CONCEPTUAL DESIGN OF A HYDROGEN PRODUCTION PROCESS FROM NATURAL GAS WITH CO₂ CAPTURE USING A Ca-Cu CHEMICAL LOOP

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Abstract

This work presents a conceptual design of a novel method to obtain hydrogen and/or electricity from natural gas and a concentrated stream of CO₂ suitable for permanent geological storage. The method is based on the well known Sorption Enhanced Reforming (SER) principles for H₂ production using a CaO/CaCO₃ chemical loop. A second chemical loop of Cu/CuO is employed to solve the problem of endothermic CaCO₃ calcination in order to regenerate the sorbent and release the concentrated CO₂. The reduction reaction of CuO with natural gas, CO or H₂ is shown to be feasible for providing the necessary heat for calcination. A preliminary design of the process has been carried out based on the principles of fixed bed operation and high temperature PSA, making use of the information offered by the literature to define the operating best conditions for the key gas-solid reaction steps and assuming ideal plug flow behaviour in all the reactors during the chemical reactions and gas-solid heat transfer. This makes it possible to define the precise operating windows for the process, so that the reactors can operate close to neutrally thermal conditions. Special material properties (particularly the Ca/inert and Cu/inert ratios) are required, but these are shown to be within the limits of what have been reported in the literature for other gas/solid reaction

processes using the same reactions. The conclusion is that there is a great potential for achieving a high degree of energy efficiency with the proposed process by means of a sequence of reactions under the conditions described in this work.

Keywords: CO₂ capture, carbonation, chemical looping, sorption enhanced reforming

1. Introduction

Hydrogen production for both chemical and energy industries is continuously increasing and fossil fuels are currently the main sources of hydrogen. Steam methane reforming (SMR) is the established and most economical method employed to produce hydrogen on a large scale (Rostrup-Nielsen and Sehested, 2002). There is also great interest in developing efficient CO₂ capture technologies for large scale hydrogen production and/or power generation (precombustion CO₂ capture technologies from natural gas) (Metz et al., 2005). As with other CO₂ capture technologies, the main challenge is to reduce the overall energy penalties and the cost of existing equipment. It is also possible to envisage new technologies that might drastically reduce the high CO₂ capture cost with respect to more developed H₂ production processes. This paper focuses on this second type of emerging precombustion CO₂ capture processes.

The commercial steam methane reforming process is divided in two stages: one at high temperature and pressure (typically 800 °C-1000 °C and 20 atm - 35 atm) in which the reforming reaction takes place, Eq. (1), followed by an additional shift reaction at lower temperature (typically 200 °C - 400 °C) in order to maximize the CO conversion by means of Eq. (2). Both of them are equilibrium limited, so that it is impossible to achieve the complete conversion of CH₄ and CO in conventional steam reforming.

Moreover, the global reaction is strongly endothermic, so a large supply of energy is required to maintain stationary conditions in the reactor.

In the sorption enhanced reforming (SER) using CaO, Eq. (3), CO₂ is removed in-situ by CaO as soon as it is formed from gas phase. In the reactor, the reforming catalyst is combined with CaO, so that the reforming, Eq. (1), and shift, Eq. (2), reactions occur simultaneously together with CO₂ capture.

The presence of a CO₂ sorbent, according to Le Chatelier's principle, shifts the equilibrium to the right, with the result that the almost complete conversion of methane and CO is achieved, leading to a higher hydrogen yield under relatively mild conditions of pressure and temperature, Eq. (3).

In addition, the process can be simplified and reduced to one step, as the overall reaction, Eq. (4), is slightly exothermic so that no supplemental energy is required for the production of H₂. The other benefits derivable from the SER have already been referred to by several authors in the literature (Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 1999; Lee et al., 2004; Yi and Harrison, 2005; Yoon et al., 2007; Li and Cai, 2007; Lysikov et al., 2008; Harrison, 2008; Martavaltzi and Lemonidou, 2010).

In order to allow multicycle operation in the SER process for H₂ production, it is necessary to regenerate the sorbent by calcining the CaCO₃ formed in Eq. (4) to form

CO₂ and CaO. This reaction is highly endothermic and it must be performed in a CO₂-rich atmosphere if the process aims at zero emission by introducing the subsequent steps of CO₂ purification, compression and geological storage. Additional energy is required to reach the high calcination temperatures that equilibrium demands (above 900°C in pure CO₂ and at atmospheric pressure). If the partial pressure of CO₂ during the calcination step is lower than the equilibrium pressure of CO₂ (which is determined by the operating temperature), the equilibrium in Eq. (3) shifts to the left and total sorbent calcination is achieved. This condition may be established by reducing the total operating pressure, increasing the operating temperature and feeding in a purge flow of steam. When calcination is carried out close to atmospheric pressure, the demand for purge steam and the temperature swing are reduced. Thus a lower energy consumption and greater system efficiency can be achieved (Solieman et al, 2009). Various solutions have been proposed as a means of providing the heat required for the CaCO₃ calcination with minimum efficiency penalties and favorable production costs. High temperature streams of combustion gases and steam may be used to raise the temperature of a depleted solid bed after the SER operation (Stevens et al., 2007). Steam regeneration has the advantage of transferring more energy to the bed at the same molar flow rate since the heat content (mc_p) is higher than that of the combustion gases. However, the thermal efficiency is lower because the latent heat of water cannot be fully recovered from this stream of steam (Stevens et al., 2007). Both alternatives have the drawbacks of low thermal efficiency and high equipment cost due to the need for additional pre-combustors and boilers.

Other alternatives developed for sorbent regeneration include the lime enhanced gasification (LEGS), a process that consists of two coupled fluidized beds: a gasifier in which CO₂ is captured by CaO to produce a H₂-rich gas from coal, and an oxygen-fired

regenerator in which the sorbent is calcined above 900°C, generating a CO₂-rich stream suitable for storage. The heat required for the calcination in the regenerator is supplied by the combustion of the residual char and the exothermic oxidation of CaS to CaSO₄ (both the char and the CaS formed in the gasifier) (Weimer et al., 2008). Another solution proposed in the literature is the ZEG technology, which couples a solid oxide fuel cell (SOFC) to the sorption enhanced reforming process. This hybrid concept entails the production of hydrogen and electricity from natural gas (Meyer et al., 2011) or coal (Boshu et al., 2008), employing the waste heat from the fuel cell through an internal heat transfer loop in order to perform the CO₂ sorbent calcination at around 900°C. This technology requires specific materials for the SOFC stacks (Ni-based and (La, Sr)MnO₃-based electrodes) that must exhibit a high stability and low degradation rates under conditions of high temperature and pressure.

A number of works have been published by General Electric (Lyon, 1996; Kumar et al., 2000) on alternative reforming processes in packed beds with CaO as a CO₂ sorbent. These systems use a redox chemical loop to solve the problem of the energy supply in the endothermic regeneration of the CaCO₃ formed (see also Dupont et al., 2008). This process, called “unmixed reforming”, involves the use of a metal (Fe, Ni) as oxygen carrier, which transfers oxygen from the air to the fuel, thereby avoiding direct contact between the fuel and the air as is the case in “chemical looping combustion” processes (Hossain and De Lasa, 2008). Then, the exothermic oxidation of the metal with air supplies the heat required for the decomposition of CaCO₃, thereby regenerating the CO₂ sorbent for the next cycle. By coupling an endothermic and an exothermic reaction in the same bed matrix, a higher efficiency and lower equipment cost can be achieved, since the heat is transferred directly from the metal particles to the carbonate. However, although a H₂-rich stream free of CO₂ is obtained in these processes, it must be

emphasized that the CO₂ generated in the calcination of CaCO₃ leaves the reactor highly diluted by N₂, so the problem of a large part of CO₂ emissions to the atmosphere remains unsolved.

The process discussed in the present work also uses a second chemical loop of Cu/CuO to solve the problem of the endothermic CaCO₃ calcination and to release the CO₂ captured during the sorption enhanced reforming step. However, the necessary heat for calcination is supplied by the exothermic reduction of CuO using natural gas, CO or H₂, which produces a gas stream rich in CO₂ and readily separable H₂O. Carbon deposition can be considered negligible in this stage in case of feeding a reducing gas with high content of steam or high H₂/CH₄ ratio, as seen in the literature (Tavares et al., 1996; de Diego et al., 2004). Likewise, the presence of calcium in the material may avoid the carbon formation from methane decomposition, even at high temperatures (Choudhary et al., 1998; Bellido et al., 2009). Moreover, several authors in chemical looping combustion that employ Cu-based materials as a oxygen carrier didn't find carbon deposition during the CuO reduction with CH₄ (Mattison et al., 2003; Abad et al., 2010).

