [4]. In this case, whereas the steam gasification proceeds in minutes, the CO_2 gasification time is of the order of hours. As for the gasification agent, most studies have used steam. If CO_2 was used, the energy required for steam production is avoided. CO_2 can be re-circulated from the flue gases. The use of CO_2 has been proposed for highly reactive solid fuels, such as low-rank coals or biomass [20]. Sub-bituminous and lignite coal char have shown gasification rates using CO_2 as high as for H_2O [21]. Dennis et al. [22] tested the feasibility of using pure iron oxide and a lignite fuel gasified by CO_2 in a batch fluidized-bed reactor. They stated that although the oxygen-carrier used (pure Fe_2O_3) was not optimized, it was still able to burn most of the CO produced by the gasification of the carbon. Using these types of coal could be advantageous because recirculated CO_2 could be used as fluidizing agent. Besides, dry gasification of a lignite [23] was found to be as fast as the steam gasification of bituminous coal [24] using Fe-based oxygen-carriers. On the whole, the CO_2 recirculation can be an interesting option when highly reactive solid fuels, that is, sub-bituminous coal, solid waste or biomass, or high-sulphur coals are used.

The effect of the solids circulation rate and the resulting mean residence time of the oxygen-carrier particles has been to date only tested experimentally for continuous CLC with gaseous fuels [25,26,27]. Markström et al.[28] developed a model for solid fuels that determined the circulation mass flow, the residence time and residence-time distribution of particles in the fuel-reactor for a number of operational cases previously done in a 10 kWth rig for solid fuels with different particle circulation. With the model and experimental results they established a relation between the system performance versus residence time using data of batch and continuous tests feeding pet coke and a South African coal at fuel-rector temperature of 950ºC.

In this work, the CLC technology with a Colombian bituminous coal was investigated in a continuous 500 W_{th} rig using ilmenite as oxygen-carrier. The aim of this work was to study the conversion of coal in the fuel-reactor under different operating conditions, which has been not tested to date in a continuous facility. The effect of operating conditions such as the solids circulation rate, the coal flow feed and the gasification agent flow were investigated on the combustion efficiency and the extent of gasification in the fuel-reactor. The fluidizing gas, which also acts as gasification agent, was steam. Besides, the influence of using CO_2 as gasification agent was assessed by doing experiments with different CO_2:H_2O mixtures. The results obtained are analyzed and discussed in order to be useful for the scale-up of a CLC process fuelled with coal.

2. Experimental section

2.1. Bed material and fuel

Norwegian ilmenite has been the most used material for Chemical-Looping coal Combustion. The bed material in this study was ilmenite with particle size of +150-300 μm. Ilmenite is a common mineral found in metamorphic and igneous rocks. The ilmenite used is a concentrate from a natural ore. It is mainly composed of $FeTiO_3$ ($FeO \cdot TiO_2$) and some free Fe_2O_3, where iron oxide is the active phase that behaves as the oxygen-carrier. A semi-quantitative analysis performed by XRD of a oxidized sample showed that the used ilmenite was composed by 11.7% Fe_2O_3, 53.2% Fe_2TiO_5 and 29.5% TiO_2. More details about the physical properties of the ilmenite particles used and their behaviour can be found elsewhere [13,14]. Ilmenite

undergoes an activation process during continuous operation in the plant and reaches a maximum reactivity, which is studied in previous work [14]. The experiments have been carried out with activated ilmenite, so the reactivity was maximum and constant and did not affect in the evaluation of other parameters. The porosity of the initial sample was 12.3%. The oxygen transport capacity, which is the mass fraction of oxygen that can be used in the oxygen transfer, was measured to be 3.9% for this CLC process with solid fuels.

The fuel used was a bituminous Colombian coal "El Cerrejón". The coal was subjected to a thermal pre-treatment for pre-oxidation in order to avoid bed agglomeration problems or pipes clogging, as El Cerrejón coal had shown high swelling behaviour. Hence, coal was placed in trays in layers of about 3 mm height and exposed to heating at 180ºC in air atmosphere for 28 hours. Ultimate and proximate analyses of the used pre-treated coal are shown in Table 1. Three different coal particle sizes were used: +74-125, +125-200 and +200-300 μm.

Table 1. Properties of the used pre-treated Colombian coal.

Pre-treated Colombian coal			
C	65.8 %	Moisture	2.3 %
H	3.3 %	Volatile matter	33.0 %
N	1.6 %	Fixed carbon	55.9 %
S	0.6 %	Ash	8.8 %
O	17.6 %		
		Low Heating Value: 21899 kJ/kg	

2.2. 500 W_{th} CLC facility for solid fuels

A schematic view of the plant is shown in Figure 1. The set-up was basically composed of two interconnected fluidized-bed reactors joined by a loop seal, a riser for solids transport from the air-reactor to the fuel-reactor, a cyclone and a solids valve to control the flow rate of solids fed to the fuel-reactor. This design allowed the variation and control of the solid circulation flow rate between both reactors.

The fuel-reactor consisted of a bubbling fluidized bed with 5 cm of inner diameter and 20 cm bed height. The fluidizing gas was H_2O or CO_2, which are also gasifying agents. Coal is fed by a screw feeder at the bottom of the bed above the fuel-reactor distribution plate in order to

maximize the time that the fuel and volatile matter is in contact with the bed material. The screw feeder has two steps: the first one with variable speed to control the coal flow rate, and the second has high rotating velocity to avoid coal pyrolysis inside the screw. A small N_2 flow is fed in the beginning of the screw to avoid possible volatile reverse flow or entrance of steam. In the fuel-reactor the oxygen-carrier is reduced by the volatile matter and gasification products of coal. Reduced oxygen-carrier particles overflowed into the air-reactor through a U-shaped fluidized bed loop seal with an inner diameter of 50 mm, to avoid gas mixing between fuel- and air-reactors. The oxidation of the carrier took place in the air-reactor, consisting of a bubbling fluidized bed with 8 cm of inner diameter and 10 cm bed height, and followed by a riser. Secondary air was introduced at the top of the bubbling bed to help particle entrainment. N_2 and unreacted O_2 left the air-reactor and went through a high-efficiency cyclone and a filter before the stack. The oxidized solid particles recovered by the cyclone were sent to a solids reservoir, which acts as a loop seal, setting the oxygen-carrier ready to start a new cycle. The regenerated oxygen-carrier particles returned to the fuel-reactor by gravity from the solids reservoir through a solids valve which controlled the flow rates of solids entering the fuel-reactor. A diverting solids valve located below the cyclone allowed the measurement of the solids flow rates at any time. The total ilmenite inventory in the system was 3.5 kg and the solids inventory in the fuel-reactor was 0.8 kg ilmenite.

