Chemical looping combustion process in fixed-bed reactors using ilmenite as oxygen carrier

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Abstract

A process scheme based on a series of fixed-bed reactors is presented as a possible alternative for carrying out the chemical looping combustion of methane at high pressure with ilmenite as oxygen carrier. The oxygen carrier is stationary and it is alternately exposed to reducing and oxidizing atmospheres by means of the periodic switching of the gas feeds (i.e., methane and air, respectively). Cyclones and filters for the separation of gases and solids are not needed in fixed-beds, which allows a more compact reactor design. Moreover, the operation at high pressure permits the use of highly efficient power cycles. However, more complex heat management strategies and switching valves able to function at very high temperatures are required in these systems. The continuous cyclic operation of a packed-bed chemical looping combustion process is described using a basic reactor model. A sequence of four stages: reduction, steam reforming, oxidation and heat removal ensures the production of a continuous high temperature and high pressure gas stream able to efficiently drive a gas turbine for power generation in combination with a steam cycle. At the same time, a concentrated stream of CO₂ suitable for transport and storage is also produced. The use of suitable recycles of the product gases makes it possible to control the progression of the reaction and the heat exchange fronts, which improves the heat management of the CLC process. The inclusion of steam methane reforming in the process allows the conversion of the ingoing methane to syngas, which enhances the reduction kinetics of the ilmenite and the overall combustion efficiency of the process. A preliminary design for an inlet flow of 10 kg/s of methane (500 MWt) has shown that a minimum of five reactors, 10 m long, with an inner diameter of 6.7 m, would be required to fulfil the overall process assuming cycles of 10 minutes with maximum pressure drops per stage of less than 6 %. These results demonstrate the potential of this novel technology for power generation in combination with CO₂ capture.

Keywords: CO₂ capture, chemical looping combustion, adiabatic fixed-bed, ilmenite, reforming, gas recycle, heat management

1. Introduction

The potential increase in world energy demand over the next few decades and the alarming signs of global warming make it necessary to drastically reduce greenhouse gas emissions from anthropogenic sources [1]. Of the different strategies directed at mitigating CO₂ emissions developed in recent years, Carbon Capture and Storage (CCS) is considered as a valid mid-term solution [2]. CO₂ capture is nowadays the most energy-intensive step in CCS, and as a result, there is growing interest in the development of new CO₂ capture technologies, especially in large-scale power production in order to address the problem of energy penalties and the cost of existing equipment [3].

Of the different technologies proposed in the literature, Chemical Looping Combustion (CLC) represents one of the most promising alternatives for achieving a very high CO₂ capture efficiency with reduced energy penalties [4]. This concept consists in the transfer of oxygen from air to the fuel by using a solid oxygen carrier (typically a metal oxide) and so avoiding any direct contact between the fuel and air. The dilution of the combustion products with nitrogen is avoided and the resulting gas is highly concentrated in CO₂. CLC was firstly conceived in the 1950s [5], but it was not until the 1990s when it was proposed as a CO₂ capture system [6]. Most of the CLC configurations proposed consist of interconnected fluidized-bed reactors, where the oxygen carrier is reduced in the fuel reactor and rapidly transported to the air reactor to be regenerated [7-14]. The small size of the particles used in fluidized beds ensures that there is good contact between the gas and solids, as a result of which the kinetics of the reactions involved in the process are considerably enhanced. Furthermore, rapid mixing of the solids ensures an adequate control of the temperature, which is of fundamental importance in the energy-intense reactions characteristic of CLC processes. The application of the CLC concept in fluidized-beds has been widely studied in recent years in several experimental units at different pilot scales [13-20]. However, the use of interconnected fluidized-beds in CLC has several drawbacks. Operation at high pressure is required to enable a CLC system to be integrated in a combined cycle to increase the energy efficiency [21]. Several works have been published in recent years about CLC performed in fluidized-beds at high pressure [22-24], but this concept still faces critical challenges, such as the difficulty in maintaining a stable circulation of solids between the pressurized reactors, in order to demonstrate its feasibility on a large scale.

Moreover, a high-temperature and high-pressure solids filtering system is required to eliminate the fines resulting from particle attrition, since the presence of particles in the exiting gas from the CLC unit could have a negative effect on the performance of the downstream gas turbine [4].

An alternative for CLC applications at high pressure is the use of configurations based on dynamically operated fixed-bed reactors, where the oxygen carrier remains stationary and the gas feed (fuel gas and air, respectively) is periodically alternated in order to perform the reduction and oxidation stages. As can be seen from Fig. 1, the use of at least two reactors operating in parallel ensures: (1) the production of a continuous high-temperature and high-pressure stream of gas, that is able to drive a gas turbine for power generation, and (2) a concentrated stream of CO₂ suitable for transport and subsequent geological storage. In fixed-bed systems, attrition in the oxygen carriers can be expected to be negligible, and therefore, cyclones and filters downstream are not required. Moreover, the oxygen carrier can be better utilized, because operating in fixed-beds allows a larger degree of conversion between the reduced and oxidized forms. In contrast, heat management strategies for controlling the changes in temperature as the reaction fronts advance through the bed and switching valves able to function with gases at high temperature are required in fixed-bed systems. Although there is a wide experience in industry with pressure and temperature swing adsorption systems, there are very few works that deal with the feasibility of CLC in fixed-bed configurations [25-28]. Early works on chemical looping processes carried out in fixed-beds [25] showed that the oxidation and reduction reactions involved can proceed very fast in narrow reaction fronts. During chemical looping combustion, both reaction and heat exchange fronts are formed and move forward at different velocities depending mainly on the concentration and molecular weights of the reactants and on the stoichiometry of the reactions [26], which is a similar phenomenon to the catalytic oxidation of a fuel gas when it is carried out at different operating temperatures [29]. Several heat management strategies have been proposed in the literature in relation with CLC for controlling the increase in temperature in the reaction fronts, while the product gas is discharged at nearly constant temperature and mass flow rate to protect the gas turbine from thermal and mechanical stress, and also to ensure that the temperature profiles of the solids are sufficiently high to allow fast reaction rates and total gas and solids conversion from the very beginning of the operation.

Fig. 1. Representation of a CLC system with alternating fixed-bed reactors for power generation.