If CO is employed as reducing gas, the Cu/CaO molar ratio needed to reach neutral conditions in the reduction-calcination step will be minimum, taking into account the enthalpies of reduction of CuO with these gases. Nevertheless, a readily available source of CO or H₂ is necessary for the process, as will be discussed in more detail below.

When the SER operation is completed, the subsequent oxidation of Cu with air, Eq. (8), is required in order to obtain an adequate proportion of CuO to carry out the chemical loop for the calcination of CaCO₃.

This reaction must proceed at temperature conditions so that the calcination of CaCO₃ is minimal, in order to avoid the loss of CO₂ in the stream of O₂ depleted air leaving the Cu oxidation reactor. The basic idea of this process has been explained in a previous paper (Abanades et al., 2010) and is briefly outlined in Fig. 1 and in more detail in the next section of this paper.

The sequence of reactions in Fig. 1 is implemented as a series of steps carried out in fixed bed reactors, where pressure and temperature conditions will have to be modified to permit the required reaction fronts outlined above, in order to obtain a hydrogen-rich stream for power generation employing CH₄ as the only energy source. The objective of this work is to develop a full conceptual design of the process, in which the operation strategy and conditions are clearly defined in each of the process reaction steps, considering ideal models for the reactors such as fixed beds operating in plug flow mode and incorporating thermodynamic and rate limitations known from the application of similar systems reported in the literature. Finally, the sensitivity of the process model to the operating conditions, material properties and other limiting conditions is discussed.

2. Material requirements and reactor operating conditions

To carry out the process outlined in Fig. 1 these reactors require functional materials with the right proportions of Cu and CaO to ensure that all the reactions take place in

the different reaction stages. Since the reactions involving Cu and CaO in the SER step (A in Fig. 1) and the Cu oxidation step (B in Fig. 1) are proceeding independently of each other, the Cu/Ca molar ratio in the material is best defined on the basis of the heat requirements in the calcination step (C in Fig. 1). Assuming thermal neutrality in the reaction in step C, and taking into account both enthalpies of reaction at 1123 K, a Cu/Ca molar ratio of 3.1 is required if a pure stream of CH₄ is fed into the reactor C. This assumes that all of the CO₂ has been captured as CaCO₃ in the reforming stage, no CaCO₃ has been lost during Cu oxidation and all reactants have arrived at the reaction front at the same temperature at which they left the reaction front (Abanades et al., 2010). If pure CO is employed as reducing agent, this ratio will decrease to 1.3 and therefore a smaller Cu/Ca ratio will be required for the overall process. If a syngas consisting of CO and H₂ is fed in stage C, the Cu/Ca proportion in the solids will be between the 1.3-1.9 interval depending on the H₂/CO ratio. It is important to note here that the use of CO/H₂ as a fuel gas in the calcination step C can only be justified if there is a suitable source of these synthetic gases within the process. Apart from the obvious potential synergy obtained from syngas derived from coal gasification processes or other industrial processes, we propose in this work a method of producing this gas just after step C has been completed. This is because the sorbent regeneration step C leaves the solid bed at a very high temperature (higher than 850°C) since high temperatures are required for the decomposition of CaCO₃ into CO₂ and CaO. In fact, this temperature is so high that it must be reduced to just above 600°C before the process can be re-started with a new SER step (step A in Fig. 1), because temperatures higher than 800°C would lead to much lower hydrogen yields. For this reason, the overall process is completed by an additional steam methane reforming (SMR) step that acquires sensible heat directly from the hot solids resulting from the calcination step. This steam methane reforming

carried out under adequate conditions of temperature and a suitable S/C molar ratio cools down the solids and produces a stream rich in CO and H₂ that may be employed as a reducing gas in the reduction-calcination step C. As will be explained in more detail below, this additional step affords a significant advantage for the global process as it permit lower Cu/Ca ratios (between 1.3 and 1.9) than when CH₄ is used alone as a fuel in the calcination step C (Abanades et al., 2010).

Regardless of the final Cu/Ca ratio and the chemical activity, these materials will have to be synthesized into shapes, such as extrudates, pellets, rings or beads in order to minimize the pressure drop inside the fixed bed reactors. These shapes will then have to gather the necessary mechanical strength to minimize attrition and a sufficiently high thermal and mechanical stability to withstand numerous cycles, since the process entails severe temperature and pressure swing operations. The materials employed can be combined in different manners to achieve the most efficient performance. The integration may be performed at length scale between mm (separate pellets or powders mixed and pelletized together) and nm (composites) as described in Fig. 2. In principle, composites and mixtures of particles provide a closer contact with the reactants and are therefore a better guarantee for the overall thermal neutrality of the simultaneous reactions required by the SER (step A) and the sorbent regeneration (step C). However, these options are in need of more detailed investigation in materials which is not possible at present and may be not necessary for large scale applications. Stevens et al. (2007) obtained good results in a SER operation carried out in fixed beds made up of individual pellets of CaO-based sorbent separated from pellets of reforming catalyst. Van Selow et al. (2009) also operated the sorption enhanced water gas shift (SEWGS) process in fixed beds where the functional materials were in the form of individual pellets. This is all consistent with the good heat transfer characteristics of a typical large

scale reforming bed catalyst beds (Dybkjaer, 1995; Rostrup-Nielsen and Sehested, 2002). Indeed, it would seem reasonable to start off with the option of the fixed bed using separate pellets (with CaO and Cu as the functional material). Furthermore, if this option is adopted, we shall have at our disposal all the information available in the literature on the reactivity and stability of these types of materials in separate applications.

Irrespective of the content of the functional Cu and Ca materials, there will always be an inert support for these active species, that must be quantified in order to conduct mass and energy balances in the reactors. There is important information available in the literature relating to both CaO and Cu based synthetic materials for applications similar to those expected of the process presented in this paper. Manovic and Anthony (2008, 2009) reported on low cost CaO-based sorbents that maintain a high residual activity (>0.3 mol fraction) even after many carbonation/calcinations cycles. Other more elaborated synthesis routes exist to obtain materials with an even higher reactivity and stability (Stevens et al., 2007; Blamey et al., 2010). Natural limestones, with residual activities of around 0.1, can therefore be ruled out as sorbent candidates for this process.

In relation with Cu-supported materials, de Diego et al. (2004) reported on the high stability of Cu-based materials for chemical looping combustion supported over silica, sepiolite, titania and zirconia with Cu contents of up to 80 wt%. Likewise, Lee et al. (2004) achieved high H_2 yields by methanol steam reforming over a commercial Cu/ZnO/Al₂O₃ catalyst (64 wt% of Cu). Therefore, as will be discussed later in relation to quantitative examples, it seems feasible to assume the availability of materials with sufficiently high contents of Cu and Ca to fulfill the energy requirements of the reaction fronts at each step of the process.

A third pellet loaded with reforming catalyst (e.g. Ni or noble transition metals) (Jones et al., 2008) may be required in the reactors for the reforming step A. However, this material is not considered in the present work because different authors (Storch and Pinkel, 1937; Idakiev et al. 1987) have shown that Cu-based catalysts are able to promote high hydrogen yields in the water-gas shift reaction (WGS). Alstrup et al. (1998) also found that the addition of high proportions of copper to nickel catalysts prevents the deposition of carbon in the SMR, keeping the catalytic activity for longer periods of time. Furthermore, Podbrscek et al. (2009) proved that Cu-catalysts provide enough activity to carry out SMR up to 700 °C. Thus, we may assume that a fair level of catalytic activity will be derived from the use of Cu-materials in the SER reaction (step A in Fig. 1).

