Optimized design and operation strategy of a Ca-Cu chemical looping process for hydrogen production

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Abstract

This work describes the performance of an improved Ca-Cu looping process to produce H₂ and/or power from natural gas while generating a CO₂ suitable for its reuse and/or permanent storage. The core of the process relies on an arrangement of fixed-bed reactors performing adiabatically. A sequence of five stages: sorption enhanced reforming (SER), Cu oxidation, solid/gas heat exchange, CuO reduction/CaCO₃ calcination and steam methane reforming (SMR) is used. A continuous flow rate of O₂-depleted gas is produced at sufficiently high pressure and high temperature to efficiently drive a gas turbine for the generation of power. The optimization of the process carried out in this work allows the number of reactors to be reduced to five. The energy requirements for the reduction/calcination step can be reduced, thanks to the use of the PSA off-gas resulting from the H₂ purification step and the syngas generated in a SMR stage. This also allows a reduction in the Cu/Ca molar ratio of bed composition to a value around 2. A dynamic reactor model partially validated in a previous work has been used to simulate in detail a complete cycle of the Ca-Cu looping process under large scale conditions. Simulations indicate that the advance of the reaction and heat exchange fronts can be regulated by means of the partial recirculation of the product gases. A process design for a base case with a reference output of 30,000 Nm³/h of pure H₂ (88.5 MW_{th}), which is the typical production of fired tubular reformers installed in refineries, shows that reactors of 6 m long and 2.9 m of inner diameter could be sufficient to carry out the overall process, assuming a cycle duration of 15 minutes and a maximum pressure drop per stage of 10% (referred to the inlet pressure). A hydrogen production efficiency of 76% is achievable, which is 5 net points above the efficiency of benchmarks based on fired tubular reformers that use amines (MDEA) to remove the CO₂. A CO₂ capture efficiency of about 96% is obtained, which is 11 net points higher than those typically estimated in reference H₂ plants that use MDEA absorption.

1. Introduction

Carbon capture and storage (CCS) remains as a promising alternative to drastically reduce CO₂ emissions from industries using fossil fuels or biomass [1]. Precombustion capture systems retain great theoretical advantages for new CCS systems in power and industry, as H₂ offers the flexibility and energy density of fossil fuels with a potential low carbon footprint [2, 3]. Nowadays, hydrogen is almost entirely used as feedstock in refining and chemical industries, but the demand of H₂ is expected to rise in coming years because of the increase in its application in hydrocracking and hydroprocessing processes, metallurgy, glass production and also in most recent applications, such as

fuel for gas turbines, fuel cells and combustion engines [4]. Steam methane reforming (SMR) is the dominant H_2 production technology at commercial scale [4]. SMR involves the endothermic conversion of methane and steam into H_2 and CO, typically performed inside fired tubular reformers (FTR), where natural gas is fired in external burners to supply the necessary thermal power. The process requires high pressures (up to 35 bar) and high temperatures (between 800 and 900 °C) to overcome the thermodynamic constraints of reforming reaction and thus reach high H_2 yield [5]. Steam reforming is a highly efficient process (compared to other alternatives such as the partial oxidation, the autothermal reforming or coal gasification), but it requires a complex arrangement composed of several stages carried out in different conditions and using different catalysts in order to improve the fuel conversion to H_2 [4, 5].

The combination of reforming reaction with CO_2 separation to produce hydrogen in a single stage is gaining in importance in recent years, because higher hydrogen yields are achievable with a simplified process [6-9]. In the Sorption Enhanced Reforming (SER), the use of a calcium-based material in combination with a reforming catalyst allows the CO_2 to be removed from the gas phase as soon as it is produced, forming $CaCO_3$ [10]. The CO_2 sorption reaction (i. e. the CaO carbonation) is exothermic and supplies “in situ” the heat required to carry out the endothermic reforming reaction. Moreover, the steam reforming and the WGS reactions are both shifted towards H_2 formation, with the result that very high conversions of methane to H_2 can be achieved in one single stage under moderate temperatures (600-700 °C) [11]. The SER allows a product gas with almost pure H_2 (higher than 90 vol.% on a dry basis) to be obtained directly from the reformer, which simplifies the downstream purification procedure. Shift catalysts are not required and the operation at a lower temperature favours the use of cheaper materials [12, 13]. However, the CO_2 -sorbent needs to be continuously regenerated to carry out a multicycle operation. The calcination of $CaCO_3$ is an endothermic reaction that demands temperatures around 900 °C in pure CO_2 at 1 atm. Therefore, the main challenge for the development of the SER technology at a large scale lies in finding a process scheme that allows the heat transfer required for the calcination of $CaCO_3$ in rich CO_2 atmospheres. Various alternatives have been proposed in the literature. These mainly include the oxy-combustion of additional fuel in the regenerator [14-16], the external heating through high temperature heat transfer surfaces [17-19] or the heating by direct contact with hot solids from an air-blown combustion chamber [20, 21]. Another recent alternative for indirect calcination of $CaCO_3$ is the use of chemical looping combustion (CLC) systems. In the CLC, oxygen is transferred from air to the fuel by means of an oxygen carrier (typically a metal oxide) [22-25]. This avoids the dilution of the combustion products with nitrogen and generates a product gas highly concentrated in CO_2 . General Electric initially proposed the “unmixed reforming” concept to calcine $CaCO_3$ in a reactor where the oxidation of nickel with air was simultaneously taking place [26]. The coupling of both endothermic and exothermic reactions in one single stage allows for higher integration as the heat is directly transferred from the oxygen carrier to the calcium carbonate without the need for intermediate heat exchange devices. However, this system generates CO_2 highly diluted

by N_2 , which makes the capture of CO_2 unfeasible without additional steps. More recent CLC configurations have been envisaged to accomplish the $CaCO_3$ calcination with inherent CO_2 capture making use of the large heat-transfer capacity of NiO [27] or of iron oxides [28] that come from an oxidation stage at temperatures above 1000 °C.

We recently described a novel Ca-Cu chemical looping process [29] to produce H_2 on the basis of the SER concept, which incorporates a Cu/CuO chemical loop to generate the heat needed for the $CaCO_3$ calcination. The critical difference with other previous looping concept with similar objective is that in this case the heat supply for calcination does not come from an oxidation step of the oxygen carrier, but comes from the exothermic reduction of CuO with gaseous fuels, generating a highly concentrated stream of CO_2 and $H_2O(v)$. The basic Ca-Cu looping process consists of a sequence of three reaction steps (see Fig. 1), which are adiabatically carried out in fixed-bed reactors operating in parallel. In the first stage, an enriched stream of H_2 is produced by the sorption enhanced reforming (SER) of methane in the presence of a reforming catalyst, a CaO-based sorbent and a copper-based solid (that acts as inert in this stage). This takes place at 600-750 °C, steam-to-carbon molar ratios between 2.5 and 5, and pressures between 10 and 35 bar in order to achieve high H_2 production yields with high CO_2 capture efficiencies [30]. In the next step, the copper-based particles are oxidized with diluted air at a high pressure. A low content of oxygen in the feed moderates the increase in temperature during the oxidation of Cu to CuO, thereby avoiding the decomposition of $CaCO_3$ by partial calcination [31]. In the following reaction stage, the calcination of the $CaCO_3$ formed during the SER is accomplished by means of the simultaneous reduction of CuO with a gaseous fuel at atmospheric pressure. A suitable CuO/ $CaCO_3$ molar ratio in bed composition has to be selected to ensure that the heat released during CuO reduction is sufficient to completely decompose the $CaCO_3$ without any external energy supply [32-34].