One option is to use an oxygen carrier with a sufficiently low content of active phase that allows the oxidation stage to be accomplished without exceeding the maximum allowable temperature (i. e. up to 1200 °C depending on the oxygen carrier in order to avoid solids deactivation). Under these circumstances, the reaction front proceeds very quickly along the reactor, leaving behind the solid/gas heat exchange front. A large amount of inert material makes it possible to separate the advance of the reaction and heat exchange fronts so that there will be a larger mass of solids between them able to absorb the heat released from the oxidation reaction. When oxygen carriers with a high carrying capacity and a high oxidation enthalpy, such as Ni or Cu, are used, very low metal loadings (lower than 20 wt.%) are required to limit the increase in temperature during the operation, which means that larger high-pressure reactors are required for a given flow of fuel gas fed into the system. This option has been studied assuming methane [26-28, 30, 31] and syngas [32-34] to be the fuel gas. Another alternative is to control the increase in temperature during the oxidation stage by recycling a large amount of the cooled N₂ product gas in order to dilute the O₂ fed into the air reactor [35, 36]. In these conditions, the reaction front advances at a slower velocity than the heat exchange front, which allows the oxidation stage to be carried out with a higher amount of active oxygen carrier content without exceeding the maximum allowable temperature in the reaction front. This alternative permits a more compact reactor design at the expense of a higher energy requirement and equipment cost due to the recirculation of part of the product gas to the air reactor inlet.

Many materials have been evaluated as oxygen carriers for CLC, including synthetic materials, mixed oxides, minerals and waste materials [37-47]. Ni-based and Cu-based carriers have been the most extensively studied materials in the literature because of their favourable characteristics for chemical looping applications, such as their high oxygen carrying capacity, high reactivity with methane and syngas, good chemical stability after multiple redox cycles at high temperatures and also few thermodynamic restrictions for allowing the complete fuel conversion to CO₂ and H₂O [37-42, 46]. Despite these advantages, Ni-based materials are expensive oxygen carriers (see Fig. 2), they have a low resistance to carbon deposition and emissions of their trace compounds must at all costs be avoided because of their potential risks to human health and the environment. With regards to Cu-based materials, they have a relatively low melting point (1085°C) and therefore cannot be used at the highest temperature range for CLC (1100-1200 °C) in order to prevent their deactivation through agglomeration [39, 40].

Fig. 2. Approximate cost and carrying capacity of the main oxygen carriers used in chemical looping combustion.

The main advantage of using natural materials as oxygen carriers is their lower cost in comparison to synthetic materials, though at the expense of a lower oxygen transport capacity (see Fig. 2). Several studies have been published on the suitability of using these materials (iron ore, ilmenite, manganese ore, etc) in CLC applications [43-48]. Manganese ore is reasonably cheap and has a relatively high reactivity with methane and syngas, but after repeated redox cycles it shows poor mechanical stability [47]. Iron-based materials are most stable at high temperatures but their oxygen carrying capacity is very limited and their reactivity with methane is moderate [47, 48]. In general, oxygen carriers with a low oxygen transport capacity require a large amount of active phase in

fixed-bed CLC configurations in order to reach a sufficiently high temperature in the oxidation front that allows the generation of power at a high efficiency [26]. However, active contents greater than 60 wt.% can cause a drastic reduction in mechanical stability after multiple redox cycles [4]. Moreover, the extremely low carrying capacity of many iron-based materials makes the CLC operation unfeasible in a single oxidation stage [33]. Therefore, the use of low-cost carriers in fixed-bed CLC systems requires a substantial effort to find appropriate heat management strategies for this technology to be feasible on a large scale. Ilmenite is a common mineral found in metamorphic and igneous rocks that is mainly composed of iron and titanium oxides. The reduced form of ilmenite in CLC applications is FeTiO_3 , whereas the most oxidized form is Fe_2TiO_5 . Of all the natural materials studied for CLC, ilmenite is one of the most attractive options because of its low price (around 0.3 \$/kg) [49], its reasonably effective oxygen transport capacity (up to 0.05 kg/kg), its good chemical and mechanical stability at temperatures up to 1200 °C and its poor tendency towards carbon deposition during the reduction stage [43]. Although ilmenite reacts rapidly with CO and H_2 , several works have demonstrated that it allows a moderate conversion of CH_4 to CO_2 and H_2O [43, 48, 50]. A previous calcination [45] and the addition of a small amount of Ni (lower than 5 wt.%) [51, 52] to the ilmenite have been proposed in the literature as a way to improve its reactivity with methane in order to achieve combustion efficiencies close to 100%.

This study proposes a fixed-bed process scheme as a valid alternative to carry out the chemical looping combustion of methane using ilmenite as oxygen carrier. We outline a heat management strategy in which the gradients of temperature at the different reaction stages are controlled by suitable gas recycles. Moreover, a steam reforming stage is incorporated to the system as a source of syngas that promotes the reduction kinetics of ilmenite and enhances the combustion efficiency of the overall process. The process design proposed envisages a compact system with a minimum number of reactors able to carry out the entire synchronized operation.

2. Reactor design and process description

The process proposed in this work requires a system of fixed-bed reactors dynamically operated in order to produce a continuous gas stream at a sufficiently high temperature and pressure to efficiently drive a gas turbine for power generation. Only two reaction stages are not sufficient to complete this novel CLC configuration because the conditions at the end of one stage (especially in terms of temperature profiles) do not

satisfactorily meet the requirements to carry out the next stage. Additional stages are needed between the oxidation and reduction steps in order to accommodate the temperature of the solids and gases present in the process, to carry out the reactions involved and fulfill the energy requirements of the process.

A basic reactor model is adopted to represent the performance of the fixed-beds in each stage of the process. Reaction rates are assumed to be sufficiently fast to take place in narrow reaction fronts that move forward as the oxygen carrier is converted. Moreover, an ideal plug flow pattern and negligible axial gas dispersion are assumed to approximately represent the cyclic operation of the CLC system. These assumptions, that are typical of many fixed-bed catalytic systems [53-55], have also been adopted in recent works to describe the performance of dynamically operated fixed-bed systems in CLC [26, 27, 36, 56] and sorption enhanced reforming applications [35, 56-58]. Heat exchange fronts are also formed when the process is not thermally neutral and/or when the temperatures of the gases and solids in contact are different. Both the reaction fronts and heat exchange fronts advance during the operation at different velocities (u_r and u_e , respectively), that can be estimated by solving the heat balances in each front. The variation of temperature in the reaction front ($\Delta T_{\max}$) can be calculated assuming that heat (released or consumed depending on whether the reaction is exothermic or endothermic, respectively) is taken by or from the solids when the gas reacts with them [26]. The reactor model equations considered in this work are listed in Table 1.

Table 1. Equations used in the model [26].

