CHEMICAL-LOOPING COMBUSTION OF COAL USING ILMENITE AS OXYGEN-CARRIER

TESIS DOCTORAL - PhD

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CHEMICAL-LOOPING COMBUSTION OF COAL
USING ILMENITE AS OXYGEN-CARRIER

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Abstract

Chemical-Looping Combustion, CLC, is a promising combustion technology with inherent capture of the greenhouse gas CO\textsubscript{2} at low cost for fossil-fuelled power units. In CLC the oxygen from air is transferred to the fuel by a solid oxygen-carrier that circulates between two interconnected fluidized-bed reactors: the fuel- and the air-reactor. Thus, the direct contact between air and the fuel is avoided and CO\textsubscript{2} is obtained in a separate stream from N\textsubscript{2} in air. In the application of CLC for solid fuels, the oxygen-carrier oxidizes the products of the fuel gasification, which can be carried out ex-situ or in-situ the CLC system. The process where coal gasification takes place in the fuel-reactor is here called in-situ gasification Chemical-Looping Combustion, iG-CLC. The spent oxygen-carrier is transported to the air-reactor where it is oxidized by air, being ready to start a new cycle. The CO\textsubscript{2} capture efficiency depends on the char conversion in the reactor.

This study is focused on the development and assessment of the feasibility of the CLC process for solid fuels, using ilmenite as oxygen-carrier. Ilmenite, a natural mineral composed of FeTiO\textsubscript{3}, is a low cost and promising material for its use on a large scale in CLC.

The performance of ilmenite in the iG-CLC technology for solid fuels was studied from the smaller to the larger scale. The reactivity of ilmenite with CH\textsubscript{4}, H\textsubscript{2} and CO as the main products of coal devolatilization and gasification under different operating conditions of temperature and gas concentration was analyzed in well-defined conditions in TGA and fluidized bed reactor in batch mode. Although initially ilmenite particles present a rather low reactivity, ilmenite was found to undergo an activation process in its reaction rate, whose final value is adequate for the use of ilmenite in iG-CLC. The reaction kinetics of ilmenite for the main reduction and oxidation reactions were determined. The chemical
and physical changes of ilmenite after many redox cycles, as well its fluid-dynamic behavior in fluidized beds were studied in batch fluidized bed reactor. No agglomeration problems and adequate attrition rates were found. The char gasification kinetics of El Cerrejón bituminous coal was determined, and furthermore the char gasification process in presence of ilmenite particles was evaluated in batch fluidized bed reactor at different temperatures and H₂O-CO₂ mixtures as gasification agents, since the gasification rate was found to increase in presence of the oxygen-carrier.

The process performance was studied in continuous testing with different coals from lignite to anthracite in a 500 Wₘₚ and a 10 kWₘₚ facility. The effect of several operation parameters on the performance of iG-CLC process was analyzed. Thus, different experiments were carried out by varying the fuel-reactor temperature, the coal particle size, the solids recirculation rate, the coal feeding flow, and the flow and type of gasification agent. There are unburnt gases that get out of the system, which were found to come from the volatile matter, because they have poor contact with the oxygen-carrier bed. To get high carbon capture it is necessary to work at high fuel-reactor temperatures, desirably above 950°C, and to have enough residence time to increase the extent of char gasification.

The feasibility of application of the iG-CLC technology with fuels of different rank was proven. Furthermore, the effect of the type and characteristics of the solid fuel was assessed. It was found that higher carbon captures are obtained with coals of lower rank which are more reactive and gasify faster. Using H₂O as gasifying agent is desirable to enhance char conversion in case of most types of coals. The use of some using CO₂ is admissible, depending on the resulting gasification rate with CO₂ with the fuel used. Big differences in carbon capture were found depending on the coal. At 900°C and with an average residence time of the solids of 14.4 minutes and steam as gasification agent, the carbon capture obtained were 90% for lignite, 48% for bituminous Colombian coal, 54% for bituminous South African coal and 29% for anthracite. The corresponding combustion efficiencies in the fuel-reactor were in all cases above 70% and at 950°C with bituminous Colombian coal, a combustion efficiency as high as 95% was reached with an inventory of 3100 kg/MWₘₚ. For all types of solid fuels the combustion efficiency can be increased when working at high temperatures and high inventories. The influence in the process of
limestone addition was also studied and a slight improvement in the gas conversion could be seen after limestone addition, which can be explained by limestone catalyzing the Water Gas Shift reaction.

To predict and optimize the iG-CLC process, a simplified model based on mass balances and kinetics of the reactions involved in the process was developed. The performance of the iG-CLC process considering El Cerrejón bituminous coal as fuel was analyzed as a function of the main operating parameters such as the fuel-reactor temperature, the solids inventory in the fuel-reactor, the oxygen-carrier-to-fuel ratio, or the gasification agent to fixed carbon ratio. It was found that it is highly beneficial to increase the solids inventory up to 1000-2000 kg/MWth, but further increase gives no relevant improvement. Because of the low char gasification rate, to get high carbon capture efficiency, a carbon separation system should be implemented to separate unconverted char and recirculate it back to the fuel-reactor. To have a high efficient carbon separation system was found to be determining for the process and can lead to carbon capture values above 90%. The contact of the volatile matter with the oxygen-carrier should be improved with some design solutions. Besides, the implementation of a second fuel-reactor is proposed as a very promising option to fully burn the volatile matter and besides to avoid another oxygen polishing step.

On the whole, the good results confirm the feasibility of the iG-CLC technology with solid fuels and that ilmenite appears to be a suitable material to be used for solid fuel combustion, considering its chemical and physical properties, its lack of toxicity and low market cost.

**Keywords:** CO$_2$ Capture, Chemical-Looping Combustion, ilmenite, coal, oxygen-carrier.
List of Papers

This thesis is based on these following papers that are referred by roman numbers:


Others:


Contribution report

I, III, IV, V, VI, VII and IX. Principal author, responsible for experimental work, data evaluation and writing.

VIII. Principal author, responsible for model developing, data evaluation and writing.

II: Co-author, responsible for experimental work, data evaluation and writing.

X: Co-author, responsible for part of the experimental work, data evaluation and revision of writing.

Congress contributions


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CERTIFICAN:

que la presente memoria, titulada: “Chemical-Looping Combustion of coal using ilmenite as oxygen-carrier”, ha sido realizada bajo nuestra dirección en el Instituto de Carboquímica (ICB-CSIC) por Dña. Ana Cuadrat Fernández, autorizando su presentación como compendio de publicaciones.

Y para que así conste, firmamos el presente certificado en Zaragoza a 2 de febrero de 2012.

Fdo: Dr. Juan Adánez Elorza  Fdo: Dr. Alberto Abad Secades
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Appendix – Papers
1 Introduction
1.1 Greenhouse effect and CO$_2$ mitigation

According to the IPCC (IPCC, 2007), “warming of the climate system is unequivocal”, considering that eleven of the recent years (1995-2006) rank among the twelve warmest years in the instrumental record of global surface temperature since 1850. It is also clear that climate change can strongly modify the earth biodiversity (IPCC, 2002). Among the possible causes, it seems that most of the warming observed over the past 50 years is attributable to human activities, as a consequence of the gases emitted to the atmosphere, the so-called greenhouse gases (GHG) (IPCC, 2001). Among them, CO$_2$ is considered the gas making the largest contribution to the global warming, because CO$_2$ represents the largest emissions of all the global anthropogenic GHG emissions, with percentage values as high as 75% (Archer, 2005), and due to its high residence time in the atmosphere.

The CO$_2$ concentration in the atmosphere has increased strongly over the few past decades as a result of the dependency on fossil fuels for energy production. The global atmospheric CO$_2$ concentration increased from a pre-industrial value of about 280 ppm to 390 ppm in 2010 (NOAA-ESRL, 2010). To assure the increase in average temperatures was lower than 2 $^\circ$C –which it is considered as the limit to prevent the most catastrophic changes in earth– the CO$_2$ concentrations must not exceed 450 ppm. Therefore, it is generally accepted that a reduction in emissions of greenhouse gases is necessary as soon as possible. In 1997, the nations participating in the United Nations Framework Convention on Climate Change drafted the historic agreement known as the Kyoto Protocol (United Nations, 1998). After ratification in 2005, its provisions include a mean reduction in the GHG emissions of the developed countries of 5.2% over the period 2008-2012 compared to 1990 levels.

As for the IPCC, the largest growth in global GHG emissions in the last years has come from the energy supply sector. Energy from fossil sources -gas, oil and coal-, which cause CO$_2$ emissions, will still satisfy over 80% of the demand during the first part of the 21st century. Furthermore, IEA predicts 57% increase of energy demand from 2004 to 2030 (IEA, 2007). Fossil-fueled power units are responsible for roughly 40% of total CO$_2$
emissions, coal-fired units being the main contributor (Carapellucci and Milazzo, 2003). Unfortunately these energy sources will not yet be ready to be substituted massively in the near future (IEA, 2007).

The abatement of GHG emissions can be achieved through a wide portfolio of measures in the energy, industry, agriculture and forest sectors. Up to now, the technological options for reducing net CO₂ emissions to the atmosphere have been focused on (IPCC, 2005): 1) increasing the efficiency of energy conversion and/or utilization; 2) switching to less carbon intensive fuels, e.g. natural gas; 3) increasing the use of renewable energy sources (biofuel, wind power, etc.) or nuclear energy, and 4) the use of technologies of CO₂ Capture and Storage (CCS) also appears as a relevant option to reduce the emissions of GHG, see Figure 1. It is clear that no single technology option will provide all of the emissions reductions needed.

Figure 1. Illustrative example of the global potential contribution of CCS as part of a mitigation portfolio. Global CO₂ emissions in grey and corresponding contributions of main emissions reduction measures in color (IPCC, 2007).

According to the analysis made by the IPCC and IEA (IPCC, 2005; IEA, 2006), CCS could contribute 15–55% to the cumulative mitigation effort worldwide until 2100, averaged over a range of baseline scenarios (see Figure 1), to stabilize climate change at a reasonable cost. It is likely that there is enough technical potential for geological storage. CCS must provide 20% of the global CO₂ cuts required by 2050, according to the IEA (IEA, 2006).
1.2 CO₂ Capture and Storage

The purpose of CCS technology is to produce a concentrated stream of CO₂ from industrial and energy-related sources, transport it to a suitable storage location, and then store it away from the atmosphere for a long period of time. Thus, if CO₂ is transported and stored appropriately, it will not further contribute to the greenhouse effect. The IPCC Special Report on Carbon Dioxide Capture and Storage (IPCC, 2005) gives an overview of the different options available both for the capture, transport and storage processes. Figure 2 shows sources for which CCS might be relevant and CO₂ transport and storage options.

Figure 2. Schematic diagram of possible CCS options.

For CCS to achieve the estimated economic potential, several hundreds to thousands of CO₂ capture systems would need to be installed over the coming century, each capturing 1–5 MtCO₂ per year. One aspect of the cost competitiveness of CCS systems is that CCS technologies are compatible with most current energy infrastructures, being the implementation of these technologies more feasible and readily achievable in stationary power units. Thus, CCS is an essential component of a portfolio of technologies and measures to reduce global emissions and help to avoid the most serious impacts of climate change.
change (IPCC, 2005; IEA, 2010). Costs for CO$_2$ capture include the capture process, plus the conditioning and compression/liquefaction of the captured CO$_2$ required for transport. Implementing CCS will of course have an impact on the cost for the electricity production. Estimations on using commercially available technologies indicate an increase in the cost of produced electricity by 37-85% in natural gas combined cycle power units and 43-91% in pulverized coal power units (IPCC, 2005).

Among the three steps involving CCS (capture, transport and sequestration), CO$_2$ capture is the most costly. The development of CO$_2$ capture systems with low economic and energetic penalty has the mayor potential to reduce the global cost of the CCS process. Three main approaches were considered for CO$_2$ capture in industrial and power generation applications: post-combustion systems, oxy-fuel combustion, and pre-combustion systems. A brief overview of the current situation of these technologies can be found in the work of Toftegaard et al. (2010). However, most of the technologies that reduce CO$_2$ emissions have high energy penalty using commercial technologies available. This leads to a lower overall energetic efficiency and an increase in the energy price.

The Zero Emissions Platform (ZEP) report about the costs of CCS on existing pilot and planned demonstration projects concluded that for hard coal-fired power units, the addition of CO$_2$ capture and the processing of CO$_2$ for transport is equivalent to CO$_2$ avoidance costs of 30-40€/t (Zero Emissions Platform, 2011). They found no clear difference between any of the analyzed capture technologies and all could be competitive in the future if successfully demonstrated. The conclusion of the study was that, following the European Union’s CCS demonstration program, CCS will be cost-competitive with other sources of low-carbon power, including on-/offshore wind, solar power and nuclear. Further decrease in the CCS cost will be possible by developing CO$_2$ capture technologies with low energetic and economical penalty.

1.2.1 Post-combustion capture

It consists in separating the CO$_2$ from the flue gas after the combustion step. Amine absorption/desorption is often used for this purpose. With this method, the flue gas is led
to a scrubber where the liquid solvent absorbs the CO₂ and the rest of the flue gas is released to the atmosphere. Solvent regeneration is obtained by temperature changes which release CO₂. The separation is not inherent to the combustion step and since this method requires extra energy consumption, the process efficiency is affected. It has been estimated that CO₂ capture by post-combustion in coal power units would reduce their efficiency from 8 to 16% and for a natural gas combined cycle from 5 to 10% (Ghoniem, 2011). To decrease costs, there are several technologies in development, such as the chilled ammonia process by ALSTOM or the calcination-carbonation cycle.

1.2.2 Pre-combustion capture

In a first step, the fuel is converted to a mixture of CO, CO₂, H₂ and H₂O using O₂ and/or H₂O by reforming natural gas or gasifying coal. The next step is to shift CO and H₂O producing CO₂ and H₂. Removing CO₂ from the mixture, using e.g. physical absorption with solvents, yields almost pure H₂ which can be used as a carbon-free fuel in a combined gas and steam turbine cycle. As a result, no carbon containing gases are released. However, as for the post-combustion technology, this method is energy consuming. The technology required for pre-combustion capture is widely applied in fertilizer manufacturing and in hydrogen production. Although the initial fuel conversion steps of pre-combustion are more elaborate and costly, the higher concentrations of CO₂ in the gas stream and the higher pressure make the separation easier. The estimated efficiency reduction in a coal gasification unit is about 7 to 13% and in a natural gas reforming unit is 4-11% (Ghoniem, 2011). The integration of this process with a combined cycle can be beneficial, reaching high energetic efficiencies. Besides, membrane technologies are in development.

1.2.3 Oxy-fuel or O₂/CO₂ combustion

In this method, the combustion step is achieved using a mixture of oxygen and recirculated flue gases, i.e. carbon dioxide, instead of air. In the flue gases, almost only CO₂ and H₂O are present. By condensing steam, almost pure CO₂ is obtained. The carbon capture efficiency, nearly 100%, is thus considerably higher than the efficiency of the post-combustion treatment. However, an Air Separation Unit is required for the oxygen
production, which induces to extra cost and energy penalties. The estimated efficiency reduction in a coal gasification unit is 6-9% and in a natural gas unit is 5-12% (Ghoniem, 2011). Membrane technologies are also in development.

1.2.4 CCS demonstration projects

As for projects in the bigger scale focused on storage in CCS, the first application started in 1996 within the Sleipner CO₂ storage project from the former Norwegian company Statoil, now StatoilHydro. The CO₂ contained in the natural gas from the Sleipner gas field is injected into a deep saline aquifer called the Utsira formation located in the North Sea between Norway and Scotland, at a depth of around 1000 meters. Around 1 million tones CO₂ is annually injected in the sand stone formation since the project start (IPCC, 2005).

There are several projects on CCS worldwide in operation to date. The most important are the following: The Weyburn Project since 2000 from US and Canada on CO₂ geological storage; the In Salah gas project in South Algeria on CO₂ post-combustion and storage in an underground aquifer; the Snøhvit project in the Norwegian Sea on CO₂ storage in a sandstone; the Callide ‘A’ Power Station project in Australia on oxy-fuel capture and storage on a gas field; the project at Schwarze Pumpe, Germany, which has a 30MWth oxyfuel coal boiler and the CIUDEN foundation which accounts with a 30 MWth circulating fluidized bed and a 20 MWth pulverized oxyfuel coal boilers in El Bierzo, Spain.

1.3 Chemical-Looping Combustion

The previous technologies involve expensive and energy demanding gas separation processes. Thus, new processes and further research are being developed to reduce the energy penalty of these technologies. To address this issue and since the main cost comes from the separation of CO₂ from N₂, an alternative is to use a process where the combustion air and the fuel are never mixed, so that no nitrogen is present in the combustion exhaust gases. The CO₂ separation is then inherent to the combustion step.
This principle could be called unmixed combustion and requires a way to transfer oxygen from air to fuel. The process on which this thesis is based, Chemical-Looping Combustion (CLC), also belongs to this category.

The CO₂ Capture Project (CCP) –Phase I– decided at the beginning of 2000 to collaborate with governments, industry, academic institutions and environmental interest groups to develop technologies that greatly reduce the cost of CO₂ capture (Thomas and Benson, 2005). The objective was to identify the most promising technologies that had the potential to deliver performance and efficiency improvements resulting in close to a 50% reduction in the cost of CO₂ capture. Among them, the Chemical-Looping Combustion (CLC) process was suggested among the best alternatives to reduce the economic cost of CO₂ capture (Kerr, 2005). If the environmental impact is also considered, CLC is preferred against other CO₂ capture options (Petrakopoulou et al., 2011). Moreover, the IPCC in their special report on Carbon Dioxide Capture and Storage made a comparative economic evaluation of the different technologies (Thambimuthu et al., 2005). The CLC process, with a cost of 14 US$ per ton of CO₂ avoided, was one of the cheapest technologies. The main drawback attributed to CLC was a very low confidence level as a consequence of the lack of maturity of the technology. This is an emerging technology although during the last 10 years has undergone a great development.

Chemical-Looping Combustion (CLC) is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen-carrier, avoiding direct contact between fuel and air. Lyngfelt et al. (2001) proposed the use of two interconnected fluidized beds for a CLC system with the oxygen-carrier circulating between them. Ideally, the stream of combustion gases from the fuel-reactor contains primarily CO₂ and H₂O, although some unburnt compounds can also appear (e.g. CO, H₂, CH₄). In this case, an oxygen polishing step can be necessary for complete combustion to CO₂ and H₂O. After that, water can be easily separated by condensation and a highly concentrated stream of CO₂ ready for compression and sequestration is achieved. The CO₂ capture is inherent to this process, as the air does not get mixed with the fuel, and no additional costs or energy penalties for gas separation are required. The gas stream from the air-reactor is oxygen-depleted and consists in N₂ and some unreacted O₂.
Important progress has been made in CLC for gaseous fuels, i.e., natural gas and syngas, to date. Most of the oxygen-carriers proposed in the literature are synthetic materials. In general, the oxygen-carrier is based on a transition state metal oxide, e.g. CuO, NiO, Co₃O₄, Fe₂O₃ or Mn₃O₄, which is supported on different inert materials, as Al₂O₃, SiO₂, TiO₂ or ZrO₂. A selection of oxygen-carrier materials for natural gas and syngas combustion has been summarized by Hossain and de Lasa (2008) and Lyngfelt et al. (2008) and recently by Adánez et al. (2011).

The feasibility of this process has been successfully demonstrated in different CLC prototypes in the 10-140 kWth range using oxygen-carriers based on nickel, copper and cobalt oxides (Ryu et al., 2005; Lyngfelt and Thunman, 2005; Adánez et al., 2006; Linderholm et al., 2008 and 2009; Kolbitsch et al., 2009). Regarding the intensive use of coal for energy generation, there is an increasing interest for CLC using this fuel.

1.3.1 CLC with solid fuels

There are three options for the use of the CLC technology with coal. The first one is to carry out previous coal gasification and subsequently to introduce the produced gas in the CLC system. This option needs pure O₂ for the gasification step and thus an air separation unit and an external gasifier are required. Simulations performed by Jin and Ishida (2004) and Wolf et al. (2001) showed that this process has the potential to achieve an efficiency of about 5-10% points higher than a similar combined cycle with conventional CO₂ capture technology working under pressure. Several oxygen-carriers based on Ni, Cu, Fe and Mn oxides have shown good reactivity with syngas components, i.e. H₂ and CO (Mattisson et al., 2007; Abad et al., 2007a), and the use of syngas in a CLC system has been successfully accomplished in 300-500 Wth continuous CLC units (Johansson et al., 2006a; Abad et al., 2006, 2007b; Dueso et al. 2009; Forero et al., 2009). The second possibility for the use of coal in CLC is the direct feeding in the CLC process, that is, avoiding the need of an external gasifier and the corresponding gaseous oxygen requirement (Cao and Pan, 2006; Dennis et al., 2006). The reactor scheme for this CLC configuration is shown in Figure 3. In this option coal is physically mixed with the oxygen-carrier in the fuel-reactor which is
fluidized by a gasification agent. As the gasification of coal happens inside the fuel-reactor, this process has been referred as the in-situ gasification CLC (Adánez et al., 2011).

The in-situ gasification of the solid fuel is carried out in the fuel-reactor and the carrier reacts with the gas products from steam coal gasification, where H₂ and CO are main components. Thus, the volatiles release and the solid fuel gasification proceed in the fuel-reactor according to reactions (1-3) and the resulting gases are oxidized through reduction of the oxidized oxygen-carrier, MeₓOᵧ, by reaction (4). The oxygen-carrier reduced in the fuel-reactor, MeₓOᵧ₋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.

Coal → Volatile matter + Char  
Char + H₂O → H₂ + CO  
Char + CO₂ → 2 CO  
H₂, CO, Volatile matter + n MeₓOᵧ → CO₂ + H₂O + n MeₓOᵧ₋₁  
MeₓOᵧ₋₁ + ½ O₂ → MeₓOᵧ

It is expected that the gasification process was the limiting step in the fuel-reactor, so the stream of solids that exits from the fuel-reactor contains some unconverted char together with the oxygen-carrier. To increase the mean residence time of char and to avoid ungasified char to enter the air-reactor, the char particles can be separated from the oxygen-carrier in a carbon separation system and re-introduced to the fuel-reactor, as shown in

Figure 3. Reactor scheme of the iG-CLC process for solid fuels (optional stream).
Figure 3. It is necessary to point out that the transference of char to the air-reactor does not reduce the energetic efficiency of the process but it decreases the carbon capture efficiency of the system because some CO₂ will exit with the exhaust gas from the air-reactor.

Moreover, as a consequence of the ash present in the solid fuel it is necessary to drain ashes from the system to avoid its accumulation in the reactors. The drain stream will also contain some oxygen-carrier. Thus, the lifetime of this material is expected to be limited by the losses together the drain stream rather than for its degradation.

For direct CLC with solid fuels, there are three particular aspects to be taken into account: (1) high combustion efficiencies in the fuel-reactor should be reached, (2) the system must be optimized to get maximum ash separation and minimum carrier losses, and (3) the carbon separation system should be optimized. Thus, the efficiency of char conversion in the fuel-reactor and the separation of ashes from the oxygen-carrier seem to be key factors for the development of this process.

Recently, a third option has been proposed: the Chemical-Looping with Oxygen Uncoupling process (CLOU) (Mattisson et al., 2009). In the CLOU process the oxygen-carrier releases oxygen in gas phase, and this gaseous oxygen reacts with the fuel. CLOU allows solid fuels to be burnt in gas-phase oxygen without the need for an energy-intensive air separation unit. A key issue for the development of the CLOU process is to develop suitable materials with oxygen uncoupling properties.

### 1.3.2 Oxygen-carriers for iG-CLC

The selection of the oxygen-carrier is a key factor for the CLC technology development. Suitable oxygen-carriers must show high reaction rates and oxygen transport capacity, complete fuel conversion to CO₂ and H₂O, negligible carbon deposition, avoidance of agglomeration, and sufficient durability as well as good chemical performance. These properties must be maintained during many reduction and oxidation cycles. In addition, the cost of the oxygen-carrier, environmental characteristics and health aspects are also
important for its use with coal, as it is predictable a partial loss together with the coal ashes when removing them from the reactor to avoid their accumulation in the system.