Fig. 1. Illustration of a process for hydrogen production using the Ca-Cu chemical looping reaction concept.

In recent years, high-performance materials with direct application to the Ca-Cu looping process have been developed for other applications. Thus, novel CaO-based solids with stable CO_2 sorption capacity higher than 30 wt.% of active content have been obtained by using different synthesis routes [35-38]. Copper-based oxygen carriers with very

high active content (higher than 60 wt.%) [39, 40] have been proven to be resistant to agglomeration and deactivation in long duration cyclic tests. Even mixed materials that combine in the same solid matrix CaO/CuO [41, 42] and reforming catalyst/CaO [43, 44] have shown very promising results. From the point of view of reactor design and operation, a very substantial progress has taken place recently in the CLC field in packed beds [45-57] that is most relevant for the novel Ca-Cu process. Fixed beds for CLC systems undergo very energy intensive reactions in relatively narrow reaction fronts, which require an adequate heat management strategy in order to approach the complete conversion of the solids and avoid hot spots during the operation. Several works have been recently published, in which dynamic reactor models are developed to study the transient behaviour of these systems and identify suitable operational windows [47, 50-57]. Previous work under an European FP7 project, DEMOCLOCK [58], have demonstrated experimentally some of these strategies in an pseudo-adiabatic pilot reactor that can reach a temperature and pressure of 1200 °C and 10 bar, respectively. In a more recent FP7 project, ASCENT [59], we have also demonstrated experimentally the viability of the critical reduction/calcination stage at a laboratory scale under pseudo-adiabatic conditions [60]. From a process perspective, simulations integrating of the Ca-Cu looping process to power systems [61-63] have shown that high CO₂ capture efficiencies are achievable with moderate efficiency penalties respect to NGCC systems without capture. The application of the Ca-Cu chemical loop in post-combustion capture systems has also been assessed by some authors [64, 65], although there is a fundamental limitation that makes them less viable: the use of natural gas in any combustion system at atmospheric pressure introduces a large inherent penalty when compared to benchmarks at high pressure (i.e. NGCC). Despite the progress outlined above, several difficulties are known to exist for a future scale up of the Ca-Cu technology and, by extension, of other technologies relying on the operation of switching fixed beds operating at very high temperatures unlike commercial PSA systems. The need for high-temperature valves is usually pointed out as a common obstacle for these technologies, although water cooled equipment and/or special ceramic materials are close to commercial scale in other applications [66] very demanding in temperatures and pressures.

In the present work, we propose an optimized process of the Ca-Cu looping concept that leads to a more compact configuration, with just five reactors to carry out the complete process, while our original scheme contained 15 reactors [61] of lower size volume but requiring an excessive number of high-temperature valves. More fundamental problems at material and reactor level also exist: the mechanical properties of materials inside the reactor may deteriorate under sharp changes in temperatures and/or reaction fronts. In particular, it has been already pointed out that hydration of CaO at the conditions in the SER reactor may lead to severe breaking of the pellets due to the swelling associated to Ca(OH)₂ formation [61, 63]. To avoid this phenomenon, we have chosen in this work to operate the SER stage at relatively low steam-to-carbon (S/C) molar ratio and pressure, as explained below. Finally, a more accurate estimation of temperature profiles is required to prevent temperature excursions and hot spots in the bed. This problem is

tackled using a more elaborated reactor model, similar to those applied in CLC applications [47, 50, 57] and that has been partially validated against experimental data from a small pilot reactor [60] during the reduction/calcination stage. A full simulation of the dynamic behaviour of the large scale fixed beds during a complete cycle of the novel Ca-Cu looping process is carried out in this work, assuming that the initial conditions of each reaction stage are the result of the previous stage. The selection of appropriate operating conditions and the heat management strategies adopted for each stage of the process are also discussed.

2. Process description and optimized reactor design

Fig. 2 shows a simplified scheme of the process under consideration in this work, including elements already described in [61] together with a series of important changes to achieve the objectives set up above. In the SER stage, the following global reaction takes place, resulting from simultaneous reactions of steam reforming, water gas shift and carbonation:

Fig. 2. Illustration of the modified Ca-Cu looping process in an arrangement of fixed beds for H₂ production (RF and HF are referred to reaction front and heat exchange front, respectively).

The production of H₂ by the SER of methane is favoured at low pressures because of the increase in the number of gas moles in Eq. (1). However, it is usually required to operate at high pressure to favour the efficient use of H₂ downstream in the chemical industry and power generation [10]. Attending to SER equilibrium (see Fig. 3), the use of high temperatures in SER operation would allow higher conversions of CH₄ to be obtained, but temperatures above 750 °C would make the CO₂ capture by CaO carbonation less effective and a lower amount of H₂ would be produced. On the other

hand, a high value of S/C molar ratio of 5 in the feed promotes H_2 production (up to 95 vol.% of H_2 on a dry basis in the outlet gas) even for the relatively high operating pressure of 20 bar. The reduction of steam in the feed to reach a S/C molar ratio of 3, while maintaining the pressure at 20 bar, would reduce the CH_4 conversion to around 72%, with the result that the H_2 content in the product gas would be reduced to 90 vol.% (see Fig. 3). However, with a lower operating pressure of 10 bar, it is possible to reach a H_2 content in the product gas higher than 93 vol.% (on a dry basis) with a S/C of 3 (see Fig. 3).

On the other hand, as it has been mentioned above, a potentially serious problem for any SER system is that CaO hydration may occur at high temperatures and partial pressures of water vapour [61, 63]. Although the hydration of calcium oxide can increase the CO_2 sorption capacity of CaO-based sorbents in calcium looping systems [67, 68], several studies with Ca-based materials carried out at high temperatures and high pressures revealed the formation of melts that could cause agglomeration [69, 70]. Moreover, the increase in carbonation conversion after hydration disappears when the sorbent performs at temperatures higher than 700 °C [71]. Therefore a S/C molar ratio of 3, a temperature at around 700 °C and 10 bar of total pressure in the SER reactor seems a good compromise to avoid CaO hydration [72] and lead to a product gas (stream 3 in Fig. 2) with a H_2 content higher than 90 vol.% (on a dry basis) and negligible amounts of CO and CO_2 (see Fig. 3). These are the target conditions adopted in this work for the reactor simulation described later. The product gas from SER can be then cooled down and enter a pressure swing adsorption (PSA) unit at ambient temperature, that delivers virtually pure H_2 (stream 4 in Fig. 2). The resulting PSA off-gas, which mainly contains unconverted CH_4 , CO and H_2 , can partially recirculated to the SER stage (stream 5 in Fig. 2) or used as a fuel input to the CuO reduction and $CaCO_3$ calcination stage.