Energy balance:	$(\rho_g u_g x_{i,g})/M_{i,g} (-\Delta H)_{i,r} = \epsilon \rho_s c_{p,s} (u_r - u_e) (T_{\max} - T_0)$
Variation of temperature in the reaction front:	$\Delta T_{\max} = \frac{-\Delta H_r}{\frac{c_{p,s} M_s}{x_s \phi} - \frac{c_{p,g} M_g}{x_g}}$
Maximum temperature:	$T_{\max} = T_{s0} + \Delta T_{\max}$
Velocity of reaction front:	$u_r = \frac{\rho_g u_g x_g M_s}{\epsilon \rho_s x_s M_g \phi}$
Velocity of heat exchange front:	$u_e = \frac{\rho_g u_g c_{p,g}}{\epsilon \rho_s c_{p,s}}$

Fig. 3 shows the fixed-bed CLC process proposed in this work. Assuming an intense heat transfer between the gases and solids, the temperature of the gases and solids will

be similar at any point of the beds, and therefore, the dynamic behavior of each stage of the process can be represented by using a single axial temperature profile. A base case with a reference inlet flow of 10 kg/s of methane (stream 1 in Fig. 3) is examined to show the feasibility of this CLC process on a large scale. An ilmenite-based oxygen carrier with an active content of about 35 wt.% has been chosen as being an intermediate value for the ilmenite contents of most oxygen carriers studied in the literature for CLC applications [43-45]. Around 5 wt.% of Ni in the packed-bed composition is assumed in order to promote ilmenite reactivity and allow a steam reforming stage. The contribution of the Ni-based material in the mass and heat balances is assumed to be negligible at every stage of the CLC process.

Fig. 3. Evolution of the temperature profiles during the stages of the proposed fixed-bed CLC process (r: reaction front, e_i: heat exchange front, white zone: reduced oxygen carrier, grey zone: oxidized oxygen carrier).

A maximum temperature of 1200 °C is assumed in order to maintain the chemical and mechanical stability of the carrier after multiple redox cycles [43-45]. An operating pressure of about 20 bar has been selected in order to achieve the highest energy

efficiency in the downstream gas turbine [21]. Table 2 summarizes the input operating conditions chosen for the case study and Table 3 indicates the temperature, flow rate and composition of the gas streams obtained by solving the mass and heat balances at each stage of the CLC process.

Table 2. Operating conditions and reactor characteristics for the reference case study.

Parameters	Values
Inlet CH ₄ mass flow, kg/s	10
Pressure, bar	20
Inlet gas temperature, °C	370
Ilmenite content, wt. %	35
Ni content, wt. %	5
Particle size, m	0.005
Bed porosity	0.5
Bed bulk density, kg/m ³	1950

Table 3. Temperature, flow rate and composition of the gas of the CLC process for the operating conditions listed in Table 2.

Streams	1	2	3	4	5	6	7	8	9	10	11	12	13
T, °C	550	370	370	370	370	370	370	370	550	550	370	370	1200
Flow, kmol/s	1.25	2.42	4.0	4.10	2.50	1.58	5.94	7.84	6.59	4.69	1.90	13.21	13.21
Composition (vol. %)													
CH ₄	50	2	1	-	-	-	-	-	-	-	-	-	-
CO	-	24	15	-	-	-	-	-	-	-	-	-	-
H ₂	-	72	44	-	-	-	-	-	-	-	-	-	-
CO ₂	-	-	10	25	25	25	-	-	-	-	-	-	-
H ₂ O	50	2	30	75	75	75	-	-	-	-	-	-	-
N ₂	-	-	-	-	-	-	79	84	100	100	100	100	100
O ₂	-	-	-	-	-	-	21	16	-	-	-	-	-

2.1. Reduction stage

At the beginning of the reduction stage (stage A in Fig. 3), it is assumed that the active phase of the ilmenite-based oxygen carrier is completely oxidized (Fe₂TiO₅) and that the bed is divided into two parts at different temperatures, as a result of the preceding stage

explained below. A part of the packed bed is at 1200 °C (T_{s1} in Fig. 3), while the rest of the solids are at 370 °C (T_{s2} in Fig. 3). A stream of syngas (stream 2 in Fig. 3) of about 2.4 kmol/s is fed in at the part of the bed that is at 1200 °C, which is a sufficiently high temperature to ensure the fast and complete oxidation of the syngas to CO₂ and steam from the very beginning of the process [43-45]. The syngas, which is mainly composed of H₂ (73 vol.%) and CO (24 vol.%), is obtained from a subsequent steam methane reforming stage (B) that is described below. It is assumed that the Fe₂TiO₅ contained in the bed is reduced to FeTiO₃ during stage (A) and that there is no total reduction to FeTiO₂ (Fe+TiO₂). The presence of pure Fe would reduce the selectivity of syngas to CO₂ and steam, resulting in a higher carbon slip and therefore a lower CO₂ capture efficiency. Moreover, the formation of pure Fe would cause the partial deactivation of the oxygen carrier because Fe tends to agglomerate at the usual temperatures of CLC [32]. Side reactions of the syngas during the reduction stage (carbon deposition by the Boudouard reaction and WSG) are assumed to be negligible. When the syngas comes into contact with oxidized solids, it rapidly reacts to form a narrow reduction front (r) that will move forward at a velocity (u_r) (indicated in Fig.3 as the transition between the white and grey zones). For the syngas composition of this reference case the reduction of the ilmenite is slightly endothermic, and therefore, a small drop in temperature (ΔT_{red} in Fig. 3) is produced at the reduction front (see Table 1). As the stage starts with the solids bed being at two different temperatures (T_{s1} and T_{s2}) and the syngas is also fed in at another temperature ($T_{gin,1}$), two heat exchange fronts (e_1) and (e_2) are formed, and they move forward at velocities (u_{e1}) and (u_{e2}), respectively. Under the conditions chosen for the reduction stage (A), the reduction front moves forward faster than the heat exchange fronts ($u_r/u_e > 1$), and consequently, a heat plateau (at T_1) forms in the bed. In this situation, the syngas arrives at the reaction front already preheated by the reduced solids, which in turn have been cooled down from T_{s1} to T_1 because of the heat consumed in the endothermic reduction of the ilmenite with the syngas. Downstream of the reduction front (r), the intense heat transfer between gases and solids causes the product gas to be emitted at the initial temperature of the solids located near the reactor exit ($T_{s2}=370$ °C). In the conditions listed in Table 2, a product gas (stream 5 in Fig. 3) of around 2.5 kmol/s is emitted during stage (A), which is composed of 75 vol.% of H₂O and 25 vol.% of CO₂.

The recirculation of a part of the product gas (stream 6 in Fig. 3) will increase the flow rate into the reduction stage (stream 3 in Fig. 3), which will accelerate the advance of the heat exchange fronts (e_1 and e_2) along the bed (bringing u_r/u_e closer to 1). Moreover, the presence of a large amount of steam and CO_2 in the feed will prevent carbon deposition and the over-reduction of Fe_2TiO_5 to pure Fe will be kept to a minimum during stage (A) [32]. The recirculation of gas can be designed in a manner such that both the reaction front (r) and the heat exchange front (e_2) reach the reactor exit at the same time. This will allow the reduction stage (A) to be initiated with only a portion of the bed at $1200\text{ }^\circ\text{C}$ (T_{s1} in Fig. 3), and therefore, a higher amount of the heat generated in the subsequent oxidation stage (C) can be used for power generation (as explained below). However, the shorter distance between the advance of the reaction front (r) and the heat exchange front (e_1) will cause a higher drop in temperature in the reduction front (ΔT_{red}), because there will be fewer solids at $1200\text{ }^\circ\text{C}$ (T_{s1} in Fig. 3) to supply the necessary heat for the endothermic reduction of the ilmenite (see Fig. 3). Furthermore, a reasonable recirculation ratio must be chosen in order to avoid the excessive dilution of the syngas that would lead to a dramatic decrease in the reduction rate. H_2 and/or CO contents lower than 30 vol.% in the feed will significantly reduce ilmenite reactivity [50], and therefore the assumption of narrow reduction fronts during stage (A) would be erroneous. Fig. 4 shows the effect of the recirculation ratio on these variables for the conditions chosen in this case study.