Synthetic materials have been proposed as oxygen-carriers in CLC for solid fuels, e.g. coal, petroleum coke, biomass or solid wastes (Cao et al., 2006; Scott et al., 2006; Leion et al., 2007; Yang et al., 2007; Chuang et al., 2008; Shen et al., 2009a;b;c; Siriwardane et al., 2009). There are studies made on the reactivity of synthetic oxygen-carriers mainly based on CuO (Cao et al., 2006), Fe₂O₃ (Scott et al., 2006; Leion et al., 2007; Wu et al., 2010) and NiO (Zhao et al., 2008) for in-situ gasification of the solid fuel. However, for CLC with solid fuels, the use of low-cost natural minerals or industrial waste products seems to be more suitable, as it is predictable a partial loss of the oxygen-carrier together with the coal ashes.

At the beginning of this thesis in 2008, there were only a few studies about this technology. There were some studies on the suitability of using low cost minerals such as ilmenite, an iron based natural ore. Leion et al. (2008a,b) analyzed the reactivity of ilmenite in a batch fluidized bed for solid fuels combustion. Ilmenite gave high conversion of CO and H₂ but moderate conversion of CH₄. They observed a gain in ilmenite reactivity as increasing redox cycles, and eventually reactivity as high as for a synthetic Fe₂O₃-based oxygen-carrier was reached. Ilmenite showed high stability in its reactivity after repeated redox cycles. They also saw that defluidization occurred only when the ilmenite particles were in a highly reduced state (Leion et al., 2008b), which is not expected at CLC operation. These were first approaches of the ilmenite performance as oxygen-carrier in iG-CLC. In order to advance in this technology, a more comprehensive analysis of the properties of ilmenite as oxygen-carrier is needed. An assessment of the conditions in which the gain in reactivity occurs as well as the reactivity and properties of ilmenite after a high number of redox cycles, the evaluation of the intrinsic kinetics in the oxidation and reduction reactions and a study on the gasification reaction under iG-CLC conditions are required. A deeper study on the behavior in fluidized bed of the oxygen-carrier material is also essential.

The proof of the concept of the iG-CLC process in a continuously operated prototype was carried out by Berguerand and Lyngfelt (2008a; b) using ilmenite as oxygen-carrier. Due to the characteristics of this facility with over-bed coal feeding, the volatiles do not get in
good contact with oxygen-carrier particles. Thus, only the conversion of gases from steam gasification (CO and H₂) was analyzed. A CO₂ capture within the range 65-82% was obtained for South African coal as fuel at 900-950°C. Petcoke was also used as a fuel with low volatile content, for which CO₂ capture was 60-75% at 900-950°C, with an oxygen demand around 25%. The performance of this prototype could be improved by increasing the residence time of the particles in the fuel-reactor to get higher CO₂ capture and by increasing the separation efficiency of the cyclone after the fuel-reactor. Also, the incomplete gas conversion resulted into the presence of unconverted gases in the fuel-reactor outlet stream that demanded 29-30% of the total oxygen needed to fully burn coal to H₂O and CO₂. The gas conversion could be improved by a polishing step with O₂ after the fuel-reactor. Due to the promising good behavior observed for ilmenite, in this work the iG-CLC process for solid fuels using ilmenite as oxygen-carrier was evaluated. Since to date only the effect of the temperature had been analyzed by doing experiments at two temperatures. To evaluate the influence of different operating variables in the system is necessary for the progress of this technology, as well as to try other types of fuels with different ranks. Besides, the combustion of the devolatilization products should be analyzed. While this thesis was developed, more studies about ilmenite and other possible oxygen-carriers –natural ores and industrial products, most of all- for iG-CLC in different scales were done concurrently, where different types of fuels were used. The main results obtained in other later studies will be commented along this thesis.

1.4 Objective

The aim of this work was to study the feasibility and performance of the Chemical-Looping Combustion technology for solid fuels and to evaluate the conditions and key parameters that improve the efficiency of the process, in order to get a technically and economically competitive combustion technology with CO₂ capture.

This was investigated by performing tests in a thermogravimetric analyzer, a batch fluidized bed reactor for gaseous fuels, a batch fluidized bed reactor for solid fuels and a continuous CLC unit for solid fuels, all these devices are placed at the Instituto de
Carboquímica (ICB-CSIC) in Zaragoza (Spain). Tests in a 10 kW\textsubscript{th} continuous CLC unit for solid fuels built at Chalmers in Göteborg (Sweden) were also done. Focus was made on analyzing the behavior and suitability of ilmenite as oxygen-carrier in CLC with solid fuels by in-situ gasification CLC (iG-CLC), on assessing the operation performance using different solid fuels and evaluating the effect of operational parameters on carbon capture and combustion efficiency. Furthermore, with the experimental information gathered, a theoretical simplified model for the fuel-reactor was developed to analyze the effect of the main operating variables in the CLC process performance.

This thesis is based on nine papers. Paper I analyzes the behavior of ilmenite as oxygen-carrier in CLC and its activation process. Changes in its properties through redox cycles in a thermogravimetric analyzer were also assessed. In Paper II the kinetics of ilmenite as oxygen-carrier for the reduction and oxidation reactions taking place in CLC with the main gas products of coal devolatilization and gasification were determined. In Paper III the reactivities with different mixtures of reducing agents and the variation of chemical and physical characteristics of ilmenite particles during high number of consecutive redox cycles in fluidized-bed was assessed. In Paper IV the char gasification step and subsequent conversion of the gasification products was studied in a fluidized bed using a bituminous coal char as fuel at different temperatures and using various H\textsubscript{2}O-CO\textsubscript{2} mixtures as gasification agent and ilmenite as oxygen-carrier. Papers V, VI and IX explain results obtained in a continuous facility fuelled with coal. In Paper V the effect of temperature and coal particle size of a bituminous coal on the process performance was assessed. Char gasification and combustion of both gasification products and volatile matter were also evaluated. In Paper VI the effect of operating conditions such as the solids circulation rate and oxygen-carrier residence time, the coal flow feed and the gasification agent flow and type were investigated. In Paper IX the variation in the system performance and feasibility of the technology when using different types of coals is investigated. In Paper VII the influence of limestone addition to ilmenite as oxygen-carrier was tested in a continuous 10 kW\textsubscript{th} CLC pilot using petroleum coke as fuel at different temperatures and solids circulation rates. Based on experimental results, in Paper VIII a simplified model that describes the fuel-reactor of an iG-CLC system was developed. The model includes the possibility of using a carbon separation system.
2 Experimental
2.1 Oxygen-carrier

Ilmenite is a common mineral found in metamorphic and igneous rocks. Ilmenite is mainly composed of FeTiO₃ (FeO·TiO₂), where iron oxide is the active phase that behaves as an oxygen-carrier.

The ilmenite used in this study is a concentrate from a Norwegian natural ore and it has a purity of 94.3%. The particle size used was 150-300 μm. Fresh ilmenite and calcined ilmenite particles were initially used in this work. Calcined ilmenite was obtained after a thermal treatment of fresh ilmenite at 950 °C in air during 24 hours.

Ilmenite particles were physically and chemically characterized by several techniques. Table 1 shows the main physical and chemical properties of the Norwegian ilmenite used as oxygen-carrier in the experiments of this research. Both fresh and calcined ilmenite are characterized. As it is later explained, the oxygen-carrier undergoes an activation process with the number of cycles. Therefore, the properties of the here called “activated ilmenite” are also analyzed. As an example of an activated ilmenite, the properties of the activated ilmenite after 20 redox cycles in fluidized bed with 25 vol.% CH₄ + 10 vol.% H₂O as reducing agent at 900 °C are also given in Table 1. Both calcined and activated ilmenite were used for the determination of ilmenite reaction kinetics. The true density of the particles was measured with a Micromeritics AccuPyc II 1340 Helium picnometer. The force needed to fracture a particle was determined using a Shimpo FGN-5X crushing strength apparatus. The mechanical strength was taken as the average value of at least 15 measurements undertaken on different particles of each sample randomly chosen. Particle porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by powder X-ray diffraction (XRD) patterns acquired in an X-ray diffractometer Bruker AXS D8ADVANCE using Ni-filtered Cu Ka radiation equipped with a graphite monochromator. Semi-quantitative percentages of the different components in each sample were obtained through normalization by means of a ratio between the intensity peaks of the main component and a substance of reference.
Table 1. Composition (%wt.) and physical properties of fresh, calcined and activated ilmenite after 20 redox cycles in fluidized bed (Reducing agent: 25 vol.%CH₄+10 vol.%H₂O).

<table>
<thead>
<tr>
<th></th>
<th>Fresh ilmenite</th>
<th>Calcined ilmenite</th>
<th>Activated ilmenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density (kg/m³)</td>
<td>4580</td>
<td>4100</td>
<td>4250</td>
</tr>
<tr>
<td>$R_{O,ilm}$ (%)</td>
<td></td>
<td>4.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Grain radius (µm)</td>
<td>0.5</td>
<td>0.5</td>
<td>1.25</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>0</td>
<td>1.2</td>
<td>12.7</td>
</tr>
<tr>
<td>BET Surface (m²/g)</td>
<td>0.6</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Crushing strength(N)</td>
<td>2.4</td>
<td>2.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XRD (main species)</th>
<th>FeTiO₃, Fe₂O₃, TiO₂</th>
<th>Fe₂TiO₅, Fe₂O₃, TiO₂</th>
<th>Fe₂TiO₅, Fe₂O₃, TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃ (%wt.)</td>
<td>14.8</td>
<td>11.2</td>
<td>22.0</td>
</tr>
<tr>
<td>Fe₂TiO₅ (%wt.)</td>
<td>-</td>
<td>54.7</td>
<td>38.5</td>
</tr>
<tr>
<td>TiO₂ (%wt.)</td>
<td>14.0</td>
<td>28.6</td>
<td>34.0</td>
</tr>
<tr>
<td>FeTiO₃ (%wt.)</td>
<td>65.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inert (%wt.)</td>
<td>5.7</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The XRD analysis revealed ilmenite (FeTiO₃), hematite (Fe₂O₃) and rutile (TiO₂) as major components of fresh ilmenite. Besides, SEM-EDX analyses revealed a Fe:Ti molar ratio around 1:1. During the thermal treatment ilmenite (FeTiO₃) was fully oxidized to pseudobrookite (Fe₂TiO₅). Calcined ilmenite consists of a mixture of ferric pseudobrookite (Fe₂TiO₅), rutile (TiO₂) and some free hematite (Fe₂O₃), which confirms the literature data indicating that iron compounds in ilmenite are in the most oxidized state after calcination at 950ºC (Rao and Prototypeaud, 1975). Minor amounts of oxides and silicates can be found, mainly MgSiO₃ and MnO₂.

The oxygen transport capacity of ilmenite $R_{O,ilm}$ corresponds to the reduction of the Fe₂TiO₅ and Fe₂O₃ present in ilmenite, being the reduced species FeTiO₃ and Fe₃O₄, respectively. Although the oxidized species can get further reduced, the thermodynamic equilibriums indicate that Fe₂TiO₅ and Fe₂O₃ should be only reduced up to FeTiO₃ and Fe₃O₄ respectively in order to reach full conversion to CO₂ and H₂O of the reducing gases,
which is the objective of a CLC process. Low values of BET surface area were measured, but a slight increase was observed after calcination. Mercury porosimetry of both fresh and calcined ilmenite exhibit low porosity development. This ilmenite has shown good reactivity and properties from batch fluidized bed testing (Leion et al., 2008a,b; 2009a,b; Bidwe et al., 2011). It has also been tested with solid fuels in a 10 kW unit at Chalmers University of Technology (Berguerand and Lyngfelt, 2008a; b; 2009a; b) and with gaseous fuels in a 10 kWth unit (Bidwe et al., 2011) and a 120 kWth unit (Pröll et al., 2009).

2.2 Fuels

In this thesis both gaseous and solid fuels were used. As gaseous fuels, pure gases such as CH₄, H₂ or CO were used, considered as main products of coal devolatilization and gasification. A range of coals with different behavior was used as fuels: a Spanish anthracite, a Spanish lignite and two bituminous coals from Colombia and South Africa. Following the ASTM characterization, South African coal is a medium volatile (MV) bituminous coal, whereas Colombian coal is a high volatile (HV) bituminous coal. Mexican petcoke was also used. The properties of all these solid fuels are gathered in Table 2. Three different particle sizes of Colombian coal were used: +74-125, +125-200 and +200-300 μm. The particle size used for lignite, South African coal and anthracite was +200-300 μm and for petcoke was +90-200 μm.

The HV bituminous Colombian coal was subjected to a thermal pre-treatment for pre-oxidation to reduce its swelling properties. Thus, coal was placed in trays in layers of about 3 mm height and exposed to heating at 180 °C in air atmosphere for 28 hours. The use of pre-treated coal eliminates the swelling properties and avoids the pipe clogging and coal particles agglomeration showed when fresh coal was used. Pre-oxidation causes an increase in oxygen content and a decrease in the heating value.

Char of bituminous South African and pre-treated Colombian bituminous coal were produced and used (see properties in Table 3). They were done by devolatilizing batches of
500 g of coal particles in a fluidized-bed reactor. The reactor was fluidized by N\textsubscript{2} and it was heated up from room temperature to 900 °C with a temperature ramp of 20 °C/min and afterwards cooled down. The N\textsubscript{2} flow was correspondingly reduced as the temperature increased to ensure bubbling bed conditions and to avoid elutriation of particles. The particle size for South African coal char used was +100-200 μm and for bituminous Colombian coal it was +125-200 μm.

Table 2. Proximate and ultimate analysis and low heating value of solid fuels used.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture,%wt.</td>
<td>12.5</td>
<td>6.2</td>
<td>2.3</td>
<td>4.2</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Volatile matter,%wt.</td>
<td>28.7</td>
<td>33.4</td>
<td>33</td>
<td>25.5</td>
<td>7.6</td>
<td>9.9</td>
</tr>
<tr>
<td>Fixed carbon,%wt.</td>
<td>33.6</td>
<td>48.5</td>
<td>55.9</td>
<td>56</td>
<td>59.9</td>
<td>81.6</td>
</tr>
<tr>
<td>Ash,%wt.</td>
<td>25.2</td>
<td>11.9</td>
<td>8.8</td>
<td>14.3</td>
<td>31.5</td>
<td>0.5</td>
</tr>
<tr>
<td>LHV,kJ/kg</td>
<td>16252</td>
<td>25878</td>
<td>21899</td>
<td>26434</td>
<td>21878</td>
<td>31750</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>45.4</td>
<td>68</td>
<td>65.8</td>
<td>69.3</td>
<td>60.7</td>
<td>81.3</td>
</tr>
<tr>
<td>Fresh Bit. Colomb.</td>
<td>2.5</td>
<td>4.2</td>
<td>3.3</td>
<td>4</td>
<td>2.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Pret. Bit. Colomb.</td>
<td>0.5</td>
<td>1.6</td>
<td>1.6</td>
<td>2</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>MV Bit. S.African</td>
<td>5.2</td>
<td>0.6</td>
<td>0.6</td>
<td>1</td>
<td>1.3</td>
<td>6</td>
</tr>
<tr>
<td>Anthracite</td>
<td>8.6</td>
<td>7.5</td>
<td>17.6</td>
<td>5.2</td>
<td>2.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Petcoke</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Composition of the chars used in this work.

<table>
<thead>
<tr>
<th></th>
<th>C(%wt.)</th>
<th>H(%wt.)</th>
<th>N(%wt.)</th>
<th>S(%wt.)</th>
<th>O(%wt.)</th>
<th>Ash(%wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pret. Bit. Colomb</td>
<td>79.8</td>
<td>0.7</td>
<td>1.3</td>
<td>0.6</td>
<td>4.0</td>
<td>13.6</td>
</tr>
<tr>
<td>South African</td>
<td>75.2</td>
<td>0.9</td>
<td>1.6</td>
<td>0.7</td>
<td>2.3</td>
<td>19.3</td>
</tr>
</tbody>
</table>
2.3 Thermogravimetric analyzer

The oxidation and reduction reaction rates of the different samples analyzed during this thesis, as well as the kinetics of the reduction and oxidation reactions for the calcined and activated ilmenite were determined through thermogravimetric analysis in a CI Electronics thermobalance, see Figure 4.

TGA experiments allowed analyzing the reactivity of the oxygen-carriers under well-defined conditions, by means of measuring the weight variation versus time or temperature during reaction with gases. The reactor consists of two concentric quartz tubes (24 mm i.d. and 10 mm i.d.) placed in an oven. The sample-holder was a wire mesh platinum basket (14 mm diameter and 8 mm height) designed to reduce mass-transfer resistance around the solid sample. The temperature and sample weight were continuously collected and recorded in a computer. The reacting gas mixture (25 L\textsubscript{N}/h) was measured and controlled by electronic mass flow controllers.

Figure 4. CI thermobalance layout.

For the measurement of the reaction rates, the ilmenite particles were loaded in a platinum wire basket. The sample weight used for the experiments was about 50 mg. The oxygen-carrier particles were heated up to the desired temperature in an air atmosphere. Once the set temperature was reached, the experiment started by exposing the oxygen-carrier to the
desired conditions for the reduction step. When a subsequent oxidation was made to measure the oxidation rate, in order to avoid the mixing of combustible gas and air, nitrogen was introduced for 2 min between the oxidizing and the reducing period. A mass value of 100% is assumed to be the sample in its most oxidized state and the mass loss is considered to be exclusively due to oxygen transfer.

In this thesis, the reactivity with the main reacting gases considered present in a CLC system, i.e. CH₄, CO and H₂ was analyzed for a wide variety of samples. If steam was used, before entering the reactor the reacting gases were directed through a water deposit which was heated at a set temperature so that the generated steam had the desired partial pressure.

Data evaluation

The conversion for the reduction, \( X_r \), and the oxidation, \( X_o \), reactions with time for consecutive cycles of ilmenite are calculated from the mass variations registered in TGA as:

\[
X_r = \frac{m_o - m_r}{m_o - m_v}
\]

\[
X_o = 1 - X_r
\]

The difference between the fully oxidized and reduced form of the oxygen-carrier defines its oxygen transport capacity, \( R_{OC} \), which is the mass fraction of the oxygen-carrier that is used in the oxygen transfer:

\[
R_{OC} = \frac{m_o - m_r}{m_o}
\]

For the specific case of ilmenite as oxygen-carrier, the oxygen transport capacity of ilmenite is this thesis is designated as \( R_{OC,ilm} \). The mass based conversion of ilmenite, \( \omega \), indicates only the oxygen transfer and is independent of the oxygen transport capacity of the oxygen-carrier. It is expressed as:
To facilitate a comparison of reactivity between different oxygen-carriers a rate index is often used as a normalized rate at a fuel gas concentration of 15% (Johansson et al., 2006b). The rate index, expressed in %/min is calculated as:

$$\omega = \frac{m}{m_o} = 1 + R_{O,ilm} (X_o - 1) = 1 - R_{O,ilm} X_r$$  \hspace{1cm} (9)$$

The rate index is calculated as:

$$Rate\ index\ (%) = 100 \cdot 60 \cdot \left( \frac{d\omega}{dt} \right)_{norm} = 100 \cdot 60 \cdot R_{O,ilm} \left( \frac{dX_i}{dt} \right)_{norm}$$  \hspace{1cm} (10)$$

The normalized reactivity is calculated as:

$$\left( \frac{dX_i}{dt} \right)_{norm} = \frac{p_{ref}}{p_{TGA}} \left( \frac{dX_i}{dt} \right)$$  \hspace{1cm} (11)$$

$P_{ref}$ is a reference partial pressure that has been used in previous studies and it is 0.15 atm for reduction and $P_{ref}=0.10$ atm for oxidation (Johansson et al., 2006b). $P_{TGA}$ is the partial pressure of the fuel gas used in the TGA experiments.

### 2.4 Batch fluidized bed reactor for gaseous fuels

Several reduction-oxidation cycles with different reducing gases were performed in a batch fluidized-bed to investigate the gas product distribution and the variation of the chemical and physical properties of ilmenite particles with the number of cycles.

Figure 5 shows the experimental setup. It consists of a system for gas feeding, a fluidized-bed reactor (55 mm i.d.) made of Kanthal, two filters that recover the solids elutriated from the fluidized-bed working alternatively, and the gas analysis system. The whole fluidized-bed reactor is inside an electrically heated furnace. The gas feeding system allowed the feeding of the fuel gas (mixtures of CH₄, CO, CO₂, H₂, H₂O and N₂) during the reducing
period and a mixture of air or N₂ for oxidation of ilmenite. N₂ was introduced between the two periods during 2 min to purge and avoid the contact between the gas fuel and air. For the supplying of the steam there is a liquid flow controller for water which is subsequently heated up and evaporated with a resistance heater and swept away by the rest of the reducing gas. Changes of gases during reduction, oxidation or purge were done by a three-way valve.

Figure 5. Experimental setup used for multicycle tests in a fluidized-bed reactor.

The differential pressure drop in the bed is measured by means of two pressure taps connected to the bottom and top of the reactor, and are used to detect possible agglomeration problems in the bed. The reaction progress is determined from gas analysis at the reactor outlet. The gas analysis system consists of several online gas analyzers. CH₄, CO and CO₂, dry basis concentrations are measured using non-dispersive infrared analysis (NDIR) and H₂ by thermal conductivity. O₂ concentration is determined using a paramagnetic analyzer. Water content is measured via Fourier Transform Infrared (FTIR Gasmet Cx-4000) analyzer. All data were collected by means of a data logger connected to a computer. The gas concentration was corrected considering the flow dispersion through the sampling line and the analyzers. Thus, the actual concentration of the gases at the bed exit was obtained by a deconvolution method similar to that found in Abad et al. (2006).
To measure the attrition rate, particles elutriated from the fluidized-bed reactor were retained in a filter, and were taken every 10 cycles.

Data evaluation

From the gas product distribution, it is possible to know the rate of oxygen transferred, \( r_O(t) \), from ilmenite to the fuel gas in case of the reduction reaction, and from the oxygen in the air to ilmenite in case of the oxidation reaction, as a function of reaction time:

For CH\(_4\), CO and H\(_2\):

\[
2 \cdot y_{\text{CO}_2} \cdot (y_{\text{CO}_2} + 2y_{\text{H}_2}) \cdot F_{\text{out}} - (y_{\text{H}_2} + 2y_{\text{CO}_2}) \cdot F_{\text{in}}
\]

For O\(_2\):

\[
2 \cdot (y_{\text{O}_2}) \cdot F_{\text{out}} - 2 \cdot (y_{\text{O}_2}) \cdot F_{\text{in}}
\]

where \( F_{\text{in}} \) and \( F_{\text{out}} \) are the molar flows of the respectively inlet and outlet gas streams and \( y_i \) the molar fraction of the gas \( i \).

The mass based conversion, \( \omega \), can be calculated as follows, where \( \omega_{\text{red}} \) and \( \omega_{\text{ox}} \) are the reduced and oxidized conversions reached in the previous period, correspondingly.

For reduction:

\[
\omega(t) = \omega_{\text{ox}} - \frac{M_o}{m_{\text{ox}}} \int_{t_{p}}^{t} r_O(t) dt
\]

For oxidation:

\[
\omega(t) = \omega_{\text{red}} - \frac{M_o}{m_{\text{ox}}} \int_{t_{p}}^{t} r_O(t) dt
\]

A normalized rate index was used to evaluate the reaction rates of all the gaseous fuels tested with ilmenite before and after the activation period, and also for comparison purposes. It is very similarly defined as for the TGA analysis section, and in this case the normalized rate was calculated from the experimental rate considering plug flow and that the reaction order is 1:

\[
\text{Rate index (%/min)} = 60 \cdot 100 \left( \frac{d\omega}{dt} \right)_{\text{norm}} = 60 \cdot 100 \left( \frac{d\omega}{dt} \right)_{\text{exp}} \frac{P_{\text{ref}}}{P_{\text{m}}}
\]
being $P_m$ the mean partial pressure of the gaseous fuel in the reactor, which is calculated with the coefficient of expansion of the gas mixture $\varepsilon_g$, and the partial pressures of the gaseous fuel at the reactor inlet and outlet.

\[
P_m = \frac{(P_m - P_{out})}{(P_m + \varepsilon_g \cdot P_{out})}
\]

For comparison purposes among different experiments, the oxygen yield parameter is proposed, which gives the idea to what extend the fuel has been oxidized at each instant of the reducing period. The oxygen yield, $\gamma_O$, is defined as the oxygen gained in the fuel for its oxidation divided by the oxygen needed to fully oxidize the fuel, as follows:

\[
\gamma_O(t) = \frac{\gamma_o(t)}{(4\gamma_{CH_4} + \gamma_{CO} + \gamma_{H_2})_{in} \cdot F_{in}}
\]

### 2.5 Batch reactor fluidized bed for solid fuels

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 (FB) reactor and the gas analysis system. A schematic layout of the laboratory setup is presented in Figure 6. The fluidized-bed reactor (55 mm i.d. 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. Possible 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 that 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.