Fig. 3. Effect of temperature, pressure and steam-to-carbon molar ratio on SER equilibrium.

The Cu oxidation stage runs at high pressure, as described in previous works [61], to enable the O_2 -depleted air obtained at the reactor exit to be expanded in a gas turbine. A pressure of 20 bar for this stage is a reasonable compromise, and this value will be used in the simulation of the oxidation reactor in the reference case below. The Cu oxidation front must advance sufficiently separated from the resulting heat exchange front in order

to accomplish the bed oxidation avoiding excessively high temperatures. The maximum temperature achieved during the Cu oxidation must be kept below 900°C to minimize the carbon losses by partial CO₂-sorbent calcination, the side reactions of the copper-based material and the loss of activity of the calcium oxide. The temperature profiles can be moderated by reducing the temperature of the inlet gas and the concentration of O₂. The dilution of oxygen in the feed is achieved by recirculating a large fraction of the product gas (stream 8 in Fig. 2). When the operation is carried out at these conditions, the Cu oxidation front (RF in Fig. 2) advances along the bed much slower than the resulting heat exchange front (HF in Fig. 2) [31]. As a result, when the Cu-based solids are completely oxidized, the bed is left at the temperature of the feed (around 300°C to moderate the maximum temperature achieved), which is too low to initiate the following reduction/calcination step. Therefore, a heat-exchange step is then needed to transfer the excess of heat in the bed at the end of the oxidation stage to the bed just before the beginning of the reduction step. A minor improvement on this step is introduced in this work respect to alternative process schemes [29, 61], that consist in the recirculation of the gas fraction at the highest temperature (stream 10) to heat the solids bed. This reduces the mass flow rate to be fed to this stage. A blower located downstream the cooling unit is also needed to compensate the pressure drop in the gas after the Cu oxidation and heat exchange stages. For the reduction/calcination stage, the pressure must be reduced to atmospheric level to favour the complete calcination of the sorbent at a temperature around 900°C. The composition of the reducing gas strongly affects the Cu/Ca ratio required to reach the complete conversion of the solids without the need for an external energy supply. A Cu/Ca molar ratio of 3.1 would be required if pure CH₄ were used as reducing gas because of the relatively low reduction enthalpy of CuO with CH₄. However, the use of the PSA off-gas resulting from the H₂ purification step and the syngas generated in a subsequent steam reforming (SMR) stage (both with high contents of H₂ and CO) allows the Cu/Ca molar ratio needed to be lowered down to 2. Once the solids in the reduction/calcination stage are converted, most of the bed will be left at around 900°C, which hinders a suitable performance of a new SER stage. Previous works on Ca-Cu looping process [29, 61] proposed the introduction of a SMR stage to use the excess of sensible heat stored in the bed to provide a H₂/CO-rich syngas of direct use for the reduction of CuO and bring the temperature of the bed closer to the initial target for the SER stage (around 600°C). A steam-to-carbon molar ratio of 1.5 in the SMR stage will diminish the production of CO₂ during the operation, which will minimize carbonation of the CO₂-sorbent present in the reactor [29].

The detailed simulation of the reactors in each stage of the process, as conducted in the next section, requires the definition of material properties and a reference set of reactor dimension and other conditions to achieve a certain design target. For the purpose of more detailed reactor simulations of each stage, a base case with a reference output flow of 30,000 Nm³/h of pure H₂ is examined. This value corresponds to the typical H₂ production of plants based on fired tubular reformers (FTR) installed in refineries [73, 74]. A H₂ recovery efficiency of 90% is assumed in the PSA unit, which is consistent with the usual performance of PSA units in SMR processes [75]. Regarding material

characteristics, a CaO-based sorbent with 35 wt.% of active phase, a copper-based oxygen carrier with 60 wt% of active CuO and a reforming catalyst with 10 wt.% of Ni are assumed, which are reasonable values compared to those reported in the wide literature on calcium looping [35-38], chemical looping combustion [39, 40, 76] and steam reforming [77], respectively. A uniform particle size for the solids of 0.01 m has been selected for pressure drop and kinetic calculations. In these conditions, mass transfer resistances at particle level are modelled with an effectiveness factor of 0.5 [78, 79, 80]. A Ca-based sorbent/catalyst ratio of 3.5 has been chosen in bed composition to ensure a production of H₂ close to that given by SER equilibrium [30, 81]. A Cu/Ca molar ratio of 2 in solids composition is assumed in order to achieve neutral conditions during the reduction/calcination stage.

Regarding reactor characteristics, the geometry of the fixed beds has been determined considering as limiting step the Cu oxidation stage, which is by far the operation that is carried out with the highest gas flow rate due to the necessary dilution of the comburent to avoid hot spots. A first set of initial design conditions for this reactor (to be refined later by the reactor model predictions) come from the overall heat and mass balances of the oxidation step assuming sharp reaction and heat exchange fronts [29]. Assuming a content of active Cu in the bed of 30 wt.%, a concentration of O₂ in the feed of 2.2 vol.% (which means a recirculation ratio of about 91%) is required in the oxidation stage in order to moderate the maximum temperature achieved up to 860°C and minimize the loss of CO₂ by partial CaCO₃ calcination. The geometry of the beds and the gas velocities decided to perform the process must be able to accommodate the resulting flow rates. Assuming a maximum pressure drop of about 10% per stage, a diameter of 3 m is obtained in the reference case. A minimum L/D ratio of about 2 [53] leads to a reactor length of 6 m (resulting at these conditions a total reactor volume of 212 m³), with a duration of 15 minutes required to oxidize this volume of solids. The viability of these assumptions will be demonstrated below when each step is simulated in more detail with the reactor model under the chosen initial conditions. Shorter stage durations (i.e. smaller reactors) could allow the same flow gas fed into the process to be converted in smaller cross-sectional reactor at the expense of higher pressure drops. Alternatively, much lower L/D ratios would demand sharper profiles in the reaction and heat transfer fronts and a relative increase of the fraction of time operating with intermediate purges to remove unconverted species during the transition periods. In the analysis that follows, the duration of these purges is considered negligible in comparison with the 15 minutes needed to carry out every stage of the process. Taking into account the conditions chosen, a total of five fixed beds performing in parallel as in Figure 2 will be shown to be sufficient (see section 4 below) to carry out the full process from CH₄ to H₂ (or power) and CO₂ represented in Figure 4. Table 1 summarizes the input operating conditions discussed for this case study. Table 2 indicates the characteristics (i. e. average or maximum temperature, molar flow rates and molar composition) of the main gas streams of the process obtained from the mass and energy balances assuming sharp reaction and heat exchange fronts and also those obtained from the reactor model described in the next section to all stages.