Turning our attention to the operating conditions in the reactors we will focus now on the scheme of the process (Fig. 3), which has been designed for large scale H₂ production and/or power generation. The basic series of steps are indicated in Fig. 1. These are carried out in fixed bed reactors, that will have to alternate pressure and temperature conditions to accommodate the required reaction fronts outlined above, in order to obtain a hydrogen-rich stream for power generation with CH₄ as the only overall energy source. Two important intermediate steps are shown in Fig. 3 to accommodate the necessary changes in the temperature of the solids bed in the reactor before a new reaction step is carried out.

The first stage of the process (step A in Fig. 3), involves the production of a hydrogen-rich stream via the sorption enhanced reforming of CH₄ with steam and the simultaneous carbonation of CaO with the CO₂ produced from the reforming reaction. It is assumed that the reaction rates of the reforming reactions and the absorption of CO₂

by CaO are sufficiently rapid to approach equilibrium when the operation is carried out at the space velocities normally employed in steam reforming. A neat reaction front is thus established that advances as the CaO is consumed while a bed of CaCO₃ is left behind the reaction front. As can be seen in Fig. 3, a stream of CH₄ and steam (11) is fed into the reforming reactor (A) that contains the composition of solids shown in Table 1. In the SER, the equilibrium limits of Eq. (1) and Eq. (2) shift to the right, so that a higher CH₄ conversion may be attained at lower temperatures (Fig. 4).

Balasubramanian et al. (1999) achieved 90% of CH₄ conversion working at 650°C and 15 atm. Under similar working conditions, it is possible to obtain a stream (12) with a hydrogen content of about 95% (dry basis). At this temperature and pressure, we can assume that almost all the CO and CO₂ generated is removed by the carbonation of CaO and that the primary impurity left in stream (12) is CH₄. Furthermore, a lower concentration of CO and higher concentration of H₂ in the product stream reduce carbon deposition, which is a serious problem in SMR as it leads to catalyst deactivation and the blockage of the reforming reactor (Tavares et al., 1996). Although the use of higher temperatures in reactor A would allow higher conversions of methane, CO₂ capture efficiency would decrease and H₂ production would remain stable and close to its maximum at temperatures below 750°C (Fig. 5). The fact that the hydrogen yield is not dependent on temperature is a result of the thermal neutrality of Eq. (4). Above 850°C, CO₂ separation is not effective and the equilibrium product composition is the same as that of a stream obtained by conventional steam methane reforming (Balasubramanian et al., 1999; Harrison, 2008).

As with other reforming processes, increasing the steam/methane molar ratio in reactor A tends to enhance the CH₄ conversion (Balasubramanian et al., 1999), but an

additional amount of energy to produce the steam is required. In practice, steam to carbon ratios of around 3-5 are common (Harrison, 2008) which also ensures that no coke is formed during the reaction.

With respect to the operating pressure, as indicated in Fig. 5 (left) hydrogen production in the SER is favored if the operation is carried out at low pressure because of the rise in the number of gas moles associated with Eq. (4). However, high-pressure performance in the range of 15-35 atm, has been found to be economic in spite of the adverse effect of pressure on the equilibrium (Harrison, 2008). This is particularly interesting from the point of view of power generation applications of the H_2 rich gas coming from reactor A, which may be employed to raise the temperature and the gas flow at the turbine inlet (stream 23 in Fig. 3). This situation is common in other pre-combustion CO_2 capture technologies for natural gas (Metz et al., 2005), because the high energy cost of H_2 compression would make it highly inefficient to generate H_2 at atmospheric pressure.

After the breakthrough in reaction step A, a new reaction step begins when diluted air is fed into reactor B in order to oxidize Cu to CuO with the minimum calcination of $CaCO_3$ formed during step A. Thus, stream 21 is introduced into the packed bed B, where it reacts with the Cu present according to Eq. (8). The oxidation reaction in reactor B is one of the main outputs of energy from this process. In the scheme of Fig. 3, a part of the flue stream 22 from reactor B is fed into a gas turbine in order to generate electricity. In order to maximize energy efficiency through the expansion of the gas in this turbine, the oxidation in reactor B needs to be carried out at high pressure and at the highest allowable temperature. At the same time, it is essential to avoid hot spots that would lead to an irreversible loss of Cu activity and the partial calcination of

the CaCO_3 present in the packed bed. The trade-off between these two requirements will be quantitatively analyzed in the next section in a case study. However, a preliminary discussion on the limits of the operating conditions in this reactor is important to understand the design and material requirements of the process. The starting point of step B is a bed of solids with a temperature of around 650-750°C resulting from step A, a temperature that allows the rapid and complete oxidation of Cu to CuO (Garcia-Labiano et al., 2004; de Diego et al., 2004). Cu maintains an excellent chemical stability even after a large number of successive oxidation/reduction cycles, as can be seen in the literature on chemical looping combustion (Garcia-Labiano et al., 2004; de Diego et al., 2004; Hossain and De Lasa, 2008), but it loses its active surface by agglomeration and volatilization at around 1000°C. The same occurs with the CaO sorbent, which tends to sinter and to lose its activity in this temperature range (Gonzalez et al., 2005). Therefore, it can be anticipated that reactor B will operate between 20-35 atm and at around 850°C, where very fast oxidation rates are reached (Garcia-Labiano et al., 2004; de Diego et al., 2004). In this range, the production of CO_2 by calcination will be moderate. The maximum CO_2 loss by sorbent calcination is established by the equilibrium. Under the operating conditions mentioned above, the maximum partial pressure of CO_2 is lower than 0.5 atm, which means maximum CO_2 content in the flue gas from 1 to 2.5%. However, the high flow rate fed into oxidation reactor and the high operating pressure make that the calcination of the CaCO_3 formed during SER operation will not occur appreciably during the oxidation stage. Several authors have found that high operating pressures decelerate the calcination rate, even if there is no CO_2 in the reacting atmosphere. The main cause of this decrease is due to an inhibition of gas diffusion in the porous of the sorbent at high pressures (Dennis and Hayhursts, 1987; García-Labiano et al., 2004).

On the other hand, it can be assumed that the fast reaction rates and suitable gas space times in reactor B will allow the total conversion of oxygen. Therefore, the flue gas (stream 22) will contain mainly N_2 , which can be used to dilute the O_2 in stream 21 by recirculating part of stream 22. The temperature and the oxygen concentration in 21 are the key to avoiding hot spots in the oxidation reactor as will be shown quantitatively in the next section which deals with how to solve the necessary mass and heat balances in the oxidation reaction front.

As the reaction front moves towards the end of reactor B, solids at low temperature are left behind because the temperature of stream 21 has to be low (between 150 and 300°C) as indicated above. By the end of the oxidation stage, the solids in reactor B will have reached a sufficiently low temperature to impede the reduction of CuO with CH_4 , CO or H_2 . It is therefore essential to include an intermediate heat exchange step (B' in Fig. 3) between stages B and C for the purpose of raising the temperature of the packed bed at the end of reaction step B to a value that allows the reduction of CuO to Cu and the subsequent calcination of $CaCO_3$. Furthermore, it is important to extract heat from stream 25 before it is mixed with stream 27. Compact fixed-bed regenerators are widely used in some industries to cool down hot gases and subsequently provide the stored heat to cold streams (Zarrinehkfash and Sadrameli, 2004). The quantitative details of this operation will be provided in the next section by solving the necessary mass and heat balances at the heat transfer front that is assumed will form during the heat transfer operation B' (see Fig. 3).

The next reaction step in the process involves the regeneration of the $CaCO_3$ formed in the SER step A, by means of the reduction of the CuO obtained in stage B. As indicated above, if a suitable Cu/CaO molar ratio is employed, the heat released in the

reaction front by the exothermic reduction of CuO with CH₄, CO or H₂ is equivalent to the energy required for the endothermic calcination of CaCO₃ and no supplementary fuel will be needed in reactor C. The reaction rates of the CuO reduction with CH₄ have been reported to be sufficiently high at temperatures over 700°C (Abad et al., 2010), and if H₂ or CO are fed in, the kinetics are even faster, with the result that the time required to convert CuO to Cu is significantly lower (Garcia-Labiano et al., 2004). However the operating pressure must decrease to atmospheric pressure in order to allow the decomposition of CaCO₃ to CaO at reasonable temperatures. Likewise, stream 31 must be fed in at a sufficiently high temperature (above 800°C, as this is the temperature of the product gas from stage C') in order to accelerate the reduction of CuO and the calcination of CaCO₃. During the prebreakthrough period, the exit gas (stream 32) is assumed to contain only CO₂ and H₂O. Therefore, only one subsequent H₂O condensation step is needed to obtain pure CO₂ with the minimum supply of energy.