Figure 6. Schematic layout of the laboratory setup.

The gas feeding system had different mass flow controllers connected to an automatic three-way valve. This way it was possible to feed alternatively air, N₂ or a mixture of steam/CO₂. 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. As in most of cases gas is mainly composed by steam, a downstream N₂ flow of 90 LN/h is introduced to ensure a continuous dry gas flow feeding the analyzers. This N₂ is also used to calculate the outlet gas flow by a balance to N₂.
Data evaluation

The evolution of char conversion, \( X_{\text{char}} \), with time is calculated by integrating the rate of char conversion, \( r_C(t) \), which is obtained from a mass balance to carbon in gaseous form in the reactor.

\[
X_{\text{char}}(t) = \frac{1}{N_{C,\text{char}}} \int_0^t r_C(t) dt
\]  
(19)

\[
r_C(t) = (y_{CO_2} + y_{CO}) F_{\text{out}} - F_{CO_2,\text{in}}
\]  
(20)

\( N_{C,\text{char}} \) being the mol number of carbon fed into the reactor. The instantaneous rate of conversion of the char, \( r_{C,\text{inst}}(t) \), is calculated as the rate of gasification per amount of non-gasified carbon that is still in the reactor.

\[
r_{C,\text{inst}}(t) = \frac{r_C(t)}{N_{C,\text{char}} - \int_0^t r_C(t) dt}
\]  
(21)

The conversion of ilmenite in the fluidized bed for reduction reaction, \( X_r \), can be calculated from the integration of \( r_O(t) \) with time:

\[
X_r(t) = \frac{1}{N_{O,\text{ilm}}} \int_0^t r_O(t) dt
\]  
(22)

\( r_O(t) \) is the rate of oxygen transferred from ilmenite to the fuel gas, and is calculated by means of the oxygen balance:

\[
r_O(t) = \left[ F_{\text{out}} (2y_{CO_2} + y_{CO}) - 2F_{CO_2,\text{in}} \right] + \left[ F_{H_2O,\text{out}} - F_{H_2O,\text{in}} \right]
\]  
(23)

\( N_{O,\text{ilm}} \) is the molar amount of oxygen in ilmenite active for CLC process, calculated as:
The conversion of gasification products, i.e. CO and H₂, to CO₂ and H₂O by reaction with ilmenite particles was evaluated by the combustion efficiency, $\eta_c$. It is defined as the oxygen gained by the fuel for its oxidation divided per the oxygen needed to fully oxidize the fuel. Here, $\eta_c$ is calculated with Eq. (25).

$$\eta_c(t) = \frac{r_O(t)}{2r_C(t)}$$  \hspace{1cm} (25)

### 2.6 Continuous ICB-CSIC-s1 unit for solid fuels

A schematic view of the continuous ICB-CSIC-s1 facility for solid fuels used in this thesis is shown in Figure 7. The CLC system was basically composed of two interconnected fluidized-bed reactors, the fuel-reactor (FR) (1) and the air-reactor (AR) (3) joined by a loop seal (2), a riser (4) for solids transport from the air- to the fuel-reactor, a cyclone to recover the entrained solids (5) and a solids valve (7) to control the flow rate of solids fed to the fuel-reactor.

The fuel-reactor consisted of a bubbling fluidized bed with 5 cm of inner diameter and 20 cm bed height. Coal (8) is fed by a screw feeder at the bottom of the bed above the fuel-reactor distributor plate in order to maximize the time that volatile matter is in contact with the bed material. The screw feeder (9) has two steps: the first one with variable speed to control the coal flow rate, and the second one has high rotating velocity to avoid coal pyrolysis inside the screw. A small N₂ flow of 18 L N/h is fed at the beginning of the screw to avoid possible volatile reverse flow or entrance of steam. The coal flow was varied from 33 to 100 g/h. The thermal power reached in the unit was between 200 and 580 Wth in the experiments done in this PhD. The fuel-reactor was fluidized by steam-CO₂ mixtures, which act also as a gasifying agent. In the fuel-reactor a gasification agent flow range from 110 to 190 L N/h was introduced (corresponding to gas velocities of 0.07-0.12 m/s at 900
°C). 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 5 cm, to avoid gas mixing between fuel and air. It was fluidized with 75 L/h N₂. Since this prototype has no carbon separation system, unconverted char from the fuel-reactor goes to the air-reactor and is fully burnt there, releasing the CO₂ that is measured in the air-reactor.

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 that uses air as fluidizing gas. In this reactor air was used to oxidize the oxygen-carrier coming from the fuel-reactor. The gas flows introduced in the air-reactor were 2100 L/h as primary air and 400 L/h as secondary air at the top of the bubbling bed to help particle entrainment into the riser and later to the cyclone. That corresponded to gas velocity in the air-reactor of 0.1 m/s and a total gas velocity in the riser of 4.2 m/s at 900 °C. N₂ and unreacted O₂ leaving the cyclone passed through a filter before the stack. The oxidized solid particles were recovered by the cyclone and sent to a solids reservoir, setting the oxygen-carrier ready to start a new cycle. These particles act as a loop seal avoiding the leakage of gas between the fuel-reactor and riser. 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 circulation flow rate was varied and controlled from 1.0 to 11.6 kg/h. The total ilmenite bed mass in the system was 3.5 kg and the solids bed mass in the fuel-reactor was 0.8 kg ilmenite, as the solids level in the fuel-reactor is fixed and the exceeding overflows and is directed to the air-reactor.

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. The temperature in the air-reactor was maintained at around 940 °C and the fuel-reactor temperature was varied from 820 °C to 950 °C. The fuel-reactor freeboard is kept constant at about 900 °C in all the experiments. The pressure drops in important locations of the system, such as the fuel-reactor bed, the air-reactor bed and the loop seal were monitored.
Figure 7. Schematic diagram of the coal-fuelled CLC facility.

CO\textsubscript{2}, CO\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}, and O\textsubscript{2} were continuously analyzed in the exit streams from the fuel- and air-reactors. All data were collected by means of a data logger connected to a computer. In some selected experiments the tar amount present in fuel-reactor product gases was determined following a tar protocol (Simell et al., 2000). Collection of moisture and tar was performed in a series of eight impinger bottles by absorption in isopropanol and later cooling in external baths. Two different cooling baths were used. The first was an ice bath, where the first two impingers were located. The first was empty and the second contains isopropanol. In addition, the second bath contains six impingers at -18 °C. These impingers recover the majority of moisture and aromatic tar compounds (styrene, indene, benzene, etc.) and light Polycyclic aromatic hydrocarbons (PAHs). Several gaseous samples from the fuel-reactor stream were also taken in bags in order to measure the components through gas chromatography analysis.

Data evaluation

The parameters that indicate the performance of the process are the carbon capture and the combustion efficiency. The carbon capture is the 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, $\eta_{\text{CC}}$, is here
defined as the fraction of the carbon fed in that is converted to gas in the fuel-reactor.

$$\eta_{\text{CC}} = \frac{\{F_{\text{CO}_2,\text{FR}} + F_{\text{CO},\text{FR}} + F_{\text{CH}_4,\text{FR}}\}_{\text{out}} - \{F_{\text{CO}_2,\text{FR}}\}_{\text{in}}}{\{F_{\text{CO}_2,\text{FR}} + F_{\text{CO},\text{FR}} + F_{\text{CH}_4,\text{FR}}\}_{\text{out}} + F_{\text{CO}_2,\text{AR}} - \{F_{\text{CO}_2,\text{FR}}\}_{\text{in}}} \quad (26)$$

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.

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 during
some experiments. The elutriated char flow was calculated as the difference between the
coal carbon fed 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, and it was used as the char fed to the fuel-reactor in the calculations. Note that in
case of an industrial unit the possible elutriated char will be collected in a cyclone and
reintroduced to the fuel-reactor.

To do a deeper study of the system behavior on the carbon capture, the gasification step
should be assessed. The char conversion, $X_{\text{char}}$, is defined as the fraction of carbon in the
char which is gasified and released to the fuel-reactor outgoing gas stream:

$$X_{\text{char}} = \frac{F_{\text{C, char eff}} - F_{\text{C, char eff}}}{F_{\text{C, char eff}}} = \frac{\{F_{\text{CO}_2,\text{FR}} + F_{\text{CO},\text{FR}} + F_{\text{CH}_4,\text{FR}} - F_{\text{C, vol}}\}_{\text{out}} - \{F_{\text{CO}_2,\text{FR}}\}_{\text{in}}}{\{F_{\text{CO}_2,\text{FR}} + F_{\text{CO},\text{FR}} + F_{\text{CH}_4,\text{FR}} + F_{\text{CO}_2,\text{AR}} - F_{\text{C, vol}}\}_{\text{out}} - \{F_{\text{CO}_2,\text{FR}}\}_{\text{in}}} \quad (27)$$

$F_{\text{C, char eff}}$ is the carbon in the effective char flow introduced in the CLC system. 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. The carbon content
of the volatiles is directly calculated using the analysis of coal.
An approximation to the char gasification rates can be obtained, if a simplified model is used. The fuel-reactor is considered to follow a continuous stirred-tank reactor (CSTR) model. The char is assumed to be in perfect mixing of the solids in the fuel-reactor and to react at a mean rate \((-r_c)\) which is proportional to the mass. With these considerations, \((-r_c)\) is calculated from a carbon balance in the fuel-reactor:

\[
\frac{1}{m_{\text{char}}} \frac{dm_{\text{char}}}{dt} = k \quad \Rightarrow \quad (-r_c) = \frac{X_{\text{char}}F_{C,\text{char eff}}M_C}{m_{\text{char,FR}}} \tag{28}
\]

being \(M_C\) the carbon atomic weight. \(m_{\text{char,FR}}\) is the mass of carbon in char in the fuel-reactor, which can be calculated with the mass of ilmenite in the fuel-reactor \(m_{\text{ilm,FR}}\), the solids circulation rate \(F_{\text{ilm}}\):

\[
\frac{m_{\text{char,FR}}}{m_{\text{ilm,FR}}} = \frac{F_{\text{CO2,AR}}}{F_{\text{ilm}}} \tag{29}
\]

Connected to the char conversion, the mean residence time of char, \(t_{m,\text{char}}\), is calculated as:

\[
t_{m,\text{char}} = \frac{m_{\text{char,FR}}}{F_{C,\text{char eff}}M_C} = \frac{X_{\text{char}}}{(-r_c)} \tag{30}
\]

Besides, the mean residence time of ilmenite, \(t_{m,\text{ilm}}\), is calculated by Eq. (31).

\[
t_{m,\text{ilm}} = \frac{m_{\text{ilm,FR}}}{F_{\text{ilm}}} \tag{31}
\]

The fuel-reactor combustion efficiency, \(\eta_{\text{comb FR}}\), is a measure of the 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. $\eta_{\text{comb FR}}$ was calculated as:

$$\eta_{\text{comb FR}} = \frac{[0.5 \cdot F_{\text{H2O,FR}} + F_{\text{CO2,FR}} + 0.5 \cdot F_{\text{CO,FR}}]_{\text{out}} - [0.5 \cdot F_{\text{H2O,FR}} + F_{\text{CO2,FR}} + 0.5 \cdot O_{\text{coal,eff}}]_{\text{in}}}{O_2 \text{ demand coal,eff} - F_{\text{CO2,AR}}}. \quad (32)$$

$O_{\text{coal,eff}}$ is the oxygen contained in the effective coal flow. $O_2 \text{ demand coal,eff}$ or the oxygen demand of the effective coal flow is the oxygen flow needed to fully burn the fuel.

An oxygen demand $\Omega_{\text{OD}}$ can be defined as the fraction of oxygen lacking to achieve full combustion to $CO_2$ and $H_2O$ of the fuel-reactor product gas in comparison to the oxygen demand of the devolatilization and gasification products. It is the only fraction of oxygen required in the iG-CLC process to reach full combustion of the fuel that must be supplied in a subsequent polishing step as pure $O_2$. However in this thesis $\eta_{\text{comb FR}}$ is usually used because it is conceptually a simpler parameter.

$$\Omega_{\text{OD}} = 1 - \eta_{\text{comb FR}} \quad (33)$$

The rate of oxygen transferred by ilmenite, $(-r_O)$, measures the oxygen transfer rate from ilmenite to the fuel. $(-r_O)$ is calculated as the increased flow of oxygen in the oxygen-containing gases ($CO$, $CO_2$ and $H_2O$), divided by the ilmenite hold-up:

$$(-r_O) = \frac{([F_{\text{H2O,FR}} + 2F_{\text{CO2,FR}} + F_{\text{CO,FR}}]_{\text{out}} - [F_{\text{H2O,FR}} + 2F_{\text{CO2,FR}} + O_{\text{coal,eff}}]_{\text{in}}) \cdot M}{m_{iln,FR}}. \quad (34)$$

The oxygen-carrier to fuel ratio, $\phi$, is a measure of how much oxygen is available in the circulating oxygen-carrier compared to the oxygen needed to burn the fuel fed. In stoichiometric conditions the ratio $\phi$ is equal to one. It is defined as follows:

$$\phi = \frac{F_{\text{lim}} \cdot R_{O,\text{lim}}}{2 \cdot M \cdot O_{2 \text{ demand coal,eff}}} \quad (35)$$
2.7 Continuous 10 kWth CLC unit for solid fuels

The 10 kWth unit used is designed for CLC with solid fuels and located at Chalmers University of Technology. Figure 8 shows a scheme of the whole pilot unit. The reactor system consists of two interconnected fluidized beds: (a) the fuel-reactor (FR), where the fuel is gasified with steam and gasification products are oxidized by the oxygen-carrier, and (b) the air-reactor (AR), where the oxygen-carrier particles are oxidized. The regenerated oxidized particles are led through (c) a riser above the air-reactor, which ends up in (d) a cyclone that brings the solids flow back to the fuel-reactor. There are also two loop-seals fluidized by nitrogen placed after the cyclone (d) and in the connection leading from fuel-to air-reactor. The role of these upper and lower loop-seals is to eliminate gas leakages between the reactors. Represented in Figure 8 are also the particle filters, as well as the fuel feeding, steam production unit and a water seal used to collect condensates and to balance the pressure in the fuel-reactor. The system is not self-supporting in energy and it is therefore enclosed in an oven that keeps and controls the temperature.
The fuel-reactor has three main sections: (1) a low-velocity section, which is operated as a bubbling bed. This chamber is divided into two parts separated by a wall with an opening at the bottom, through which the particles are conducted; (2) a carbon-stripper with the purpose to separate char particles from the solids flow going from the fuel-reactor to the air-reactor; and (3) a high velocity section that gives the opportunity to increase the flow in the internal loop by increasing the entrainment of the oxygen-carrier from the fuel-reactor. This option was however not used in the tests enclosed in this thesis. The low-velocity section is fluidized with steam and in this bed all reactions related to char are expected to take place, that is, fuel gasification and reaction of the gasification products with the oxygen-carrier.

The fuel is fed by a vertical fuel chute that ends above the reactor bed. Thereby, most of the volatiles are released above the bed and have little contact with the oxygen-carrier. Thus, this unit is useful to know the behavior towards char gasification with different solid fuels, but does not give information about the conversion of volatile matter. A detailed description of the 10 kW pilot is given elsewhere (Berguerand and Lyngfelt, 2008a; b). The solids inventory in the low-velocity section was around 6 kg and the total ilmenite hold-up in the unit was 15 kg of ilmenite with bulk density of about 2100 kg/m$^3$ and particle size of +90-250 μm. To assess the effect of limestone in the process, 4 kg of a Mexican limestone used in the Tamuin Power Unit were added. Its density was about 1900 kg/m$^3$ and the particle size +90-200 μm.

The pilot is equipped with 40 pressure transducers to monitor the pressures. The temperatures in the air-reactor, fuel-reactor and the air-reactor cyclone are also measured. Gas sampling outlets are located on both chimneys. At the air-reactor outlet concentrations of CO, CO$_2$, and O$_2$ are measured online and at the fuel-reactor outlet concentrations of CO, CO$_2$, O$_2$ and CH$_4$ are measured online with Sick Maihak Sidor analyzers and registered. The H$_2$ concentration could also be measured online with a Rosemount NGA2000 analyzer. Bag samples of the product gas flow from the fuel-reactor were also
taken and analyzed with a gas chromatograph Varian Micro-GC CP4900; this was used to confirm the results from the other analyzers.

The flows for the fuel-reactor and the loops seals were kept constant during all experiments and are shown in Table 4. The fluidizing gas flows are controlled and monitored by mass flow controllers. The steam flow to the low-velocity section is controlled by a steam generator. $F_{\text{LOVEL}}$ is the steam flow in the low-velocity section in the fuel-reactor, $F_{\text{CS}}$ is the $N_2$ flow in the carbon-stripper, $F_{\text{HIVEL}}$ is the $N_2$ flow in the high-velocity section in the fuel-reactor, $F_{\text{HILS}}$ is the $N_2$ flow in the higher loop-seal, $F_{\text{LOLS}}$ is the $N_2$ flow in the lower loop-seal and $F_{\text{FRLS}}$ is the $N_2$ flow in the small fuel-reactor loop-seal.

Table 4. Flows for the fuel-reactor and the loop-seals, in $L_N/min$.

<table>
<thead>
<tr>
<th>$F_{\text{LOVEL}}(H_2O)$</th>
<th>$F_{\text{CS}}(N_2)$</th>
<th>$F_{\text{HIVEL}}(N_2)$</th>
<th>$F_{\text{HILS}}(N_2)$</th>
<th>$F_{\text{LOLS}}(N_2)$</th>
<th>$F_{\text{FRLS}}(N_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

The data evaluation in this facility is the same as for the ICB-CSIC-s1 unit.
3 Results and discussion
3.1 Properties of ilmenite as oxygen-carrier

The aim of this section (studies published in Papers I and III) is to analyze the main characteristics of ilmenite as oxygen-carrier in CLC and the changes in its properties through redox cycles under well-defined conditions. Before this thesis started, there was little work done about ilmenite in its use in CLC. Leion et al. (2008a,b) proved the feasibility of using ilmenite as oxygen-carrier to oxidize gaseous fuels. They saw that the reaction rate of ilmenite increases after several redox cycles, but this activation process was not analyzed. They also observed that ilmenite is more reactive with CO and H₂ than with CH₄, but this study was done in batch fluidized bed and not in TGA, where the reactivity can be analyzed under well-defined conditions and without diffusional limitations. To assess the properties of ilmenite as oxygen-carrier, experiments consisting of reduction-oxidation cycles in a thermogravimetric analyzer (TGA) and in batch fluidized bed were carried out using the main products of coal devolatilization and gasification, that is, CH₄, H₂ and CO, as reducing gases. The reaction rates of ilmenite with these fuels were assessed, as well as the change on reactivity after hundred of redox cycles. Tests with different H₂:CO ratios were also made in order to see the reciprocal influence of both reducing gases in the reaction rate. The oxidation of ilmenite was also studied.

Both fresh and previously calcined at 950 °C ilmenite were used as initial oxygen-carriers in TGA but only calcined ilmenite was used as initial material for the experiments in the batch reactor. The properties of fresh, calcined and samples of ilmenite after different number of redox cycles and using different reacting gases were determined. The structural changes of ilmenite, as well as the variations in its behavior with a high number of cycles were also evaluated with a 100 cycle test in batch reactor. The attrition rates and fluidization performance of ilmenite in fluidized bed operation was also assessed.

In its use in iG-CLC, the components of ilmenite that can be used for the oxygen transfer are, considering the components in their oxidized form, Fe₂TiO₅ and Fe₂O₃. Table 5 shows the maximum oxygen yields at equilibrium conditions for every step in the reduction reaction. Thermodynamic calculations show that by reducing Fe₂TiO₅ with CH₄, H₂ or CO it is possible to reach very near full combustion of fuel gas into H₂O and CO₂ when it
is reduced FeTiO$_3$, i.e. $\gamma_O$ can be considered 1 for practical purposes. Further reduction is prevented in a CLC system to avoid low fuel gas conversion. Besides, there is risk of agglomeration in the FeO or Fe oxidation (Cho et al., 2006).

Table 5. Oxygen yields at equilibrium conditions for different reducing gases in presence of Fe$_2$TiO$_5$ and Fe$_3$O$_5$ at 900ºC.

<table>
<thead>
<tr>
<th>Oxidized</th>
<th>Reduced</th>
<th>CH$_4$</th>
<th>CO</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$TiO$_5$</td>
<td>FeO·TiO$_2$</td>
<td>0.998</td>
<td>0.997</td>
<td>0.998</td>
</tr>
<tr>
<td>FeO·TiO$_2$</td>
<td>Fe+TiO$_2$</td>
<td>0.308</td>
<td>0.085</td>
<td>0.067</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Fe$_2$O$_4$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fe$_2$O$_4$</td>
<td>Fe$^{0.947}$O</td>
<td>0.741</td>
<td>0.615</td>
<td>0.675</td>
</tr>
<tr>
<td>Fe$^{0.947}$O</td>
<td>Fe</td>
<td>0.523</td>
<td>0.325</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Thus, both components that carry out the oxygen transfer would react with H$_2$ as an example of reduction reaction according to reactions (36-37) and the subsequent oxidation as for the reactions (38-39).

\[
\text{Fe}_2\text{TiO}_5 + \text{TiO}_2 + \text{H}_2 \leftrightarrow 2 \text{FeTiO}_3 + \text{H}_2\text{O} \quad (36)
\]

\[
3 \text{Fe}_2\text{O}_3 + \text{H}_2 \leftrightarrow 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad (37)
\]

\[
4 \text{FeTiO}_3 + \text{O}_2 \leftrightarrow 2 \text{Fe}_2\text{TiO}_3 + 2 \text{TiO}_2 \quad (38)
\]

\[
4 \text{Fe}_3\text{O}_4 + \text{O}_2 \leftrightarrow 6 \text{Fe}_2\text{O}_3 \quad (39)
\]

### 3.1.1 Ilmenite reactivity: Activation

**Activation with CH$_4$, CO and H$_2$ in TGA**

The investigation of the conditions in which the activation process of ilmenite occurs, how fast and whether the improved reaction rate is maintained after many redox cycles was carried out. Several reduction-oxidation cycles were carried out in TGA to analyze the reactivity of fresh and calcined ilmenite. Reducing and oxidizing times for each cycle were
set to 30 minutes. The reducing agents used were 15% CH₄+20% H₂O, 15% H₂+20% H₂O or 15% CO+20% CO₂. In these conditions all the Fe³⁺ of ilmenite was reduced to Fe²⁺, that is, the main final species were FeTiO₃ and FeO. Figure 9 shows the mass variations undergone by fresh ilmenite in this TGA experiment using CH₄ as reducing gas and subsequent oxidation with air. At the beginning, ilmenite was not completely reduced or oxidized after the fixed reacting time. However, there is an increase in both the reduction and oxidation extension during the repeated redox cycles. The mass loss is considered to be exclusively due to oxygen transfer and stabilized after 4 cycles.

Figure 9. Mass variations during redox cycles in TGA starting from fresh ilmenite. Reduction and oxidation time: 30 min. Reducing gas: 15%CH₄+20%H₂O. T=900°C.

In this study a normalized conversion is used to analyze the changes in ilmenite reactivity. It is calculated considering that normalized conversion is 1 when the Fe³⁺ present in ilmenite was reduced to Fe²⁺. In this condition, the mass loss due to the oxygen transferred is 4.8%, as it can be seen in Figure 9. Figure 10 show the normalized conversion for the reduction, X₉₅, and the oxidation, X₉₅, reactions with time for consecutive cycles of fresh ilmenite. The reducing gas was 15% CH₄+20% H₂O and the oxidations were done in air.