Because of its small size, the system is not auto-thermal and is heated up with various ovens to get independent temperature control of the air-reactor, fuel-reactor, and fuel-reactor freeboard, which is kept constant at about 900ºC in all the experiments. During operation, temperatures in the bed and freeboard of the fuel-reactor, air-reactor bed and riser were monitored as well as the pressure drops in important locations of the system, such as the fuel-reactor bed, the air-reactor bed and the loop seal.

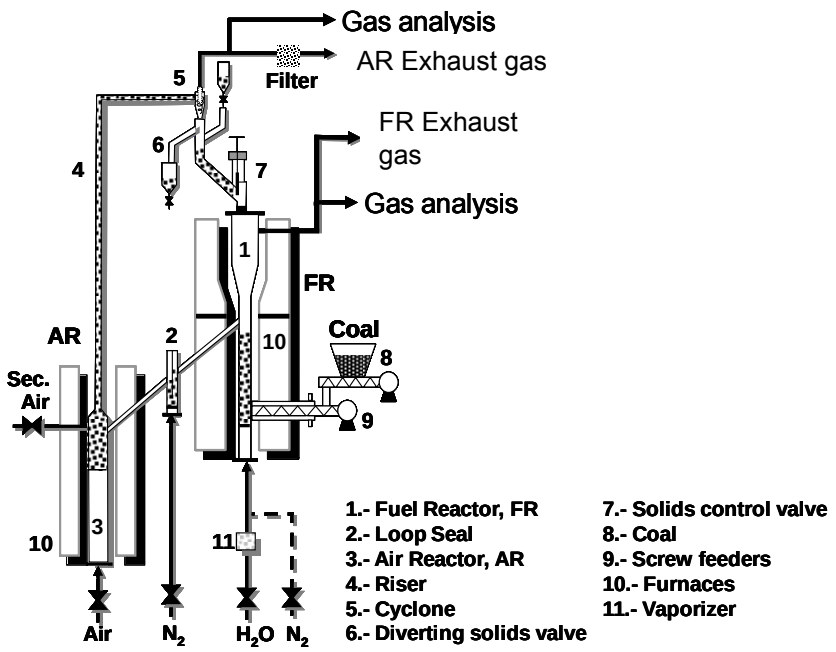

Figure 1. Schematic diagram of the coal-fuelled CLC facility.

CO, CO_2, H_2, CH_4, and O_2 were continuously analyzed in the exit streams from the fuel-reactor and from the air-reactor. In some selected experiments the tar amount present in fuel-reactor product gases was determined following the tar protocol. Some samples of the fuel-reactor outlet stream were taken and analyzed by gas chromatography in order to measure hydrocarbons.

The gas flows introduced in the air-reactor were 400 L_N/h as primary air and 2100 L_N/h as secondary air, corresponding to a total gas velocity in the air-reactor of 0.6 m/s. The loop-seal was fluidized with 75 L_N/h of N_2 and a flow of 18 L_N/h N_2 was introduced in the screw-feeder. The minimum gasification agent flow fluidizing the fuel-reactor tested was 110 L_N/h and the maximum was 190 L_N/h. For these flows, the gas velocities at 900ºC in the fuel-reactor were, respectively, 0.07 and 0.12 m/s. The minimum fluidization velocity for the ilmenite particles used at 900ºC was 0.022 m/s. Most experiments were done with steam as fluidization agent in the fuel-reactor, and H_2O-CO_2 mixtures were also used as fluidization agents in a series of tests. At least every condition was maintained stable during 30 minutes. A total of 30 hours of continuous operation feeding fuel and 36 hours of continuous fluidization were made. Table 2 shows the conditions for the series of experiments carried out. The temperature in the air-reactor was maintained at around 950ºC and the fuel-reactor temperature was kept at around 890ºC for some experiments and about 940ºC for other tests. In the series of experiments A

the coal flow rate was varied from 33 to 83 g/h, corresponding to a thermal power variation between 200 to 505 W_{th}; in the series of experiments B the solids circulation flow rate was varied from 1.0 to 11.6 kg/h for 3 different coal particle sizes; in the series of experiments C the gasification agent flow was varied from 110 to 190 L_N/h and in the series of experiments D several H_2O:CO_2 mixtures were used as gasification agent. Tests C and D were done with low solids circulation rate in order to work at high fuel-reactor temperatures.

Table 2. Conditions for the series of experiments. A) Variation of coal flow rate; B) Solids circulation flow rate variation for different coal particle sizes; C) Variation of the gasification agent flow; D) Variation of the gasification agent type (H_2O:CO_2 mixtures).

Exp.Type	Coal particle size,µm	T_{FR},ºC	Coal feed, g/h	Solids circ. Flow rate,kg/h	Gasification agent flow,L_N/h	H_2O,%	CO_2,%
A	74-125	890	33-83	8.4	190	100	0%
B1	74-125		41.1	1.2–11.6			
B2	125-200	890	46.7	1.0–3.6	190	100	0%
B3	200-300		38.5	1.6–11.3			
C	125-200	940	161	2.5	110-190	100	0
D	125-200	935	72	3.3	190	100-0	0-100

3. Data evaluation

The evaluation of the fuel-reactor performance is carried out by the analysis of two main parameters: the carbon capture efficiency and the combustion efficiency. The purpose of the data evaluation is to assess the performance of the process in the different experiments, using the measured values of the gas concentrations, temperature and solid circulation rates. The absence of a carbon stripper facilitates the interpretation of the effect of these operational conditions on the results obtained, specially the effect of the mean residence time.

The efficiencies that indicate the performance of the process are defined as follows. The carbon capture is the physical removal of carbon dioxide that would otherwise be emitted into the atmosphere. Getting high carbon capture during energy generation is the motivation of this technology. The carbon capture efficiency, η_{CC}, is here defined as the fraction of the carbon introduced that is converted to gas in the fuel-reactor.

$$\eta_{CC} = \frac{[F_{CO2,FR} + F_{CO,FR} + F_{CH4,FR}]_{out} - [F_{CO2,FR}]_{in}}{[F_{CO2,FR} + F_{CO,FR} + F_{CH4,FR} + F_{CO2,AR}]_{out} - [F_{CO2,FR}]_{in}} \quad (6)$$

$F_{CO2,FR}$, $F_{CH4,FR}$ and $F_{CO,FR}$ being the flows in the fuel-reactor of CO_2, CH_4, and CO. The carbon of the unreacted char flowing towards the air-reactor is the CO_2 gas flow in the air-reactor, $F_{CO2,AR}$. For the experiments using CO_2 as fluidization agent, the inlet CO_2 flow must be subtracted. The carbon captured in the system is the carbon contained in the volatiles plus the carbon in the char that is gasified. Thus, the carbon capture efficiency depends on the fraction of char that has been gasified.