Once the CaO has been regenerated, the solids in reactor C reach a temperature of around 850°C, that impedes the optimal performance of a new SER step (this requires much lower temperatures as pointed out above). It is therefore necessary to extract heat from the bed before the re-pressurization that precedes the beginning of a new cycle A. On the other hand, once the CuO has been completely converted to Cu, the bed will contain the right amount of catalyst to carry out an additional step of methane steam reforming. This endothermic reaction, Eq. (1), may be used to extract a certain amount of heat from the solids and leave the bed at a favourable operating temperature for the SER. Likewise, the inclusion of the final stage C' will provide an easily available source of CO and H₂ that can be used in step C, in order to reduce the amount of Cu required for the process and also to accelerate the reduction of CuO to Cu. The steam reforming in C' must be accomplished with a low S/C molar ratio (around 1) in order to

prevent the formation of CO_2 that could carbonate part of the CaO present in the bed when the temperature inside is close to 650°C .

3. Basic reactor design

Although this is a new process, the performance of the reactors in each of the different reaction stages discussed above can be approximately estimated using basic reactor models, assuming that the reaction rates of the main reactions involved are sufficiently fast for solid-gas reactions to take place on narrow reaction fronts, which advance through the fixed-bed reactors as the feeding gases are introduced and the solid products are consumed (Fig. 3). This assumption was previously considered by Noorman et al. (2007) to analytically describe the cyclic chemical looping combustion performance in fixed-bed reactors. There is also experimental evidence that this is what happens in fixed bed experiments in the reforming and CO_2 absorption reactions with CaO (Balasubramanian et al., 1999; Lopez-Ortiz and Harrison, 2001; Lee et al., 2004; Harrison, 2008) and in similar chemical looping combustion experiments (Kumar et al., 2000; Dupont et al., 2008). A plug flow assumption is therefore adopted for a preliminary description of the different model steps. In addition, when the reactions involved are not thermally neutral and/or when the temperatures of the gases and the solids in contact are different, a heat exchange front is also established, moving like a plug flow through the fixed bed as the reaction time increases. Numerous correlations for estimating the fluid-solid heat transfer coefficient (h_{fs}) have been mentioned in the literature (Holman, 1976; Dixon, 1979; Borman et al., 1992). All of them predict for the high superficial velocities employed in this stage (around 2 m/s) a fast gas-solid heat transfer. Therefore, the assumption that there is no difference between fluid and solid temperatures is reasonably valid. In other words, we can assume an intense heat transfer

between gases and solids and that the temperatures of the gases and the solids are close along the entire bed. This makes it possible to explain each cyclic operation using a simple and transparent model that helps to identify the main design constraints in this new process.

All of the gas-solid reactions involved in the process of Fig. 3 may be represented by the general expression:

which can also be expressed in diagram form as follows.

Fig. 6 represents an exothermic solid-gas reaction in which a molar flow of A (n_A) is fed into a fixed-bed at a temperature ($T_{g,in}$). In this particular example and snapshot in time, the mass flow rate of A and the concentration of B in the solid bed are such that the gas entering the bed first finds a bed of solids at its own temperature $T_{g,in}$ (the solids were originally at T_{s0} but they have been cooled down to temperature $T_{g,in}$ by the gas that carries A and that has passed through the bed before this particular point in time).

When the gas reaches the reaction front, the reaction between A and B proceeds very rapidly, in a narrow reaction front, without offering any relevant resistance to mass transfer. This results in an exit gas stream that is carrying the product of reaction C, leaving behind solids that are converted to product D. The velocities can be expressed by means of a mass balance as:

$$u_r = \frac{b \cdot n_A}{a \cdot A \cdot \rho_B} \quad (10)$$

Since the gas densities are typically between two to three orders of magnitude lower than the solid densities, and the solids are highly concentrated in reactant B, the speed at

which the reaction front moves towards the right is much slower than the gas velocity ($u_g = n_A / A \cdot \rho_A$). In Fig. 6, hot gases abandon the reaction front at high temperature and move towards the exit until they reach the lower temperature solids at heat transfer front (still at temperature T_{s0} if the assumption of a neat heat transfer front is adopted). The speed at which this heat transfer front moves towards the exit of the reactor can be estimated by means of a heat balance for this heat transfer front, assuming as stated above, that heat transfer coefficients are very high and the temperature drop in the gas beyond the heat exchange front is equal to the temperature increase in the solids before and after the reaction front.

$$u_e = \frac{n_A \cdot M_A \cdot c_{pA}}{A \cdot \rho_B \cdot M_B \cdot c_{pB}} \quad (11)$$

As indicated by Eq. (10) and Eq. (11) both fronts move forward at different velocities, depending on the stoichiometry of the reactions, the concentration of reactants, the specific heat capacities of the gases and solids and the operating pressure and temperature. Thus it is possible to distinguish between two different situations depending on the value of the u_r/u_e ratio:

$$\frac{u_r}{u_e} = \frac{b \cdot M_B \cdot c_{pB}}{a \cdot M_A \cdot c_{pA}} \quad (12)$$

The maximum adiabatic temperature increase in the bed ($\Delta T_{\max}$, in Fig. 6) is a very important parameter in this analysis. It can be calculated by means of an energy balance at the reaction front but the formulation of this heat balance depends on the relative positions of the reaction and heat transfer fronts.

If the heat exchange front moves ahead of the reaction front ($u_r/u_e < 1$), as in Fig. 6, the gas will arrive at the reaction front at the inlet gas temperature ($T_{g,in}$) and heat up due to the exothermic reaction taking place at the reaction front and the hot solids arriving at the reaction front as the front moves forward towards the exit of the reactor. In this case, the maximum adiabatic temperature increase can be calculated by Eq. (13).

$$\Delta T_{max} = \frac{\Delta H_r}{m_A \cdot C_{pA} - m_B \cdot C_{pB}} \quad (13)$$

There is also an important maximum temperature, T_{max} , which is defined under adiabatic conditions as:

$$T_{max} = T_{g,in} + \Delta T_{max} \quad (14)$$

This equation represents a situation like the one depicted in Fig. 6, where the solids ahead of the reaction front have already been heated to the maximum temperature by the flow of hot gases leaving the reaction front from the beginning of this reaction stage. In these conditions of maximum temperature, the lower temperature gas arriving at the reaction front has to accommodate not only the heat of the reaction but also the sensible heat of the solids moving “through” the reaction front (at a speed of u_r) when they have cooled down from T_{max} to $T_{g,in}$.

As will be shown later in quantitative examples, by means of this heat balance represented by Eq. (13) and Eq. (14), it is possible to regulate the maximum temperature in the bed by modifying $T_{g,in}$ and thereby prevent the formation of hot spots of

temperatures higher than $T_{\max}$. This is particularly important in the oxidation reaction stage of Cu (step B in Fig. 3).

Fig. 7 represents three different states of the bed during the operation of the reactor, derived from this simple modeling exercise. At the beginning of the reaction stage, $t=t_1$, the solids entering the reaction front are at a temperature lower than $T_{\max}$ and higher than T_{s0} (at $t=0$, this temperature would be the temperature of the initial bed of solids T_{s0}). As the heat of reaction is released at the reaction front, it is transported forward by the gas leaving the reaction front and transfers heat to the solids downstream. As a result, the solids downstream the reaction front will gradually increase their temperature. Once these solids have reached the maximum temperature allowed by Eq. (14), the heat released during the reaction will be retained by an expanding fraction of solids at $T_{\max}$ as the heat transfer front moves forward. The area at $T_{\max}$ under the points R and E in Fig. 7 increases at a rate given by the u_r/u_e ratio ($t=t_2$). Close to the end of this reaction stage, when the reaction front is approaching the end of the bed, most of the solids are left behind at the temperature of the incoming gases, while the product gases abandon the bed at $T_{\max}$ ($t=t_{\text{end}}$ in Fig. 7).