Fig. 4. Effect of the recirculation ratio on: a) the amount of solids at high temperature initially required for the reduction stage and drop in temperature at the reduction front, b) the dilution of syngas and the ratio between the reaction and heat exchange front velocity.

As can be seen in Fig. 4, the recirculation of around 40 % of the product gas to the reactor inlet (recirculation ratio of around 0.4) causes the reaction front (r) to advance only 1.7 times faster than the heat exchange front (e_2), predicted by the equations listed in Table 1. It will therefore be possible to completely reduce the solids bed by initiating the reduction stage with around 40% of the bed at 1200°C (T_{s1}) and the remaining 60% of the bed at 370 °C (T_{s2}). Under these conditions, the decrease in temperature in the reduction front will be around 13 °C, and therefore the reduced solids will be left behind the reaction front at 1187 °C (T_1 in Fig. 3). At this recirculation ratio, the inlet flow rate (stream 3 in Fig. 3) will increase to 4 kmol/s, with a composition of 43 vol.% of H_2 and 14 vol.% of CO. Once the solids bed has been completely reduced ($t=t_{end}$ in Fig. 3), the part of the bed that has been traversed by all the fronts will be left at the temperature of the inlet gas (370 °C). This section of the bed is around 60 wt.% for the conditions of the reference case and a recirculation ratio of 0.4. The rest of the bed (around 40 wt.%) will remain at 1187 °C (T_1 in Fig. 2).

2.2. Reforming stage

Since the oxidation of ilmenite with air is moderately exothermic, the fact that much of the bed is initially at a very high temperature (1187 °C) may cause the temperature to rise above the maximum allowable value during the oxidation stage, which would have a negative effect on the properties of the oxygen carrier [32]. We therefore propose for this study the addition of a steam reforming stage (B), which would allow the solids bed to cool down to a suitable temperature before the next oxidation stage (C) begins. The excess of sensible heat stored in the solids after the reduction step is used to convert the inlet flow of methane and steam (stream 1 in Fig. 3) fed into the system into a product gas (stream 2) that contains a large amount of H_2 and CO. This stream (2) can then be used as reducing gas in stage (A), which will enhance the kinetics of the reduction of Fe_2TiO_5 to $FeTiO_3$, while ensuring at the same time the total conversion of the syngas to CO_2 and steam. As mentioned above, the reactivity of ilmenite with methane is slower, even at very high temperatures and gives a moderate conversion to CO_2 and H_2O , resulting a carbon slip during the reduction stage. A flow of methane of about 0.625 kmol/s (10 kg/s of CH_4) with steam is supplied at 550 °C (T_{gin2} in Fig. 3) and 20 bar to stage (B) through the part of the reactor where the solids are at the highest temperature, 1187 °C (T_1 in Fig. 3). Under these conditions, the steam methane reforming reaction (SMR) will be favoured [59], and therefore, a narrow reaction front will be formed.

Since the reforming reaction is highly endothermic, the solids at the highest temperature will supply the heat needed to maintain the advance of the reaction front (r) through the bed, causing a dramatic drop in temperature (ΔT_{ref} in Fig. 3). As the reaction front moves forward, the solids will be left behind at the temperature of the incoming gas, 550 °C (T_{gin2} in Fig. 3). At this temperature, the kinetics of steam methane reforming will be too slow [59][61], and therefore, the conversion of methane to syngas behind the reaction front (r) will be negligible.

Fig. 5. Equilibrium compositions at 20 bar in steam methane reforming as a function of the S/C molar ratio (a) and as a function of the temperature, S/C=1 (b).

The composition of the syngas (stream 2) will be determined by the SMR equilibrium at the temperature of the reaction front (1187 °C) and it will strongly depend on the steam-to-carbon (S/C) molar ratio fed into stage (B). As shown in Fig. 5, the S/C molar ratio fed into stage (B) must be around 1 in order to promote the conversion of methane to H₂ (which will accelerate the reduction kinetics of the ilmenite in stage (A) and minimize the consumption of steam in the process. Under the conditions selected for stage (B), the reaction front (r) will advance much faster than the heat exchange front (e), labelled in Fig. 3 as the transition T_1/T_{gin1} . As a result, the reaction front will catch up with the heat exchange front before it reaches the reactor exit. The syngas produced during stage (B) therefore can be assumed to be discharged at a constant temperature of 370 °C (T_{gin1} in Fig. 3). At the end of stage (B), the entire bed will have cooled down to 550 °C, which is still a sufficiently high temperature to start a rapid oxidation of the ilmenite-based carrier in the following stage (C) [50].

2.3. Oxidation and heat removal stages

Once stage (B) has finished, the subsequent oxidation stage (C) is initiated by feeding in air (stream 7 in Fig. 3), which is supplied by the compressor of the turbine at 20 bar and

370 °C (T_{gin1} in Fig. 3). A flow rate of about 5.9 kmol/s of air (stream 7) is assumed to be sufficient for the complete oxidation of the solids bed in a similar cycle time as that needed for the reaction stages (A) and (B) with only a moderate pressure drop. Given the operating conditions listed in Table 2, the reaction front (r) will advance much faster than the heat exchange front (e) and the solids located between both fronts will absorb the heat released in the reaction front, resulting in an increase in their temperature. Under these conditions, the air stream will arrive at the reaction front already preheated by the oxidized solids up to the maximum temperature reached in the reaction front (T_{max} in Fig. 3). This temperature will allow the solids and oxygen to achieve a complete conversion in a narrow reaction front, and consequently, the product gas will contain pure nitrogen (stream 9 in Fig. 3). Meanwhile, the solids that have already been oxidized are left behind at the inlet gas temperature (370 °C). As happened in the previous reaction stages, the fast solid/gas heat transfer will allow the nitrogen produced in stage (C) to be discharged at the temperature of the solids situated closest to the reactor exit ($T_{\text{gin2}}=550$ °C).