To do a deeper study of the system behavior, the gasification and combustion steps should be assessed. The char gasification efficiency, η_{gas}, is defined as the fraction of carbon in the effective char fed to the fuel-reactor which is released to the fuel-reactor outgoing gas stream:

$$\eta_{gas} = \frac{[F_{CO2,FR} + F_{CO,FR} + F_{CH4,FR} - C_{vol}]_{out} - [F_{CO2,FR}]_{in}}{[F_{CO2,FR} + F_{CO,FR} + F_{CH4,FR} + F_{CO2,AR} - C_{vol}]_{out} - [F_{CO2,FR}]_{in}} \quad (7)$$

The gasified char in the fuel-reactor was calculated as difference of the carbon in gases in the fuel-reactor outgoing flow, and the carbon flow coming from the volatile matter, C_{vol}. The carbon content of the volatiles is directly calculated using the ultimate and proximate analyses of both the coal used and char.

The carbon measured in the gases coming from the fuel-reactor and the air-reactor is less than the carbon present in the introduced coal, because there is elutriation of char. However, in case of an industrial plant the possible elutriated char will be collected in a cyclone and reintroduced in the fuel-reactor. The elutriated char flow was calculated as the difference between the fed coal carbon and the measured carbon in the fuel-reactor and air-reactor outlet gas flows. The effective char was calculated as the fed char that had not been elutriated from the fuel-reactor.

The combustion efficiency, η_{comb}, is a measure of gas conversion in the fuel-reactor and represents the extent of oxidation of volatiles and gasification products by the oxygen-carrier. It is defined as the fraction of the oxygen demanded by the volatile matter and gasification

products that is supplied by the oxygen-carrier in the fuel-reactor. It is therefore dependent on the reaction rate of ilmenite with the gaseous fuels and on the amount of gases generated in the fuel-reactor from coal. The oxygen supplied by ilmenite in the fuel-reactor is calculated through the oxygen containing species in the fuel-reactor product gas. The sum of volatile matter and gasified char is calculated as the effective coal introduced minus the char flowing towards the air-reactor, $F_{CO2,AR}$. The combustion efficiency was calculated as:

$$\eta_{comb} = \frac{[0.5 \cdot F_{H2O,FR} + F_{CO2,FR} + 0.5 \cdot F_{CO,FR}]_{out} - [0.5 \cdot F_{H2O,FR} + F_{CO2,FR} + 0.5 \cdot O_{coal,eff}]_{in}}{O_{2\ demand\ coal,eff} - F_{CO2,AR}} \quad (8)$$

$O_{coal,eff}$ is the flow of oxygen contained in the effective coal introduced. The oxygen introduced by the gasification agent, i.e. H_2O and/or CO_2, must be removed in the analysis. $O_{2\ demand\ coal,eff}$ or the oxygen demand of the effective coal flow is the oxygen flow needed to burn the fuel completely and is calculated with the volatile matter in the coal feeding flow and the effective char flow.

The oxygen demand, Ω_{OD}, has also been used to evaluate the gas conversion in the fuel-reactor of a CLC system [7,8,9]. In this case, the oxygen demand would be defined as $\Omega_{OD} = 1 - \eta_{comb}$.

To evaluate the char conversion in the fuel-reactor, the mean residence time of char particles was calculated. Considering perfect mixing of the solids in the fuel-reactor, the residence time of ilmenite and char would be the same, but since there is char elutriation, the mean residence time of char, $t_{m,char}$, should be lower than the residence time for ilmenite particles. So, the mean residence time of ilmenite, $t_{m,ilm}$, is calculated by equation (4).

$$t_{m,ilm} = \frac{m_{ilm,FR}}{F_{ilm}} \quad (9)$$

$m_{ilm,FR}$ being the fuel-reactor bed mass or solid hold-up in the fuel-reactor, and F_{ilm} the solids circulation rate. However, the residence time for char particles was calculated as the mass of char in the fuel-reactor, $m_{char,FR}$, divided by the char flow that exits the fuel-reactor, sum of the

carbon flow from the elutriated char, $C_{char\ elutr}$, and the carbon flow from the char to the air-reactor, $C_{char,AR}$.

$$t_{m,char} = \frac{m_{char,FR}}{C_{char,AR} + C_{char\ elutr}} = \frac{\frac{x_{char,FR}}{1-x_{char,FR}} \cdot m_{ilm,FR}}{C_{char,AR} + C_{char\ elutr}} \tag{10}$$

$x_{char,FR}$ is the carbon concentration from char in the fuel-reactor, which is calculated considering the carbon flow in the air-reactor exiting gases.

The oxygen-carrier to fuel ratio, ϕ, is a measure of how much oxygen can be supplied by the circulating oxygen-carrier compared to the oxygen needed to burn the fuel fed. In stoichiometric conditions the ratio ϕ is equal to one, when the oxygen-carrier is fully oxidized. It is defined as follows:

$$\phi = \frac{F_{ilm} \cdot R_{O,ilm}}{M_{O_2} \cdot O_{2\ demand\ coal,eff}} \tag{11}$$

$R_{O,ilm}$ is the transport capacity of ilmenite and M_{O_2} is the oxygen molecular mass.

The rate of oxygen transferred by ilmenite, $(-r_O)$ is a measure of how much and how fast oxygen is transferred from ilmenite to the fuel and is calculated as the flow of the generated oxygen containing species of the fuel-reactor that were generated due to the oxygen transferred by ilmenite, i.e., the generated CO, CO_2 and H_2O, divided by the ilmenite hold-up:

$$(-r_O) = \frac{([0.5 \cdot F_{H2O,FR} + F_{CO2,FR} + 0.5 \cdot F_{CO,FR}]_{out} - [0.5 \cdot F_{H2O,FR} + F_{CO2,FR} + 0.5 \cdot O_{coal,eff}]_{in}) \cdot M_{O_2}}{m_{ilm}} \tag{12}$$

4. Results and discussion

The influence of varying different operation parameters on the CLC process with solid fuels was determined. In a previous study it was determined that the temperature in the fuel-reactor had a great influence on coal conversion [10], which agreed with the results showed by other works [9,11]. All continuous experiments of CLC with solid fuels to date are focused on the

influence of the fuel-reactor temperature as operational variable. In this work, a wide range of operation conditions was reached, by changing several different operational variables such as the coal feeding rate, the solids circulation flow rate with different particle sizes of coal, the gasification agent flow and the composition of the gasification agent, as several CO_2:H_2O mixtures were introduced to fluidize the fuel-reactor.