Table 1. Operating conditions that have been used for the analysis of the reference case assuming sharp reaction and heat exchange fronts.

Conditions	Value
Solids properties	
CaO active content in CO ₂ -sorbent, wt.%	35
CuO active content in O ₂ carrier, wt.%	60
Ni active content in reforming catalyst, wt.%	10
Particle size (d_p), m	0.01
Bed porosity (ϵ)	0.5
SER stage	
CO ₂ -sorbent/catalyst mass ratio	3.5
Inlet bed temperature, °C	600
Pressure, bar	10
S/C molar ratio	3
Feed temperature, °C	700
Inlet molar flow rate, mol/s	563
Cu oxidation stage	
Inlet bed temperature, °C	520
Pressure, bar	20
O ₂ content in the feed, vol.%	2.2
Feed temperature, °C	300
Inlet molar flow rate, mol/s	4533
Solid/gas heat exchange stage	
Inlet bed temperature, °C	300
Pressure, bar	20
Feed temperature, °C	860
Inlet molar flow rate, mol/s	1372
Reduction/calcination stage	
Cu/Ca molar ratio	2
Inlet bed temperature, °C	860/300
Pressure, bar	1
Feed temperature, °C	700
Feed composition, vol.%	58 H ₂ ; 24 CH ₄ ; 10 CO (+CO ₂ +H ₂ O)
Inlet molar flow rate, mol/s	118
Steam methane reforming stage	
Inlet bed temperature, °C	900/700
Pressure, bar	1
Feed temperature, °C	700
S/C molar ratio	1.5
Inlet molar flow rate, mol/s	40

Table 2. Main characteristics of the gas streams of the process obtained from the mass and energy balances assuming sharp reaction and heat exchange fronts together with those obtained from the dynamic reactor model solutions described below (underlined numbers correspond to average values obtained during the duration of each stage of the process; numbers in brackets correspond to maximum values).

Gas streams from the mass and energy balances assuming sharp reaction and heat exchange fronts															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Flow, mol/s	558	563	666.7	372	4.9	496	4533	4484	2707	1372	76	118	40	44	362
T, °C	150	700	<u>670</u> (780)	30	30	25	300	<u>715</u> (860)	<u>640</u> (860)	860	30	700	700	900	<u>695</u> (900)
P, bar	10	10	9.9	9	1.1	1	20	18	18	18	1.1	1.1	1.15	1.1	1.05
Composition (vol.%)															
CH ₄	24.7	24.9	<u>2.7</u> (3.5)	-	43.1	-	-	-	-	-	43.1	23.7	40.0	-	-
CO	-	0.04	<u>3.5</u> (4)	-	4.3	-	-	-	-	-	4.3	9.7	-	18.2	-
H ₂	-	0.4	<u>62</u> (64)	100	50.9	-	-	-	-	-	50.9	58.0	-	61.8	-
CO ₂	-	0.01	<u>1.8</u> (2)	-	1.7	-	1.0	<u>0.7</u> (2.5)	<u>0.6</u> (2.5)	2.5	1.7	5.6	-	11.8	<u>40</u> (52)
H ₂ O	75.9	74.6	<u>30</u> (32)	-	-	-	-	-	-	-	-	3.0	60.0	8.2	<u>60</u> (95)
O ₂	-	-	-	-	-	21.0	2.2	-	-	-	-	-	-	-	-
N ₂	-	-	-	-	-	79.0	96.8	<u>99.3</u> (99.9)	<u>99.4</u> (99.9)	97.5	-	-	-	-	-
Gas streams calculated from the dynamic reactor model															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Flow, mol/s	545	558	656	372	13	479	4370	4295	2584	1280	75	112	40	37	371

T, °C	150	700	<u>658</u> (730)	30	30	25	300	<u>721</u> (860)	<u>654</u> (854)	860	30	700	700	<u>860</u> (900)	<u>691</u> (920)
P, bar	10	10	9.9	9	1.1	1	20	18	18	18	1.1	1.1	1.15	1.1	1.05
Composition (vol.%)															
CH₄	24.1	24.7	<u>5.2</u> (6)	-	47.2	-	-	-	-	-	47.2	31.6	40.0	-	-
CO	-	0.09	<u>1.2</u> (2.8)	-	3.9	-	-	-	-	-	3.9	14.4	-	<u>35</u> (37)	-
H₂	-	1.1	<u>63</u> (65)	100	47.2	-	-	-	-	-	47.2	39.9	-	<u>25</u> (30)	-
CO₂	-	0.04	<u>0.6</u> (1.2)	-	1.6	-	1.0	<u>0.6</u> (1.8)	<u>0.5</u> (1.8)	1.6	1.6	5.4	-	<u>13</u> (25)	<u>38</u> (55)
H₂O	75.9	74.1	<u>30</u> (33)	-	-	-	-	-	-	-	-	9.0	60.0	27.0	<u>62</u> (98)
O₂	-	-	-	-	-	21.0	2.3	-	-	-	-	-	-	-	-
N₂	-	-	-	-	-	79.0	96.7	<u>99.4</u> (99.9)	<u>99.5</u> (99.9)	98.4	-	-	-	-	-

As can be seen in Table 2, the simplified approach assuming sharp fronts gives in general similar results in comparison to those obtained from the application of the more rigorous reactor model to every stage of the process that will be described in next section. Regarding the SER stage, the sharp front model predicts a higher increase in temperature (about 50 °C above the maximum calculated by the dynamic model) in the SER reaction front because of the assumptions of very fast reaction kinetics and a uniform temperature profile in the bed (i. e. 600 °C) at the beginning of the stage. The dynamic reactor model calculates more moderate temperature profiles since it takes into account real kinetics taken from literature, possible diffusional effects, possible axial dispersion and it also considers a non-uniform starting temperature profile, in which more than half of the bed is at temperatures slightly lower than 600 °C (as a result of a previous SMR stage). Under these conditions, the dynamic model predicts a slightly lower conversion of methane and lower selectivity to CO but higher selectivity to H₂ in comparison to the sharp fronts approach. As a result of this, the process simulated with the dynamic model requires a little lower input of methane (see Table 2) to achieve the targeted output flow of hydrogen in the reference case. The dynamic model also predicts more moderate temperature profiles during the oxidation stage. This allows the Cu oxidation to be accomplished with a minimum increase in the concentration of O₂ in the feed (i. e. 2.3 vol.% O₂, which means a slightly lower recirculation of the product gas) maintaining a maximum temperature of 860 °C in the oxidation front. The composition of the syngas (stream 14 in Fig. 2) generated in the steam methane reforming (SMR) stage significantly differs in both models. In the sharp front approach, the composition of the product gas is assumed to be given by the SMR equilibrium at 900 °C. However, the dynamic reactor model predicts a more transient operation in this stage and both outlet temperature and gas composition will change in the course of the SMR step (as it is widely explained in a section below). As a consequence of this, the syngas calculated from the dynamic model and the reducing gas resulting from the mixture of this syngas and the PSA off-gas are enriched in CO but with a lower content of H₂ compared to the compositions predicted by the sharp fronts approach (see Table 2). However, despite the different gas compositions, the reduction enthalpy of the fuel gas obtained from the dynamic model is very similar to that calculated from the simpler model, and therefore, the Cu/Ca molar ratio required in the dynamic model is 2, as it is assumed in the sharp fronts model.