Although ilmenite presents initially a rather low reactivity, the oxygen-carrier has a gradual gain in its reduction reaction rate as well as in oxidation rate. The reactivity increases up to a maximum value after 4 cycles and stabilizes. This increase is more pronounced in the reduction reaction than in the oxidation reaction, because the initial
reactivity for the oxidation of ilmenite for the first oxidation step is relatively high, with $X_{N,0} = 0.25$ in less than 9 seconds for fresh ilmenite. After 4 cycles carried out in TGA a value for the normalized conversion of 0.8 is reached in 120 s for reduction and 180 s for oxidation reaction. At this point, it can be considered that ilmenite had achieved maximum conversion rate in both reduction and oxidation reactions. Therefore, an activation process was observed which made the reactivity increase during the initial redox cycles. Also, it can be seen that the oxidation rate decreases gradually at high conversion values ($X_{N,0} > 0.8$), and full conversion is reached in 30 min. This fact indicates that a change in the resistance control has happened or the oxidation reaction proceeds via two consecutive steps.

![Figure 10](image.png)

Figure 10. Normalized conversion during a) reduction and b) oxidation periods in TGA of fresh ilmenite vs. time through several cycles. Reducing gas:15%CH$_4$+20%H$_2$O. $T = 900^\circ$C.

Similar behavior was observed for redox cycles using H$_2$ and CO as reducing gases. The main consequence of ilmenite being more reactive with the number of cycles in the activation period is that fewer inventories of oxygen-carrier in the reactors are necessary.

**Effect of pre-oxidation on activation**

Samples of fresh and calcined ilmenite were subjected to alternating reduction-oxidation cycles using CH$_4$, H$_2$ or CO as reducing gases in TGA. Hundred cycles were performed and the reducing and oxidizing periods were one minute. Both fresh and calcined ilmenite achieve the same conversion variation after activation, but calcined ilmenite reached earlier
the activated state. When using CH$_4$ as reducing gas, 40 cycles were necessary for the activation and stabilization for fresh ilmenite, whereas about 30 cycles were enough to activate calcined ilmenite. Therefore, a previous calcination has a positive effect on both the reactivity of the oxygen-carrier and the activation rate during the activation period. Similar behavior was found when the activation was carried out using 15 vol.% H$_2$ or 15 vol.% CO as reducing gases, but in these cases calcined ilmenite activated in 9 cycles with H$_2$ and in 20 cycles with CO.

**Activation with CH$_4$, CO, H$_2$ and syngas in fluidized bed**

The activation of ilmenite was also analyzed in batch fluidized bed with the main gases involved in the process, because the reactions occur in conditions similar to the real process. The effect of the activation process of ilmenite, through consecutives redox cycles on the gas product distribution, was analyzed in a fluidized-bed reactor. CH$_4$, H$_2$ or CO were used as reducing gases. The total solids hold-up in the reactor was 500 g of calcined ilmenite. The oxygen-carrier was exposed to alternating reducing and oxidizing conditions at a temperature of 900 ºC. The reducing conditions of the experiments performed are shown in Table 6. All reducing gaseous flows have the same oxygen demand. Thus, the resulting gas velocity for tests with CH$_4$ was 0.15 m/s and for all other tests it was 0.3 m/s.

**Table 6. Experimental conditions during reduction period in the batch fluidized-bed reactor for experiments 1 to 4. N$_2$ to balance. T=900 ºC.**

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Composition (vol.%)</th>
<th>H$_2$:CO</th>
<th>Reducing time (s)</th>
<th>Number of cycles</th>
<th>Solids inventory (kg/MWth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_4$: 25 - - 10 -</td>
<td>-</td>
<td>300</td>
<td>23</td>
<td>670</td>
</tr>
<tr>
<td>2</td>
<td>- - H$_2$: 50 - 20</td>
<td>0:100</td>
<td>240</td>
<td>20</td>
<td>480</td>
</tr>
<tr>
<td>3</td>
<td>- 50 - CO: 20 -</td>
<td>100:0</td>
<td>180</td>
<td>20</td>
<td>560</td>
</tr>
<tr>
<td>4</td>
<td>- 21.5 H$_2$: 28.5 8.2</td>
<td>43:57</td>
<td>240</td>
<td>100</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 11 shows the CO$_2$ concentration in dry basis or H$_2$O concentration during consecutive reduction periods when using CH$_4$, CO and H$_2$ as reducing gases. The
corresponding maximum CO₂ or H₂O fractions if full combustion was reached are also represented. For every tested reducing gas, there was an increase in the percentage of CO₂ and/or H₂O in the product gas with the cycles because ilmenite had a gradual gain in its reaction rate. After several redox cycles, ilmenite reactivity stabilized and the CO₂ and/or H₂O concentrations achieved the highest values. Thus, an activation process is seen during the initial redox cycles.

Figure 11. CO₂ or H₂O fractions in the product gas (wet basis) during consecutive reduction periods in batch FB, for a) CH₄, b) CO and c) H₂ as reducing gases. The intervals between reducing periods are removed. Cₘₐₓ: maximum CO₂ or H₂O fraction if full combustion was reached. Experimental conditions in Table 6. T=900ºC.

Reaction with H₂ is faster than with CO, and near full H₂ conversion was obtained in the fluidized-bed reactor. Lower reactivity was found for CH₄, being CH₄ the most unconverted gas. In this case, negligible amounts of H₂ or CO were observed during CH₄ combustion. Ilmenite activation process depended on the gas used as fuel, i.e., CH₄, H₂ or CO. Thus, when using CH₄ it activated after about 20 cycles, for CO after about 10 cycles and it was faster for H₂, as it took 3-4 cycles. The more reactive is the fuel gas, the lower is the number of cycles to activate ilmenite particles.
A long test in fluidized bed was done: 100 redox cycles with syngas as reducing gas was performed (see conditions in Table 6). The syngas composition is in Water-Gas Shift equilibrium. Very little H₂ in the outlet gas was seen at the beginning of the reducing cycles: about 1-2%. The CO content was about 2.4%. Figure 12 shows the variation of the oxygen yield, \( \gamma_0 \), with the solids conversion for various reducing periods from the 100 redox cycles. The oxygen yield is a parameter that gives the idea to what extent the fuel has been oxidized at each instant of the reducing period. \( \gamma_0 = 1 \) corresponds to complete conversion of fuel gas to CO₂ and H₂O. When focusing only in the first 1.5 minutes of each reducing period, it can be seen that the oxygen yield increases within the first 10 cycles approximately and reach a maximum value of 98%, which is due to the activation of ilmenite. This maximum value is kept throughout the cycles, which indicates that ilmenite maintains its reaction rate and does not deactivate. This corresponded to a \( \omega \) about 0.99.

![Figure 12. Oxygen yield variation vs. ilmenite mass based conversion for several reduction periods in a 100 redox cycle test in batch FB with syngas as reducing agent. T=900°C.](image)

On the other hand, after about 1.5 minutes and mass based conversions \( \omega \) further than 0.99, there was a decrease in the oxygen yield from the cycle 20. In Figure 12 it can be seen that the \( \gamma_0 \) reached after many cycles was close to the corresponding \( \gamma_0 \) for the Fe₃O₄ ↔ FeO equilibrium. This means that the oxygen transport capacity decreased with
the number of cycles, because reduction of Fe₃O₄ to FeO is not suitable in a CLC system in order to get complete combustion to CO₂ and H₂O.

Activation of ilmenite with coal char

Since this process is really applied to solid fuels, the activation process of ilmenite was also studied using solid fuels in batch fluidized bed. 16 consecutive redox cycles in batch fluidized bed were carried out using calcined ilmenite as starting material. Steam was used as fluidizing gas. Every reduction period consisted of two consecutive loads of 1.5 g of char. The second load in the same period was fed to get further reduction of the oxygen-carrier. After the reduction period, the bed material was oxidized by air. As in experiments with gaseous fuels (TGA and batch fluidized bed) an activation process was also seen using char as fuel. Effectively, there was a decrease in the unconverted gasification product CO (see Figure 13), which was similar for H₂, with the number of cycles accompanied by an increase in the production of CO₂. After several redox cycles no further substantial decrease on CO or H₂ concentration or increase on CO₂ concentration were observed and the CO₂ concentration achieved the highest value. This proved that ilmenite undergoes an activation process in its reactivity using char as fuel during the initial 6 or 7 cycles.

![Figure 13. Molar flow evolution with time of CO in the gas product during the initial 10 reduction cycles. Every cycle consisted of 2 loads of char, 1.5 g each one, in batch FB. The intervals between reducing periods are removed. Gasification agent: steam. T=900 °C.](image-url)
Activation for oxidation

The activation in the oxidation reaction was also studied in the 100 cycle test performed in fluidized bed and using a syngas mixture as reducing agent (21.5% H₂+28.5% CO+8% H₂O+8.2% CO₂), with reducing periods of 4 minutes. After every reducing period, the ilmenite bed was fully re-oxidized with diluted air (10% O₂) in the oxidation period with a gas velocity of 0.23 m/s. At the beginning of the oxidation period no oxygen could be seen in the produced gas, since it reacted with the reduced ilmenite. After this period, the breakthrough curve of oxygen appeared. This curve is different depending on the reactivity of the bed material (Adánez et al., 2005). For higher number of cycles this second step of reaction appeared later and at higher oxidizing conversions (see Figure 14.a)) until roughly equal breakthrough curve is obtained, this being the activation period. This behavior was also in line with TGA results. For a mass based conversion of 0.975 in the previous reduction periods, the activation in the oxidation reaction took about 8 cycles. The oxidation reaction was fast and fully oxidized ilmenite was reached in every cycle. Oxidation seems to happen in two steps. From Figure 14.b) it could be seen that if the area under the O₂ curve was integrated, the oxygen amount taken by ilmenite with the number of cycles was slight but gradually decreasing. That is because in the previous reducing period ilmenite was less reduced, as the oxygen transfer capacity was gradually decreasing.

Figure 14. O₂ profiles in the product gas for a) the first 20 oxidation periods and b) subsequent oxidations in batch FB from cycle 20 to cycle 100. Previous reductions with syngas up to conversion ω ~ 0.975. Oxidations with 10% O₂. T=900 °C.
3.1.2 Characterization of ilmenite

Table 1 shows the main physical and chemical properties of the fresh, calcined and activated Norwegian ilmenite used as oxygen-carrier in the experiments of this research.

The major change with respect to the initial ilmenite was that porosity increased substantially with the redox cycles. For the 100 cycle test using syngas as reducing agent in batch fluidized bed, the initial porosity of calcined ilmenite was 1.2%, after 20 cycles it was 27.5% and after 100 cycles it reached the value of 38%. The pore distribution shown in Figure 15 confirms that the minimum pore size is about 30 nm, but as porosity increases, the pore size distribution locates at higher pore diameters and the average pore diameter gradually increases with the number of cycles and higher size pores are formed.

![Pore size distribution](image)

Figure 15. Pore distribution of different samples of ilmenite samples taken after several redox cycles in Batch FB using syngas as fuel (conditions in Table 6): Calcined, after 8 cycles, after 18 cycles and after 100 cycles.

Figure 16 shows SEM microphotographs of the general overview and external surface of several particles that confirm the low pore development for fresh and calcined ilmenite and the gain of granular shape on the surface and porosity after several redox cycles.
Figure 16. SEM images of a) a general overview of several particles, b) the external surface of particles of fresh, calcined ilmenite and ilmenite after undergoing several redox cycles.

Figure 17 shows the evolution of porosity by SEM photographs of cross-cut particles of different samples taken from the 100 cycle experiment done using syngas as reducing agent in batch fluidized bed. Throughout the reduction-oxidation cycles, there is a continuous appearance of porosity, since the final porosity after 100 redox cycles was measured to be 38%. Moreover, a gradual generation of an external layer slightly separated from the rest of the particle which grows with the number of cycles could be clearly observed. This space between the layer and the core also enhances the porosity measured for the particle.

Figure 17. SEM-EDX images of cross-cut ilmenite particles a) calcined and after b) 16, c) 50 and d) 100 redox cycles, using syngas as reducing agent in batch FB.

EDX analyses were done to determine Fe and Ti distributions throughout the particles, see Figure 18. In fresh and calcined ilmenite distributions of both elements were uniform,
which agrees with the XRD analysis that reveals Fe$_2$TiO$_5$ as main component. For activated ilmenite the particle core is titanium enriched, whereas the external part is iron enriched. XRD analyses to the external part found that this region is composed only by iron oxide, whereas XRD to the internal core revealed the existence of TiO$_2$ and Fe$_2$TiO$_5$. Thus, the external shell formed during activation period was Fe enriched, likely due to a physical segregation of Fe$_2$TiO$_5$ and subsequent migration phenomenon of Fe$_2$O$_3$ towards the external part of the particle, where there is no TiO$_2$ to form iron titanates. The diffusion of iron—or titanium, depending on the conditions—within the ilmenite particles was already reported by Rao and Prototypeaud (1975). However, this iron migration or layer formation did not appear in other ilmenite samples that were activated in a different way, for example in case of the samples activated in batch fluidized bed using char as fuel, or even in case of ilmenite that was used for about 100 hours of operation using coal as fuel (see Figure 19). This is because in those tests the reduction degree of ilmenite was low, compared to the higher conversion reached in the experiments done using syngas as fuel.

![Figure 18. EDX line profiles of Fe and Ti in a) calcined and b) activated ilmenite particle.](image)

![Figure 19. SEM-EDX images of cross-cut ilmenite particles a) activated ilmenite in batch FB using char as fuel after 16 cycles, b) activated ilmenite used for about 100 hours of operation using coal as fuel in the 10 kWth CLC facility.](image)
To evaluate the fraction of Fe as Fe$_2$TiO$_5$ or Fe$_2$O$_3$ as a function of the number of redox cycles, particles subjected to different numbers of redox cycles (up to 100 cycles) in TGA with 15 vol.% H$_2$, CO or CH$_4$ as fuel gas during the reduction period were analyzed by XRD. Figure 20 shows the semi-quantitative mass fractions of Fe$_2$TiO$_5$ and Fe$_2$O$_3$ in the oxidized ilmenite particles as a function of the number of cycles when H$_2$ was used as reducing gas. It can be seen that the Fe$_2$TiO$_5$ fraction decreases with the number of cycles whereas the Fe$_2$O$_3$ fraction increases.

![Graph showing the mass fraction of Fe$_2$O$_3$ and Fe$_2$TiO$_5$ in ilmenite after several redox cycles in TGA up to 100 cycles. Oxidation and reduction periods: 1 min. Reducing gas used: 15% H$_2$ + 20% H$_2$O. T = 900 ºC.]

**Figure 20.** Mass fraction of Fe$_2$O$_3$ and Fe$_2$TiO$_5$ in ilmenite after several redox cycles in TGA up to 100 cycles. Oxidation and reduction periods: 1 min. Reducing gas used: 15% H$_2$ + 20% H$_2$O. T = 900 ºC.

Initial and activated ilmenite particles after 20 cycles in batch fluidized bed using syngas as fuel had relatively high values of crushing strength; because it varied from 2.2 N to 2.9 N. The values of crushing strength obtained are similar to other Fe-based oxygen-carriers and they are acceptable for the use of these particles in circulating fluidized bed (Johansson et al., 2006b). However, particles after 50 and 100 cycles in fluidized bed show a decrease in the crushing strength down to a value of 1 N after 100 cycles (see Figure 21).
1 N is considered to be the minimum value for the use of a material in interconnected fluidized-beds (Johansson et al., 2004). Nevertheless, since in these particles there was formation of an external layer, the normal strength under which the particles are subjected could break this layer and not the whole particles.

**Variation of the oxygen transport capacity, R_{\text{O,ilm}}**

The oxygen transport capacity is a fundamental property of the oxygen-carrier since it determines the recirculation rate and solids inventory in the system, and therewith the suitability of ilmenite as oxygen-carrier in CLC. The oxygen transport capacity is the oxygen fraction of the total oxygen-carrier mass that can be used in the oxygen transfer (Eq. 8). However, free Fe\textsubscript{2}O\textsubscript{3} is only capable to fully convert CO and H\textsubscript{2} into CO\textsubscript{2} and H\textsubscript{2}O when it is reduced to Fe\textsubscript{3}O\textsubscript{4}. On the other hand, Fe\textsubscript{2}TiO\textsubscript{5} can be reduced to FeTiO\textsubscript{3}.

Therefore, R_{\text{O,ilm}} depends on the relative abundance of free Fe\textsubscript{2}O\textsubscript{3} and iron titanates, which varies with the number of redox cycles. As the number of cycles increases, the fraction of free Fe\textsubscript{2}O\textsubscript{3} rises at expenses of Fe\textsubscript{2}TiO\textsubscript{5}. With these percentages the R_{\text{O,ilm}} can be calculated:

\[
R_{\text{O,ilm}} = R_{\text{O,Fe}_2\text{O}_3} \cdot f_{\text{Fe}_2\text{O}_3} + R_{\text{O,Fe}_2\text{TiO}_5} \cdot f_{\text{Fe}_2\text{TiO}_3} \tag{40}
\]

\(R_{\text{O,Fe}_2\text{O}_3}\) is the oxygen transport capacity of Fe\textsubscript{2}O\textsubscript{3} when converted to Fe\textsubscript{3}O\textsubscript{4} \((R_{\text{O,Fe}_2\text{O}_3} = 3.3\%\)\) and \(R_{\text{O,Fe}_2\text{TiO}_5}\) is the oxygen transport capacity of Fe\textsubscript{2}TiO\textsubscript{5} when converted to FeTiO\textsubscript{3} \((R_{\text{O,Fe}_2\text{TiO}_5} = 6.7\%\). \(f_{\text{Fe}_2\text{O}_3}\) and \(f_{\text{Fe}_2\text{TiO}_3}\) are the Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}TiO\textsubscript{5} mass fractions, respectively.
The initial RO,ilm value for calcined ilmenite was 4.0 %wt. However, the fraction of free Fe₂O₃ increases with the number of cycles due to the mentioned Fe₂TiO₅ segregation. As a consequence, the oxygen transport capacity decreases because free Fe₂O₃ reduction to Fe₃O₄ transfers less oxygen than its reduction to Fe²⁺. This decrease of RO,ilm was starker for the first cycles and after several cycles the decrease was slight and continuous. After 100 redox cycles in TGA with H₂ as reducing gas RO,ilm had decreased down to 2.1 %wt.

The values of RO,ilm were also measured by TGA when reducing the samples with 5%H₂ + 40%H₂O to ensure that the final reduced species are FeTiO₃ + Fe₃O₄. Figure 22 shows the RO,ilm value obtained for samples extracted from experiments in batch fluidized bed, as well as the values calculated from the measured fraction of Fe₂TiO₅ and Fe₂O₃ in the solids (in Figure 20). The results indicate a similar variation of oxygen transport capacity during cycles in TGA or batch fluidized bed. The disadvantage of having a decrease in RO,ilm is that higher solid circulating flows between reactors are needed.

![Figure 22. Measured in TGA and theoretical ROC. ROC variation with the number of cycles reduction periods in a 100 redox cycle test using syngas as reducing agent (see conditions in Table 6). T=900 °C.](image)

From all the experiments performed in TGA and batch fluidized bed, the decrease in the oxygen transport capacity was not influenced by the reducing agent used. For the different gases used, if the reduction degree of ilmenite in every cycle was the same, the final RO,ilm had the same value. It depended only on the extent of conversion reached in every cycle.
Higher conversions led to a greater extent of segregation of Fe$_2$TiO$_5$ to Fe$_2$O$_3$+TiO$_2$ and therefore stronger decrease in RO$_{ilm}$. This correlation between RO$_{ilm}$ and the extent of conversion can be seen in Figure 23, which shows the decrease in the oxygen transport capacity after around 20 cycles in the experiments in batch fluidized bed with the different gaseous fuels tested, i.e., CH$_4$, CO, H$_2$ and the CO+H$_2$ mixture, as a function of the ilmenite conversion reached in every reducing cycle. Figure 23 also includes the RO$_{ilm}$ of ilmenite particles after 35 h of continuous operation in a CLC unit fuelled with coal. The oxygen transport capacity decreased only to 3.9% and the reduction conversion in the continuous tests was about 0.23. The same occurred with the ilmenite sample that was used in the 10 kW$_{th}$ prototype: it had been used for about 100 hours of operation, where RO$_{ilm}$ was also measured to be 3.9%. Thus, working with low values of $\Delta X$ allows to maintain the initial RO$_{ilm}$ roughly constant during long time.

![Figure 23. Decrease in the oxygen transport capacity after 20 cycles as a function of the ilmenite conversion reached in every reducing cycle in the experiments in batch fluidized bed using CH$_4$, CO, H$_2$ and syngas as fuel and in continuous test with coal as fuel.](image)

### 3.1.3 Analysis of the reactivity

The reactivity of calcined and activated ilmenite was investigated using H$_2$, CO or CH$_4$ as reducing gas, in TGA as well as in batch fluidized bed. Figure 24 represents the conversion curves obtained in TGA during reductions using H$_2$, CO and CH$_4$ as reducing agents and during oxidations with air for a) calcined and b) activated ilmenite. It demonstrates that for the different reducing gases, calcined and activated ilmenite react faster with H$_2$ than with...
CO and CH₄. After the activation, for H₂ and CO the reactivity increased around 5 times, while for CH₄ this increase was about 15 times.

To analyze the reactivity of the oxidation reaction, it was necessary to reduce the sample first until the particles were composed of Fe₃O₄ and FeTiO₃, so simulating the behavior expected in a CLC system. Tests carried out by TGA showed that the oxidation rate was the same independently of the gas previously used for the reduction. The reactivity of the oxidation reaction is higher than the reactivity for the reduction with H₂, CO, and CH₄, except for the oxidation of calcined ilmenite for solid conversions higher than ≈ 0.25. After this value, the reaction rate sharply decreased for calcined ilmenite. Nevertheless, complete oxidation of calcined particles was reached after a long enough oxidizing period.

![Figure 24. Conversion vs. time curves obtained in TGA during reduction period using H₂, CO or CH₄ as reducing agent (continuous lines). Oxidation by air is showed for the reduced ilmenite (dotted lines): a) calcined and b) activated ilmenite. Reducing gas mixtures: 15% H₂ + 20% H₂O or 15% CO + 20% CO₂ or 15% CH₄ + 20% H₂O. T=900 °C.](image)

In order to assess whether ilmenite has adequate values of reactivity and oxygen transport capacity for its use in the CLC technology, the rate index is calculated for H₂, CO, CH₄ and O₂. The rate index (see Eq.10) can be used to compare ilmenite with other oxygen-carriers that have been proposed for CLC. Figure 25 shows the rate index obtained in TGA for every reacting gas as a function of the number of cycles. The rate index increased
during the activation period and eventually reached a maximum and stable value that was kept constant during the cycles. The maximum value of the rate index was around 5.1%/min for H₂, 1.6%/min for CO, 3.1%/min for CH₄ and 8.1%/min for O₂. Other iron-based oxygen-carriers previously tested by Johansson et al. (2006b) had normalized rate index values with CH₄ within the range of 0.4 to 4%/min. This fact agrees with the results showed by Leion et al. (2008a), where it was concluded that ilmenite reacts just as well as a synthetic Fe₂O₃/MgAl₂O₄ oxygen-carrier. Nevertheless, it is necessary to remark that ilmenite is a natural mineral and a considerably cheaper material than a synthetic material and it has adequate values of reactivity and oxygen transport capacity for its use in the CLC technology with solid fuels.

![Graph showing variation of rate index with cycles](image)

Figure 25. Variation of the rate index with the number of redox cycles in TGA. Oxidation and reduction periods: 1 min. Reacting gases: 15% H₂, 15% CO, 15% CH₄ and 10% O₂.

The reduction reactivity of ilmenite in fluidized bed was also assessed. Figure 26 plots the normalized rate index as a function of the mass based conversion in the reduction reaction for calcined and activated ilmenite for the gases tested and shows that the reaction rate of ilmenite increased after activation. In case of CH₄ the increase in the reaction rate is greater than with the other gaseous fuels, as the rate index raised here in batch fluidized-bed 5 times after activation. The increase in the rate index for CO and for H₂ was lower and it was about 2 times. The resulting rate index calculated from these experiments (Eq. 16) were lower compared to the values obtained in TGA because in fluidized bed there is resistance to mass transfer between the bubble and the emulsion that makes the effective concentration lower to the concentration of the gas main flow.
Figure 26. Normalized rate index as a function of the ilmenite mass based conversion, \( \omega \), for the reduction reactions with CH\(_4\), CO and H\(_2\) with calcined and activated ilmenite in batch FB. \( P_{\text{ef}} = 0.15 \). \( T = 900 \ ^\circ \text{C} \).