As representative of the gas distributions obtained in this study, the evolution with time of the gas concentrations from the fuel-reactor and the CO_2 concentration in the air-reactor as result of ungasified char escaping to that reactor is shown in Figure 2 for the experiments with increasing coal feeding rate, that is, the series of experiments A. Four coal feed flows were tested and the dotted lines indicate the moments where the coal feeding was raised. The initial period before introducing coal and the transitory period until the stationary state was reached are also represented. Concentrations in fuel-reactor are in dry basis. Steady state after any parameter change was fast reached and all the points were therefore evaluated at stable conditions. The CLC prototype was easy to operate and control, and the steady state for each operating condition was maintained for at least 60 min.

The outlet of the fuel-reactor was mainly composed of oxidized CO_2, and H_2 and CO and some CH_4 as not fully oxidized products of char gasification and volatile matter. The gas chromatography analyses of the samples taken and the tars measurements revealed there were neither hydrocarbons heavier than CH_4 nor tars in the fuel-reactor outlet flow.

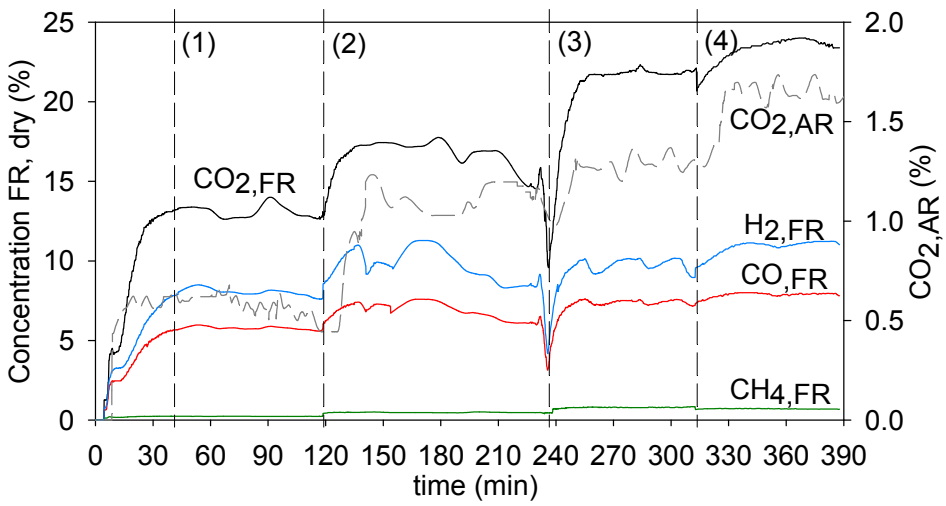

Figure 2. Gas distributions in fuel-reactor (FR) (dry basis concentrations, N_2 to balance) and CO_2 concentration in the air-reactor for rising coal feeding rate. The dotted lines indicate

increase in the fuel feed flow. Coal feed flows tested: (1) 33 g/h, (2) 45 g/h, (3) 62 g/h, (4) 83 g/h. Solids circulation flow: 4.8 kg/h. Coal particle size: +74-125 µm. T_{FR}: 890 ºC.

4.1. Effect of the coal feeding rate

The effect of the coal feeding rate on the process performance was studied. Coal feeding flow rate was changed from 33 to 83 g/h, corresponding to a thermal power of 200 W_{th} to 505 W_{th}. In these experiments the fuel-reactor temperature was maintained constant at about 890ºC and the solids circulation rate at 8.4 kg/h. This study was carried out using coal with particle size +74-125 µm.

Figure 2 gives a first idea of how the system behaves when more coal was introduced. All concentrations increased, that is, more gases were being released. Since the residence time of ilmenite was approximately kept constant and higher amount of coal was being introduced, higher flow of char escaped to the air-reactor, where higher quantity of CO_2 was generated. Besides, the yield to CO_2 in the fuel-reactor increased. The corresponding flows from all products increased with the coal feeding flow because there was more fuel to devolatilize, gasify and burn. Figure 3 shows the CO_2, CO and H_2 average concentrations from the fuel-reactor at each resulting effective carbon flow. They are represented H_2O and N_2 free to see better the yield of each released specie and the real trend. The CO_2 fraction in the air-reactor outlet is also represented. The ratio of oxygen-carrier to fuel decreased from 7 to 2.3 and in all cases the ratio steam to fixed carbon was over 2.9. At these conditions, there is oxygen as well as steam excess and the reactions are not limited by those reactants.

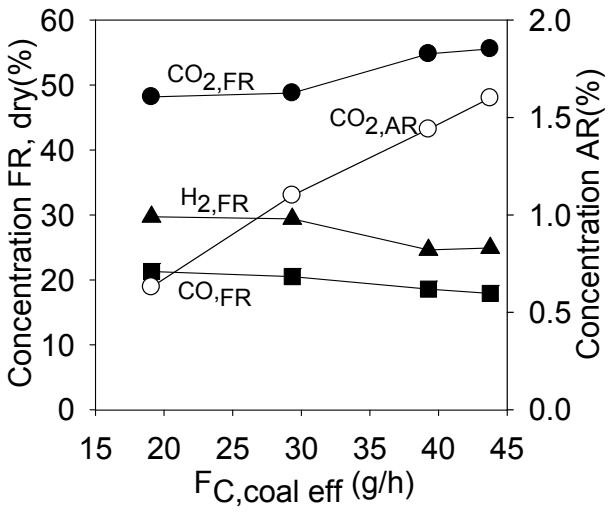

Figure 3. CO_2, CO and H_2 concentrations from the fuel-reactor, FR, in dry basis and N_2 free, and CO_2 resulting concentration from the air-reactor for increasing effective carbon in the coal feeding flow rate, $F_{C,coal,eff}$. T_{FR} = 890ºC. Average solids circulation rate = 8.4 kg/h. Particle size +74-125 µm.

Figure 4 shows the gasification and combustion efficiencies as a function of the effective carbon in the coal feeding flow. The resulting combustion efficiency for increasing coal feeding rate increased slightly. This fact was because it turned out that there was lower char elutriation when higher coal flows were fed. If lower char is elutriated, the fraction of carbon in the fuel-reactor that comes from char increases. Since char gasification products are better burnt than the released volatile matter [10], the resulting combustion efficiency slightly increases. The circulation rate and the temperature were kept constant and there was oxygen and steam excess in all cases. Char residence time was calculated to be within the range 2.7 to 6 minutes. The gasification efficiency was not really influenced by an increase in the coal feed. As there was no major increase in the residence time, but higher amount of char was being introduced, the resulting percentage of gasified char had a minor drop. Nevertheless and obviously, the char mass concentration in the fuel-reactor bed was calculated to increase from 0.16% with the coal feeding flow of 33 g/h up to 0.38% when feeding 83 g/h of coal.