Fig. 4 shows the operational diagram of the proposed Ca-Cu looping process, which is comparable to other arrangements recently proposed for sorption enhanced reforming (SER-SEWGS) [61, 82, 83] and chemical looping combustion [53, 84, 85]. The overall flow diagram proposed comprises common elements to conventional H₂ production plants, such as the cooler downstream the reforming stage (108 in Fig. 4) and the PSA unit (109), and also to combined cycles powered by natural gas (NGCC), such as the gas turbine (105), the air compressor (100) and the heat recovery steam generator (104). Moreover, additional elements are needed to ensure the optimal performance of the system, such as the cooler (112) and the CO₂ compressor (113) typically required in any CCS system, the blowers (107) and (110) needed for the re-compression of the recycled

the fraction that is used to preheat the solids in the reactor (B'), where the heat exchange step is taking place. Moreover, valve (50) is open to introduce the mixture of CH₄ and steam into reactor (C') to carry out the SMR stage. Downstream reactor (C') valve (22) is open to direct the syngas produced in (C') (together with part of the PSA off-gas) to the reactor (C), where the reduction/calcination stage is taking place.

3. Reactor model description

The operation of the five reactors illustrated in Fig. 2 and Fig. 4 has been simulated using a dynamic reactor model able to predict in each stage the evolution with time of the gas and solids conversion and the temperature profiles in the adiabatic reactors for a set of initial conditions. To dynamically simulate the process, the initial conditions of each stage are the result of the previous stage, and therefore, the model requires several iterations to achieve convergence, starting always from a first iteration with the numbers coming from the basic mass and heat balances (see Table 1 and Table 2). An adiabatic and multi-component system has been modelled, adopting the following common assumptions for all reaction stages: adiabatic reactors, ideal gas behavior, plug flow with moderate axial mass and thermal dispersion, negligible radial concentration and radial temperature gradients, absence of intra-particle concentrations and temperature gradients, a constant bed void fraction, uniform particle size and even distribution of all active species in the bed of solids. The equations used for the calculation of the mass and energy balances are listed in Table 3. Table 4 summarizes the literature taken into account in the model for the calculation of axial dispersion, equilibrium conditions and reaction kinetics. A detailed description of the reactor model used in this work can be found elsewhere [30-32]. It must be highlighted that the model has been previously validated against experimental data taken from previous works on SER [86, 88], CLC [50] and the simultaneous CuO reduction/CaCO₃ calcination [60] in fixed beds.

Table 3. Mass and energy balances in a differential control volume in the reactors.

Component mass balances

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_g \frac{\partial C_i}{\partial Z} + \frac{\partial}{\partial Z} \left([D]_{eff} \frac{\partial C_i}{\partial Z} \right) + \eta_i (1 - \varepsilon) r_i$$

Energy balance

$$\left((1 - \varepsilon) \rho_s C_{ps} + \varepsilon \rho_g C_{pg} \right) \frac{\partial T}{\partial t} = -u_g \rho_g C_{pg} \frac{\partial T}{\partial Z} + \left(\frac{\partial}{\partial Z} \left(\lambda_{eff} \frac{\partial T}{\partial Z} \right) \right) - \sum \eta_i (1 - \varepsilon) H_{r,i}$$

Momentum balance

$$dP/dZ = -150 \left(\left[\rho_{1g} u \right]_{1g} (1 - \varepsilon)^{1.2} \right) / \left(\left[d_{1p} \right]^{1.2} \varepsilon^{1.3} \right) + 1.75 \left(\left[\left[\rho_{1g} u \right]_{1g} \right]^{1.2} (1 - \varepsilon) \right) / (d_t$$

The kinetics of steam reforming and water gas shift reactions are modelled on the base of previous works about SER [79-81, 86-89]. The kinetics reported by Xu and Froment [90, 91] were assumed in this work for a typical Ni-based reforming catalyst. The carbonation of calcium oxide is described using the empirical equation obtained by [92], consistent with further studies [93, 94]. The calcination of CaCO_3 is described using the shrinking core model (SCM) under chemical reaction control proposed by [95]. The presence of CO_2 in the equilibrium is calculated using the equation obtained by [96]. For the calculation of the kinetics of Cu oxidation and CuO reduction, it is assumed that it is chemically controlled and follows shrinking core model (SCM) with cylindrical geometry [97]. The amount of Ni as reforming catalyst is small (around 1 wt.% in total bed composition), but its effect has been taken into account in the model (accounting for its oxidation and reduction in the mass and energy balances in each reaction front). A SCM with cylindrical geometry has been also assumed for nickel reactions. The effect of the operation at a high pressure on oxidation kinetics is also incorporated in the model, which was calculated by [97] for different oxygen carriers to fit experimental data.

Table 4. Summary of the literature considered in the dynamic model for the calculation of axial dispersion, equilibrium conditions and reaction kinetics.

	References
Axial mass and heat mass dispersion	[98-102]
$\text{CaCO}_3/\text{CaO}/\text{CO}_2$ equilibrium	[96]
$\text{Ca}(\text{OH})_2/\text{CaO}/\text{H}_2\text{O}$ equilibrium	[103]
Kinetics of SMR and WSG	[90, 91]
Kinetics of carbonation of CaO	[92]
Kinetics of calcination of CaCO_3	[95]
Kinetics of oxidation and reduction reactions	[97]

4. Dynamic behavior of reactors and its consequences for process operation

A simulation of the dynamic behavior of the reactors during each stage of the process represented in Fig. 4 has been carried out using the dynamic model described above. The selection of appropriate operating conditions and heat management strategies adopted to reach the results described for each stage are also discussed in this section.

4.1. Sorption enhanced reforming stage

An input flow of around 130 mol/s of CH_4 is assumed to enter in the SER stage to achieve the targeted production of H_2 . As can be seen in Fig. 2, there is a fraction of the PSA off-gas (stream 5) that is not needed for the reduction/calcination stage, and therefore, it is recirculated at the SER reactor inlet to mix with the fresh supply of CH_4 . As explained above, high S/C molar ratios increase the production of H_2 . However, very high steam partial pressures can lead to CaO hydration unless the SER operation is

carried out at temperatures higher than 750 °C [103]. Although the use of high temperatures in SER operation also favours the conversion of methane, the CO₂ capture efficiency would decrease, as a result of a reduced SER effect. Furthermore, very high starting temperatures in the bed further enhance the temperature profiles between the section of the bed where conventional steam reforming is taking place (because the Ca-based sorbent is already carbonated) and the part of the bed downstream the carbonation front (because the reacting gas arrives at the reaction front partially converted into H₂, CO and CO₂) [63]. The temperature profile at the beginning of the SER stage is the result of the previous steam reforming (SMR) stage. Most of the bed is at a temperature around 600 °C and only a small fraction of about 15% has been left at higher temperatures (see Fig. 5). This initial temperature profile and operating conditions chosen to perform at relatively low steam partial pressures (i. e. 10 bar and a S/C molar ratio in the feed of 3) should allow the SER stage to be carried out avoiding CaO hydration.