**Reactivity with syngas**

Additional redox cycles with different H\(_2\):CO ratios in fluidized bed were also done with the same activated ilmenite after the 100 cycles with syngas. The reducing periods lasted 240 seconds and the gas velocity of the reducing flow was 0.3 m/s. The solids inventory in these tests was 250 kg/MW\(_{\text{th}}\). Figure 27 plots the average rate index as a function of the fraction of H\(_2\) in the reducing agent. It can be seen that the reaction rate was higher for the experiments carried out with H\(_2\) and the lower values were obtained when using only CO. The dotted line is a theoretical rate index calculated as sum of the rate index of H\(_2\) and CO multiplied per their corresponding fractions. It can be seen that the resulting reaction rates for all syngas mixtures tested matches with the theoretical line. Therefore, the reaction rate for a syngas mixture can be actually calculated as the sum of both reducing agents reaction rates. As it has been observed with other Fe oxygen-carriers (Abad et al., 2007a). In addition, no significant displacement of the Water-Gas Shift (WGS) equilibrium towards CO or H\(_2\) formation can be deduced. If WGS reaction was relevant, more H\(_2\) could be produced by reaction of CO with H\(_2\)O in excess. As H\(_2\) is more reactive than CO, the WGS would cause an increase in the rate index compared to the theoretical rate calculated as the sum of the rates with H\(_2\) and CO.
Figure 27. Average normalized rate index as function of the fraction of H₂ in the reducing gas for different H₂:CO mixtures. T = 900 °C.

In this study, ilmenite was seen to undergo an activation process. The achieved maximum reaction rate is maintained throughout the cycles for all gaseous fuels tested. The activation is faster if ilmenite is pre-oxidized. Besides, it is also quicker if the conversion degree reached in the reducing periods of the redox cycles is higher.

3.1.4 Carbon formation and fluidizing behavior

**Carbon formation**

The deposition of carbon from carbon containing gases is a concern because it can deactivate the oxygen-carrier. It can also cause defluidization problems. Besides, if carbon is formed, it can be further directed to the air-reactor where it will be burnt, being therewith the carbon capture efficiency decreased. The conditions for which carbon formation is thermodynamically possible in the CLC process depend on the amount of oxygen added with the oxygen-carrier as well as the temperature and pressure. Nevertheless, there was no CO or CO₂ observed any time during inert or oxidation periods when using carbon-containing fuel gases, i.e. CH₄ and CO, indicating that there was not accumulation of carbon during reduction periods.
Particle integrity and attrition

The attrition rate of the carriers is an important parameter to be accounted as a criterion for using a specific oxygen-carrier in a fluidized-bed reactor. High attrition rates will decrease the lifetime of the particles increasing the reposition of the oxygen-carrier in the CLC system. 100 redox cycles were done in 56 hours of operation in fluidizing conditions. Figure 28 shows the attrition rate as a function of fluidization time. The loss of fines was considered as the recovered particles with a diameter under 40 µm. The initial value of attrition at the beginning is due to the rounding off of angular initial ilmenite particles. With the number of cycles, an external layer was formed, and that this layer is mainly composed by iron oxides. After 40 hours of operation the attrition rate stabilized to a low value: 0.076%/hour. Furthermore, XRD analysis of fines showed that they are formed only by iron oxide. This fact suggests that fines are produced by an attrition process in the particle surface, and not by the fragmentation of particles. There is particle rounding and detachment of part of the external layer, but no particle fragmentation. The resulting average lifetime of the particles was 1310 hours. This is an acceptable value. Furthermore, ilmenite particles are expected to be lost together with coal ash removal in this technology, so the continuous feeding of new oxygen-carrier will be also determined by this loss.

![Figure 28. Fine attrition rate in batch FB as a function of fluidization time. T=900 ºC.](image)

Defluidization

The behavior of ilmenite with respect to particle agglomeration in the fluidized-bed has been also analyzed in this work. Particle agglomeration must be avoided because it can lead
to bed defluidization that causes solids circulation disturbances and channeling of the gas stream through the bed, which turns the contact between gas and particles less efficient. During the experimental tests, defluidization problems were never observed. Moreover, particles extracted from the fluidized-bed at the end of the tests did not show agglomeration evidences.

3.2 Gasification in CLC with solid fuels

Char gasification is one of the crucial steps to take into account, since in this technology char must be previously gasified to react with the oxygen-carrier and get oxidized to CO₂. Leion et al. (2007) reported an enhancement of the gasification rate of a petcoke due to the presence of a Fe-based oxygen-carrier. Leion et al. (2008a) saw that the gasification rate is influenced by the temperature and the amount of gasification agent introduced. They also observed that ilmenite showed similar results than a synthetic Fe-based oxygen-carrier with different fuels. Besides, CO₂ was used as gasification agent by Leion et al. (2009c) with a bituminous Colombian coal as fuel. Their evaluation was focused on the general fuel conversion comparing both gasification agents, which was 5 times faster with steam as compared to CO₂.

To have a comprehensive knowledge of char conversion within the frame and conditions of CLC with solid fuels, the parameters that influence both the gasification rate and the later combustion of the gasification products must be deeply studied to improve the performance of the process. The study was done in a batch fluidized bed reactor as valuable information can be obtained in this device under defined conditions and as a previous facility before doing tests in a continuous prototype. The aim of this section, a study that constitutes Paper IV, is to analyze the performance of ilmenite as oxygen-carrier for iG-CLC regarding the char conversion and the conversion of gasification products. The effect of ilmenite itself and the gasification agent, i.e. H₂O, CO₂ or H₂O/CO₂ mixtures at different temperatures, on the gasification rate and on the combustion of the gasification products were evaluated. Successive redox cycles were carried out in a batch fluidized bed
using char from a South African MV bituminous coal as reducing agent. 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. In some tests, a second load of char was fed in the same reduction period to get further reduction of the oxygen-carrier.

3.2.1 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. Lower concentrations of CO and H₂ were obtained when using ilmenite as bed material compared to sand. No CH₄ was observed during any test, since the volatile matter content in the char is negligible and no methane was generated at these conditions, e.g. by methanation of hydrogasification reactions. From the concentrations obtained, an instantaneous rate of char conversion is calculated with Eq. (21), which is shown in Figure 29. Average values of char conversion rate of 10.9%/min for ilmenite and of 6.5%/min for sand were obtained at 950 ºC using steam. Thus, the use of ilmenite improves the char gasification rate because it has an effect on the gas distribution, as it reacts with CO and H₂, which are well known to be inhibitors for the char gasification reaction.

Figure 29. Instantaneous rate of char conversion, \( r_{C,\text{inst}}(t) \), as a function of the char conversion with activated ilmenite and sand as bed materials. Loads of 1.5 g char in batch FB. Gasification agent: steam. \( T = 900 \, ^\circ\text{C} \).
Solid-solid reaction between char and oxygen-carrier particles has been reported to happen at a relevant rate in TGA (Siriwardane et al., 2009). To check this possible solid-solid reaction in a fluidized bed, tests were performed using N₂ as fluidizing gas and ilmenite or sand as bed material. In both cases almost negligible CO₂ or CO concentrations were generated. This means that the possible solid-solid reaction among char and the oxygen-carrier happened at a negligible rate. A substantial increase in the rate of char gasification could be observed when a gasification agent (H₂O) was used as fluidizing gas. Therefore, the conversion of the solid fuel when is fluidized with H₂O was mainly happening through gasification as an intermediate step, with CO and H₂ as intermediate products.

### 3.2.2 Effect of the fluidizing gas composition

H₂O and CO₂ can be used as fluidizing gases because both can act as gasifying agent. CO₂ 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 if a mixture of CO₂ and H₂O was used, or even avoided if a pure stream of CO₂ was used as fluidizing gas.

Here, the effect of using a gas mixture of CO₂ and H₂O on the gasification of char particles from the South African bituminous coal was analyzed. Figure 30.a) shows the instantaneous rate of char gasification, \( r_{C,\text{inst}}(t) \), as a function of the char conversion when the reactor was fluidized by different H₂O:CO₂ mixtures, and Figure 30.b) shows the evolution with time of the char conversion working with different H₂O:CO₂ ratios. The instantaneous rate of char conversion increased significantly as higher was the H₂O 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 CO₂. 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. From these results it can be concluded that steam seems to be the more adequate fluidizing gas for bituminous South African coal to reach high char gasification conversion. This fact will depend on the type of coal used, as it will be later explained with experiments done in continuous operation with different types of fuels.
Figure 30. a) Instantaneous rate of char conversion, $r_{C,\text{inst}}(t)$, as a function of the char conversion and b) Char conversion vs. time curves with activated ilmenite as bed material with different H$_2$O:CO$_2$ ratios. Loads of 1.5 g char in batch FB. $T=900$ °C.

In this technology, the gasification products, mainly composed of CO+H$_2$, must react with the oxygen-carrier getting oxidized. Figure 31 shows the evolution of combustion efficiency, $\eta_c$, with the char conversion for different H$_2$O:CO$_2$ ratios. The combustion efficiency decreases as the CO$_2$ content in the fluidizing gas increases. Although the flow of reacting gases is lower with CO$_2$, they are enriched in CO. That is, the use of CO$_2$ as gasification agent leads to a worse combustion, since ilmenite reacts slower with CO than with H$_2$.

Figure 31. Combustion efficiency vs. char conversion for several H$_2$O:CO$_2$ ratios. Bed material: Activated ilmenite. Loads of 1.5 g char in batch FB. $T=900$ °C.
3.2.3. Effect of 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. Figure 32 shows the instantaneous rate of char conversion, $r_{C,\text{inst}}(t)$, as a function of the char conversion when the reactor temperature was 900, 950 or 1000 ºC and fluidizing gas was steam or CO$_2$. It can be seen an important increase in the rate of char conversion with temperature when steam is used as gasifying agent. The average $r_{C,\text{inst}}$ value increases from 10.9%/min at 900 ºC up to 37.3%/min at 1000 ºC. Gasification rate with CO$_2$ also increased: the average $r_{C,\text{inst}}$ value increases from 3.4%/min at 900 ºC up to 6.9%/min at 1000 ºC. The apparent activation energy, $E_a$, can be calculated from these values assuming an Arrhenius type dependence with the temperature, thus $E_a=162$ kJ/mol for steam gasification and $E_a=88$ kJ/mol for gasification with CO$_2$. The residence time that would be needed to convert 95% of char fed to the reactor is 7.8 min at 1000 ºC for the char particles when using steam, whereas 43.4 min should be necessary using CO$_2$.

![Figure 32](image)  
Figure 32. Instantaneous rate of char conversion, $r_{C,\text{inst}}(t)$, as a function of the char conversion at 900, 950 and 1000 ºC in batch FB. Fluidizing agent: a) H$_2$O; b) CO$_2$. Activated ilmenite as bed material. Loads of 1.5 g char.

As for the combustion efficiency, for both gasification agents the combustion efficiencies are promoted with the temperature, as ilmenite reacts faster at higher temperatures. However, the dependence of $\eta_c$ with temperature was of lower relevance that those showed for char gasification, see Figure 33. The combustion efficiency for steam is very
high and increases from about 89% at 900 °C to 95% at 1000 °C. Note that although the resulting \( \eta_c \) at 950°C and 1000°C is almost the same, the amount of oxidized gases is higher due to an enhanced extent of gasification. When using CO\(_2\) as gasification agent \( \eta_c \) rises from about 59% at 900 °C to 65% at 1000 °C.

![Graph](image)

Figure 33. Combustion efficiency as a function of X\(_{\text{char}}\) at 900, 950 and 1000 °C in batch FB. Fluidizing gas: a) H\(_2\)O; b) CO\(_2\). Bed material: activated ilmenite. Loads of 1.5 g char.

In conclusion, a relevant increase in the gasification rate was seen when ilmenite was used compared to an inert bed material, because ilmenite reacts with H\(_2\) and CO which are gasification inhibitors. Steam is preferred as gasification agent to CO\(_2\), since with this coal the gasification rate with steam is higher. High temperature enhanced steam gasification substantially: the residence time to convert 95% South African bituminous coal char decreased from 27.5 min at 900°C to 7.8 min at 1000°C.

### 3.3 Continuous operation of CLC with solid fuels

Up to 2011, there have been only several studies done in continuous CLC units fuelled with solid fuels. Berguerand and Lyngfelt (Berguerand and Lyngfelt, 2008a; b; 2009 a; b) used a 10 kW\(_{th}\) chemical-looping combustor with ilmenite as oxygen-carrier and South African coal and petroleum coke as solid fuels. They analyzed the combustion process focusing on char conversion. They analyzed mainly the temperature as one of the main
parameters of influence in the system performance, being higher efficiencies reached at high temperatures. Temperatures above 1000 °C were tested in some cases (Berguerand and Lyngfelt, 2009a). Combustion efficiencies from 85 to 95 % and average carbon capture efficiencies of 80% were obtained in all the experimental works at high temperatures with fuels of low volatile content. Biomass as solid fuel was evaluated by Shen et al. (Shen et al., 2009a) in a continuous 10 kWth CLC combustor using an oxygen-carrier prepared from iron oxide and CO₂ as gasification medium. Gu et al. (Gu et al., 2011) also proved the feasibility of using CLC for both biomass and a biomass/coal mixture as solid fuels in a continuous 1 kWth CLC facility using an Australian iron ore as oxygen-carrier. In order to get more knowledge about the iG-CLC process, in this thesis various series of experiments were performed in two continuous CLC units for solid fuels.

The first one is the ICB-CSIC-s1 unit placed at the Instituto de Carboquímica-CSIC, Zaragoza, Spain. The maximum thermal power reached in these experiments was 580 Wth. The two main advantages of this facility are that it allows the control and measurement of the solids circulation flow rate and that the fuel is fed at the bottom of the reactor, so the volatiles get in contact with the oxygen-carrier bed. This facility has no carbon separation system, which facilitates the evaluation of the effect of the solids mean residence time. The experiments were done with several fuels ranging from lignite to anthracite. Nevertheless, most experiments were carried out with HV bituminous Colombian coal El Cerrejón as fuel. A total of 98 hours of continuous operation feeding fuel and 122 hours of continuous fluidization were made in this prototype, where the carbon capture and combustion efficiency of the CLC process with coal was analyzed. The effect on the process of several variables of operation was assessed. Results obtained from the experiments performed in this unit are presented in Papers V, VI and IX. In Paper V the different behavior and conversion of the char and the volatile matter is analyzed, as well as the fuel-reactor temperature and the coal particle size on the system performance. Besides, the property variation of ilmenite along the operating time could be analyzed. In Paper VI the effect of variables of operation such as solids recirculation rate, coal feeding flow, and flow and type of gasification agent is studied. Paper IX evaluates the feasibility of using different types of coals, as well as the effect of the coal rank on this technology.
The second unit has a thermal power of 10 kW\textsubscript{th} and is placed at Chalmers University of Technology, Göteborg, Sweden. Since in this facility the volatiles are not efficiently mixed with the oxygen-carrier bed because of its above-bed feeding system, petcoke was used as fuel due to its low content in volatiles. A total of 4 hours of continuous operation feeding fuel and 8 hours of fluidization were made in this unit, where the influence of limestone addition to ilmenite in the CLC process with solid fuels was evaluated. Results obtained were presented in Paper VII. Both CLC prototypes were easy to operate and control, and the steady state for each operating condition was maintained stable for at least 30 min.

Table 7 shows the conditions for the series of experiments carried out with Colombian coal in the ICB-CSIC-s1 facility. One further test was done with sand as bed material with a feed flow of 75 g/h of coal and steam as fluidizing agent at 915 °C. The total sand bed mass in the system was 1.8 kg and the solid bed mass in the fuel-reactor was 0.38 kg sand.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Coal particle size(μm)</th>
<th>TFR (ºC)</th>
<th>Coal feed (g/h)</th>
<th>Solids circ. Flow(kg/h)</th>
<th>Gasif.agent flow(LN/h)</th>
<th>H\textsubscript{2}O:CO\textsubscript{2} (%):%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>74-125</td>
<td>820-950</td>
<td>42</td>
<td>3.5</td>
<td>180</td>
<td>100:0</td>
</tr>
<tr>
<td>A2</td>
<td>125-200</td>
<td>820-950</td>
<td>42</td>
<td>3.5</td>
<td>180</td>
<td>100:0</td>
</tr>
<tr>
<td>A3</td>
<td>200-300</td>
<td>820-950</td>
<td>42</td>
<td>3.5</td>
<td>180</td>
<td>100:0</td>
</tr>
<tr>
<td>B</td>
<td>74-125</td>
<td>890</td>
<td>33-83</td>
<td>8.4</td>
<td>190</td>
<td>100:0</td>
</tr>
<tr>
<td>C1</td>
<td>74-125</td>
<td>890</td>
<td>41.1</td>
<td>1.2–11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>125-200</td>
<td>890</td>
<td>46.7</td>
<td>1.0–3.6</td>
<td>190</td>
<td>100:0</td>
</tr>
<tr>
<td>C3</td>
<td>200-300</td>
<td>890</td>
<td>38.5</td>
<td>1.6–11.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>125-200</td>
<td>940</td>
<td>161</td>
<td>2.5</td>
<td>110-190</td>
<td>100:0</td>
</tr>
<tr>
<td>E</td>
<td>125-200</td>
<td>935</td>
<td>72</td>
<td>3.3</td>
<td>190</td>
<td>100:0-0:100</td>
</tr>
</tbody>
</table>

The activation process on ilmenite reactivity was observed in the continuous ICB-CSIC-s1 unit, as ilmenite samples were extracted after several hours of operation and the reactivity
was measured by TGA. It could be considered that ilmenite was already active after 3 hours for the reduction reaction. However, ilmenite was not completely activated for oxidation reaction after 35 hours operation yet and it was almost fully activated after 98 hours. This was attributed to the fact that it had not developed enough porosity. This was because in the continuous tests the ilmenite conversion variation was low.

As an example, in Figure 34 the obtained gas distributions (dry and N$_2$ free basis) in fuel- and air-reactor for tests with increasing fuel-reactor temperature in the ICB-CSIC-s1 unit are represented. The outlet of the fuel-reactor was mainly composed of oxidized CO$_2$, and H$_2$ and CO as not fully oxidized products. In case of this series of experiments, it can be observed that an increase in the fuel-reactor temperature led to an increase in the generated CO$_2$ and to a decrease in the unburnt gases in the fuel-reactor, that is, CO, H$_2$ and CH$_4$, and to a decrease in the CO$_2$ in the air-reactor, which was ungasified char coming from the fuel-reactor that was burnt in the air-reactor.

![Figure 34. Gas distributions in fuel-reactor (dry basis and N$_2$ free) and air-reactor for increasing fuel-reactor temperature in continuous test. Solids circulation flow: 3.5 kg/h. Fuel: pre-treated bituminous Colombian coal. Coal particle size: +125-200 μm.](image)

A key aspect of the process is the oxidation of the gasification products by ilmenite, as well as the released volatile matter, and possible tars formed. Experiments with char showed complete combustion of gasification products to CO₂ and H₂O. Therefore, unconverted gases should come from incomplete combustion of volatile matter.

In order to evaluate to what extent ilmenite oxidizes the volatile matter, an experiment with sand as inert bed material was done with coal as fuel at 915 °C and steam as gasification agent in the fuel-reactor. Therefore, from the comparison between the tests with ilmenite and sand as bed materials, at 915 °C the combustion efficiency of the released volatiles by the oxidation with ilmenite was 38.3% for CH₄, 35.3% for CO and 79.0% for H₂. The reaction differences between gases are due to the reaction rates of ilmenite, since it reacts faster with H₂ and slower CH₄. In addition, more oxygen transfer is needed to oxidize CH₄. Thus, the combustion efficiency of the volatile matter was 63.0%.

For sand as bed material, the GC measurement showed that the fuel-reactor product gas had compositions of 0.13% C₂H₆ and 0.04% C₃H₈. Besides, the tar content in the fuel-reactor outlet was measured to be 0.895 g/Nm³ dry gas. Although the quantities measured of both tars and higher hydrocarbons for this fuel were quite low in absence of an oxygen-carrier, ilmenite showed to promote the decomposition and later oxidation of those species, since no tars either hydrocarbons heavier than CH₄ were formed when using ilmenite.

Char gasification increased from 5.2% with sand to 48.1% with ilmenite as bed material. This can be explained through the inhibitory effect that causes the presence of high amounts of H₂ and CO in the fuel-reactor, as they do not react with the oxygen-carrier.

3.3.1 Effect of fuel-reactor temperature

The influence of the fuel-reactor temperature on the main parameters of the CLC process for 3 different coal particle sizes, i.e., +74-125 μm, +125-200 μm and +200-300 μm, was studied. Temperatures from 820 to 950 °C were used in this study. Figure 35 represents the efficiencies of carbon capture, char conversion and combustion as a function of the reactor
temperature for different coal particle sizes. As it was presumable, the results show that there is a continuous increase of all efficiencies with the temperature for all coal particle sizes. In this prototype carbon capture presented low values below 920 °C. This was because the gasification rate at these temperatures is slow and thus a relatively high amount of char went to the air-reactor. The carbon capture at 870 °C had a value of 35% and increased up to 86% at 950 °C. The increase in the carbon capture efficiency with the temperature is due to more carbon in char is being gasified in the reactor. The char conversion changed from 15% at 870 °C to 82% at 950 °C as extreme cases. If the trends are extrapolated, it could be expected that all efficiencies would reach a value close to 100% at 1000 °C, which means that most of carbon in the coal would exit with the fuel-reactor flue gases. This unit has no carbon separation system, so the ungasified char from the fuel-reactor is directed to the air-reactor where it is burnt with air. Nevertheless, the absence of a carbon stripper facilitates the interpretation of the effect of the operational conditions on the char conversion, specially the effect of the mean residence time.

Figure 35. a) Carbon capture, b) char conversion and c) combustion efficiency variation with fuel-reactor temperature for various coal particle sizes. Particle size: • 74-125 μm; ▲ 125-200 μm; ■ 200-300 μm.

The combustion efficiency varied from 70% at 870 °C to 95% at 950 °C for the middle and bigger particle sizes. It is likely that the combustion efficiencies observed for the smaller particle size were lower because relevant fraction of char was gasified in the upper part of the reactor, where gasification products are not in contact with the oxygen-carrier. Full oxidation of the outlet fuel-reactor stream was not achieved in any of the previous CLC
experiments with solid fuels performed to date (Berguerand and Lyngfelt, 2008a; b; 2009a; b; Wu et al., 2010; Shen et al., 2009a;b;c;2010). Furthermore, the extent of unburt gases was similar as if a highly Ni-based oxygen-carrier was used (Shen et al., 2009b;2009c;2010).

3.3.2 Effect of coal particle size

The effect of the coal particle size on the process performance was investigated because it is a key parameter in the operation of fluidized-bed reactors. Three different coal particle sizes were assessed: +74-125, +125-200 and +200-300 μm. Differences on combustion efficiency with the smaller particle sizes can be explained because elutriated char particles could be gasified to some extent in the reactor freeboard. There the gasification products did not get in contact with the oxygen-carrier and could not be therefore oxidized. However, the char from the smaller size could still get gasified in the freeboard. The resulting char conversions and carbon captures are similar at different particle sizes. The slight differences can be explained because smaller particles are more easily elutriated than bigger ones. For particle sizes of +74-125 μm about 35% of the introduced char was elutriated, whereas lower values than 5% were found in most cases for bigger particles. At about 900 ºC the residence time of char was 9 min for +200-300 μm, 8 min for +125-200 μm and decreased to 5 min for +74-125 μm. Figure 36 shows the calculated char gasification rates at different temperatures and for the three particle sizes used.

Figure 36. Calculated gasification rate considering the fuel-reactor as a CSTR for different fuel-reactor temperatures. Coal particle size: – 74-125 μm; – 125-200 μm; – 200-300 μm.
It can be observed that the char gasification rate increased with the temperature for every particle size.