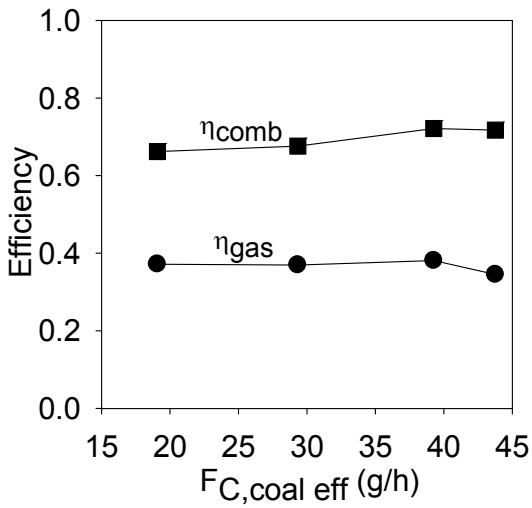

Figure 4. Gasification and combustion efficiency variation as a function of the effective carbon in the coal feeding flow rate, $F_{C,coal,eff}$. T_{FR} = 890ºC. Average solids circulation rate = 8.4 kg/h. Particle size +74-125 µm.

Figure 5 shows the rate of oxygen transferred by ilmenite for the tests preformed. When more coal was introduced in the system, the variation of ilmenite conversion and therefore the oxygen transferred increased proportionally to the coal feeding rate increase. This confirms the statement made that in this system the combustion efficiency is not limited by the reaction rate of ilmenite, but for the gasification step.

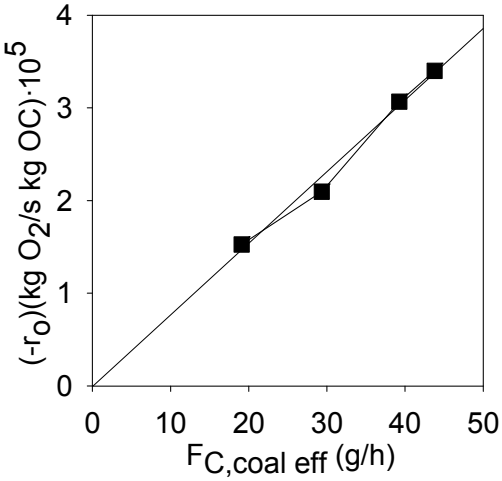

Figure 5. Rate of oxygen transferred by ilmenite for rising effective carbon in the coal feeding flow rate, $F_{C,coal,eff}$. T_{FR} = 890ºC. Average solids circulation rate = 8.4 kg/h. Particle size +74-125 μm.

4.2. Effect of the solids circulation rate

The effect of the solids circulation rate on the process performance was studied. For a CLC system based on two interconnected fluidized beds the circulation rate between them must be high enough to transfer the oxygen necessary for the fuel combustion and the heat necessary to maintain the heat balance in the system, if necessary. It must be considered that the fuel gas conversion depends on the gas-solid reaction rate in the reactor, and this is affected by the oxygen-carrier reactivity and the mean residence time of the particles in the reactor [29,30].

Solids circulation flow rates from 1.0 to 11.6 kg/h for three ranges of coal particle sizes at an average fuel-reactor temperature of 890ºC were used. This range corresponded to an ilmenite residence time range of 4.2 to 48 minutes. Considering the fuel-reactor inventory, the oxygen-carrier to fuel ratio ϕ was varied from 0.5 to 8.4. Thus, there were cases where the solids recirculation rate was lowered so much that ϕ reached values under the unity, which meant that there was not enough oxygen-carrier available to fully oxidize the fuel. In other studies, continuous experiments of CLC with solid fuels [7,8,9], were done at higher oxygen-carrier to

fuel ratios, so the effect of ϕ getting closer to the unity and even under 1, could not be therefore assessed. On the contrary, in this work a wider range of ϕ were obtained.

Figure 6 shows the carbon capture efficiency, obtained as a function of the oxygen to fuel ratio for the different coal particle sizes tested. The carbon capture efficiency decreases for increasing oxygen-carrier to fuel ratio, that is, when the recirculation rate increases. This trend is clear for ϕ closer to the unity, and when ϕ has higher values the influence is much smaller. This follows the tendency of the solids residence time, that is, the decrease in η_{CC} can be explained because coal was worse gasified, due to a lower residence time of the solids. Figure 7 shows the calculated ilmenite residence times for ϕ values resulting from the solids circulation rates set. The oxygen to fuel ratio increases when increasing the circulation rate for a constant fuel flow. Thus, the resulting ilmenite residence time increased when ϕ decreased, as $t_{r,ilm}$ is inversely proportional to the circulation rate. Berguerand et al. [31] obtained the same trend of CO_2 capture decrease for increasing circulation rate, but with batch feeding of coal to the CLC reactor. The model developed by Markström et al. [28] that predicted the carbon capture efficiency versus residence time presented the same trend of increasing η_{CC} when the residence time was higher.

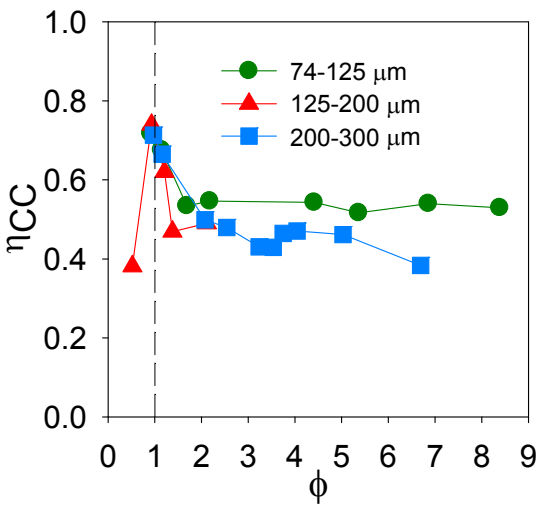

Figure 6. Carbon capture efficiencies with different oxygen-carrier to fuel ratio, ϕ, and for different coal particle sizes. T_{FR} = 890ºC.