Fig. 5 shows the evolution of the axial profiles of gas composition, solids conversion and temperature during the SER operation for the reference case. The mixture of methane and steam is preheated at 700°C and it is fed into the SER reactor by the part at the highest temperature, which favours a rapid conversion of CH₄ (and H₂O) to produce H₂ via the SMR and WGS reactions. In the part of the bed where the CaO-based sorbent is still unconverted, the CO₂ is almost completely removed from the gas phase via Eq. (1), which increases the conversion of CH₄ and promotes the H₂ yield, as the SER equilibrium predicts and the fast reforming and carbonation reactions allow. As the carbonation front moves forward, the Ca-based sorbent are left behind totally carbonated ($X_{CaO}=0.35$ in Fig. 5). In this part, the fixed bed performs as a conventional SMR reformer, and therefore, the methane conversion and the production of H₂ are lower. As shown in Fig. 5, the curves of steam partial pressure given by the reactor model evolve during the operation below the CaO/Ca(OH)₂ equilibrium line in the part of the bed downstream the carbonation front, which indicates that CaO hydration would be avoided during the SER stage.

Regarding axial temperature profiles, there is rapid drops from the initial 700 °C to about 600°C ($t=1$ min) because the reforming reactions (highly endothermic) are faster than the CaO carbonation reaction (highly exothermic). As the sorbent is progressively converted, the bed is left at a temperature around 520 °C given by the SMR equilibrium for the conditions of the reference case. The CO₂ formed via the SMR is mostly captured downstream in a narrow carbonation front and the heat supplied by the carbonation raises the temperature up to 730 °C. The heat from the carbonation reaction is transported downstream and a heat plateau is formed at around 730 °C between the carbonation front and the resulting heat exchange front that advances ahead. Part of the CO₂ not captured due to the high temperature reached in the heat plateau is subsequently removed from the gas stream downstream, where the temperature is lower. As a result of that, there will be a partial carbonation in the solids bed downstream the heat plateau before the arrival of the carbonation front.

Fig. 5. Dynamic profiles of gas composition, solids conversion and temperature inside the fixed bed during the SER operation (RF is carbonation front).

Fig. 6 represents the temperature profiles and composition of the gas resulting from the SER stage. During the first 8 minutes of operation, the temperature of the product gas decreases from 700 °C to a minimum of 590°C. During this period, the gas composition at the exit of the reactor is quite uniform and contains around 92 vol.% of H₂, 9 vol.% of CH₄ and negligible amounts of CO and CO₂ (on a dry basis). When the heat exchange front resulting from the carbonation of CaO arrives at the reactor exit ($t > 8$ min), the temperature of the product gas rapidly increases up to 730°C. At these conditions, the amount of H₂ in the gas slightly decreases (resulting from the SER equilibrium) to around 87 vol.%, while the amounts of CO and CO₂ increase (4 vol.% and 0.6 vol.% on

a dry basis, respectively). After 15 minutes of operation, the carbonation front approaches the reactor exit and the CO₂ capture efficiency starts to decrease dramatically because the Ca-based sorbent is close to its total conversion. The SER stage ends at this moment (breakthrough period), before the H₂ content in the feed falls below 80 vol.% of H₂ purity in the product gas. If the operation continues far beyond the breakthrough period (see Fig. 6), the separation of CO₂ by CaO would be low and only the SMR and WSG reactions would take place. The bed would perform as a stationary steam reformer generating a product gas at 520 °C composed of 50 vol.% of H₂, 41 vol.% of CH₄ and 8 vol.% of CO₂ (given by the SMR equilibrium).

Fig. 6. Evolution of temperature and composition (on a dry basis) of the product gas during the SER operation.

4.2. *Cu oxidation stage*

In the reference case, the solids bed contains around 30 wt.% of active Cu. Under these conditions, the recirculation of approximately 90% of O₂-depleted air, which dilutes the concentration of O₂ in the feed to 2.3 vol.%, makes it possible to limit the temperature profiles up to a maximum value of about 860 °C (see Fig. 7). A flow of air of about 479 mol/s (stream 6 in Fig. 2) is assumed in the reactor model to carry out the Cu oxidation stage. The air is supplied at 20 bar and 300 °C and subsequently mixed with the recirculated O₂-depleted air forming an inlet stream of 4370 mol/s (stream 7). At the reactor exit, a flow of 4295 mol/s is emitted (stream 8), which is mainly composed of nitrogen (around 99 vol.%). The fraction of the product gas that is not recirculated (430 mol/s) can be directed to a downstream gas turbine for power generation. After the SER stage, most of the bed is left at a temperature higher than 520°C. As can be seen in Fig. 7, this temperature is suitable to achieve from the beginning the complete conversion of O₂ in a sharp front even with the very low amount of O₂ in the feed. The gas approaches the oxidation front (R in Fig. 7) at the inlet temperature (300 °C) and it is rapidly heated up thanks to the energy released from the oxidation of Cu to CuO. The oxidation front progressively rises the temperature of the solids as it advances along the bed. The high

dilution of the O_2 in the feed makes the heat exchange front (HE in Fig. 7) advance ahead and a heat plateau is formed, which moderates the maximum temperature achieved to around 860 °C. As the gas flows through the bed, the moderate temperatures and the presence of a low amount of CO_2 in the gas avoids the partial calcination of $CaCO_3$. Only in the last quarter of the bed, where the maximum temperature is achieved, the calcination is favoured and part of the Ca-based sorbent is calcined, resulting in a slight increase in the CO_2 content in the product gas.

Fig. 7. Evolution of gas composition, temperature and solids conversion inside the fixed-bed reactor during the Cu oxidation stage.

Fig. 8 shows the dynamic profiles expected during the Cu oxidation stage. In the course of the prebreakthrough period ($t < 10$ min), the O_2 reacts completely and the product gas is virtually pure N_2 with a very low content of CO_2 . While the heat exchange front (HF) advances inside the bed ($t < 4$ min), the temperature of the product gas gradually decreases from 725 °C to a minimum of 545 °C, as a result of the initial solids temperature profile. When the heat exchange front reaches the reactor exit, the temperature of the product gas rapidly increases up 860 °C (i. e., the temperature of the heat plateau) and the content of CO_2 also increases until it reaches a maximum of 1.8 vol.% (given by the equilibrium of the calcination reaction). The Cu oxidation stage

ends after 15 min of operation. At this time, the Cu present in the bed is almost completely oxidized (see Fig. 7) and the content of O₂ in the outlet gas is very close to 2.3 vol.% (i. e. the O₂ content in the feed). A large part of the solids bed is left at a temperature around 300 °C, which is insufficient to carry out the regeneration of the Ca-based sorbent in the reduction/calcination stage. Therefore, it is necessary a heat-exchange step, as mentioned above.