As explained above, ilmenite is an oxygen carrier with a moderate carrying capacity and its oxidation enthalpy is lower than that of other common carriers used in CLC applications, such as Ni or Cu. For the reference case of this work (35 wt.% of active phase in the oxygen carrier), the increase in temperature in the oxidation front (ΔT_{ox} in Fig. 3) will be around 600 °C (see Table 1). Since the temperature of the solids ahead of the reaction front (T_{gin2} in Fig. 3) is 550 °C, the maximum temperature achieved during the oxidation stage (T_{max}) will be around 1150 °C (see Table 1), which is lower than the maximum limit (1200 °C) that can be reached without the performance of the ilmenite-based material being affected. As a result, the flue gas generated in the subsequent heat removal stage (D) will be sent to the gas turbine at 1150 °C (well below the nominal inlet temperature of modern combined cycles), and therefore, the efficiency of the CLC process will diminish. As can be seen in Fig. 6, the ratio between the reaction and heat exchange front (u_r/u_e) mainly depends on the contents of ilmenite and O_2 in the solids bed and in the gas feed, respectively. The dilution of the O_2 fed into stage (C) will allow the reaction and heat exchange fronts to approach each other (u_r/u_e closer to 1). Consequently, there will be a smaller mass of solids located between them to absorb the heat released from the oxidation reaction, which will cause the temperature in the reaction front to increase. A suitable gas recycle (stream 11 in Fig. 3) in the oxidation

stage (C) will permit the desired temperature increase in the oxidation front even in fixed-bed CLC systems that use oxygen carriers with a low carrying capacity and/or low oxidation enthalpy (such as many manganese and iron-based oxygen carriers).

Fig. 6. Reaction and heat exchange front velocity ratio as a function of the ilmenite content in the oxygen carrier and the O₂ content in the feed during the oxidation stage.

The effect of the recirculation ratio on the increase of temperature in the oxidation front (see Table 1) and on the dilution of O₂ in the feed is illustrated in Fig. 7. For the reference case of this study, a recirculation ratio of around 0.3 will increase the inlet flow rate (stream 8 in Fig. 3) up to 7.8 kmol/s, with an O₂ content of around 16 vol.%, which means that the reaction front (r) will advance approximately 4 times faster than the heat exchange front (e). In these conditions, the maximum increase in temperature in the oxidation front will be around 650 °C, and therefore, the resulting maximum temperature reached during the oxidation stage will be 1200 °C. The approach of the reaction and heat exchange fronts during the operation will decrease the amount of bed that is left at the maximum temperature once the oxidation has finished ($t=t_{\text{end}}$ in Fig. 3). For a recirculation ratio of about 0.3, the part of the bed that is left at 1200 °C will be around 76 wt.%. The rest of the bed (around 24 wt.%) will remain at 370 °C (T_{ginl} in Fig. 3).

Once the oxidation stage (C) has finished, the heat stored in the solids bed will be removed in a subsequent heat removal stage (D) by a gas flow (stream 12 in Fig. 3), which will be released at 1200 °C and later expanded in a combined cycle for power generation. The inlet gas will be supplied to stage (D) at 20 bar and 370 °C. For this purpose, air from the compressor of the turbine can be used. Another option would be to recirculate and re-compress a large fraction of the exhaust gas (N₂) from the HRSG of the combined cycle, which is a similar operation to the partial recirculation of the flue

gas that is employed in NGCC to increase the concentration of CO₂ in the exit gas before it enters postcombustion capture systems [60]. During stage (D), the solids bed will gradually cool down from 1200 °C ($T_{\max}$) to 370 °C (T_{ginl}) as the heat exchange front (e) moves forward. However, not all the heat stored in the bed can be blown out of the reactor for power generation. As explained above, a sufficient amount of bed needs to be left at a very high temperature (T_{sl} in Fig. 3) so that a new reduction stage (A) can be initiated. For the conditions of the reference case, stage (D) will finish when around 40 wt.% of the bed is at 1200 °C and the remaining 60 wt.% of the bed at 370 °C. A flow rate of about 13.2 kmol/s of nitrogen (stream 12) is considered to be necessary to carry out stage (D) for a reasonable cycle duration and pressure drop.

Fig. 7. Influence of the recirculation ratio on the increase in temperature in the oxidation front and on the dilution of O₂ in the feed (in the conditions of the reference case).

2.4. Process design

The CLC process proposed in this work needs to ensure the production of a continuous stream of nitrogen at high temperature and high pressure for its expansion in a combined cycle. This stream must be generated at a nearly constant temperature and mass flow rate in order to protect the gas turbine expander from thermal and mechanical stress [32]. The number of reactors required for the complete process (following the sequence of four stages explained above) must be kept to a minimum in order to minimize the equipment cost. However, a larger number of reactors may be needed, since the gas flow rates calculated for every stage must be accommodated at reasonable gas velocities in order to avoid excessive pressure drops. Taking into account the operating conditions listed in Table 2 and the inlet flow rates calculated for each stage (see Table 3), a total of five reactors operating in synchronized mode will be required, i.

e., one reactor for stage (A), one reactor for stage (B), one reactor for stage (C) and two reactors for stage (D). Very short rinse/purge steps can be introduced to remove traces of unconverted species after the oxidation and reduction stages in order to avoid unwanted reactions during the transition periods. The duration of the purges can be considered negligible in relation to the duration of each stage of the process because from industrial experience only five times the total reactor volume of inert gas will be required for a complete rinse [61]. The operational diagram of the proposed CLC system is represented in Fig. 8, which is similar to other configurations used in sorption enhanced reforming (SER) and other CLC applications [61-64].

1	A	B	C	D	D
2	D	A	B	C	D
3	D	D	A	B	C
4	C	D	D	A	B
5	B	C	D	D	A

Fig. 8. Operational diagram of the proposed fixed-bed reactor configuration for the chemical looping combustion of methane using an ilmenite-based carrier with nitrogen recycling (the dotted line represents a snapshot of the process at a specific point in time as shown in Fig. 9).

The overall flow diagram of the proposed CLC configuration (see Fig. 9) comprises elements that are common to conventional natural gas combined cycles (NGCC), such as an air compressor (101), a gas turbine (107), a heat recovery steam generator (HRSG, 108 in Fig. 9) and a compressor (109) for the recirculation (to the oxidation and heat removal stages) of the N₂ discharged downstream of the HRSG. A topping cycle can also be introduced in order to maximize the efficiency of the gas turbine. A small flow of methane and pressurized air can be burned to increase the temperature of the gas sent to the combined cycle up to the optimum value (1400-1450 °C), at the expense of a slightly lower CO₂ capture efficiency [65]. Moreover, additional elements are introduced to ensure optimal performance in each stage of the CLC process. Blowers (102) and (105) are required to re-compress the recycled streams of CO₂ with steam and N₂, respectively. Heat exchangers (100), (103) and (106) are needed to condition the temperature of the inlet feed of methane and the temperature of the inner recycles incorporated into the process.

Fig. 9. Process flow diagram of the proposed fixed-bed system for the chemical looping combustion of methane using an ilmenite-based oxygen carrier with nitrogen recycling (white valves are open and black valves are closed for a specific point in time).