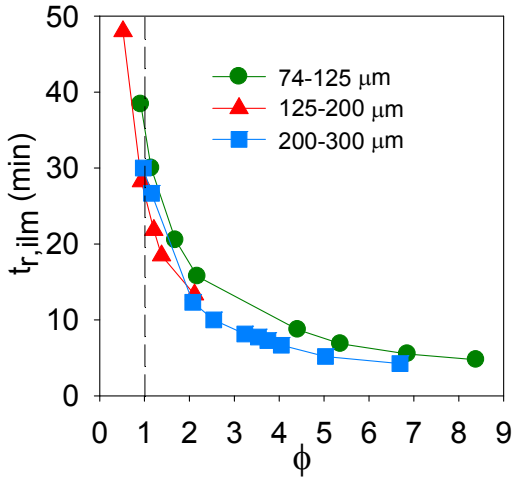

Figure 7. Calculated ilmenite residence times for the oxygen-carrier to fuel ratio, ϕ, resulting from the solids circulation rates tested for different coal particle sizes. T_{FR} = 890ºC. Average coal mass flow = 42 g/h.

Figure 8 shows the gasification efficiencies for increasing ilmenite residence times. One of the main parameters that determine the gasification efficiency is the char residence time -as it was seen for the carbon capture efficiency-, which depends on the solids recirculation rate set. For decreasing oxygen to fuel ratio, the solids residence time increased and the char from the fuel had more time to be gasified and the gasification efficiency increased from about 27% with ϕ = 8 and an ilmenite residence time $t_{m,ilm}$ of 4.2 minutes to 63% with ϕ = 1.1 and $t_{m,ilm}$ = 30 minutes. This type of char needs around 20-30 minutes to fully gasify with pure steam at 890ºC [32]. For the range of coal particle size used in these experiments, i.e. 74-300 μm, the gasification efficiency is independent of the coal size used.

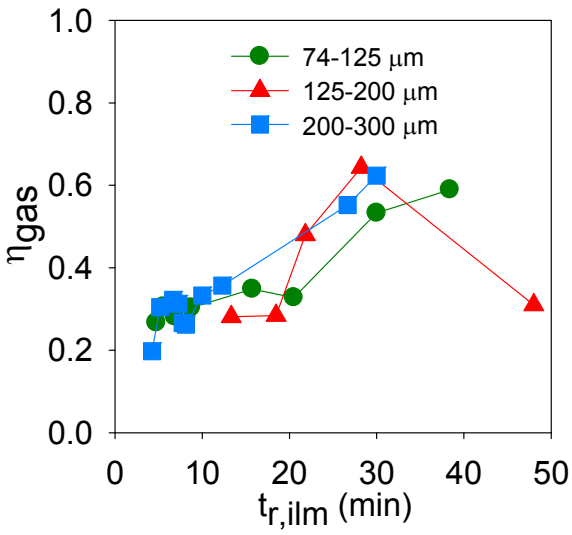

Figure 8. Gasification efficiencies for increasing ilmenite residence times for different particle sizes. T_{FR} = 890ºC.

Figure 9 shows that the combustion efficiency had some increase for lower ϕ and resulting higher residence times: from 75% with ϕ = 8 to 86% with ϕ = 1.1. The explanation of this slight benefit was related to the enhanced gasification as the average reactivity of ilmenite particles increased. The circulation rate of solids directly affects to the variation of solids conversion between the reactors, which directly affects the average reactivity of solids in the reactor [29]. Thus, as the circulation rate increases, i.e. ϕ increases, the average reactivity increases and the combustion efficiency of the generated gaseous fuels increases. In previous work in this facility [10] it was seen that the combustion of the gasification products has very high efficiencies, and their full combustion can be reached at high temperatures. Thus, with higher ϕ the char conversion increased, which were almost fully converted, and the percentage of unconverted gases -mainly coming from volatiles- decreased, as the relative importance of the gasification products in the reacting gases increased. Therefore, higher gasification efficiencies will lead to enhanced combustion efficiencies (see).

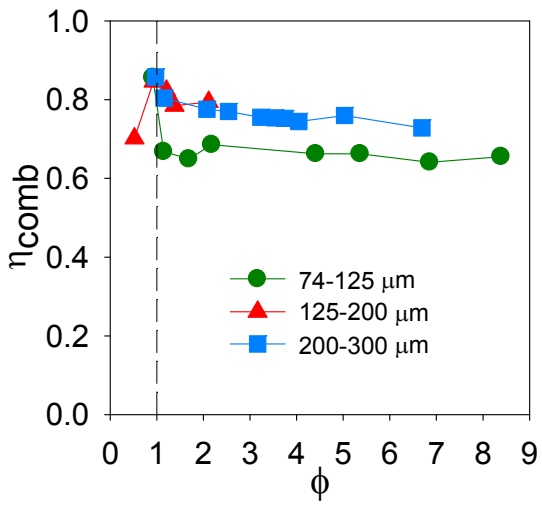

Figure 9. Combustion efficiencies with different oxygen-carrier to fuel ratio, ϕ, and for different coal particle sizes. T_{FR} = 890ºC.

This conclusion for CLC with solid fuels is opposite to the results and trends found for CLC with gaseous fuels, for which it was found that higher ϕ leads to better performance of the system, for Ni-based oxygen-carriers [25,26] as well as for Cu-based oxygen carriers [27]. For gaseous fuels the determining factor is to have oxygen available to fully oxidize the fuel,

whereas for solid fuels more factors come into consideration. The fact that there must be enough residence time for gasification and that gasification products are better burnt than the volatile matter determine this resulting trend for solid fuels in this facility. However, if the system had a carbon stripper with 100% separation efficiency, the trend followed regarding the oxygen to fuel ratio would be the same as for gaseous fuels and the combustion efficiency would increase for higher ϕ.

In Figure 9 it is showed that lower combustion efficiencies were obtained for the +74-125 μm particles, which were also seen and evaluated in previous tests [10]. It is because for the smaller particles there was higher elutriation and there was some gasification happening in the reactor freeboard where the gasification products did not get in contact with the oxygen-carrier and could not be therefore oxidized.

Nevertheless, the combustion efficiencies were not greatly influenced by the solids circulation rate. This indicates that the process is actually controlled by the gasification, although the amount or reactivity of the oxygen-carrier has also some influence in the system. This occurred in almost all the cases where the ratio of oxygen-carrier to fuel was higher than 1.1, that is, all the experiments were made with excess of oxygen for the reaction and to have more oxygen-carrier does not affect the reaction rate or the conversion.