In other words, during the period of time which it takes the heat exchange front to reach the end of the bed, the gas products are released at T_{s0} (Fig. 7). During the rest of the prebreakthrough period, the gas is emitted at the maximum temperature ($T_{\max}$). It is also possible to estimate the average exhaust gas temperature ($T_{g,\text{out ave}}$) during the operation by taking into consideration the enthalpy of reaction and the heat transfer between solid and gas phases, as follows:

$$T_{mg,\text{out ave}} = T_{g,\text{in}} + \frac{\Delta H_r + (m_B \cdot c_{pB})_0 \cdot (T_{s,0} - T_{g,\text{in}})}{(m_A \cdot c_{pA})_{\text{out}}} \quad (15)$$

where $(m_B \cdot c_{pB})_0$ refers to the initial conditions of solid B and $(m_A \cdot c_{pA})_{out}$ to the outlet conditions of gas A. Finally, when the solid is totally depleted ($t=t_{end}$), the reactor is at $T_{g,in}$.

It is also possible to operate the reaction steps with solid beds in which the starting temperature is not uniform (T_{s01} and T_{s02} in Fig. 7, below). As mentioned above, when the heat exchange front moves ahead of the reaction front, the incoming gas (which is at a lower temperature) arrives at the reaction front and cools the solids in the reaction front from T_{max} down to $T_{g,in}$. As T_{s0} has no influence on T_{max} , as indicated in Eq. (14), the highest temperature reached during the operation will be identical to the maximum temperature achieved when the reactor is performing at only T_{s0} (Fig. 7, above).

If the reaction front advances first and leaves behind the heat exchange front ($u_r/u_e > 1$), the gas will arrive at the reaction front (R) having already been preheated by the depleted solids (in E, see Fig. 8), which in turn have been heated by the heat released in the exothermic reaction since the beginning of this reaction stage. In this case, the maximum adiabatic temperature increase can be calculated by means of an energy balance at the reaction front, as follows:

$$\Delta T_{max} = \frac{\Delta H_r}{m_B \cdot c_{pB} - m_A \cdot c_{pA}} \quad (16)$$

In addition, the maximum temperature achieved (T_{max}), can be determined by ΔT_{max} and by the initial temperature of the solids (T_{s0}), Eq. (17).

$$T_{max} = T_{s0} + \Delta T_{max} \quad (17)$$

In adiabatic conditions, the solids ahead of the reaction front (which are at a lower temperature than the reaction front) heat up and absorb the heat of reaction and the sensible heat of the gas that arrives already preheated from the heat exchange front. As a result after passing through the reaction front, the gas cools down to the initial temperature of the solids. For this reason, during the prebreakthrough period ($t < t_{\text{end}}$), the gas abandons the bed at a constant temperature corresponding to the initial temperature of the solids ($T_{\text{g,out}} = T_{\text{s0}}$). When the bed is close to total conversion ($t = t_{\text{end}}$), the part of the solids that has been crossed by both fronts (E and R in Fig. 8) is left at the temperature of the incoming gas ($T_{\text{g,in}}$), while the rest of the solids, which have not been reached by the heat exchange front, remain at T_{max} .

As mentioned above, when the reaction front advances ahead ($u_r/u_e > 1$) of the heat exchange front, the solids at lower temperature receive the heat from the reaction and the sensible heat from the gas, so that maximum temperature is achieved (T_{max}), Eq. (17). As indicated in Fig. (8) (below), there may be situations where two different temperatures are present at the beginning of the reaction stage (see T_{s01} and T_{s02} in Fig. 8 when $t = t_1$). In order to avoid temperatures above a certain value of T_{max} , this variable has to be calculated with Eq. (17) using the maximum initial solid temperature, T_{s02} in the example of Fig. (8).

The previous analysis covers all the different possible scenarios detected in the operation of the reaction steps outlined in Fig. 3. Both the reaction fronts and the heat exchange fronts evolve through the bed of solids and depend only on the initial conditions of the solids (which are in turn determined by the final conditions of these solids from the previous reaction step) and the flow rates, compositions and preheating temperatures of the gas streams fed in at the different reaction stages. A concrete case

study is presented in the next section to illustrate the procedure used to design the process.

4. Case study

In order to demonstrate the applicability of the process to a particular set of operating conditions, the models described in the previous paragraphs have been used to estimate the performance of the reactors together with the mass and energy flows entering and leaving the system. This has been accomplished by solving the mass and energy balances described in the previous sections. Table 1 summarizes the set of input operating conditions and reactor compositions chosen for a conceptual design based on feeding 10 kg/s of CH₄ into to the reformer reactor. Table 1 also includes the operating pressures, the initial temperatures of the reaction fronts established in the different reaction stages and the maximum temperatures calculated for these reactors by means of Eq. (14) and Eq. (17). Reasonable space velocities have been employed that lead to reasonable reactor volumes, comparable to those values achieved in similar operations in steam reforming (Rostrup-Nielsen and Sehested, 2002).

Table 2 shows the composition of CaO and Cu-based materials used for the case study. These have already been referred to in the literature for CO₂ capture and reforming applications (Manovic and Anthony, 2009; Lee et al., 2004). Likewise, a reasonable pellet equivalent diameter, bed porosity and reactor length have been chosen in order to keep the pressure drop in the gas streams through the reactors at any reaction stage below 1 atm. Since the process proceeds under adiabatic and autothermal conditions, making an external energy supply unnecessary, it is possible to employ larger reactor diameters than those used normally in steam methane reforming at industrial scale.

A carbon balance based on the results summarized in Table 1 points to an overall CO₂ capture efficiency of 87.5%, expressed as the amount of CO₂ obtained in stream 32 (stage C) divided by the total amount of CH₄ fed into the process (streams 11 and 33).

The following paragraphs deal with the main implications of adopting these conditions and the methodology used at each reaction stage taking into account the mass output and energy flows.

4.1. Sorption enhanced reforming (step A)

The working conditions presented in Table 1 for reactor A in Figure 1 were chosen to obtain a high H₂ yield in stream 12, operating at a reasonably high pressure, comparable to that of some existing commercial reforming processes in operation, and with a temperature interval that allows maximum CO₂ absorption by CaO. Although hydrogen production is favored at low pressure, a pressure of at least 20 atm is required (35 atm in Table 1) in order to obtain a high pressure gas product stream, which may be used to feed a gas turbine for power generation. For any given operating pressure, there is an optimum reforming temperature for maximizing the purity of hydrogen after the gases have passed through the reformer. High pressures tend to reduce methane conversion and hydrogen production, and consequently the SER must be carried out at even higher temperatures, as can be seen in Fig. 5 (left).

On the other hand, although temperatures over 750°C promote higher methane conversions, there is also a greater loss of CO₂ from the calcination of CaCO₃. An adequate trade-off can be arranged by feeding in stream 11 ($T_{g,in}$) and by operating the solids bed (T_{s0}) at around 700°C. It should be possible to achieve a CH₄ conversion of over 90% and a H₂ content of more than 95% (dry basis) in stream 12, with negligible

formation of CO and CO₂ (<0.5%) by setting reactor A to operate at 35 atm and at around 700°C, Fig. (5).

Since the SER operation is accomplished at 35 atm in this case study, a high S/C molar ratio must be employed to obtain a H₂ purity in stream 12 of over 95% (dry basis), as indicated in Fig. (9). In practice, a steam-to-carbon ratio of around 5 is fed into the reforming reactor, but the amount of steam fed in must be a trade-off between the need to obtain a high degree of H₂ purity in stream 12 and overall process efficiency, because the latent heat of water cannot be totally recovered from the steam as in the SER process described by Stevens et al. (2005).

Reactor A is able to operate at elevated space velocities (over 4000 Nm³CH₄/m³cat/h) and superficial velocities of gas of around 2 m/s, in the same way as industrial tubular reformers (Rostrup-Nielsen and Sehested, 2002). It is assumed that the kinetics of the reforming process is sufficiently rapid for the equilibrium to be reached at the reaction front in these conditions (Xu and Froment, 1989).