A valve set-up is necessary to synchronize the operation of the five reactors. For the instant represented in Fig. 8 by a dotted line, valve (9) is open to introduce the methane required to carry out the reforming stage (B), while the valves responsible for feeding air/ N_2 into this reactor are closed. Downstream of the reactor that is performing as stage (B), valves (46) and (42) are open in order to allow the syngas produced in (B) to be fed into the reactor that is operating as stage (A). Subsequently, valves (31), (26) and (21) are also open to regulate the fraction of the CO_2 and H_2O produced in stage (A) that is destined for transport and storage and the fraction that is recirculated into the process. Meanwhile, valve (8) is open in order to allow air to be fed into the reactor that is operating as stage (C). Downstream of stage (C), valve (39) is open to allow the recirculation of the N_2 produced during the oxidation. The heat exchanger (106) removes the excess of sensible heat from this stream before it is recompressed (no blowers operate at high temperature in this system). Moreover, valves (13-16) are open to allow the recirculated N_2 to be fed into the reactors that are performing as stage (D). Finally, valves (47) and (48) are open so that the outlet N_2 (that is being discharged from stage (D) at 1200 °C) can be sent to the combined cycle while part of the exhaust N_2 is being recirculated to the system via the compressor (109).

The reactor geometry and the duration of a single stage are also defined for the operating conditions listed in Table 2. As mentioned above, the cross-sectional area and the minimum time for accomplishing each single stage must be able to accommodate the inlet gas flows at reasonable gas velocities in order to avoid excessive pressure drops. The effect of the cycle duration on the geometry of the reactor and pressure drop has been studied assuming a maximum inlet flow per stage of 7.8 kmol/s (i.e., the inlet flow calculated for stage C), a pellet size of 0.005 m, a void fraction of 50% and a bed density of 1950 kg/m³ when the ilmenite-based carrier is completely oxidized.

Fig. 10. Effect of cycle duration on the reactor geometry and pressure drop.

As can be seen in Fig. 10, shorter cycle durations makes it possible to convert the same amount of gas fed into the system using smaller cross-sectional areas. Larger reactor lengths combined with smaller diameters (i. e. higher L/D ratios) also reduce the total area required. However, these conditions will cause higher pressure drops, resulting in an increase in the energy needed to recompress the gas streams involved in the process. For the operating conditions and reactor characteristics assumed in the reference case, a minimum duration of about 10 minutes can be considered as a reasonable time for each single stage of the CLC process. Assuming a minimum L/D ratio of about 1.5 and a maximum pressure drop of about 6% in each stage, the full process scheme to convert 10 kg/s of methane fed into the system will require 5 reactors, 10 m long with an inner diameter of 6.7 m (with a total area of around 175 m²).

Conclusions

A fixed-bed process scheme for carrying out the chemical looping combustion of methane using ilmenite as oxygen carrier has been described assuming a set of

reasonable operating conditions. The possibility of producing a gas stream at high pressure and at high temperature makes this technology feasible and easy to integrate into a highly efficient natural gas combined cycle. CLC based on fixed-bed reactors are shown to be a competitive mid-term alternative to pressurized fluidized beds, which are handicapped by problems in relation with the circulation of solids at high pressures. However, fixed-bed systems require more complex heat management strategies and high-temperature switching valves that represent a formidable challenge from a technical point of view. A basic reactor model has shown that with reasonable flue gas recycles it is possible to control the advance of reaction and heat exchange fronts, which enhances considerably the heat management of the CLC process. The partial recirculation of the CO_2 and H_2O produced in the reduction stage brings the advance of the fronts closer, which means that the operation can be initiated with a smaller fraction of solids at high temperature. Consequently, a higher proportion of the heat generated during the oxidation stage can be used for power generation in the gas turbine. By means of the same procedure, the recirculation of the nitrogen produced in the oxidation stage under suitable conditions allows the required increase in temperature in the oxidation front to be reached. The dilution of the inlet O_2 makes the heat exchange front move faster and therefore closer to the reaction front. As a result, there will be fewer solids between both fronts that can absorb the heat released from the oxidation reaction, which will facilitate the increase in temperature in the oxidation front to $1200\text{ }^\circ\text{C}$, and therefore result in a more efficient generation of power. Moreover, a steam methane reforming stage is incorporated to the system as a source of syngas that will promote the reduction kinetics of the ilmenite, enhancing the combustion efficiency of the process. A preliminary design of this configuration for an inlet flow of 10 kg/s of methane shows that a minimum of five reactors (10 m long with an inner diameter of 6.7 m) operating in cycles of 10 minutes are required for the successful completion of the process. The results of this study demonstrate the potential of this novel technology for power generation with CO_2 capture, although a substantial effort to experimentally validate the performance of the reactors is required for its development at a large scale. A detailed heat integration of this configuration lies outside the scope of this work, but the absence of process stages with a large energy penalty (apart from the purification and compression of CO_2 as in other capture technologies) is an indication of the high energy efficiency that can be expected of this novel system.

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Nomenclature

c_{pi} specific heat capacity of component i, kJ/mol °C

ΔH_r enthalpy of the reaction, kJ/mol

M_i molecular weight of component i, kg/mol

P pressure, bar

t time, s

$T_{g,in}$ inlet gas temperature, °C

T_{max} maximum temperature, °C

T_{s0} initial temperature of bed reactor, °C

ΔT_{max} maximum adiabatic temperature variation, °C

u_e heat exchange front velocity, m/s

u_g gas velocity, m/s

u_r reaction front velocity, m/s

x_i weight fraction of component i, dimensionless

Greek letters

ρ_i density of component i, kg/m³

ε porosity, dimensionless

φ stoichiometric factor, dimensionless

References

- [1] B. Metz, Controlling Climate Change, Cambridge University Press, 2010.
- [2] IPCC, climate change, The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change, [T. Stocker, D. Qin, G. Plattner, M. Tignor, S. Allen, J. Boschung, A. Nauels, Y. Xia, B. Bex, B. Midgley], Cambridge University Press, 2013.