### 3.3.3 Effect of solids recirculation rate

The effect of the solids circulation rate on the process performance was studied. Solids circulation flow rates from 1.0 to 11.6 kg/h for three coal particle sizes at an average fuel-reactor temperature of 890 °C were used. This range corresponded to an ilmenite residence time range from 4.2 to 48 minutes and the oxygen-carrier to fuel ratio $\phi$ was varied from 0.5 to 8.4. Thus, there were cases where the solids recirculation rate was lowered so much that $\phi$ reached values under the unity, which meant that there was not enough oxygen-carrier available to fully oxidize the fuel.

Figure 37.a) 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 $\phi$ closer to the unity, and when $\phi$ has higher values the influence is smaller. This follows the tendency of the solids residence time, that is, the decrease in $\eta_{CC}$ can be explained because coal was less gasified, due to a lower residence time of the solids in the fuel-reactor.

The combustion efficiencies were less influenced by the solids circulation rate. This indicates that the process is actually controlled by char gasification, although the amount or reactivity of the oxygen-carrier has also some influence in the system. Figure 37.b) shows that the combustion efficiency had some increase when $\phi$ decreases: from 75% with $\phi=8$ to 86% with $\phi=1.1$. With lower $\phi$ the char conversion increased, and since the gasification products had almost full conversion, the percentage of unconverted gases - mainly coming from volatiles- decreased, as the relative importance of the gasification products in the reacting gases increased. Thus, higher char conversions will lead to enhanced combustion efficiencies. The lower combustion efficiencies obtained for the +74-
125 μm particles are due to the higher fraction of char in the freeboard with smaller particles.

Figure 37. a) Carbon capture and b) Combustion efficiencies with different oxygen-carrier to fuel ratios for different coal particle sizes. TFR = 890 °C. El Cerrejón coal.

When oxygen-carrier to fuel ratios lower than 1 were used, the performance of the system dropped substantially although the residence time was very high. When φ decreased to 0.5 the combustion efficiency decreased because there was not enough oxygen available to burn the fuel fed and as a consequence the char conversion also dropped because the reactor got enriched in the generated H2 and CO, which are inhibitors for the char gasification rate.

3.3.4 Effect of coal feeding flow

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

When higher coal feeding flow was introduced, the corresponding flows from all products increased because there was more fuel to devolatilize, gasify and burn. However, the char
conversion was not really influenced by an increase in the coal feed because there was no major increase in the residence time, as can be seen in Fig. 4 from Paper VI.

The resulting combustion efficiency was not influenced by the coal feeding rate, as the oxygen-carrier to fuel ratio was above one. 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 (see Fig. 6 from Paper VI). 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.

3.3.5 Effect of gasification agent: flow and type

The flow of steam feed was varied from 110 to 190 L/h, corresponding to a gas velocity variation in the fuel-reactor from 0.07 to 0.12 m/s at 900 °C. The steam to fixed carbon ratio changed from 0.7 to 1.1. When the gasification products are burnt by ilmenite, H2O and CO2 are formed which can further gasify the fuel, so H2O is being regenerated in the process. The increase in the steam flow fed had some beneficial effect on the char conversion. For conditions of steam excess, there was no major effect on the char conversion, so it would not be necessary to have H2O/C over the unity. The change in the gasification agent flow did not influence the combustion efficiency.

The steam requirements for the gasification would be decreased in some extension, or even avoided if a pure CO2 stream was used as fluidizing gas. The motivation of this is that CO2 can be fed by recirculating a fraction of the product gas stream. The effect of using a gas mixture of CO2:H2O on the gasification step and the whole performance of the process was evaluated in a continuous system. The average fuel-reactor temperature was 935 °C. The total gasification agent flow was 190 L/h. The solids circulation rate was 3.3 kg/h.

The results showed that the char conversion increased for higher fraction of steam in the gasification agent, as it was previously found in batch FB experiments. With this type of fuel, gasification with steam is faster than with CO2. However, the combustion efficiency was not really influenced by the gasification agent used. When gasifying with CO2, more
CO is generated as when gasifying with steam, where H₂ is also generated. This result is opposite to that found in batch FB done with bituminous South African coal. This is because in this plant the combustion efficiency was limited by the combustion of volatiles which is not influenced by the fluidizing gas.

Limited use of CO₂ in the fluidizing gas would be desirable to maintain high gasification rates for this fuel. This was also seen in the previous tests in batch FB with Colombian South African coal. On the other hand, the implementation of a carbon separation system that increased the char residence time would offset any possible poorer system performance caused by the slower gasification rate.

### 3.3.6 Effect of limestone addition

The influence of limestone addition to ilmenite as oxygen-carrier was tested in a continuous 10 kWth CLC pilot for solid fuels. The results of it comprise Paper VII. This study was motivated by previous tests where calcined limestone addition in a batch fluidized bed had some beneficial effect on the char conversion rate and led to an enhancement on the gas conversion (Teyssié et al., 2011). Tests with an ilmenite-limestone mixture as bed material were performed, and also tests using only ilmenite as bed material were carried out in that unit for comparison. Global solids circulation was varied as it is an important operational parameter, which determines the solid fuel residence time. The tests were performed at two temperatures of the fuel-reactor: 950 ºC and 1000 ºC. The fuel flow was 479 g/h, which is a fuel power of 4.2 kWth. The particle recirculation between reactors was controlled by the air flow to the air-reactor: it was varied from 155 to 190 Lₙ/min. The fuel was petcoke, which has relative low fraction of volatile matter, 9.9%. Thus, only the gasification process and oxidation of gasification products are really the scope of evaluation in this study.

As an example of the most important results, Figure 38 shows the comparison between the obtained oxygen demand, Ω_{OD}, and carbon capture η_{CC} from the experimental conditions used, for experiments done at 950 and 1000 ºC; and using only ilmenite as bed material and...
after limestone addition. The limestone fraction in the fuel-reactor bed at the end of the experiments was weighed to be about 12 %wt.

Table 8 shows a summary of the average values for the main experiments performed: the carbon capture efficiency, $\eta_{CC}$, the oxygen demand, $\Omega_{OD}$, the oxygen-carrier to fuel ratio, $\phi$, and the oxygen-carrier average residence time in the fuel-reactor, $t_{r,ilm}$.

The conversion of gasification products after limestone addition was higher at 950 °C, as $\Omega_{OD}$ decreased from 0.33 to 0.24. For a mean residence time of 10.7 minutes, $\eta_{CC}$ was 0.79. In order to compare tests with the same residence time, an interpolated value of $\eta_{CC}$ of 0.76 was obtained for ilmenite only, for a mean value of $t_{r,ilm}$ of 10.7 minutes. Thus, $\eta_{CC}$ was somewhat lower for ilmenite only, as compared to ilmenite + limestone. At 1000 °C there was no significant difference in the gas conversion, as $\Omega_{OD}$ was quite similar after limestone addition. However, the efficiencies related to char conversion improved by the presence of limestone: $\eta_{CC}$ increased from 0.77 to 0.86, as can be seen in Table 8. As for the influence of adding limestone to the CLC process with ilmenite, at 950°C, there is a reduction in the oxygen demand, whereas no clear difference is seen at 1000°C. In all the cases char was faster converted in presence of limestone.
Table 8. Summary of the mean values obtained in the continuous experiments with petcoke as fuel and with ilmenite or a limestone-ilmenite mixture as bed material.

<table>
<thead>
<tr>
<th>T_{FR}=950 °C</th>
<th>Bed material</th>
<th>η</th>
<th>Ω</th>
<th>t_{r,ilm}(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ilmenite + Lime</td>
<td>0.79</td>
<td>0.24</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>0.7</td>
<td>0.33</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>0.83</td>
<td>0.33</td>
<td>13.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T_{FR}=1000 °C</th>
<th>Bed material</th>
<th>η</th>
<th>Ω</th>
<th>t_{r,ilm}(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ilmenite + Lime</td>
<td>0.86</td>
<td>0.28</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

The addition of some limestone was somewhat advantageous for the efficiency improvement, for gasification as well as for gas conversion due to its effect in the water-gas shift equilibrium. Figure 39 shows the fraction \( \frac{F_{\text{H}_2,FR} F_{\text{CO}_2,FR}}{F_{\text{H}_2O,FR \text{ out}} F_{\text{CO},FR}} \) obtained for experiments with ilmenite-limestone and for tests done with ilmenite only at 950 °C and 1000 °C. The equilibrium constant \( k_{\text{WGS}} \) at the temperature considered is also represented. At both temperatures the exiting gaseous flows with limestone addition were closer to the WGS equilibrium, i.e. to higher \( \text{H}_2 + \text{CO}_2 \) formation, although the difference was much more pronounced at 950 °C.

Figure 39. Fraction \( \frac{F_{\text{H}_2,FR} F_{\text{CO}_2,FR}}{F_{\text{H}_2O,FR \text{ out}} F_{\text{CO},FR}} \) for experiments with ilmenite-limestone mixture and with ilmenite as bed material at 950 °C and 1000 °C.
Thus, limestone addition causes CO and H₂O to react to give CO₂ and H₂, i.e. Ca-based compounds could act as a catalyst for the WGS reaction (Teyssié et al., 2011). This happens in the presence of an oxygen-carrier, ilmenite, which reacts faster with H₂ than with CO. Consequently, the oxidation of the gas should proceed faster, giving higher gas conversion and lower oxygen demand. This effect is clearly seen at 950 °C (see Figure 38.a)), although at a temperature of 1000 °C the improvement regarding the gas conversion was residual when CaO was present in the solids mixture (see Figure 38.b)). From results showed in Figure 39 it seems that the WGS reaction itself is fast enough at 1000 °C to happen at similar extension with and without limestone addition.

3.3.7 Effect of the coal rank

The carbon capture and combustion efficiencies as representative of the process performance were studied in continuous testing with different coals from lignite to anthracite, in order to prove the feasibility of the technology with coals of different ranks and to assess the performance of the process as a function of the solid fuel properties. Previous research studies in batch FB concluded that the char conversion is related to the reactivity of solid fuel particles (Linderholm et al. 2011), being the nature of the oxygen-carrier of lower relevance (Leion et al., 2008a; 2009d). This study is gathered in Paper IX.

Table 9 shows the conditions for the series of experiments carried out, where the fuel-reactor temperature and of the gasification agent type (H₂O:CO₂ mixtures) were varied. The average solids circulation flow rate was 3.0 kg/h and the resulting oxygen-carrier to fuel ratio for all fuels tested was about 1.0-1.1. The gasification agent flow was 190 Lₙ/h, corresponding to a gas velocity of 0.12 m/s at 900°C. The flows introduced are the same as in the tests done with the HV bituminous Colombian coal. An experiment previously performed with this coal, which had similar solids residence time and solids inventory, is included in the discussion of results.
Table 9. Conditions for the series of experiments with the different types of coals tested, i.e, lignite, Colombian and South African bituminous coals and anthracite.

<table>
<thead>
<tr>
<th>Coal type</th>
<th>T_{FR}, °C</th>
<th>Coal feed, g/h</th>
<th>Gasif. agent Fixed C</th>
<th>Gasification mixture,%H_2O</th>
<th>Thermal output, W_{th}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>870-920</td>
<td>100</td>
<td>3.0</td>
<td>100</td>
<td>450</td>
</tr>
<tr>
<td>MV Bit. S.African</td>
<td>850-915</td>
<td>79</td>
<td>2.3</td>
<td>100</td>
<td>580</td>
</tr>
<tr>
<td>Anthracite</td>
<td>870-930</td>
<td>94</td>
<td>1.8</td>
<td>100</td>
<td>570</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coal type</th>
<th>T_{FR}, °C</th>
<th>Coal feed, g/h</th>
<th>Gasif. agent Fixed C</th>
<th>Gasification mixture,%H_2O</th>
<th>Thermal output, W_{th}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>920</td>
<td>100</td>
<td>3.0</td>
<td>100;60;0</td>
<td>450</td>
</tr>
<tr>
<td>MV Bit. S.African</td>
<td>910</td>
<td>79</td>
<td>2.3</td>
<td>100;58;0</td>
<td>580</td>
</tr>
<tr>
<td>Anthracite</td>
<td>925</td>
<td>94</td>
<td>1.8</td>
<td>100;48;0</td>
<td>570</td>
</tr>
</tbody>
</table>

Continuous tests were done at different temperatures. Figure 40.a) shows the carbon capture obtained for different temperatures for the coals tested, as well as the values that were obtained for HV bituminous Colombian coal in the previous study. $\eta_{CC}$ was highly dependent on coal rank because of the gasification reactivity of the coal chars. Lignite reached the highest values of $\eta_{CC}$, followed by HV bituminous Colombian, MV bituminous South African coal and it was lower for anthracite. As an example, at 900°C $\eta_{CC}$ was 0.90 for lignite, 0.55 for Colombian coal (at 890°C), 0.54 for South African coal and 0.29 for anthracite. The carbon capture depended on the char conversion and on the ratio $F_{C,vol}/F_{C,char eff}$ of the coal considered.

Figure 40.b) shows the char conversions reached at different temperatures for the coals studied. Lignite had much higher char conversion than the other coals. The char
conversion obtained for the other coals are closer, indicating that they have more similar gasification rates, but lower that the gasification rate of lignite.

The residence time of solids was similar for all fuels tested, that is, the char from all fuels had similar time to gasify. It was around 14 minutes. From these results, it can be concluded that the gasification rates follow the order expected from the rank of the different coals: it is much faster for lignite, then HV bituminous coal, MV bituminous South African coal and it is slower for anthracite. The gasification rates in all experiments were also calculated and confirmed this statement at all temperatures tested. This was also in line with the trend of the char gasification rates expected from the rank of the coals used (Johnson, 1981).

Both char conversion and carbon capture for anthracite were similar because the volatile matter fraction is low, whereas for the other coals the values of carbon capture were higher. For lignite the differences between $X_{\text{char}}$ and $\eta_{\text{CC}}$ are not big either because $X_{\text{char}}$ is already quite high. HV bituminous Colombian and MV bituminous South African coal have similar fractions of volatiles and fixed carbon and char conversions reached, so their increase in $\eta_{\text{CC}}$ compared to $X_{\text{char}}$ is similar.
Figure 41.a) shows that for the fuels tested in this work, the fuel-reactor combustion efficiencies obtained have a slow growth with the temperature because of the increase in the reaction rate of ilmenite. Besides, for all the temperatures tested, $\eta_{\text{comb FR}}$ was higher for anthracite, followed by lignite and MV bituminous South African coal, which was similar to HV bituminous Colombian coal. As it was concluded from the experiments with the bituminous Colombian coal, the released volatiles have worse contact with the oxygen-carrier particles and are therefore less converted. On the contrary, gasification products are highly oxidized. This explains the higher $\eta_{\text{comb FR}}$ for anthracite, since the volatile fraction is lower. Although lignite has a higher fraction of volatile matter compared to South African coal, the resulting $\eta_{\text{comb FR}}$ for lignite was slightly higher because the relative fraction of gasification products compared to volatiles was higher due to the fast char gasification rate of lignite. As an example, at 900$^\circ$C $\eta_{\text{comb FR}}$ was 0.73 for Colombian coal (at 890$^\circ$C), 0.84 for anthracite 0.75 for lignite and 0.73 for South African coal. Solid residence times are similar for all coals used, around 14 minutes, although the solids inventories have some differences that also affect the results: it was 1770 kg/MWth for lignite, 1580 kg/MWth for Colombian coal, 1380 kg/MWth for South African coal and 1400 kg/MWth for anthracite.

If complete combustion of the gasification products is assumed, a combustion efficiency of the volatile matter, $\eta_{\text{comb vol}}$, can be defined, as for Eq. (41). This parameter can give an idea of how much the volatiles of each type of fuel are oxidized.

$$
\eta_{\text{comb vol}} = \frac{O_2 \text{ demand gases FR}}{O_2 \text{ demand volatiles}} = \frac{2 \cdot F_{\text{CH}_4, FR} + 0.5 \cdot F_{\text{H}_2, FR} + 0.5 \cdot F_{\text{CO}_2, FR}}{O_2 \text{ demand coal} - O_2 \text{ demand char}} \quad (41)
$$

As it can be seen in Figure 41.b), the volatile combustion efficiency was lower for anthracite and higher for lignite and very similar for both bituminous coals. This could be explained by means of the composition of volatiles of each type of fuel: the oxygen demanded by the volatiles of anthracite is higher than for lignite, then for South African and bituminous Colombian coal. The average combustion efficiency of volatiles was around 52% for lignite, 61% for HV bituminous Colombian coal, 58% for MV bituminous South African coal, 42% for anthracite.
Figure 41. a) Fuel-reactor combustion efficiency and b) volatile combustion efficiency variation with the fuel-reactor temperature for lignite, HV bituminous Colombian coal, MV bituminous South African coal, anthracite.

Since the rate of gasification of the fuel in this process is a determining factor, the effect of using a gas mixture of CO₂ and H₂O on the gasification step and the whole performance of the process with the fuels used in this work was evaluated. In case of lignite there is no change in the process performance when gasifying with CO₂, as it can be seen in Figure 42.

Figure 42. a) Carbon capture efficiency and b) Char conversion variation for different H₂O:CO₂ mixtures as gasification agent for lignite, bituminous South African coal, anthracite.
On the other hand, for anthracite the lower gasification rate of char with CO$_2$ leads to a substantial drop in the performance. The combustion efficiency is not affected by the gasification agent used. Thus, depending on the type of fuel, CO$_2$ recirculated from the outlet fuel-reactor flow can replace some of the steam as gasification agent, getting similar system performance and thereby saving energy derived from steam generation.

In this study it has been concluded that the outgoing unburnt gases in the fuel-reactor seem to come from volatile matter that had not been fully oxidized. At higher fuel-reactor temperatures, gasification and combustion reactions are faster and promoted for all types of solid fuels. The carbon capture is higher for the solid fuels with faster char gasification rates and also when the volatile content in the fuel is higher. High values of carbon capture can be obtained, but it is essential to have a highly efficient carbon separation system that reintroduced unconverted char particles back to the fuel-reactor, especially for solid fuels with slow gasification rates such as anthracites. The combustion efficiency in the fuel-reactor is higher for higher temperature, higher solids inventory and for solid fuels with lower volatile content and with faster gasification rate. Furthermore, depending on the type of fuel, some of the steam as gasification agent can be replaced by CO$_2$. 

4 Simplified model of a CLC system with solid fuels and optimization
A theoretical model is a useful tool to understand the operation of the system in a general way, as well as to predict the influence of the different variables and optimize their values. A validated model can be also used for the design of an industrial unit. In this section a theoretical simplified model for the fuel-reactor of an iG-CLC process using ilmenite as oxygen-carrier has been developed based on a simple reacting scheme. The model calculations were made considering the HV bituminous Colombian coal “El Cerrejón” as solid fuel. For the development of the simplified model of iG-CLC, it was necessary to know: (1) the reaction scheme to be considered in the mass balance; (2) the content and composition of the volatile matter in coal; (3) kinetics of char gasification with the gasification agents used; and (4) kinetics of the subsequent reaction of the gaseous compounds (CO, H$_2$, CH$_4$) with the oxygen-carrier are also required.

4.1 Gasification kinetics

For char gasification the most common gasification agents are steam and CO$_2$, through which H$_2$ and CO are generated as for the following reactions:

\[
\begin{align*}
C + H_2O & \rightarrow CO + H_2 \\
C + CO_2 & \rightarrow 2 CO
\end{align*}
\]  

(42)  \hspace{1cm} (43)

Kinetics of the gasification reactions for the bituminous Colombian coal were obtained by TGA analysis, in order to implement the kinetics in the model of the iG-CLC system. Conversion vs. time curves at different temperatures (900-1050°C), gasification agent concentrations (i.e. 20-80 vol.% H$_2$O or CO$_2$) and gas product concentrations (i.e. 0-40 vol.% H$_2$ or CO) were obtained. A similar procedure was used to those found in (Adánez et al., 1985). Char was assumed to gasify according to the homogeneous reaction model with control by chemical reaction. The surface reaction follows a Langmuir-Hinshelwood reaction model and the reaction rate is constant with the char conversion. The gasification rate ($-r_c$) is defined by Eq. (44).
\[ (-r_c) = \frac{1}{(1 - X_{\text{char}})} \frac{dX_{\text{char}}}{dt} = \frac{k_1 p_{\text{react}}}{1 + k_2 p_{\text{react}} + k_3 p_{\text{prod}}} \]  

(44)

where \( X_{\text{char}} \) is the char conversion, \( p_{\text{react}} \) is the partial pressure of the gaseous reactants, i.e. \( \text{H}_2\text{O} \) or \( \text{CO}_2 \), \( p_{\text{prod}} \) is the partial pressure of the gasification products, i.e. \( \text{H}_2 \) or \( \text{CO} \), and \( k_1 \), \( k_2 \) and \( k_3 \) are the kinetic constants. Thereby, the gasification kinetic parameters were obtained when using \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) as gasification agents and taking into account the inhibitory effect of \( \text{H}_2 \) and \( \text{CO} \).

As an example, Figure 43 shows the char conversion versus time curves for the gasification reactions with \( \text{H}_2\text{O} \) of El Cerrejón coal at different temperatures and different \( \text{H}_2 \) fractions as inhibitory agent obtained by TGA. In the TGA tests, the coal sample is heated up immediately in \( \text{N}_2 \) and pyrolysis takes place until constant weight is reached at the temperature of reaction. Later, the gas mixture for char gasification is introduced.

![Figure 43. Char conversion versus time curves for the gasification reactions with H2O of El Cerrejón coal obtained by TGA a) at different temperatures, using 20% H2O + 0% H2; and b) with 40% H2O and different H2 fractions at 1000°C.](image)

The gasification kinetic parameters were obtained when using \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) as gasification agents and taking into account the inhibitory effect of \( \text{H}_2 \) and \( \text{CO} \). The gasification kinetic constants obtained are gathered in Table 10.
Table 10. Gasification kinetic constants for char from pre-treated El Cerrejón coal. Gasification agents: H₂O/H₂ and CO₂/CO.

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁, H₂O (s⁻¹·bar⁻¹)</td>
<td>k₂, H₂O (s⁻¹·bar⁻¹)</td>
</tr>
<tr>
<td>k₀</td>
<td>52.6</td>
<td>2.81·10⁻⁶</td>
</tr>
<tr>
<td>Eₐ (kJ/mol)</td>
<td>95.1</td>
<td>-135.1</td>
</tr>
</tbody>
</table>

4.2 Reaction kinetics of ilmenite

To design a CLC system it is necessary to determine the reactivity under different operating conditions of temperature and gas concentration. Thus, the objective of this section, a study published in Paper II, was to establish the kinetic of both reduction and oxidation reactions taking place in the CLC process using ilmenite as oxygen-carrier. Because of the beneficial of the use of calcined ilmenite against fresh ilmenite and the activation of the ilmenite during the redox cycles, both the reactivity of calcined and activated ilmenite was analyzed. The reaction studied was the reduction of the components in oxidized ilmenite, Fe₂TiO₅ and Fe₂O₃ to FeTiO₃ and Fe₃O₄, and vice versa for the oxidation. The experimental tests were carried out in a thermogravimetric analyzer (TGA), using H₂, CO and CH₄ as reducing gases at different temperatures (800, 850, 900 and 950 °C) and gas concentrations (5%, 15%, 30%, 50%) to analyze the reactivity of the reduction reaction. Preliminary results showed that the reaction products, i.e, H₂O or CO₂, had no effect on the reaction rate. To analyze the reactivity of the oxidation reaction, O₂ was used as reacting gas at different temperatures (800, 850, 900 and 950 °C) and O₂ concentration from 5 to 21 vol.%. For the study of the oxidation, the sample was first reduced at a reference temperature of 900 °C in an atmosphere composed of 5 vol.% H₂+40 vol.% H₂O. The starting particles ready for oxidation were composed of Fe₃O₄ and FeTiO₃, so simulating the behavior expected in a CLC system.

The oxygen transport capacity $R_{O,ilm}$ of calcined ilmenite was 4% and $R_{O,ilm}$ was 3.3% for the activated ilmenite analyzed. However, although activated particles had other $R_{O,ilm}$
values, it was found that the oxygen transference rate $R_{O,ilm} \cdot (dX_i/dt)$ is constant. A discussion about the use of kinetics when $R_{O,ilm}$ changes during the activation process can be found in Paper II. For the kinetic determination, the data used corresponded to the first reduction or oxidation period, because the reactivity of ilmenite varies during the first cycles using calcined ilmenite. Fully activated samples had no change in the reaction rates.