According to the basic reactor models explained in the previous section, in the SER reactions in stage A, the reforming and absorption reaction front moves towards the exit of the reactor during the breakthrough period, accompanied by the resultant heat exchange front. The ratio between the two front velocities can be expressed as follows:

$$\frac{u_r}{u_e} = \frac{X_{CH_4} \cdot M_s \cdot c_{ps}}{X_{CaO} \cdot M_g \cdot c_{pg}} = 1.15 \quad (18)$$

where X_{CH_4} is the molar fraction of methane in stream 11 and X_{CaO} is the molar fraction of active CaO in the solids bed before the SER begins. The previous ratio (u_r/u_e) depends heavily on the steam supplied to stream 11 (which reduces X_{CH_4}). At industrial

scale in the SMR, the usual steam/methane ratio fed into the reforming reactor is between 2.5 and 5. Under this narrow operation range, the reaction front moves faster than the heat exchange front ($u_r/u_e > 1$ in Eq. 18), which is the situation represented in Fig. 8. Because of the slight exothermicity of the global reforming and carbonation reaction, Eq. (4), the bed temperature rises in the reaction front to a maximum value that depends on the composition of the bed and the temperature of stream 11 (in Table 1 a $T_{\max_A}$ of 733°C is achieved).

A higher $T_{g,in}$ entails a higher $T_{\max}$ during the SER operation and a lower Cu/CaO molar ratio to be able to perform close to thermally neutral conditions during the process, as shown in Fig. 10. In this case study, the temperature of stream 11 is 600°C because this value leads to a maximum bed temperature of 733°C, which is close to the optimum value for maximizing H_2 production, as indicated in Fig. 5. In these conditions, the Cu/CaO molar ratio required is 1.77 (Table 1, Fig. 11).

As mentioned above, during the prebreakthrough period, the flue gas (stream 12) leaves the reactor at T_{s0} (650°C) with the composition indicated in Table 1. Under these conditions, the heat exchange front advances just behind the reaction front so that a small portion of the solids remains at the end of the reaction stage at temperature $T_{\max}$. According to the basic reactor models proposed in the previous section, only 16% of the solids remain at $T_{\max}$ (733°C), whereas the rest of the bed has cooled down to 600°C, due to being in contact with the gas fed into the reactor ($T_{g,in}$). As can be seen in Fig. 11, the steam methane reforming is barely favored at this temperature. Therefore, this endothermic reforming reaction can hardly be expected to take place behind the reaction front once the solids have transferred their excess of sensible heat to the incoming gas.

Most of the bed (84% in weight) will remain at $T_{g,in}$ to begin the next reaction stage of Cu oxidation (stage B and B').

4.2 Cu oxidation (steps B and B')

The main purpose of this reaction step is to obtain the necessary CuO to be able to carry out the subsequent regeneration of CaO by means of the reduction of CuO with methane, CO or H₂ (stage C), without calcining the CaCO₃ formed in reaction step A. As mentioned above, the high exothermicity of Eq. (8) permits the generation of an exit gas stream at high temperature and pressure, which may be used to drive a gas turbine for power generation (see Fig. 3).

Since the starting temperature at the reaction front of the reactor is 600°C (see Table 1), the total and rapid oxidation of Cu to CuO is feasible in a narrow reaction front from the very beginning of this reaction step. Furthermore, Cu oxidation is favored by the high operating pressure (35 atm), that allows fast reaction rates even with the low content of oxygen present in stream 21. Indeed, the main problem in this reactor is that because of the high rate of reaction and the high exothermicity, the temperature in the reaction front may escalate out of control due to the adiabatic conditions at the reaction front. In order to regulate the temperature at the reaction front and limit the maximum temperature to the reasonable value of 830°C adopted in Table 1, it is necessary to have a large gas flow in contact with the reacting fixed bed, Eq. (13). As can be seen in Fig. 12, the lower temperatures needed for Cu oxidation require a higher dilution of O₂ in stream 21 and therefore a significant fraction of the exit gas from reactor B must be recycled (stream 25 in Fig. 3). High recirculation ratios increase piping requirements and compression costs. In addition, temperatures higher than 850°C will lead to a great loss of CO₂ from calcination since depressurization from 35 atm to atmospheric pressure

must precede the beginning of stage C. In consequence, a reasonable trade-off has to be found (around 830° at 35 atm) in order to obtain fast oxidation kinetics with minimal CaCO₃ calcination.

The application of the heat balance of Eq. (13) to this case shows that a dilution of the O₂ in stream 21 down to 4%, makes it possible to limit the maximum temperature. There is a nitrogen recirculation ratio ($R_N = \text{stream 25}/\text{stream 22}$) of around 0.85, which entails operating with gas velocities of around 2 m/s, taking as a reference the normal velocities at industrial scale for the steam reforming (Rostrup-Nielsen and Sehested, 2002). It is reasonable to assume that this residence time will allow total oxygen conversion inside reactor B. Consequently, the flue gas (stream 22) will contain mainly N₂ and a negligible quantity of CO₂. Moreover, the inlet of recycled CO₂ via stream 25 shifts the equilibrium of Eq. (3) to the left and therefore the formation of CO₂ is further reduced. At 35 atm and at 830°C, the calcination of CaCO₃ in B is kept to a minimum (1 v% CO₂ in stream 22).

As in the SER reaction stage A, the u_r/u_e ratio can be estimated by means of Eq. (19), where X_{O_2} is the molar fraction of oxygen in stream 21 and X_{Cu} is the molar fraction of Cu in the solids bed before the oxidation begins.

$$\frac{u_r}{u_e} = \frac{2 \cdot X_{O_2} \cdot M_s \cdot c_{ps}}{X_{Cu} \cdot M_g \cdot c_{pg}} = 0.50 \quad (19)$$

Due to the low oxygen content in the gas phase, the heat exchange front in this reactor advances much faster than the reaction front ($u_r/u_e < 1$), which makes reactor B perform as shown in Fig. 7. Under these circumstances, the inlet temperature ($T_{g,in}$) needs to be preferably low (approximately 150°C) in order to moderate T_{max} , as indicated in Eq. (13).

As mentioned above, while the heat exchange front is still inside the reactor, the flue gas temperature matches T_{s0} . Only when this front reaches the exit, is the gas product discharged at T_{max} . Although the average gas temperature ($T_{g,out ave}$) of stream 22 can be calculated from Eq. (15), it is vital in order to maximize the global efficiency of the process, to know the proportion of exhaust gas at T_{s0} and at T_{max} during the breakthrough period. Thus, a valve setup can be used to guide the gas corresponding to stream 23 towards the turbine during the period of time in which the product gas is emitted at T_{max} . The rest of the exhaust gas (stream 25) is then recirculated and mixed with stream 27, as can be seen in Fig. 3.

In order to maximize the power generation in the gas turbine, a topping cycle system may also be introduced by burning part of the H_2 produced in stage A (stream 52 in Fig. 3) or additional CH_4 (stream 51 in Fig. 3), so that the input temperature of the gas stream reaches around $1500^\circ C$. It is clear that, by increasing the temperature of 23, there will be a lower consumption of fuel (H_2 from reactor A or additional natural gas) and hence the overall energy and CO_2 capture efficiencies will rise.

On the other hand, since the reaction front lags behind the heat transfer front during the oxidation of Cu, the converted solids in reactor B will remain at $T_{g,in}$. This temperature will be too low ($150^\circ C$ in the case study of Table 1) to initiate the next reaction stage C in which the reduction of CuO to Cu and the decomposition of $CaCO_3$ must take place. For this reason, an additional heat exchange step, (B' in Fig. 3), is included in the process in order to transfer the excess heat from the recycled gas to the fixed-bed reactor, which is depleted of Cu as a result of step B, thus raising the temperature of the solids to a suitable temperature (around $830^\circ C$) for the reduction of CuO in stage C.

By changing the nitrogen recirculation ratio (R_N), the proportion of exhaust gas at T_{s0} and T_{max} can be greatly modified. With a higher R_N , the u_r/u_e ratio is reduced and the distance between both fronts increases because of the low O_2 content in stream 21 (X_{O_2}). Under these conditions, the amount of flue gas at T_{max} (830°C) will rise, making it possible to heat a larger part of the reactor up to a temperature that leaves the solids in favorable conditions for the reduction/calcination stage (C). When more than the 93% of stream 22 is recycled ($R_N > 0.93$), the O_2 in stream 21 is diluted to 1.7%. Under these working conditions, approximately 38% of the exhaust gas leaves reactor B at T_{max} , which allows the depleted bed to be heated up completely during stage B'. However, under these circumstances, the energy efficiency of the overall process may fall significantly, because of the need for a greater recirculation of gas flow. The most favorable conditions exist when the recirculation ratio is around 0.85, which corresponds with the data in Table 1. In this case, the sensible heat contained in stream 25 is unable to heat the entire bed of solids up to T_{max} and therefore the reactor is left, at the end of stage B', divided into two zones with different temperatures (26% at 830°C and 74% at 733°C). In any case, an additional heat exchanger is required downstream of reactor B' in order to remove the excess of sensible heat in stream 25', before it is allowed to mix with stream 27 and is subsequently fed back to reactor B (see Fig. 3).