Fig. 8. Evolution of temperature and composition of the product gas during the Cu oxidation stage.

4.3. *Solid-gas heat exchange stage*

As can be seen in Fig. 8, about 40% of the O₂-depleted air produced in the oxidation stage is emitted at a temperature around 860°C, as a result of the heat plateau generated at this temperature inside the bed. Only 10% of the flue gas can be directly used for power generation, and the remaining 90% must be recirculated and cooled down to 300 °C (i. e., the temperature of the feed in the oxidation stage). The solid-gas heat exchange stage has been designed to be carried out with the fraction of the flue gas emitted at the highest temperature (860 °C) that must be recirculated, that means a flow rate of about 1280 mol/s (stream 10 in Fig. 2). As shown in Fig. 9, the temperature of the bed gradually increases because the excess of sensible heat in the gas is transferred to the solids as the gas flows along the bed. During the first 5 minutes of operation, the flue gas is emitted at a temperature of 300 °C, and after that period of time, the temperature of the gas progressively increases up to reach 440 °C (for t=15 min). Since the gas stream contains a low amount of CO₂ (around 1.6 vol.%), part of the calcined particles are re-carbonated during the first minutes of the operation, as long as the temperature favours this reaction. At the end of this operation, around half of the solids bed has been left at a temperature of 860°C that allows the subsequent reduction/calcination stage to be initiated.

Fig. 9. Dynamic profiles calculated for the solid-gas heat exchange step.

4.4. Reduction-calcination stage

For the conditions of the reference case, the Ca-Cu looping process cannot produce a sufficient flow rate of both PSA and syngas in the SMR stage to be used separately in the reduction/calcination stage. Therefore, a mixture of both gas streams (stream 12 in Fig. 2) is used to perform the reduction/calcination stage, thereby giving a total inlet flow rate of 112 mol/s, that contains 40 vol.% of H_2 , 32 vol.% of CH_4 and 14 vol.% of CO, which means that a Cu/Ca molar ratio of 2 is needed to carry out a suitable operation. Fig. 10 shows the dynamic evolution of gas and solids along the fixed bed in the course of the reduction/calcination operation. A starting temperature of about 860°C in the solids bed and the feed of the reducing gas at 700 °C allow the total conversion of H_2 (and CO) to be reached in a very narrow reduction front. The temperature rapidly rises up to maximum of around 900°C due to the heat released in the reduction front. This temperature is much lower than that expected in a fixed bed without carbonated particles because a large part of the heat generated during CuO reduction is simultaneously consumed to perform the calcination of $CaCO_3$. A heat plateau at around 900°C is formed, which favours the rapid calcination of $CaCO_3$. Both reduction and calcination fronts move forward together during the operation, leaving behind the solids totally converted. As can be seen in Fig. 10, as the heat plateau moves forward, there is an increase in the CO_2 released, given by the equilibrium of the calcination reaction. Because of the high content of the reducing gases in the feed (around 86 vol.% of H_2 , CH_4 and CO in stream 12), the reduction (and calcination) fronts advance much faster than the heat exchange front resulting from the reduction of CuO to Cu. After 15 minutes of operation, the reaction fronts have reached the reactor exit. However, at that time, the heat exchange front resulting from the CuO reduction only has passed through a small fraction of the reactor, which means that approximately 85% of the bed is left at a temperature close to 900°C (see Fig. 10).

Fig. 10. Evolution of gas composition, solids conversion and temperature inside the fixed bed during the reduction/calcination stage.

During the prebreakthrough period ($t < 14$ min), the H_2 , CH_4 and CO present in the feed are totally converted and the product gas exclusively contains steam and CO_2 . According to the composition and the temperature calculated at the reactor exit (see Fig. 11), the reduction/calcination stage can be divided into two periods before the solids are completely converted. During the first 6 minutes of operation, the product gas mainly contains steam with a very low content of CO_2 (less than 3 vol.%) and the outlet temperature is lower than 500 °C, as a result of initial solids temperature profile. From that point onwards, the temperature of the product gas rapidly rises up to reach a temperature of around 900 °C after 8 minutes of operation. During this period of time, the content of CO_2 dramatically increases up to 55 vol.% due to the change in temperature that favours the calcination of $CaCO_3$. This phenomenon, explained in a previous work [32], occurs because of the rise in the molar flow rate resulting from the calcination of $CaCO_3$, which makes the resulting heat exchange front advance first, heating the solids downstream the reduction front. After 14 minutes of operation, the bed approaches its total reduction, resulting in a rapid increase in the H_2 , CH_4 and CO contents in the product gas up to reach the inlet gas composition (breakthrough period). After 15 minutes of operation, there is no CO_2 in the product gas, which means that the calcination of $CaCO_3$ is also completed.

Fig. 11. Composition and temperature of the product gas during the reduction/calcination stage.

4.5. *Steam methane reforming stage*

For the reference case, a flow rate of 40 mol/s (stream 13 in Fig. 2) with a S/C molar ratio of 1.5 comes into the fixed bed preheated at 700 °C. As can be seen in Fig. 12, the methane rapidly reacts at the reactor inlet giving rise to a dramatic drop in temperature until a minimum of about 570 °C, which is the value predicted by the SMR equilibrium at these operating conditions. The sensible heat of the incoming gas at 700 °C allows around 50% of the methane to be converted at the reactor inlet. The SMR carried out at this part of the reactor generates a small amount of CO₂ that is removed from the product gas since the lower temperature favours the carbonation reaction. As a result of that, the particles of Ca-based sorbent at the reactor inlet are progressively carbonated during the operation (see Fig. 12). When gas reaches the part of the solids bed at 900°C, the methane is totally converted and the CO₂ produced remains in the gas phase since the very high temperature in the reaction front impedes the carbonation of the Ca-based particles in the rest of the bed. As the reaction front advances, the solids are left behind at temperatures between 560 and 600 °C, which are sufficiently high temperatures to start a new SER stage in a subsequent cycle of the Ca-Cu looping process.

Fig. 12. Dynamic profiles of temperature, gas composition and solids conversion inside the fixed bed during the steam methane reforming stage.

At the reactor exit, a syngas with relatively uniform composition of CO (between 30 and 37 vol.%) and H_2 (between 20 and 30 vol.%) is produced during the SMR operation (see Fig. 13). Although most of the methane reacts in a relatively narrow reaction front, a small part of the fuel gas is finally converted downstream, so the solids located at the second half of the reactor are progressively cooled down (see Fig. 2) because of the endothermicity of the SMR reactions. For this reason, the product gas is emitted at around 900 $^{\circ}\text{C}$ during the first 5 minutes, and from that point onwards, the temperature rapidly decreases to reach 780 $^{\circ}\text{C}$ after 15 minutes of operation (that is the end of the SMR stage).