Kinetics determination

By using a particle reaction model, the kinetic parameters of the different reactions can be determined for the oxygen-carrier. The model used to determine the kinetic parameters is the grain model with uniform reaction in the particle with changing grain size model (CGSM) and with control of chemical reaction in the grain. The model assumes that the particle consists of a number of nonporous spherical grains of uniform initial radius, $r_g$. Considering that the reaction is controlled by the chemical reaction in the grain and considering spherical grains, the equations that describe this model are:

$$\frac{t}{\tau_{chr}} = \frac{1}{1 - x_i}^{1/3} \tau_{chr} = \frac{\rho_a r_g}{b k_r C_g^n}$$

This model describes the reduction kinetics of calcined and activated ilmenite, as well as the oxidation reaction for activated ilmenite. Nevertheless, the oxidation mechanism of calcined ilmenite was slightly different: it was a two-step mechanism that changed from a chemical reaction control to a diffusional control in the particle due to the loss of porosity inside the particle as oxidation proceeds. Thus, a mixed resistance between chemical reaction and diffusion in the solid product was needed. In this case, it was assumed that the reaction rate was controlled by chemical reaction in the grain, whereas the porosity of particles decreases because the volume of the solid products ($Fe_2TiO_5 + TiO_2$ and $Fe_2O_3$) is higher than that for the solid reactants ($FeTiO_3$ and $Fe_3O_4$). This chemically controlled step proceeds until the porosity collapses at a determined conversion value, $X_{chr}$, which will be determined from the conversion-time curves. From this point, it was assumed that the oxidation proceeds following a shrinking core model in the particle, and it is controlled by
the diffusion in the solid product layer. Furthermore, it was found that the oxygen concentration do not affect the oxidation rate when the reaction is controlled by diffusion through the product layer. This agrees with the work by Rao and Prototypeaud (1975), which indicates that the controlling mechanism in this diffusion is the iron ions migration towards the product layer surface. The equations that describe this oxidation step are:

\[ \frac{t}{\tau_{\text{dif}}} = 3 \left[ 1 - (1 - X_0')^{3/2} + \frac{1 - Z + (1 - Z)(1 - X_0')^{3/2}}{Z - 1} \right] \]

\[ \tau_{\text{dif}} = \frac{\rho_m r_p^2}{6 \bar{b} D_v} \] (46)

The reaction order, \( n \), with respect to each reacting gas was obtained from the calculus of \( X_{\text{chr}} \) by fitting the experimental curves conversion-time to the model equations for different gas concentrations.

From experiments done at different temperatures, values for the chemical reaction kinetic constant, \( k_s \), as a function of the temperature were obtained. The temperature dependence of the kinetic constant was assumed to be Arrhenius type. As example, Figure 44 shows plots of the effect of H\(_2\) concentration on the conversion-time curves, and Figure 45 represents plots of the effect of O\(_2\), together with the corresponding model predictions of conversion-time for calcined and activated ilmenite.

![Figure 44](image)

Figure 44. Effect of H\(_2\) concentration on the reduction reaction for (a) calcined and (b) activated ilmenite. \( T=900 \) °C. H\(_2\) concentration: • 5 vol.%; □ 15 vol.%; ◇ 30 vol.%; ▲ 50 vol.%. 20 vol.% H\(_2\)O; N\(_2\) to balance. Continuous line: model predictions.
Figure 45. Effect of O$_2$ concentration on the oxidation reaction for (a) calcined and (b) activated ilmenite. T=900 °C. O$_2$ concentration: ◊ 5 vol.%; ▲ 10 vol.%; ◆ 15 vol.%; ◇ 21 vol.%; N$_2$ to balance. Continuous line: model predictions.

It can be seen that the reaction models proposed predicted adequately the experimental results in all range of operating conditions studied for both calcined and activated ilmenite. Table 11 gathers the obtained kinetic parameters for ilmenite reduction with H$_2$, CO and CH$_4$, and oxidation with O$_2$ for both calcined and activated ilmenite. More details about the parameter calculations and kinetic model can be found in Paper II.

Table 11. Kinetic parameters for ilmenite reduction with H$_2$, CO and CH$_4$, and oxidation with air.

<table>
<thead>
<tr>
<th></th>
<th>Calcined</th>
<th>Activated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>CO</td>
</tr>
<tr>
<td>$\rho_m$ (mol/m$^3$)</td>
<td>13590</td>
<td>13590</td>
</tr>
<tr>
<td>$b$ (m)</td>
<td>0.5·10$^{-6}$</td>
<td>0.5·10$^{-6}$</td>
</tr>
<tr>
<td>$k_{o2}$ (mol$^{1-n}$ m$^{3n-2}$ s$^{-1}$)</td>
<td>5.1·10$^{-1}$</td>
<td>2.1·10$^{-1}$</td>
</tr>
<tr>
<td>$E_{cb}$ (kJ/mol)</td>
<td>109</td>
<td>113</td>
</tr>
<tr>
<td>$D_{o2}$ (mol m$^{-2}$ s$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{dif}$ (kJ/mol)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Analysis of the reactivity from the kinetic data

To analyze the reactivity of ilmenite and to compare it with other oxygen-carriers, a preliminary estimation of the solids inventory needed for the gaseous fuels H₂, CO and CH₄ is calculated. To do that, the reaction kinetics of ilmenite were introduced in the model proposed by Abad et al. (2007a). The simplified model considers perfect mixing of solids, no restriction for the gas-solid contact and the solid reaction following the shrinking core model. This model considers the effect of residence time distribution of ilmenite on its reactivity. The kinetic parameters can be introduced in this model describing the reactors of a CLC system with gaseous fuels.

Minimum solid inventories showed in Table 12 can be compared to the solids inventory calculated for several synthetic oxygen-carriers (Abad et al., 2007a; Zafar et al., 2007a,b). For comparison purposes with other oxygen-carriers, only the minimum solids inventory for activated particles is considered, as activation is expected to occur quickly in the CLC system. The solids inventories calculated for the air-reactor (30-47 kg/MWth) are in the range of those calculated for other Ni-, Cu-, Mn- and Fe-based oxygen-carriers, which were in the range 10-60 kg/MWth. On the contrary, the calculated solids inventories in the fuel-reactor for ilmenite were usually higher than those obtained for other oxygen-carriers. For ilmenite the solids inventories were in the range 42-66 kg/MWth for H₂, 105-189 kg/MWth for CO and 167-461 kg/MWth for CH₄. For a highly reactive synthetic Fe-based oxygen-carrier the solids inventory obtained for H₂ and CO were 12 kg/MWth and 29 kg/MWth, respectively; whereas the solids inventory for CH₄ was 950 kg/MWth. Nevertheless, lower solids inventories were calculated for methane using other oxygen-carriers, e.g. in the range 10-20 kg/MWth for Ni-based oxygen-carriers, 52 kg/MWth for a Cu-based oxygen-carrier or 85 kg/MWth for a Mn-based oxygen-carrier (Abad et al., 2007a; Zafar et al., 2007a,b). Note that these values were obtained without considering bubble-emulsion resistance, but are useful for comparison purposes.
Table 12. Minimum solids inventory data for calcined and activated ilmenite (kg of solids per MWth of fuel), calculated for $\Delta X = 0.5$.

<table>
<thead>
<tr>
<th></th>
<th>Calcined</th>
<th></th>
<th>Activated</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>CO</td>
<td>CH$_4$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>$\bar{C}_g$ (% of fuel)</td>
<td>14.5</td>
<td>14.5</td>
<td>5.3</td>
<td>14.5</td>
</tr>
<tr>
<td>T</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900ºC</td>
<td>299</td>
<td>955</td>
<td>4481</td>
<td>66</td>
</tr>
<tr>
<td>950ºC</td>
<td>197</td>
<td>619</td>
<td>2337</td>
<td>52</td>
</tr>
<tr>
<td>1000ºC</td>
<td>135</td>
<td>416</td>
<td>1285</td>
<td>42</td>
</tr>
</tbody>
</table>

|                     | H$_2$    | CO      | CH$_4$    | H$_2$   | CO      | CH$_4$ |
|                     |          |         |           |         |         |        |
| Air-Reactor         |          |         |           |         |         |        |
| 900ºC               | 75       | 64      | 90        | 39      | 33      | 47     |
| 950ºC               | 74       | 63      | 89        | 37      | 31      | 44     |
| 1000ºC              | 74       | 63      | 89        | 35      | 30      | 42     |

The use of ilmenite for the combustion of methane is not adequate, but the use of ilmenite for syngas combustion could be interesting. Thus, the first approach for solid inventories needed for ilmenite take acceptable values for the main products of coal devolatilization and gasification, in the same range as the values observed for synthetic oxygen-carriers with proven suitability for CLC (Zafar et al., 2007a). Thus, the use of ilmenite for coal it is highly recommended because ilmenite is harmless for the environment and a considerably cheaper material than a synthetic material.

4.3 Theoretical approach on the CLC performance with solid fuels

The objective of this section, which constitutes Paper VIII, was to optimize the operating conditions for direct CLC with solid fuels using ilmenite as oxygen-carrier. Two of the key parameters in the design of a CLC system are the solids circulation rate and the solids inventory and they are therefore considered below. This section approaches the design of an iG-CLC system using HV bituminous Colombian coal El Cerrejón as fuel.
4.3.1 Calculation of the solids circulation rate

Figure 46 shows the solids circulation rate calculated as a function of the solid conversion variation between air- and fuel-reactors, $\Delta X$, considering “El Cerrejón” coal as fuel. A solids circulation rate value of $m_{oc} = 16$ kg/s per MW$_{th}$ is considered to be the maximum circulation rate feasible in a CLC unit without increased costs according to commercial experience on CFB systems (Abad et al., 2007c). That is, the solids circulation rate that can be used with el Cerrejón coal is between 2.04 and 16 kg/s per MW$_{th}$. The result is that $\Delta X$ can be within the range 0.13-1.

![Figure 46. Solids circulation rate as a function of the solid conversion variation between air- and fuel-reactors, $\Delta X$. Fuel: “El Cerrejón” coal.](image)

4.3.2 Calculation of the solids inventory in the fuel-reactor

In this section a theoretical model for the fuel-reactor has been developed based on a simple reacting scheme for the flow patterns of gas and solids, but describing the complex chemical processes happening in the fuel-reactor. The gasification kinetics of El Cerrejón coal for both H$_2$O and CO$_2$ as gasification agents and the kinetics of the reduction reaction of ilmenite with H$_2$, CO and CH$_4$ are incorporated to the model. The model also includes the possibility of using a carbon separation system to recirculate unreacted char particles that exit from the fuel-reactor. The simulated results have been first compared to experimental results from tests performed in the ICB-CSIC-s1 unit. Simulations were done afterwards to study the effect of the main operating variables of the fuel-reactor (e.g.
temperature, solids inventory, efficiency of the carbon separation system, oxygen-carrier to fuel ratio, or flow and type of gasification agent) on the combustion and carbon capture efficiencies. The effect of the main operating variables in the iG-CLC process can be analyzed in a simpler way than using a detailed model.

**Differential mass balances in the fuel-reactor**

The differential mass balances are defined according to Eqs. (47)-(49), which are the scheme of ilmenite reduction reactions happening simultaneously in the fuel-reactor:

\[
\begin{align*}
\text{M}_x\text{O}_y + \text{CH}_4 & \rightarrow \text{M}_x\text{O}_{y-1} + \text{CO} + 2 \text{H}_2 \quad (47) \\
\text{M}_x\text{O}_y + \text{H}_2 & \rightarrow \text{M}_x\text{O}_{y-1} + \text{H}_2\text{O} \quad (48) \\
\text{M}_x\text{O}_y + \text{CO} & \rightarrow \text{M}_x\text{O}_{y-1} + \text{CO}_2 \quad (49)
\end{align*}
\]

The pattern of gas and solids here assumed were based on the previous results obtained in the ICB-CSIC-s1 unit fuelled with the bituminous Colombian coal “El Cerrejón”. In these experiments, it was found that unconverted CH₄, CO and H₂ from the fuel-reactor were mainly coming from unconverted volatile matter. However, neither tars nor other hydrocarbons than CH₄ were found. Also, gasification products were highly converted to CO₂ and H₂O. A bad contact between volatile matter and oxygen-carrier particles was proposed as the main reason for incomplete combustion.

Based on these results, a model of the system was developed to predict and optimize the combustion and carbon capture efficiencies of the CLC process as a function of various operational parameters. The oxygen-carrier bed in the fuel-reactor was considered to be divided into two separated zones: one zone is in contact with the volatiles, with reducing species CO, H₂ and CH₄; and the other zone reacts with the generated gasification products, CO and H₂. Both gaseous flows are assumed to be independent and in plug flow. The gas flow inside the reactor is simplified and the bubble-emulsion two-phase theory is not considered. In order to solve the whole system, the reactor was considered to be divided into compartments with differential bed mass. Figure 47 shows a scheme of this assumed flow pattern. The gasification products generated in the dense bed have good
contact with the oxygen-carrier particles. The volatiles are released in a plume and they have poorer contact with the oxygen-carrier. To take this into account, the parameter $\chi_{OC,v}$ is introduced as the fraction of the oxygen-carrier bed that is in contact with the volatiles. It is considered that there is perfect mixing of the solids and no constrictions for the gas-solid reactions. This model assumes that there is no gas exchange between the flow of gasification products in the dense bed and volatile plume. Also, the model assumes that the only reducing species in the dense bed are H$_2$ and CO, whereas CH$_4$ also appears in the flow coming from the volatile plume.

Figure 47. Mass flows changes of the gases involved in the process –products of gasification and devolatilization- for a fuel-reactor element of differential mass, $dm_{OC}$.

The changes of the mass flow in a differential mass of the reactor have been considered in the model. The reaction of the oxygen-carrier with the volatile matter species and char gasification products is considered separately, to take into account that they are generated in a different location and have different contact with the oxygen-carrier. Therefore, the differential mass balances for the H$_2$ and CO generated from char gasification are expressed by Eq. (50) and (51), respectively. For the volatile matter released reducing species, i.e., CH$_4$, H$_2$ and CO, the mass balances are Eqs. (52-54). These equations show the variation of the molar flows of H$_2$, CO and CH$_4$ - $F_{H2}$, $F_{CO}$ and $F_{CH4}$, respectively, for the gasification and devolatilization products in a differential bed with mass inventory $dm_{OC}$. Neither sulfur nor nitrogen present in the fuel were considered in this simple model.

Mass balances in dense bed:

$$\frac{\partial F_{H_2}}{\partial m_{OC}} + \left[ \frac{1}{2d \cdot M_D} \left( -r_{lim,H_2} \right) - f_c \left( -r_c \right)_{H_2O} \frac{1}{M_C} \right] = 0$$

(50)
\[
\frac{\partial F_{CO}}{\partial m_{OC}} + \left[ \frac{1}{2d \cdot M O} (-r_{\text{ilm,CO}}) - \frac{f_C}{1-f_C} (-r_C)_{H_2O} \frac{1}{M_C} - 2 \frac{f_C}{1-f_C} (-r_C)_{CO_2} \frac{1}{M_C} \right] = 0
\]  
(51)

Mass balances in volatile plume:

\[
\frac{\partial F_{CH_4}}{\partial m_{OC}} + \frac{1}{2d \cdot M O} (-r_{\text{ilm,CH}_4}) \chi_{OC,v} = 0
\]  
(52)

\[
\frac{\partial F_{H_2}}{\partial m_{OC}} + \frac{1}{2d \cdot M O} (-r_{\text{ilm,H}_2}) \chi_{OC,v} + 2 \frac{\partial F_{CH_4}}{\partial m_{OC}} = 0
\]  
(53)

\[
\frac{\partial F_{CO}}{\partial m_{OC}} - \frac{1}{2d \cdot M O} (-r_{\text{ilm,CO}}) \chi_{OC,v} + \frac{\partial F_{CH_4}}{\partial m_{OC}} = 0
\]  
(54)

\((-r_C)_{H_2O} \) and \((-r_C)_{CO_2} \) are the char gasification rates with \(\text{H}_2\text{O} \) and \(\text{CO}_2 \), respectively. \(f_C \) is the carbon fraction in the fuel-reactor bed. Char is supposed to have constant concentration throughout the reactor and it is uniformly distributed in the bed in perfect mixing. The gasification takes place simultaneously with the reaction of the released volatile matter and gasification products with ilmenite. \((-r_{\text{ilm,H}_2}) \), \((-r_{\text{ilm,CO}}) \) and \((-r_{\text{ilm,CH}_4}) \) are the reaction rates of ilmenite with \(\text{H}_2 \), \(\text{CO} \) and \(\text{CH}_4 \), respectively.

To solve the mathematical model it was assumed that the coal devolatilization takes place instantaneously at the coal feeding level. The composition of the released volatiles from “El Cerrejón” coal was obtained experimentally by devolatilization in a fluidized bed using silica sand as bed material and \(\text{H}_2\text{O} \) or \(\text{CO}_2 \) as fluidizing gas, see Table 13. To do so, additional char gasification experiments were done in sand to subtract the corresponding \(\text{CO} \), \(\text{H}_2 \), \(\text{CO}_2 \) and \(\text{H}_2\text{O} \) quantities that come from this process.
Table 13. Mass (g) of the different gaseous species generated from the release of the volatile matter of 100 g of El Cerrejón coal after CH₄ reforming, for different H₂O-CO₂ mixtures as gasification agent.

<table>
<thead>
<tr>
<th>Gasification agent</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂O</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% H₂O</td>
<td>5.7</td>
<td>42.8</td>
<td>7.1</td>
<td>-27.8</td>
<td>5.5</td>
</tr>
<tr>
<td>50% H₂O + 50% CO₂</td>
<td>23.1</td>
<td>12.7</td>
<td>8.8</td>
<td>-14.7</td>
<td>3.4</td>
</tr>
<tr>
<td>100% CO₂</td>
<td>46.5</td>
<td>-29.1</td>
<td>9.9</td>
<td>4.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The difference between the released devolatilized species for different H₂O:CO₂ composition is because there is some CH₄ reforming taking place with. In some cases of the compositions given the values of H₂O or CO₂ have negative values, because some H₂O and CO₂ was taken from the gasification agent flow for the partial CH₄ reforming.

The implementation of a carbon separation system to obtain high carbon capture was also assessed. The use of a highly efficient carbon separation system with high efficiency, $\eta_{CS}$, ensures high extent of gasification, and thereby high carbon capture, by increasing char residence time in the fuel-reactor. $\eta_{CS}$ is defined as the fraction of carbon in char that is separated and recirculated back to the fuel-reactor with respect to the carbon in the char that exits the fuel-reactor together the flow of oxygen-carrier particles. Figure 48 represents a scheme of the carbon flows involved in the fuel-reactor and carbon separation system.

![Figure 48. Scheme of carbon flows in the fuel-reactor and carbon separation system.](image)

(F₄,hp) is the carbon flow of char in the coal feed; (F₄,char)out is the carbon flow of ungasified char that exits the fuel-reactor; (F₄,hp) is the flow of carbon contained in the
products of char gasification; and \((F_{c,\text{vol}})_{\text{out}}\) is the flow of carbon in volatiles. \((F_{c,\text{char}})_{\text{out}}\) depends on the solids recirculation rate, \(\dot{m}_{\text{DC}}\), which is the oxygen-carrier circulation rate. Thus, the carbon capture depends on the solids circulation rate.

The global balance to the whole reactor is done by integrating the differential equations over the total bed mass inventory. To solve the system of simultaneous differential equations, the Runge–Kutta–Merson method was used. To find the solution of the system, a value of ilmenite conversion variation \(\Delta X\) and of carbon fraction in the bed \(f_c\) are initially assumed and the system is solved in two interconnected loops. In the internal loop, with the assumed value of \(f_c\) the system of differential equations is integrated and with these data the outlet gaseous flows are obtained, as well as the carbon flow that returns from the carbon separation system and that leaves the fuel-reactor. With the last carbon flow \(f_c\) is recalculated, until the convergence is reached after successive approaches. Once the carbon balance has converged, the oxygen balance that would give the value of \(\Delta X\) for the fixed ilmenite circulation rate must be accomplished. With this new value the calculations are repeated until the simultaneous convergence for both \(f_c\) and \(\Delta X\) is reached.

Initially, a value of the oxygen-carrier conversion variation \(\Delta X\) is assumed. Thus, considering an initial value of carbon fraction in the fuel-reactor bed \(f_c\), the values of the flows of \(H_2\), \(CO\), \(CH_4\), \(CO_2\) and \(H_2O\) outgoing the reactor are obtained. To solve the whole equation system, the flow of carbon that exits the fuel-reactor must fulfill the carbon mass balance in the system, as shown in Figure 48. This carbon flow depends on \(f_c\) and the total outlet flow of the fuel-reactor is determined by the ilmenite circulation rate. Iterations on \(f_c\) must be done until the carbon mass balance is fulfilled. From the final outlet gaseous flows a new value of \(\Delta X\) is obtained. And the iterative method must be used again until both parameters converged to obtain the solution to the mathematical model.

The model was developed and applied to the natural mineral ilmenite as oxygen-carrier and El Cerrejón bituminous Colombian coal as fuel. More details about the model are found in Paper VIII. Predictions of the coal conversion in the ICB-CSIC-s1 unit used in the experimental work were carried out with the model.
The direct application of the model predicted the experimental values of char conversion and carbon capture, see Figure 49.a), but it predicted full combustion. The fraction of oxygen-carrier in contact with the volatile matter $\chi_{OC,v}$ that predicts the combustion efficiencies obtained experimentally at different temperatures is 0.53%, see Figure 49.b). $\chi_{OC,v}=0.53\%$ is a rather low value, that is, the volatile matter released in the plume in the experimental facility had indeed bad contact with the oxygen-carrier.

Figure 49. Experimental values obtained for a) Carbon capture and b) Combustion efficiency compared to the theoretical with the model simulated values at different temperatures ($T_{FR}: 880-925^\circ C$). Inventory: 3100 kg/MWth. $\eta_{CS}=0$.

As an example of the model predictions, Figure 50 represents the evolution of CH₄, H₂, CO, CO₂ and H₂O molar flows within the fuel-reactor bed, expressed as mass fraction of the bed, $m_{OC}/m_{OC,tot}$, for a solids inventory of 3100 kg/MWth, as used in the experimental work. Figure 50.a) shows the flows in the dense bed, that is, derived from the gasification; Figure 50.b) represents the evolution of the volatile matter species released in the plume; and the total sum of the flows of both phases is shown in Figure 50.c).
Figure 50. Evolution of the a) in the dense bed b) in the plume and c) total CH₄, H₂, CO, CO₂ and H₂O molar flows within the fuel-reactor bed, for a solids inventory of 3100 kg/MWth. TFR=900 °C. H₂O/C=0.7. φ=2. ηCS=0. Xo,in=0. χOC,v =0.53%.

In the dense bed all the gasification products, i.e., H₂ and CO, are fully oxidized by the oxygen-carrier and the dense bed is only composed by increasing CO₂ from char oxidation and the H₂O as gasification agent. In the plume both CH₄ and H₂ decrease when the reactor mass increases. CH₄ comes only as part of the released volatile matter species and is gradually consumed by its oxidation with the oxygen-carrier. H₂ and CO come from volatile matter release and as intermediates of CH₄ oxidation. H₂ disappears along the bed mass as it is quickly oxidized by ilmenite, while the CO profile has a smooth maximum because there is competition between the CO generation in the CH₄ conversion and its slower reaction with ilmenite.

After seeing that there is a good agreement between the values predicted by the model and the experimental results with a determined χOC,v, simulation and process optimization can be performed. The effect of the main variables in CLC with solid fuels was analyzed, taking the solids inventory as independent variable.

**Influence of the fuel-reactor temperature, solids inventory and implementation of a carbon separation system**

The following calculations were made on the basis of 1 MWth fuel power (see coal analysis in Table 2). Simulations showed that ηCC, Xchar and ηcomb FR increase with increasing solids
inventory in the fuel-reactor for all temperatures simulated (see Figure 51). For all the temperatures simulated and up to a solids inventory of 2000 kg/MWth all efficiencies increased substantially. For higher inventories the beneficial effect was not so intense. Gasification and combustion reactions are promoted with the temperature, and thus Xchar, \( \eta_{CC} \) and \( \eta_{comb \; FR} \), increased at higher temperatures.