Therefore, the char conversion was highly influenced by the residence time of char particles in the fuel-reactor. Residence times of char particles were plotted against residence times of ilmenite in Figure 10. Obviously, $t_{m,char}$ increases with $t_{m,ilm}$. However, the residence time of char was in all cases lower because there was char entrainment. The difference in the deviations of $t_{m,char}$ compared to $t_{m,ilm}$ for the different coal particle sizes was a consequence of the char elutriation. For the bigger coal particle size the residence time of char was very close to ilmenite residence time and the deviation was higher for the smaller particles because the fraction of elutriated particles was higher. Thus, the char residence time did not increase in the same extension as ilmenite particles did when decreasing the circulation rate. However, the increase in $t_{m,char}$ had as a consequence the increase seen in the gasification efficiency and somewhat in the combustion efficiencies.

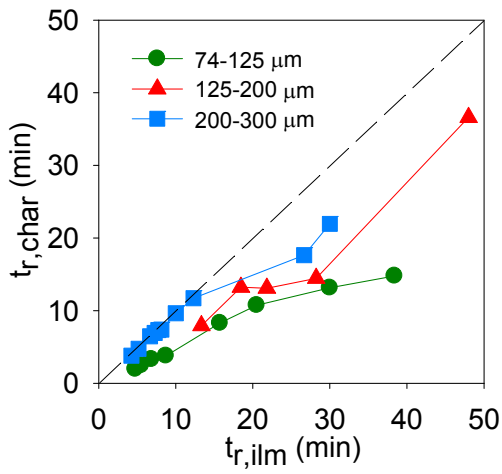

Figure 10. Difference in the residence time of char and ilmenite in the fuel-reactor for different coal particle sizes. T_{FR} = 890ºC.

When oxygen-carrier to fuel ratios lower than 1 were obtained, the performance of the system dropped substantially although the residence time was very high. Both gasification and combustion efficiencies decreased when ϕ decreased to 0.5 as can be seen in Figures 8 and 9: the combustion efficiency decreased because there was not enough oxygen available to burn the fuel fed and as a consequence the gasification efficiency also dropped because the reactor got enriched in the generated H_2 and CO, which are inhibitors for the gasification.

4.3. Effect of the gasification agent flow

The flow of steam feed was varied from 110 to 190 L_N/h, corresponding to a gas velocity variation in the fuel-reactor from 0.07 to 0.12 m/s at 900ºC. Steam acts as both fluidization and gasification agent. These experiments were done with a feeding of 161 g/h, equivalent to a thermal power of 980 W_{th}. The steam to fixed carbon ratio was varied from 0.72 to 1.09. The coal used in these tests was +125-200 µm and the average fuel-reactor temperature was 940ºC. The circulation rate was around 2.5 kg/h.

In all cases the oxygen-carrier to fuel ratio ϕ was under the unity and around 0.5, which indicated that these tests were under stoichiometric conditions. The reason of working in these conditions was that the scope of these experiments was to have low values of H_2O/C. To achieve that, the coal feed flow was raised, which caused a decrease in ϕ. Furthermore, in order to maintain high fuel-reactor temperatures, the solids circulation rate was kept at lower values, which led to work under stoichiometric conditions. However, the results are

considered valid to assess the effect of the gasification agent flow, but they are not representative of desirable operation conditions.

In Figure 11 it can be seen that for the lower steam flows tested, increasing H_2O flow corresponding to a steam to fixed carbon ratio, from 0.72 to 1.09, the increase in the fed steam flow had some beneficial effect on the gasification efficiency. However, for conditions of steam excess, there was no major effect on the gasification efficiency. When the gasification products are burnt by ilmenite, H_2O and CO_2 are formed that can further gasify the fuel, so it would not be necessary to have H_2O/C over the unity. The change in the gasification agent flow did not influence the combustion efficiency.

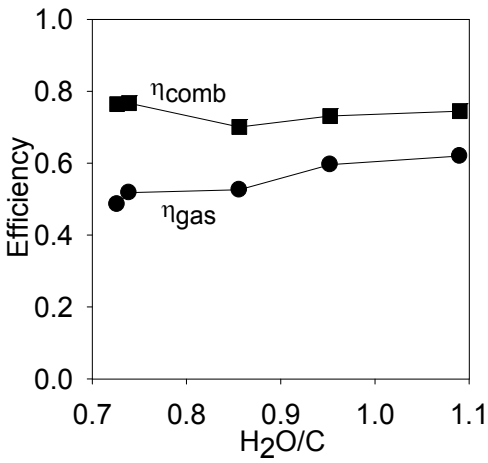

Figure 11. Gasification and combustion efficiencies variation as a function of the H_2O/C ratio.

Note that since the value of ϕ is calculated with all the coal fed to the system, with a ϕ of 0.5 combustion efficiencies as high as 0.77 could be obtained. This was because the gasification efficiencies were about 0.6 and the coal in the fuel-reactor that could be burnt in the fuel-reactor was only part of the total fuel fed.

4.4. Effect of the gasification agent: H_2O-CO_2 mixtures

Here, the effect of using a gas mixture of CO_2 and H_2O on the gasification step and the whole performance of the process with "El Cerrejón" coal was evaluated. The motivation of using H_2O-CO_2 mixtures is that CO_2 can be fed by recirculating a fraction of the product gas stream. Thus, the steam requirements for the gasification would be decreased in some extension, or

even avoided if a pure stream of CO_2 was used as fluidizing gas. The coal feeding flow was 72 g/h with a coal particle size of +125-200 μm. The average fuel-reactor temperature was 935ºC. The total gasification agent flow was 190 L_N/h. The circulation rate was 3.3 kg/h. The tested H_2O:CO_2 mixtures tested were 100:0, 90:10, 71:29, 51:49 and 0:100.

Figure 12 shows that the gasification efficiency increased for higher fraction of steam in the gasification agent. With this type of fuel, gasification with steam is faster than with CO_2 [4]. However, the combustion efficiency was not really influenced by the gasification agent used and the changes seen in η_{comb} could be explained by the slight differences in the oxygen-carrier to fuel ratios and average ilmenite residence times, being higher combustion efficiencies reached for higher ilmenite residence times, which is in concordance with the results showed in section 4.2. When gasifying with CO_2, more CO is generated as when gasifying with steam, where H_2 is also generated. Although ilmenite is more reactive with H_2 than with CO, the conclusion is that it has enough reactivity to oxidize CO and H_2 fast enough, compared to the velocities at which they are generated.