- [3] M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernandez, M. C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao, P. S. Fennell, Carbon capture and storage update, *Energy Environ. Sci.* 7 (2014) 130-189.
- [4] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L. F. de Diego, Progress in chemical-looping combustion and reforming technologies, *Prog. Energy Combust. Sci.* 38 (2012) 215-282.
- [5] W. K. Lewis, E.R. Gilliland, W.P. Sweeney, Gasification of carbon - metal oxides in a fluidized powder bed, *Chem. Eng. Prog.* 57 (1951) 251-257.
- [6] M. Ishida, H. Jin, A new advanced power-generation system using chemical-looping combustion, *Energy* 19 (1994) 415-422.
- [7] A. Lyngfelt, B. Leckner, T. Mattisson, A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion, *Chem. Eng. Sci.* 56 (2001) 3101-3113.
- [8] M. Ishida, M. Yamamoto, T. Ohba, Experimental results of chemical-looping combustion with NiO-NiAl₂O₄ particle circulation at 1200 (degree) C, *Energy Conv. Manag.* 43 (2002) 1469-1478.
- [9] B. Kronberger, A. Lyngfelt, G. Löffler, H. Hofbauer, Design and fluid dynamic analysis of a bench-scale combustion system with CO₂ separation—chemical-looping combustion, *Ind. Eng. Chem. Res.* 44 (2005) 546-556.
- [10] A. Abad, T. Mattisson, A. Lyngfelt, M. Rydén, Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier, *Fuel* 85 (2006) 1174-1185.
- [11] E. Johansson, T. Mattisson, A. Lyngfelt, H. Thunman, A 300 W laboratory reactor system for chemical-looping combustion with particle circulation, *Fuel* 85 (2006) 1428-1438.
- [12] L. F. de Diego, F. García-Labiano, P. Gayán, J. Celaya, M. J. Palacios, J. Adánez, Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO-Al₂O₃ oxygen carrier, *Fuel* 86 (2007) 1036–1045
- [13] C. Linderholm, A. Abad, T. Mattisson, A. Lyngfelt, 160 h of chemical-looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier, *Int. J. Greenhouse Gas Control* 2 (2008) 520-530.
- [14] L. S. Fan, L. Zeng, W. Wang, S. Luo, Chemical looping processes for CO₂ capture and carbonaceous fuel conversion - prospect and opportunity, *Energy Environ. Sci.* 5 (2012) 7254-7280.
- [15] A. Lyngfelt, H. Thunman, Construction and 100 h of operational experience of a 10-kW chemical-looping combustor, in: D.C. Thomas (Ed.) *Carbon Dioxide Capture for Storage in Deep Geologic Formations*, Elsevier Science, Amsterdam, 2005, pp. 625-645.
- [16] J. Adánez, P. Gayán, J. Celaya, L. F. de Diego, F. García-Labiano, A. Abad, Chemical looping combustion in a 10 kWth prototype using a CuO/Al₂O₃ oxygen carrier: effect of operating conditions on methane combustion, *Ind. Eng. Chem. Res.* 45 (2006) 6075-6080.
- [17] C. R. Forero, P. Gayán, L. F. de Diego, A. Abad, F. García-Labiano, J. Adánez, Syngas combustion in a 500 Wth chemical-looping combustion system using an impregnated Cu-based oxygen carrier, *Fuel Process. Technol.* 90 (2009) 1471-1479.
- [18] P. Kolbitsch, J. Bolhàr-Nordenkamp, T. Pröll, H. Hofbauer, Operating experience with chemical looping combustion in a 120 kW dual circulating fluidized bed (DCFB) unit, *Int. J. Greenhouse Gas Control* 4 (2010) 180-185.

- [19] A. Lyngfelt, Oxygen carriers for chemical looping combustion 4000 h of operational experience, *Oil Gas Sci. Technol.* 66 (2011) 161-172.
- [20] S. P. Sit, A. Reed, U. Hohenwarter, V. Horn, K. Marx, T. Proell, Cenovus 10 MW CLC field pilot, *Ener. Proc.* 37 (2013) 671-676.
- [21] O. Brandvoll, O. Bolland, Inherent CO₂ capture using chemical looping combustion in a natural gas fired power cycle, *J. Eng. Gas Turbines Power* 126 (2004) 316-321.
- [22] R. Naqvi, O. Bolland, Multi-stage chemical looping combustion (CLC) for combined cycles with CO₂ capture, *Int. J. Greenhouse Gas Control* 1 (2007) 19-30.
- [23] R. Xiao, Q. Song, M. Song, Z. Lu, S. Zhang, L. Shen, Pressurized chemical-looping combustion of coal with an iron ore-based oxygen carrier, *Combust. Flame* 157 (2010) 1140-1153.
- [24] A. Bischi, Ø. Langørgen, I. Saanum, J. Bakken, M. Seljeskog, M. Bysveen, J. X. Morin, O. Bolland, Design study of a 150 kWth double loop circulating fluidized bed reactor system for chemical looping combustion with focus on industrial applicability and pressurization, *Int. J. Greenhouse Gas Control* 5 (2011) 467-474.
- [25] R. Kumar, R. Lyon, J. Cole, Unmixed Reforming: A Novel Autothermal Cyclic Steam Reforming Process, in: C.E.L. Grégoire Padró, Francis (Ed.) *Adv. Hydrogen Energy*, Springer US, 2002, pp. 31-45.
- [26] S. Noorman, M. van Sint Annaland, J. A. M. Kuipers, Packed bed reactor technology for chemical-looping combustion, *Ind. Eng. Chem. Res.* 46 (2007) 4212-4220.
- [27] S. Noorman, F. Gallucci, M. van Sint Annaland, J. A. M. Kuipers, A theoretical investigation of CLC in packed beds. Part 2: Reactor model, *Chem. Eng. J.* 167 (2011) 369-376.
- [28] S. Noorman, F. Gallucci, M. van Sint Annaland, J. A. M. Kuipers, Experimental Investigation of a CuO/Al₂O₃ Oxygen Carrier for Chemical-Looping Combustion, *Ind. Eng. Chem. Res.* 49 (2010) 9720-9728.
- [29] D. Dissanayake, M. P. Rosynek, K. C. C. Kharas, J. H. Lunsford, Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/Al₂O₃ catalyst, *J. Catal.* 132 (1991) 117-127.
- [30] S. Noorman, F. Gallucci, M. van Sint Annaland, J. A. M. Kuipers, A theoretical investigation of CLC in packed beds. Part 1: Particle model, *Chem. Eng. J.* 167 (2011) 297-307.
- [31] S. Noorman, F. Gallucci, M. van Sint Annaland, J. A. M. Kuipers, Experimental investigation of chemical-looping combustion in packed beds: A parametric study, *Ind. Eng. Chem. Res.* 50 (2011) 1968-1980.
- [32] V. Spallina, F. Gallucci, M. C. Romano, P. Chiesa, G. Lozza, M. van Sint Annaland, Investigation of heat management for CLC of syngas in packed bed reactors, *Chem. Eng. J.* 225 (2013) 174-191.
- [33] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, A novel reactor configuration for packed bed chemical-looping combustion of syngas, *Int. J. Greenhouse Gas Control* 16 (2013) 1-12.
- [34] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, CLC in packed beds using syngas and CuO/Al₂O₃: Model description and experimental validation, *Appl. Energy* 119 (2014) 163-172.
- [35] J. R. Fernández, J. C. Abanades, R. Murillo, G. Grasa, Conceptual design of a hydrogen production process from natural gas with CO₂ capture using a Ca-Cu chemical loop, *Int. J. Greenhouse Gas Control* 6 (2012) 126-141.