4.3. CuO reduction and CaCO₃ calcination reaction (steps C and C')

In this final step of one full cycle, it is necessary to attain the total decomposition of the CaCO₃ and leave the bed of solids at a suitable temperature for the sorption enhanced reforming to be able to operate in a multicycle operation. In order to shift the equilibrium of Eq. (3) to form CO₂ it is necessary to reduce the pressure in the reactors to a low pressure (atmospheric pressure in the case study of Table 1). A valve system

(equivalent to the technology used in the pressure swing adsorption process) is required to reduce the working pressure in reactor C from 35 atm to atmospheric pressure. Once the bed has been depressurized, a reducing gas, such as H₂, CO and/or methane (stream 31) will be fed in to allow the exothermic reduction of CuO and the calcination of CaCO₃.

At atmospheric pressure, even allowing for larger gas velocities through the fixed bed reactor (10 m/s in the case study of Table 1) the mass flow rates of the gas reactants are much lower than in the previous stages. The u_r/u_e ratio can be calculated from Eq. (20), where X_{red} is the molar fraction of the reducing gas in stream 31 and X_{CuO} is the molar fraction of CuO in the solids bed before reduction commences.

$$\frac{u_r}{u_e} = \frac{b \cdot X_{red} \cdot M_s \cdot c_{ps}}{X_{CuO} \cdot M_g \cdot c_{pg}} = 8.90 \quad (20)$$

Stream 31 must contain just a low proportion of steam in order to avoid the reforming of the CH₄ that is fed into reactor C. With low values of S/C, the $u_r/u_e \gg 1$ (8.90 in the case study of Table 1), and therefore, the heat exchange front will move much more slowly behind the reaction front, Fig. 8. Once the sorbent has been regenerated and stage C is completed, most of the solids left in the reactor will be at temperatures over 850°C, which would not be suitable (as it would be too high) for the reforming step A that must follow the regeneration step C. For this reason, we propose in this work an additional steam methane reforming (SMR), step C' in Fig. 3, that allows the solid bed to cool down to an appropriate temperature for the SER (step A). Furthermore, the product gas of reactor C' (stream 34), that contains a large amount of H₂ and CO, can be fed into reactor C in order to reduce the Cu/CaO molar ratio to a value suitable for the overall process. The high temperature of stream 34 also leads to

faster kinetics which favours the reduction of CuO to Cu and also accelerates the calcination of the CaCO₃ present in reactor C.

The operating temperature of reactor C must rise to over 850°C in order to favor the rapid decomposition of CaCO₃ to CaO and CO₂. Higher calcination temperatures entail a higher supply of Cu to the overall process and CH₄ to stage C', as shown in Fig. 13. Moreover, temperatures greater than 900°C may cause CaO deactivation via sinterization and unwanted reactions of Cu (Mattison et al., 2003; de Diego et al., 2004; Chuang et al., 2008). A maximum temperature of 870°C for reactor C is envisaged as a reasonable trade-off.

In addition to the reasons given above, the S/C molar ratio fed into reactor C' (stream 33) must be low (around 1) in order to drastically reduce the formation of CO₂ during the steam methane reforming and to avoid the partial carbonation of the CaO present in reactor C' when the temperature of the solids is approaching to 650°C behind the reaction front. At these working conditions, almost total CH₄ conversion is achieved (95%) in the reaction front and the flue gas (stream 34) contains the highest concentration of H₂ and CO (73% and 24% respectively), as shown in Fig. 14 (left). This reduces the amount of Cu needed to regenerate the sorbent, which in turn requires less CH₄ to accomplish step C'.

As the reaction front moves forward in reactor C' at 870°C, the solids are left behind the reaction front at a lower temperature thanks to the endothermic SMR reaction and the heat exchange between the solids and the incoming gas at 650°C. SMR kinetics are not favored at this temperature (Fig. 11). Hence it can be assumed that steam reforming only takes place in the vicinity of the reaction front. The composition of stream 31 is given by the SMR equilibrium at 870°C and it is considered constant during the

operation. Even if the reforming reaction took place at lower temperatures, the composition of stream 31 would hardly change. When the SMR is accomplished at a S/C ratio of around 1, equilibrium compositions barely change even over a wide range of temperatures, as indicated in Fig. 14 (right).

At the end of stage C', the entire bed-reactor has been cooled down to 650°C. This temperature allows a new cycle of SER to commence in conditions that are optimal for hydrogen generation and CO₂ capture.

In a continuous industrial process, all the reaction stages described above must be accomplished in a system of adiabatic packed beds operating in a cycling manner by switching the feeds between the reactors. Multiple beds are necessary in order to produce a continuous stream of hydrogen and CO₂. With the reactor dimensions and the reference flow of 10 kg CH₄/s adopted for the case study in Table 1 and Table 2, it can be estimated that a minimum of 13 reactors operating in parallel would make a continuous looping operation feasible. Fig. 15 shows an example of a pressure and temperature swing cycle, similar to other recently published configurations for novel processes for producing hydrogen with CO₂ capture (Manzolini et al., 2011; Wright et al., 2011).

The relative duration of each step has been calculated with the help of the data from Table 1. A theoretical cycle time for step A in these conditions, for a single reactor with the dimensions and composition presented in Table 2 would be 5.5 minutes. A theoretical minimum time for the completion of one cycle would be 67 minutes (12.2 times the reaction time of step A). In order to make discrete reaction steps in each reactor, without any overlapping between the different reaction stages, it is necessary to increase slightly the reaction time allowed for the remaining steps or reduce slightly the

gas velocity in each step other than A. Therefore, the minimum ideal number of reactors to complete all the reaction and heat exchanging steps involved in the process is 13, as can be seen in Fig. 15. In view of these results, it is clear that one of the objectives when designing the system would be to keep steps B and B' as short as possible, since this would enable the size of the overall system for a given flow of natural gas to be kept to a minimum. This highlights the need for materials with a very high reactivity and a large amount of active components (i. e. Ca and Cu). The need for an inert support to sustain CaO and Cu, or a third solid with catalytic properties for the reforming reactions, must be kept to the minimum allowed by the sorbent preparation method, in order to minimize the demand for additional heat in the calcination step and to reduce the thermal ballast effect of the solids that would prolong the B and B' steps.

The hydrogen production efficiency of the system described in Fig. 3 and Table 1 is 0.725 defined as the LHV of the hydrogen coming out from reactor A divided by the LHV of the total CH₄ fed into reactors A and C (0.625 discounting the fraction of H₂ produced in step A that is used to increase the turbine inlet temperature). The comparison is favourable with the H₂ efficiency in steam reforming processes without capture, which is around of 0.71 (Ochoa-Fernandez et al., 2007). CO₂ capture efficiency in these conditions (total flow of CO₂ coming from step C divided by total flow of CH₄ entering the system) is 0.875. The carbon losses in the system are to be found in the unconverted methane and in the CO formed in the reforming step (7.9 points), in the calcination of CaCO₃ in the Cu oxidation step (2.3 points) and in the CO₂ emitted from the combustion of the gas used to increase the inlet temperature of the gas fed into the turbine (2.3 points).

The process described in this work is at a very early stage of development and it is not yet possible to propose a detailed and complete heat integration scheme which would permit more detailed energy efficiency and CO₂ capture efficiency estimations. Further investigation is needed to develop and test suitable materials, to derive specific rate expressions and operation limits for these materials, to experimentally validate the performance of the reactors, improve reactor models and optimize the duration of the cycles. However, as in the case of other similar chemical looping processes, the absence of process steps with a heavy energy penalty (apart from the steam requirements characteristic of conventional reforming processes and the requirements imposed by the purification and compression of CO₂ as in other CO₂ capture processes) is an indication that a high level of energy efficiency can be expected from this novel system.