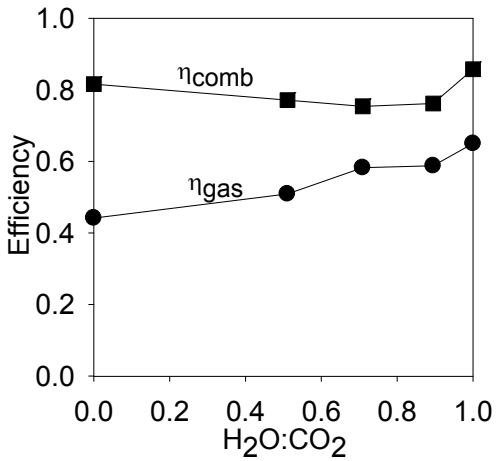

Figure 12. Gasification and combustion efficiency variation for different H_2O:CO_2 mixtures as gasification agent. T_{FR} = 935ºC. Average solids circulation rate = 3.3 kg/h. Particle size +125-200 μm.

The rates of oxygen transferred by ilmenite for the different H_2O:CO_2 mixtures tested were calculated (see Figure 13). The oxygen transferred by ilmenite is fast enough to oxidize the gasification products and the oxygen transferred is slightly higher when more gasification products are generated, that is for higher H_2O:CO_2 ratios. However it is mainly influenced by the combustion efficiency and it was therefore very similar in all cases for all mixtures tested,

as the resulting combustion efficiencies were very similar and independent of the $H_2O:CO_2$ ratio used for the gasification agent. Limited use of CO_2 in the fluidizing gas would be desirable to maintain high gasification rates for this fuel. This limitation derived from the use of CO_2 and the lower gasification rate with this gasification agent than the rate with steam was seen by Cuadrat et al. with a South African coal [4]. However, other types of fuels have higher gasification rates with CO_2 [22]. On the other hand, the implementation of a carbon stripper that increased the char residence time would offset any possible poorer system performance caused by the slower gasification rate.

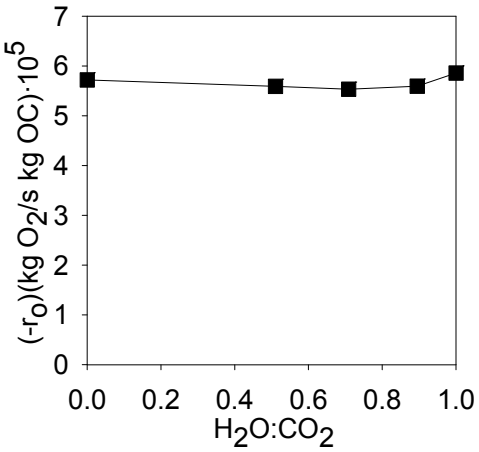

Figure 13. Rate of oxygen transferred by ilmenite for different $H_2O:CO_2$ mixtures as gasification agent.

5. Conclusions

The effect on the fuel-reactor performance of the temperature, the solids circulation rate, the coal feeding rate and the coal particle size were studied in a 500 W_{th} rig based on the CLC technology. Ilmenite was used as oxygen-carrier and the bituminous Colombian coal "El Cerrejón" as fuel. The study in this rig is based on the fuel-reactor performance and the results related to its operation were obtained.

When more coal was introduced in the system, since the circulation rate and the temperature were kept constant and there was oxygen and steam excess in all cases, the resulting combustion efficiency for increasing coal feeding rate did not change substantially. However, the conversion of ilmenite and therefore the oxygen transferred were higher and increased proportionally to the coal feeding rate increase. Thus, the coal conversion is not limited by the reaction rate of ilmenite, but by the char gasification process.

The increase in the recirculation rate and thereby a consequent increase in the oxygen-carrier to fuel ratio and decrease in the mean residence time of solids in the fuel-reactor was assessed. Lower oxygen-carrier to fuel ratios led to enhanced CO_2 capture efficiencies. That was because the increase in char residence time led to an increase in the gasification efficiency. Gasification products are more reactive with ilmenite and have better contact with the oxygen-carrier particles than the released volatile matter. Thus, regarding the combustion step, with higher oxygen-carrier to fuel ratio the combustion efficiency increases, as the relative importance of the gasification products in the reacting gases increased.

However, the combustion efficiency decreased if there was not enough oxygen available to burn the fuel fed. Consequently, the gasification efficiency also dropped because the reactor got enriched in H_2 and CO, which are gasification inhibitors.

A decrease in the gasification agent to fixed carbon ratio down to 0.7 did not influence the combustion efficiency, although the gasification efficiencies slightly increased for higher gasification agent flows closer to the stoichiometric value for gasification. From the experiments done with steam to fixed carbon ratio over 1 no substantial change in the performance of the process is expected when varying the H_2O/C ratio.

The gasification efficiency increased for higher fraction of steam in the gasification agent, although the char conversion with CO_2 could be enough high in a CLC system for solid fuels where a carbon stripper is implemented. The combustion efficiency did not seem to be influenced by the gasification agent used. These results indicate that it is feasible to decrease the gasification agent flow lower than the corresponding gasification agent to fixed carbon ratio lower than 1, and that some of the steam as gasification agent can be replaced by CO_2 recirculated from the outlet fuel-reactor flow, getting the same system performance. This would lead to energy saving derived from the extra need of evaporating steam, and thereby to enhanced total system efficiency.

Acknowledgment

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Nomenclature

$C_{char\ AR}$ carbon flow from the char that goes to the air-reactor (mol/s)

$C_{char\ elutr}$ carbon flow from the elutriated char (mol/s)

C_{vol} carbon flow coming from the volatile matter fed (mol/s)

F_i flow in the fuel-reactor of the corresponding gas i (mol/s)

$F_{C,coal,eff}$ effective carbon in the coal feeding flow rate

F_{ilm} solids circulation rate (kg/s)

H_2O/C steam to fixed carbon ratio (mol H_2O/mol C)

$m_{char,FR}$ mass of char in the fuel-reactor (kg)

$m_{ilm,FR}$ fuel-reactor bed mass or solid hold-up in the fuel-reactor (kg)

M_{O_2} oxygen molecular mass (kg/mol)

$O_{coal,eff}$ flow of oxygen contained in the effective coal introduced (moles O/s)

$O_{2\ demand\ coal,eff}$ oxygen demand of the effective coal fed (moles O_2/s)

$(-r_O)$ rate of oxygen transferred by the oxygen-carrier (kg O_2/s kg OC)

$R_{O,ilm}$ oxygen transport capacity of ilmenite

T_{FR} temperature in the fuel-reactor (ºC)

$t_{m,char}$ mean residence time of char (s)

$t_{m,ilm}$ mean residence time of ilmenite (s)

$x_{char,FR}$ carbon concentration from char in the fuel-reactor

η_{CC} carbon capture efficiency

η_{comb} combustion efficiency

η_{gas} char gasification efficiency

ϕ oxygen-carrier to fuel ratio

Ω_{OD} oxygen demand

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