If the inventory is doubled from 1000 to 2000 kg/MWth, \( \eta_{comb \; FR} \) increases from 73.1% to 89.0%. If the inventory is again doubled to 4000 kg/MWth, the increase is less substantial, \( \eta_{comb \; FR} \) is 97.2%, so it is not worth it to increase so much the solids inventory, as well as the increased pressure drop and operational cost, size and investment of such big facility. At 950°C as reference temperature, and with an inventory of 2000 kg/MWth, values obtained for char conversion and carbon capture efficiency were \( X_{char} = 0.334 \) and \( \eta_{CC} = 0.525 \).

The first simulations were done considering that there was no carbon separation system. In order to get higher extent of gasification, it was proposed to implement one. Figure 51 shows the simulated char conversion, carbon capture and combustion efficiencies with a wide range of oxygen-carrier inventories for a carbon separation system of efficiency 0%, 80%, 90% and 100%. Higher \( \eta_{CS} \) leads to higher \( \eta_{CC} \), which is essential in this process. Note the important increase in \( \eta_{CC} \) and \( X_{char} \) when using the carbon separation system. This points out the importance of implementing a carbon separation system in iG-CLC.

![Figure 51. Variation of a) carbon capture, b) char conversion and c) combustion efficiency with increasing solids inventory for \( \eta_{CS} = 0 \), 80%, 90% and 100%. \( T_{FR} = 950°C \). \( H_2O/C = 0.7 \). \( \phi = 2 \). \( X_{o,in} = 0 \). \( \chi_{OC,v} = 0.53% \).](image)
Considering an iG-CLC system with a carbon separation system of $\eta_{CS}=90\%$, the effect of the temperature and inventory is assessed. Figure 52.a) and b) represents the carbon capture and char conversion in the process, where it can be seen that to get high performance, an inventory between 1000 and 2000 kg/MW$_{th}$ seem to be necessary and reasonable. To get high gasification and oxidation rates, it is necessary to work at high temperatures. As an example, with an inventory of 2000 kg/MW$_{th}$ and $\eta_{CS}=90\%$, predictions of $\eta_{CC}$ of 79.3% at 900ºC and 90.7% at 1000ºC were obtained.

The simulated performance of the process regarding the oxidation of volatiles and gasification products is shown in Figure 52.c), where it can be seen that the fuel-reactor combustion efficiency grows with the temperature because of the increase in the oxidation rate of ilmenite. Above 900ºC, the minimum solids inventory needed to obtain $\eta_{comb\ FR}$ above 85% is 1000 kg/MW$_{th}$. As an example, with a solids inventory of 2000 kg/MW$_{th}$, the simulated resulting $\eta_{comb\ FR}$ was 86.0% at 900ºC and 94.2% at 1000ºC. For an optimum performance of the iG-CLC system, it would be best to have a carbon separation system with high $\eta_{CS}$ and to operate at temperatures above 950ºC. However, simulations showed that although the temperature of operation was high, with high oxygen-carrier inventory and high $\eta_{CS}$, there would be still some unburnt volatile matter and a subsequent oxygen polishing step would be necessary to fully oxidize the unburnt gases in the outlet stream from the fuel-reactor.

Figure 52. Variation of a) carbon capture and b) char conversion with increasing solids inventory for several fuel-reactor temperatures. ——900ºC, ——-950ºC and ——-1000ºC. H$_2$O/C=0.7. $\phi=2$. $\eta_{CS}=90\%$. $X_{o,in}=0$. $\chi_{OC,v}=0.53\%$. 
Influence of other operational parameters

Although the main parameters that turned out to determine the efficiency of the iG-CLC process are the temperature of operation, the solids inventory and the efficiency of the carbon separation system, other operational parameters also influence on the efficiency of the process, although to a lower extent.

The system was evaluated for variation the steam to fixed carbon ratio, H₂O/C, considering steam as gasification agent. It turned out that the H₂O/C ratio has no influence on the combustion efficiency and little influence on the gasification step. Although a H₂O/C ratio of 0.4 could be insufficient to ensure high gasification extent, it would be reasonable to work with a H₂O/C ratio of 0.7-1, since there is no major benefit on working with higher H₂O/C ratios.

The influence of the gasification agent type was simulated with various H₂O:CO₂ mixtures. The gasification agent type has minor effect on the combustion efficiency. When gasifying with higher fraction of CO₂ only CO is produced, whereas when gasifying with H₂O, H₂ is also generated. But although ilmenite reacts faster with H₂ than with CO, the reaction rate of ilmenite is fast if there is enough inventory and \( \eta_{\text{comb FR}} \) has no substantial change. The carbon capture increase when there is higher steam fraction in the gasification agent, being this less noticeable for higher \( \eta_{\text{CS}} \). This is because for this fuel the gasification rate with steam is faster than with CO₂.

The carbon capture efficiency decreases for higher oxygen-carrier to fuel ratio. High oxygen-carrier to fuel ratio means high solids recirculation rate and thereby low residence time, which entails a decrease in the char conversion in the bed. The lower residence time leads to lower extent of gasification and thereby lower \( \eta_{\text{CC}} \).

The effect of the reactivity of the oxygen-carrier was also evaluated. The simulations showed that \( \eta_{\text{comb FR}} \) increases with higher oxygen-carrier reaction rate, but the influence in \( X_{\text{char}} \) and \( \eta_{\text{CC}} \) is negligible. Thus, the use of an oxygen-carrier with high reactivity is
important to reach high $\eta_{\text{comb FR}}$, but is not the key factor in iG-CLC to get high $\eta_{\text{CC}}$. The major limitation to reach high $\eta_{\text{comb FR}}$ was the poor contact of the volatiles with the dense bed, and not the reactivity of the oxygen-carrier.

The fraction of oxygen-carrier in contact with the volatile matter, $\chi_{\text{OC,v}}$, resulted to be quite poor. Some design solutions can be applied in order to increase $\chi_{\text{OC,v}}$. Figure 53 shows that there is a big effect of $\chi_{\text{OC,v}}$ on the combustion efficiency and $\eta_{\text{comb FR}}$ increases from 80.8% to 99% if $\chi_{\text{OC,v}}$ increased from 0.53% to 3% with an inventory of 1000 kg/MW$_{\text{th}}$. The char conversion and carbon capture are not affected.

![Figure 53. Combustion efficiency variation with increasing $\chi_{\text{OC,v}}$ for: —— 200 kg/MW$_{\text{th}}$, —— 500 kg/MW$_{\text{th}}$ and —— 1000 kg/MW$_{\text{th}}$. T$_{\text{FR}}=950^\circ$C. H$_2$O/C=0.7. $\phi=2$. $\eta_{\text{CS}}=90\%$. $X_{\text{S,in}}=0.$](image)

A second option to fully burn the volatile matter is to implement a second step in the fuel-reactor (FR2), whose fuel would be the outlet gaseous stream of the solid fuelled fuel-reactor (FR1). It is also an alternative to the oxygen polishing step. As the fuel is gaseous, this second reactor would not be limited by the gasification step and the contact efficiency would be much higher, since the fuel would be introduced at the bottom of the reactor and not released in a plume. The simulated values obtained for the second step fuel-reactor FR2 are about 44 kg/MW$_{\text{th}}$ to fully oxidize the fuel for FR1 1000-2000 kg/MW$_{\text{th}}$, see Figure 54.
Figure 54. Minimum ilmenite inventory in the second fuel-reactor to completely oxidize the fuel for different inventories in the first fuel-reactor. $T_{FR}=950^\circ C$. Conditions in the first fuel-reactor: $H_2O/C=0.7$. $\phi=2$, $\eta_{CS}=90\%$. $X_{CS}=0$. $\chi_{OC,v}=0.53\%$.

This second step could be made by using a two-step reactor if the fuel-reactor works with bubbling bed conditions. However, if the reactor is a circulating bed, it would be necessary to install a second reactor or it would be also feasible to improve the solid-gas contact by means of internals in the diluted region.

The simulations done with the simplified model for the iG-CLC process showed that an optimized CLC system for solid fuels with ilmenite as oxygen-carrier should have a carbon separation system with high efficiency above 90\%, work at a high fuel-reactor temperature -desirably above 950$^\circ C$- and would need 1000-2000 kg/MW$_{th}$ of inventory. These parameters would lead to high carbon captures above 90\%. The contact efficiency of the volatile matter with the oxygen-carrier should be increased with some design solutions. The implementation of a second fuel-reactor whose inventory was calculated to be around 44 kg/MW$_{th}$ is proposed as a very promising option to fully burn the volatile matter and avoid an extra oxygen polishing step.
5 Conclusions
The feasibility and performance of the Chemical-Looping Combustion technology for solid fuels was studied. The natural mineral ilmenite was used as oxygen-carrier regarding its properties, low cost and because it is environmentally friendly. The conditions and key parameters that improve the process efficiency were evaluated, in order to get a competitive combustion technology with low cost CO₂ capture. This was studied by doing tests in a thermogravimetric analyzer (TGA), a batch fluidized bed reactor for gaseous fuels, a batch fluidized bed reactor for solid fuels and a continuous CLC unit for solid fuels, the ICB-CSIC-s1, all these devices are placed at the Instituto de Carboquímica (ICB-CSIC) in Zaragoza (Spain). Tests in a 10 kWth continuous CLC unit for solid fuels at Chalmers University of Technology in Göteborg (Sweden) were also done.

Focus was made on analyzing the behavior and suitability of ilmenite as oxygen-carrier in CLC with solid fuels by in-situ gasification CLC (iG-CLC). Ilmenite was seen to undergo an activation process, since it increases its reactivity with the number of redox cycles. After several cycles, reduction and oxidation rate of ilmenite reaches a maximum value which is maintained after many hours of operation. The higher is the conversion variation reached in the redox cycles, the faster is the activation. Previous calcination of ilmenite has a positive effect on the activation process. After activation, the reactivity for H₂ and CO rises around 5 times, while for CH₄ this increase is about 15 times. The activated ilmenite exhibited high reactivity in both reduction and oxidation reactions. Reaction with H₂ is faster than with CO and CH₄. Times for complete conversion at 950 °C lower than 120 s using 15% of H₂, CO or CH₄, and 30 s using 21% of O₂ in TGA.

Structural changes on ilmenite particles after activation were observed. The most remarkable is the porosity increase in the particles: for calcined particles it was 1.2% and it increased up to 38% after 100 cycles in batch fluidized bed with a conversion of 65%. It was observed the appearance of cracks and an external shell in the particle, which is Fe enriched. As activation proceeds the reactivity increases, but the oxygen transport capacity of ilmenite decreases due to the physical segregation of Fe₂TiO₅ in the oxidized ilmenite and the appearance of an external shell which is enriched in free Fe₂O₃. The higher is the conversion variation reached in the redox cycles, the faster is the segregation of Fe₂TiO₅.
and the decrease in the oxygen transport capacity. The initial oxygen transport capacity value is 4.0% and it decreased until 2.1% after 100 redox cycles in batch fluidized bed with a conversion of 65%. However, in continuous testing with an average conversion of 30%, the oxygen transport capacity after almost 100 hours of operation only decreased to 3.9%.

In comparison to other oxygen-carriers and in particular to iron-based carriers, the oxygen transport capacity and reactivity showed for ilmenite have high enough values to transfer the required oxygen from air to fuel in a CLC system. As for its fluidization properties, low attrition values were found for ilmenite during fluidized-bed operation, and no defluidization was seen for typical CLC operating conditions.

98 hours of continuous operation with coal feed and 122 hours of fluidization were made in the ICB-CSIC-s1 CLC facility. The operation performance was assessed in these tests using different solid fuels ranging from lignite to anthracite and evaluating the effect of operational parameters on carbon capture and combustion efficiency.

In all cases, unburnt compounds were found in the gas stream from the fuel-reactor. The outgoing unburnt gases in the fuel-reactor were measured when using coal as fuel, that is, CH₄, CO and H₂, which came from volatile matter that had not been fully oxidized. Gasification products were fully oxidized.

The combustion efficiency in the fuel-reactor is higher for higher temperature, higher solids inventory and for solid fuels with lower volatile content and with faster gasification rate. The combustion efficiency was not limited by the reaction rate of ilmenite, but it is limited by the low conversion of volatile matter. The combustion efficiency of the volatiles seems to depend on the composition of the released volatiles of each fuel. The average of combustion efficiency of volatiles was around 52% for lignite, 61% for HV bituminous Colombian coal, 58% for MV bituminous South African coal and 42% for anthracite. Combustion efficiencies had values higher than 75% at 910°C with an average inventory of 1200 kg/MWth for all the fuels tested, and for bituminous Colombian coal at 950°C the combustion efficiency was 95% with 3100 kg/MWth inventory. Thus, the oxygen polishing need is quite low.
The carbon capture efficiency was increased by increasing the char gasification rate. A relevant growth in the gasification rate was seen when ilmenite was used compared to an inert bed material, because ilmenite reacts with H\textsubscript{2} and CO which are gasification inhibitors. The temperature is one of the most influencing parameters. At higher fuel-reactor temperatures, gasification is faster and promoted for all types of solid fuels. The carbon capture is higher for the solid fuels with faster char gasification rates and also when the volatile content in the fuel is higher. High values of carbon capture can be obtained, but it is essential to have a highly efficient carbon separation system that reintroduced unconverted char particles back to the fuel-reactor, especially for solid fuels with slow gasification rates such as anthracites. Carbon capture as high as 93\% at 920ºC was obtained even without a carbon separation system with lignite, which has fast char gasification rate. In addition, lower recirculation rates and thereby lower oxygen-carrier to fuel ratios led to enhanced CO\textsubscript{2} capture efficiencies. That was because the increase in char residence time led to an increase in the char conversion.

Several CO\textsubscript{2}:H\textsubscript{2}O mixtures as gasification agent were tested. Depending on the type of fuel, some of the steam as gasification agent can be replaced by CO\textsubscript{2} recirculated from the outlet fuel-reactor flow, getting similar system performance and thereby saving energy derived from steam generation. In case of lignite there is no change in the process performance when gasifying with CO\textsubscript{2} and for bituminous coals the use of some CO\textsubscript{2} would be admissible. On the other hand, for anthracite the lower gasification rate of char with CO\textsubscript{2} leads to a substantial drop in the performance.

Continuous tests carried out in a 10 kW\textsubscript{th} CLC facility fuelled with petcoke found that the addition of some limestone to a bed of ilmenite led to some improvement in the process performance. This beneficial effect could be explained by lime catalyzing the water-gas shift equilibrium, and subsequent faster reaction of H\textsubscript{2} with ilmenite.

With all the experimental information gathered, a theoretical simplified model for the fuel-reactor was developed, based on the differential mass balances with reaction in the fuel-
reactor. The model includes the kinetics of coal char gasification and reaction of the gasification and devolatilization products with the oxygen-carrier.

The kinetic parameters of calcined and activated particles were obtained by determining the reactivities of the reduction reaction with H₂, CO or CH₄, as main gases of coal devolatilization and gasification, and the oxidation reaction by oxygen were determined by thermogravimetric analysis. The grain model with uniform reaction in the particle and reaction in the grains following a changing grain size model with chemical reaction control was used to determine the kinetic parameters. In addition, to predict the behavior of the oxidation of calcined ilmenite, a mixed resistance between chemical reaction and diffusion in the solid product was needed.

The model results were compared and validated with results from tests done in the ICB-CSIC-s1 facility fuelled with bituminous Colombian coal and ilmenite as oxygen-carrier. The limitation to obtain full combustion in the fuel-reactor was assigned to poor contact of the volatile matter with the oxygen-carrier. The fraction of fuel-reactor bed in contact with the volatiles in that facility was calculated to be 0.53%. After that, the most relevant operating conditions for iG-CLC were optimized by analyzing their effect on the performance of the system.

The carbon capture was directly related to the gasification extent, which is promoted by increasing the temperature or the residence time of char in the fuel-reactor, which agrees with experimental results. It is highly beneficial to increase the solids inventory to 1000-2000 kg/MWth, but further increase leads to no relevant improvements. To further enhance the carbon capture, the implementation of a carbon separation system was proposed, whose separation efficiency was found to be a key factor to reach high values of char conversion. With 1000 kg/MWth inventory at 900°C, the simulated carbon capture increased from 45.2% with 0% separation efficiency to 79.8% with 90% separation efficiency.

High oxygen-carrier to fuel ratio means high solids recirculation rate and thereby lower residence time, which leads to a decrease in carbon capture efficiency. The negative
influence of the gasification step as the oxygen-carrier to fuel ratio increases had lower relevance as the efficiency of the carbon separation system increased.

To have a high reactive oxygen-carrier is important to reach high combustion efficiencies, but is not the key factor to get high performance of the process. Lower influence was observed for the gasification agent to fixed carbon ratio or the type of gasification agent (for different H₂O:CO₂ mixtures).

The experience from the smaller to the larger lab-scale experiments and the simulation with a wide range of conditions showed that an optimized CLC system for solid fuels with ilmenite as oxygen-carrier should have a carbon separation system with high efficiency above 90%, work at a high fuel-reactor temperature -desirably above 950°C- and would need 1000-2000 kg/MWth of inventory. The contact efficiency of the volatile matter with the oxygen-carrier should be increased with some design solutions or the implementation of a second fuel-reactor is proposed as an option to fully burn the volatile matter and avoid an extra oxygen polishing step. With these measures and parameter values, carbon capture efficiency higher than 90% and full combustion can be reached with a wide range of solid fuels.
6 Acronyms, notations and symbols
AR air-reactor

$C_{\text{max}}$ maximum CO$_2$ or H$_2$O fraction if there is full combustion (%)

$C_{\text{avg}}$ average concentration of fuel gas in the reactor (%)

CLC Chemical-Looping Combustion

$E_a$ activation energy (kJ/mol)

$F_{\text{exp}}$ experimental

FB fluidized bed

$f_{C}$ carbon concentration from char in the fuel-reactor (kg/kg)

$F_{C_{\text{char eff}}}$ flow of effective carbon char introduced (mol/s)

$(F_{C})_{\text{ep}}$ flow of carbon contained in the products of char gasification (mol/s)

$F_{C_{\text{vol}}}$ carbon flow coming from the volatile matter (mol/s)

$F_{C_{\text{OAR}}}$ CO$_2$ flow in the air-reactor outlet (mol/s)

$F_{C_{\text{OFR, FR, F, H$_2$O, FR, F, H$_2$, FR, F, CH$_4$, FR, F, CO, FR}}$ flows of CO$_2$, H$_2$O, H$_2$, CH$_4$, and CO in the fuel-reactor, respectively (mol/s)

$F_{C_{\text{SS}}}$ flow in the carbon-stripper (mol/s)

$F_{R_{\text{O}}}$ and $F_{R_{\text{TiO$_3$}}}$ mass fractions of Fe$_2$O$_3$ and Fe$_2$TiO$_5$ in ilmenite, respectively (%wt.)

$F_{F_{\text{RILS}}}$ flow in the small fuel-reactor loop-seal (mol/s)

$F_{H_{\text{ILS}}}$ flow in the higher loop-seal (mol/s)

$F_{H_{\text{VEL}}}^\text{fuel}$ flow in the high-velocity section in the fuel-reactor (mol/s)

$F_{S_{\text{ILS}}}$ solids circulation rate (kg/s)

$F_{o_{\text{in}}}$ and $F_{o_{\text{out}}}$ molar flows of the respectively inlet and outlet gas streams (mol/s)

$F_{\text{LOLS}}$ flow in the lower loop-seal (mol/s)

$F_{\text{LOVEL}}$ steam flow in the low-velocity section in the fuel-reactor (mol/s)

FR fuel-reactor

FR1 first fuel-reactor

FR2 second fuel-reactor

H$_2$O/C steam to fixed carbon ratio (mol/mol)

HV high volatile

i.d. internal diameter (m)

iG-CLC in-situ Gasification Chemical-Looping Combustion

$k$ constant value of char gasification rate ($s^{-1}$)

$k_c$ chemical reaction kinetic constant (mol$^{-a}$ m$^{-3n}$ s$^{-1}$)

$k_{1}$ and $k_{2}$ kinetic constants of the char gasification model ($s^{-1}bar^{-1}$)

$k_3$ kinetic constant of the char gasification model ($s^{-1}$)

LHV low heating value (kJ/kg)

$m$ oxygen-carrier instantaneous mass (kg)

$m_{\text{O}_{\text{Y}}, \text{fr}}$ oxidized oxygen-carrier

$m_{\text{O}_{\text{Y}}, \text{r}}$ reduced oxygen-carrier

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

$m_{\text{ilm}, \text{FR}}$ ilmenite mass in the fuel-reactor (kg)

$m_{\text{C}}$ atomic weight of carbon (kg/mol)

$m_{\text{O}}$ atomic weight of oxygen (kg/mol)

$m_{\text{OC}}$ mass inventory of the oxygen-carrier in the fuel-reactor (kg)

$m_{\text{ro}}$ mass of fully oxidized oxygen-carrier (kg)

$m_{r}$ mass of fully reduced oxygen-carrier (kg)

$m_{\text{OC}}$ solids circulation rate (kg/s per MWth)

MV medium volatile

$n$ reaction order

$N_{O_{\text{ilm}}}$ molar amount of oxygen in ilmenite active for CLC process (mol O)

$N_{C_{\text{char}}}$ mol number of carbon fed into the reactor (mol C)

OC oxygen-carrier

$O_{\text{2, dem coal, eff}}$ oxygen demand of the effective coal fed (mol O$_2$/s)
O_{coal,eff} flow of oxygen contained in the effective coal introduced (mol O/s)

$P_{in}$ and $P_{out}$ partial pressures of the gas at the reactor inlet and outlet, respectively

$P_{in}$ mean partial pressure of the gaseous fuel in the reactor

$p_{prod}$ partial pressure of the gaseous products

$p_{react}$ partial pressure of the gaseous reactants

$p_{ref}$ reference partial pressure

$p_{TGA}$ partial pressure of the fuel gas used in the TGA experiments

$r_{C}$ char gasification rate (s$^{-1}$)

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

$r_{g}$ grain radius (m)

$(-r_{ilm, i})$ reaction rate of ilmenite with the gas i (s$^{-1}$)

$(-r_{O})$ rate of oxygen transferred by ilmenite (kg O$_2$/s kg oxygen-carrier)

$R_{0,Fe}_2O_3$ oxygen transport capacity of Fe$_2$O$_3$ when it is reduced to FeO$_3$ (kg/kg)

$R_{0,Fe}_2TiO_5$ oxygen transport capacity of Fe$_2$TiO$_5$ when it is reduced to Fe$_2$TiO$_5$ (kg/kg)

$R_{O,ilm}$ oxygen transport capacity of ilmenite (kg/kg)

$R_{OC}$ transport capacity of an oxygen-carrier (kg/kg)

$t$ time (s)

$T$ temperature ($^\circ$C)

$T_{FR}$ fuel-reactor temperature ($^\circ$C)

TGA thermogravimetric analyzer

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

$\tau_{i, 0}$ is the initial time when the considered reaction begins (s)

WGS Water-Gas Shift

$X_{char}$ char conversion

$X_{char}$ conversion value for which porosity collapses in ilmenite oxidation

$X_o$ conversion for the oxidation reaction

$X_r$ conversion for the reduction reaction

$\Delta X$ oxygen-carrier conversion variation

$y_i$ molar fraction of the gas i

$\varepsilon_{g}$ coefficient of expansion of the gas mixture

$\Omega_{OD}$ oxygen demand

$\phi$ oxygen-carrier to fuel ratio

$\chi_{OC, V}$ fraction of the oxygen-carrier bed that is in contact with the volatile matter

$\gamma_{O}$ oxygen yield

$\eta_c$ combustion efficiency

$\eta_{CC}$ carbon capture efficiency

$\eta_{comb, FR}$ combustion efficiency in the fuel-reactor

$\eta_{CS}$ efficiency of the carbon separation system

$\rho_m$ molar density (mol/m$^3$)

$\omega$ mass based conversion (kg/kg)

$\omega_{red}$ and $\omega_{ox}$ reduced and oxidized mass based conversions of ilmenite reached in the previous period, correspondingly
7 References


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NOAA-ESRL, 2010. National Oceanic and Atmospheric Administration in the US. Average concentration of CO₂ in the atmosphere (Mauna Loa Observatory) for 2010 was posted September 8, 2011


Appendix – Papers