4. Conclusions

A strong synergy has been demonstrated between sorption enhanced reforming (SER) processes for H₂ production using a CaO/CaCO₃ chemical loop and a second chemical loop of Cu/CuO added to solve the problem of the endothermic calcination of the CaCO₃ formed in the H₂ production step. The reduction of CuO with natural gas, CO or H₂ has been shown to provide the necessary heat for calcination, generating a stream rich in CO₂ for disposal. The basic reaction models formulated in this work to describe the overall process have yielded very promising results by exploiting the high reaction rates and heat transfer characteristics of similar high temperature reactors systems reported in the literature. Narrow and precise operating windows have been defined, in which the reactors perform close to thermally neutral conditions with minimum energy penalties and under conditions that are reported to be feasible for the functional materials required to operate the reactors. The hydrogen production efficiency is 0.625

and the overall CO₂ capture efficiency is about 0.875 when CH₄ is the only fuel used in the reactors. These results confirm the potential of the proposed process and the need for further research to bring it to completion.

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Nomenclature

a	stoichiometric coefficient for gas A
A	transverse area of bed reactor, m ²
b	stoichiometric coefficient for solid B
c_{pi}	specific heat capacity of component i, kJ/kmol K
h_{fs}	fluid-solid heat transfer coefficient, kJ/m ² s K
m_i	mass flow of component i, kg/s
M_i	molecular weight of component i, kg/kmol
n_i	molar flow of component i, mol/s
P	pressure, atm
R_N	recirculation ratio, dimensionless
t	time, s
$T_{g,in}$	inlet gas temperature, K
$T_{g,out}$	exit gas temperature, K
$T_{g,out ave}$	average exhaust gas temperature, K
T_{max}	maximum temperature, K
T_{s0}	initial temperature of bed reactor, K

u_e	heat exchange front velocity, m/s
u_g	gas velocity, m/s
u_r	reaction front velocity, m/s
X_i	molar fraction of component i, dimensionless
Greek letters	
ρ_i	density of component i, mol/m ³
ΔH_r	enthalpy of the reaction, kJ/mol
$\Delta T_{\max}$	maximum adiabatic temperature increase, K

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Figure captions

Fig. 1 - General scheme of the Cu/Ca three step chemical loop.

Fig. 2 - Different pellet structures for the Ca/Cu chemical looping process.

Fig. 3 - Illustration of the Ca/Cu chemical loop for power generation employing CH_4 as energy source.

Fig. 4 - Effect of the pressure and temperature in hydrogen production (left) and methane conversion (right) on the steam methane reforming (SMR) and sorption enhanced reforming (SER) equilibriums; (S/C=5).

Fig. 5 - Effect of P on the optimum temperature in SER; (S/C=5) (left) and equilibrium compositions in SER as a function of T; (P=35 atm, S/C=5) (right).

Fig. 6 - General description of temperature profiles and reaction/ heat exchange fronts in solid-gas reactions in a fixed-bed where an exothermic reaction, as described in Eq. (9), is taking place.

Fig. 7 - Evolution of temperature profile and the reaction and heat exchange fronts for an exothermic reaction in a fixed-bed reactor with uniform T_{s0} (above) and with different initial temperatures (below) when $u_r/u_e < 1$. (E: heat exchange front, R: reaction front).

Fig. 8 - Evolution of the temperature profile and the reaction and heat exchange fronts for an exothermic reaction in a fixed-bed reactor with uniform T_{s0} (above) and with different initial temperatures (below) when $u_r/u_e > 1$. (E: heat exchange front, R: reaction front).

Fig. 9 - Effect of the S/C molar ratio and temperature on H₂ purity and methane conversion (P=35 atm).

Fig. 10 - Effect of $T_{g, in}$ on T_{max} in the SER stage and on the Cu/CaO molar required for the entire process; (S/C=5).

Fig. 11 - Effect of temperature on the kinetics of steam methane reforming: k_1 for Eq. (1) and k_2 for Eq. (2).

Fig. 12 - Influence of $T_{\max}$ on the dilution of O_2 in the incoming gas (stage B).

Fig. 13 - Effect of the calcination temperature on the Cu/CaO molar ratio required and on the distribution of the CH₄ fed into the process.

Fig. 14 - Equilibrium compositions at atmospheric pressure in SMR as a function of the S/C molar ratio (left) and as a function of the temperature (S/C=1) (right).

Fig. 15 – Ideal operational diagram of the Ca/Cu chemical loop process for hydrogen and power generation (step A = 5.5 min duration, with 13 steps for each full cycle).

Reactor Number	1	A	B				B'			C	C'
	2	C'	A	B				B'		C	
	3	C	C'	A	B				B'		C
	4	C		C'	A	B				B'	
	5	B'	C		C'	A	B				B'
	6	B'		C	C'	A	B				B'
	7	B'			C	C'	A	B			B'
	8	B'				C	C'	A	B		
	9	B	B'				C	C'	A	B	
	10	B		B'			C	C'	A	B	
	11	B			B'			C	C'	A	B
	12	B				B'			C	C'	A B
	13	B				B'			C	C'	A

Table 1 - Temperature, pressure and composition of reactors and mass streams in Figure 1 (T*: average temperature).

BED REACTORS		Stage A		Stage B		Stage B'		Stage C		Stage C'							
Initial Temperature (°C)		650		600/733		150		733/830		870							
Final Temperature (°C)		600/733		150		733/830		870		650							
Maximum Temperature (°C)		733		830		830		870		870							
Pressure (atm)		35		35		35		1		1							
Superficial velocity (m/s)		2		2		2		10		10							
Duration (min)		5.5		23.5		19.5		10.5		8							
<u>Initial Composition (% w)</u>																	
CaO (active)		16.6		2.0		2.0		2.3		2.3							
CaO (inert)		24.9		22.3		22.3		20.9		20.9							
CaCO ₃		-		23.1		23.1		20.7		20.7							
Al ₂ O ₃		25.2		22.7		22.7		21.2		21.2							
Cu		33.3		29.9		29.9		-		-							
CuO		-		-		-		34.9		34.9							
GAS STREAMS		Stage A		Stage B		Stage B'		Stage C		Stage C'		Air compressor			Gas turbine		
		11	12	21	22	25	25'	31	32	33	34	41	27	42	23	52	35
Temperature (°C)		600	650	150	751*	748*	324*	870	830	650	870	20	150	150	1500	650	150
Pressure (atm)		35	35	35	35	35	35	1	1	1	1	1	35	35	35	35	35
Molar flow (kmol/s)		3.75	4.31	14.53	14.00	11.9	11.9	1.08	1.63	0.57	1.11	3.46	2.63	0.83	3.44	0.58	0.03
<u>Composition (% v)</u>																	
H ₂ O		83.3	47.0	-	-	-	-	1.0	51.0	50.0	1.0	-	-	-	18.0	47.0	1.0
O ₂		-	-	3.8	-	-	-	-	-	-	-	21.0	21.0	21.0	-	-	-
CO ₂		-	0.2	0.8	1.0	1.0	1.0	0.3	49.0	-	0.3	-	-	-	1.2	0.2	0.3
N ₂		-	-	95.4	99.0	99.0	99.0	-	-	-	-	79.0	79.0	79.0	80.8	-	-
CH ₄		16.7	1.7	-	-	-	-	1.3	-	50.0	1.3	-	-	-	-	1.7	1.3
H ₂		-	51.1	-	-	-	-	73.3	-	-	73.3	-	-	-	-	51.1	73.3
CO		-	-	-	-	-	-	24.1	-	-	24.1	-	-	-	-	-	24.1

Table 2 - CaO/Cu-based material compositions and reactor properties.

<u>CO₂ SORBENT</u>	<u>(% w)</u>
CaO	85
Binder	15
CO ₂ carrying capacity	35
<u>Cu-BASED MATERIAL</u>	<u>(% w)</u>
Cu	65
Binder	35
<u>REACTORS</u>	
Pellet equivalent diameter (m)	0.022
Reactor length (m)	7
Reactor diameter (m)	0.3
Bed Porosity (-)	0.5