Fig. 13. Evolution of the composition and temperature at the reactor exit during the steam methane reforming stage.

A summary of the simulation results for a complete cycle of the proposed scheme of the Ca-Cu looping process is represented in Fig. 14 and Fig. 15. The axial temperature profiles achieved at the end of each stage of the process are showed in Fig. 14. The evolution of the composition and temperature of the outlet gases during the entire cycle for the conditions chosen in the case study are depicted in Fig. 15. As can be seen, the heat management proposed in this work for the process makes it possible to achieve the required solid temperature and conversion and produce the gaseous streams at the optimal operating conditions. The main consequences of using this operation strategy are as follows:

1) in the SER stage, the feed of the inlet gas in countercurrent by the part of the bed at the highest temperature (end of SMR in Fig. 14) allows, from the very beginning, a product gas with 65 vol.% of H_2 to be obtained (i. e. about 92 vol.% H_2 on a dry basis, that is close to the maximum value given by the SER equilibrium). Moreover, the maximum temperature achieved is 730 °C, which highly reduces the emission of CO_2 during this stage (around 0.6 vol.% CO_2 on average).

2) in the Cu oxidation stage, the initial temperature profile (end of SER in Fig. 14), allows the complete conversion of O_2 to be achieved in spite of the high dilution of the O_2 in the feed. The conditions chosen for the oxidation stage limit the maximum temperature at around 860 °C, which minimizes the presence of CO_2 in the product gas by $CaCO_3$ calcination and allows the formation of a large heat plateau (see Fig. 15). The fraction of the O_2 -depleted air which is directed to a gas turbine for the generation of power will be at nearly constant mass flow rate and temperature, which are the conditions required to preserve the expander of the combined cycle from mechanical and thermal cycling stress [102].

3) in the heat exchange stage, the excess of sensible heat of the recirculated O_2 -depleted air is used to increase the temperature of the oxidized bed (end of Oxidation in Fig. 14)

up to 860 °C in large part of the reactor (end of Heat Exchange in Fig. 14), while the outlet gas is emitted close to the inlet temperature required for the Cu oxidation stage (see Fig. 15).

4) in the reduction/calcination stage, the feed of the reducing gas by the part of the bed at the highest temperature ensures the total conversion of the fuel gases to CO₂ and steam (see Fig. 15), thereby obtaining a rich-CO₂ stream easily separable for its subsequent reuse and/or permanent storage.

5) in the steam reforming stage, the great excess of sensible heat left in the bed (end of Reduction/Calcination in Fig. 14) is used to generate a syngas at high temperature (see Fig. 15) highly suitable for the reduction/calcination operation, leaving the fixed bed with a favourable temperature profile (end of SMR) for a new SER stage.

Fig. 14. Axial temperature profiles at the end of every stage of the Ca-Cu looping process for the conditions of Table 1.

Fig. 15. Gas product distribution in each stage of the Ca-Cu looping process for the conditions of Table 1.

The H₂ production efficiency and the CO₂ capture efficiency are two indexes that show the potential and feasibility of a pre-combustion system. For the operation strategy proposed in this work and the conditions of the reference case, a hydrogen production efficiency of 76% could be obtained, defined as the ratio between the energy of the hydrogen produced and the energy of the methane fueled into the system (both based on LHV). This value is close to that calculated by Martinez et al. [61] using a simpler model assuming sharp reaction and heat exchange fronts, and 5 net points higher than the efficiency of conventional fired tubular reformers (FTR) that uses chemical absorption with methyldiethanolamine (MDEA) to separate the CO₂ [61]. Moreover, a CO₂ capture efficiency of about 96% could be obtained, calculated as the ratio between the amount of CO₂ produced in the reduction/calcination stage and the amount of CO₂ associated to the inlet CH₄. The carbon losses of the system are due to the CO₂ emitted in the gas turbine coming from the partial calcination of the Ca-based sorbent during the oxidation stage. The CO₂ capture efficiency obtained in the proposed Ca-Cu looping process is also considerably higher than those typically estimated in reference H₂ plants with MDEA absorption (around 85 %) [61].

Conclusions

A sequence of five stages in the Ca-Cu looping process, that includes (1) sorption enhanced reforming (SER), (2) Cu oxidation, (3) solid/gas heat exchange, (4) the simultaneous reduction of CuO and calcination of CaCO₃ and (4) steam methane reforming (SMR), ensures the continuous production of pure H₂ and a high-temperature and high-pressure O₂-depleted gas suitable for power generation in a gas turbine. In the reduction/calcination stage, a rich-CO₂ product gas is obtained, which is highly suitable for CO₂ reuse applications and/or for CO₂ permanent storage. The performance of the SER stage at 10 bar with a S/C molar ratio in the feed of 3 and starting with the temperature profile in the solids resulting from the previous SMR stage (i. e. most of the bed at around 600 °C) allows a product gas with about 90 vol.% of H₂ (on a dry basis) to be obtained. These operating conditions avoid the CaO hydration downstream the carbonation front and limit the maximum temperature achieved up to 730 °C, which highly reduces the emission of CO₂ during the SER operation (less than 1.2 vol.% of CO₂ in the product gas). A starting temperature of around 520 °C in the bed (resulting from the previous SER stage) allows the rapid oxidation of Cu in a narrow reaction front. The complete conversion of O₂ is reached in spite of the very low content of O₂ in the feed (around 2.3 vol.%). The recirculation of about 90% of the O₂-depleted air generated during the oxidation stage allows the maximum temperature achieved to be regulated at around 860 °C, which minimizes the partial calcination of the Ca-based sorbent during the oxidation stage. The composition of the fuel gas used for the regeneration of the CO₂-sorbent highly affects the CuO/CaCO₃ ratio required. The use of the PSA off-gas resulting from the H₂ purification step and the syngas generated in the SMR stage as fuel gas during the reduction/calcination stage highly reduces the

Cu/Ca molar ratio, which improves the performance of the Ca-Cu looping process. An optimized process design for a base case with a reference output of 30,000 Nm³/h of pure H₂ allows the number of reactors required for the process to be reduced to a minimum of five (i. e. one for each stage), which are 6 m long and 2.9 m of inner diameter, assuming cycles of 15 minutes and a pressure drop per stage lower than 10%. On the basis of the gas streams produced in the process for the reference case, a hydrogen production efficiency of 76% (based on LHV) is estimated, which is 5% points above the H₂ efficiency of a FTR plant for H₂ production including the CO₂ capture with MDEA. Furthermore, a CO₂ capture efficiency of about 96% is obtained, which is 11% points higher than those typically estimated in reference FTR plants that use MDEA absorption. The results of this study demonstrate the potential of the Ca-Cu looping process as a promising H₂ production technology with CO₂ capture.

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