- [36] J. R. Fernández, J. C. Abanades, Conceptual design of a Ni-based chemical looping combustion process using fixed-beds, *Appl. Energy* 135 (2014) 309-319.
- [37] R. Villa, C. Cristiani, G. Groppi, L. Lietti, P. Forzatti, U. Cornaro, S. Rossini, Ni based mixed oxide materials for CH₄ oxidation under redox cycle conditions, *J. Mol. Catal. A: Chem.* 204–205 (2003) 637-646.
- [38] M. Johansson, T. Mattisson, A. Lyngfelt, Investigation of Fe₂O₃ with MgAl₂O₄ for chemical-looping combustion, *Ind. Eng. Chem. Res.* 43 (2004) 6978-6987.
- [39] L. F. de Diego, F. García-Labiano, J. Adánez, P. Gayán, A. Abad, B. M. Corbella, M. J. Palacios, Development of Cu-based oxygen carriers for chemical-looping combustion, *Fuel* 83 (2004) 1749-1757.
- [40] P. Cho, T. Mattisson, A. Lyngfelt, Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion, *Fuel* 83 (2004) 1215-1225.
- [41] T. Mattisson, M. Johansson, A. Lyngfelt, The use of NiO as an oxygen carrier in chemical-looping combustion, *Fuel* 85 (2006) 736-747.
- [42] M. Johansson, T. Mattisson, A. Lyngfelt, Investigation of Mn₃O₄ with stabilized ZrO₂ for chemical-looping combustion, *Chem. Eng. Res. Des.* 84 (2006) 807-818.
- [43] H. Leion, A. Lyngfelt, M. Johansson, E. Jerndal, T. Mattisson, The use of ilmenite as an oxygen carrier in chemical-looping combustion, *Chem. Eng. Res. Des.* 86 (2008) 1017-1026.
- [44] H. Leion, T. Mattisson, A. Lyngfelt, Use of ores and industrial products as oxygen carriers in chemical-looping combustion, *Energy Fuels* 23 (2009) 2307-2315.
- [45] J. Adánez, A. Cuadrat, A. Abad, P. Gayán, L. F. de Diego, F. García-Labiano, Ilmenite activation during consecutive redox cycles in chemical-looping combustion, *Energy Fuels* 24 (2010) 1402-1413.
- [46] E. Jerndal, T. Mattisson, I. Thijs, F. Snijkers, A. Lyngfelt, Investigation of NiO/NiAl₂O₄ oxygen carriers for chemical-looping combustion produced by spray-drying, *Int. J. Greenhouse Gas Control* 4 (2010) 23-35.
- [47] R. Xiao, L. Chen, C. Saha, S. Zhang, S. Bhattacharya, Pressurized chemical-looping combustion of coal using an iron ore as oxygen carrier in a pilot-scale unit, *Int. J. Greenhouse Gas Control* 10 (2012) 363-373.
- [48] A. Fossdal, E. Bakken, B. A. Øye, C. Schøning, I. Kaus, T. Mokkelbost, Y. Larring, Study of inexpensive oxygen carriers for chemical looping combustion, *Int. J. Greenhouse Gas Control* 5 (2011) 483-488.
- [49] U. S. G. Survey, Mineral commodity summaries 2013, U.S. Geological Survey, Reston, VA, 2013.
- [50] A. Abad, J. Adánez, A. Cuadrat, F. García-Labiano, P. Gayán, L. F. de Diego, Kinetics of redox reactions of ilmenite for chemical-looping combustion, *Chem. Eng. Sci.* 66 (2011) 689-702.
- [51] M. Johansson, T. Mattisson, A. Lyngfelt, Creating a synergy effect by using mixed oxides of iron- and nickel oxides in the combustion of methane in a chemical-looping combustion reactor, *Energy Fuels* 20 (2006) 2399-2407.
- [52] M. Rydén, M. Johansson, E. Cleverstam, A. Lyngfelt, T. Mattisson, Ilmenite with addition of NiO as oxygen carrier for chemical-looping combustion, *Fuel* 89 (2010) 3523-3533.
- [53] D. Vortmeyer, W. Jahnel, Moving reaction zones in fixed bed reactors under the influence of various parameters, *Chem. Eng. Sci.* 27 (1972) 1485-1496.
- [54] G. Kolios, J. Frauhammer, G. Eigenberger, Autothermal fixed-bed reactor concepts, *Chem. Eng. Sci.* 55 (2000) 5945-5967.

- [55] R. M. Navarro, M. A. Pena, J. L. Fierro, Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass, *Chem Rev* 107 (2007) 3952-3991.
- [56] J. R. Fernández, J. C. Abanades, R. Murillo, Modeling of Cu oxidation in adiabatic fixed-bed reactor with N₂ recycling in a Ca/Cu chemical loop, *Chem. Eng. J.* 232 (2013) 442-452.
- [57] J. R. Fernández, J. C. Abanades, R. Murillo, Modeling of sorption enhanced steam methane reforming in an adiabatic fixed bed reactor, *Chem. Eng. Sci.* 84 (2012) 1-11.
- [58] J. R. Fernandez, J. C. Abanades, G. Grasa, Modeling of sorption enhanced steam methane reforming—Part II: Simulation within a novel Ca/Cu chemical loop process for hydrogen production, *Chem. Eng. Sci.* 84 (2012) 12-20.
- [59] J. Xu, G. F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, *AIChE J.* 35 (1989) 88-96.
- [60] K. Jonshagen, N. Sipöcz, M. Genrup, A novel approach of retrofitting a combined cycle with post combustion CO₂ capture, *J. Eng. Gas Turbines Power* 133 (2010) 011703-011703.
- [61] I. Martínez, M. C. Romano, J. R. Fernández, P. Chiesa, R. Murillo, J. C. Abanades, Process design of a hydrogen production plant from natural gas with CO₂ capture based on a novel Ca/Cu chemical loop, *Appl. Energy* 114 (2014) 192-208.
- [62] E. R. van Selow, P. D. Cobden, R. W. van den Brink, J. R. Hufton, A. Wright, Performance of sorption-enhanced water-gas shift as a pre-combustion CO₂ capture technology, *Ener. Proc.* 1 (2009) 689-696.
- [63] A. D. Wright, V. White, J. R. Hufton, R. Quinn, P. D. Cobden, E. R. van Selow, CAESAR: Development of a SEWGS model for IGCC, *Ener. Proc.* 4 (2011) 1147-1154.
- [64] I. Martínez, R. Murillo, G. Grasa, J. R. Fernández, J. C. Abanades, Integrated combined cycle from natural gas with CO₂ capture using a Ca–Cu chemical loop, *AIChE J.* 59 (2013) 2780-2794.
- [65] S. Consonni, G. Lozza, G. Pelliccia, S. Rossini, F. Saviano, Chemical-looping combustion for combined cycles with CO₂ capture, *J. Eng. Gas Turbines Power* 128 (2006) 525-534.