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Experimental investigation of the Ca-Cu process for H₂ production: Evaluation of reduction/calcination strategies.

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Abstract

The exothermic reduction of the CuO present in a bed of solids (39 % wt. CuO, 20 % wt. CaCO₃ and 1.5 % wt. Ni, being the rest inert materials) with a fuel gas, generated a pure CO₂ stream once steam was condensed (and free of N₂). In this way, a Cu/Ca molar ratio of approximately 2 in the bed of solids allowed for CaCO₃ calcination efficiencies of around 95 % molar basis at the reducing gases break-through. This allowed performing consecutive cycles of the main reaction steps involved in the Ca/Cu H₂ production process. The mixture CaO-based sorbent, reforming catalyst and Cu-based material was able to produce a gas stream with a 94.0 % vol. H₂ at 10 bar during the CH₄ sorption enhanced reforming stage. The Cu-based material was oxidized with a highly diluted air stream at 10 bar, reacting in a well defined reaction front. A pure CO₂ gas stream was obtained at reactor exit during the calcination/reduction stage with a fuel gas typical composition of a SMR stage at high temperature. The experimental results indicated that it was possible to cool the bed and to produce a syngas with a H₂/CO molar ratio of about 3.5 suitable for its use in the calcination/reduction stage, in a SMR stage at high temperature. It was also possible to perform the calcination/reduction and SMR in one single stage.

Keywords: Pressurized H₂ production; CO₂ capture; Ca/Cu looping process; Fixed bed reactor-

1. Introduction

Pre-combustion CO₂ capture technologies have an extremely important role in achieving the CO₂ emissions reduction agreed in the Paris Agreement, among industrial sectors powered by fossil fuel or biomass as about 90 % of the hydrogen produced worldwide is used as raw material in the ammonia production, methanol and oil refining industries [1]. Aiming the reduction of the energy penalty, and the cost associated to close to commercial CO₂ capture systems, there are new chemical processes for large scale H₂ production from fossil fuels with integrated CO₂ capture those have arisen in the recent years. Within these emerging technologies the Ca/Cu looping process is an intensified process in which, based on the reaction of CaO with CO₂ and the reversible CaCO₃ decomposition, a concentrated H₂ stream is produced with in situ CO₂ capture thanks to the Sorption Enhanced Steam Methane Reforming (SER). To regenerate the sorbent in such conditions those allow producing a CO₂ concentrated stream suitable for further purification, compression and storage, a Cu/CuO chemical loop is coupled so that energy required for the calcination of CaCO₃ is provided by the exothermic reduction of CuO with a fuel gas [2]. The use of intermediate heat exchange devices is eliminated as the heat is directly transferred within the bed of solids that

contains both the CaO-sorbent and the CuO-material. The core of the Ca/Cu looping process, that was originally proposed in 2009, consists of a series of three main reaction steps (shown schematically in Figure 1 a). The process has been designed to be operated in a number of adiabatic fixed bed reactors operating in parallel at different temperature and pressure. Each reactor will face sequentially each reaction stage, and a set of valves will be responsible of changing the gas stream entering in the reactor. Three functional materials are required within the process: a CaO based CO₂ sorbent, a reforming catalyst and a Cu based material. Early works on the basic mass and energy balances of the process determined the main materials requirements [3, 4]. Their proportion in bed will be determined by the energy balance in the calcination/reduction stage in the case of Cu-based material/sorbent, and by the CH₄ space velocity that a system is able to convert for the sorbent/catalyst ratio. In any case, it will be important to maximize the active phase in every material, as the presence of inert species in the reactor would negatively affect the efficiency of the process.

Figure 1. a) Three principal reaction steps in the Ca/Cu H₂ production process. b) Simplified Cu/Ca H₂ production process scheme that includes intermediate heating and cooling stages [5].

The first process step is the H₂ production stage, in which a methane gas stream is steam reformed in the presence of the reforming catalyst, the CaO-based CO₂ sorbent and the Cu-based oxygen carrier (SER). At the beginning of this process stage the CaO sorbent should be fully calcined and the Ni catalyst, and Cu-based material both in reduced form. Steam Methane Reforming (SMR), Water Gas Shift (WGS) and CaO carbonation reaction take place simultaneously. This last reaction allows the CO₂ to be eliminated from the gas phase as soon as it is formed to produce CaCO₃, and pushes the reforming and WGS equilibrium towards H₂ production. Product gas streams with H₂ purity over 95 % vol. (dry basis) using CaO as sorbent have been reported in the literature and predicted by the thermodynamics in the range of 650 °C to 750 °C [6]. Given the highly exothermic character of the CO₂ sorption reaction the global enthalpy of the SER stage is slightly exothermic.

To maximize CH₄ conversion to H₂ achieving high CO₂ capture efficiencies, the SER stage has been proposed to operate in the range of 600-750 °C with moderate steam-to-carbon molar ratios (S/C from 2.5 to 5), and operating pressure between 10 and 25 bar depending on the main output of the process (i.e, hydrogen or power production) [4, 7]. In the following reaction step, the Cu-based oxygen carrier (and the reforming catalyst) is oxidized with a gas stream with very low O₂ content at a high pressure. The reaction of Cu with O₂ is highly exothermic ($\Delta H_{298\text{K}} = 156 \text{ kJ/mol}$), and an strict control of the temperature in the reactor will be needed to reduce the possibility of high temperature spots that could compromise the stability of the Cu-based oxygen carrier (either loss of reactivity or

agglomeration) in the reactor and to minimize the CaCO_3 decomposition that would result in CO_2 emitted to the atmosphere. The strategy to moderate the bed temperature, is to limit the oxidant content at the inlet of the reactor thanks to the recirculation of a high fraction of the O_2 depleted stream obtained from this stage, and to reduce the gas temperature at reactor inlet [8]. Finally, in the third main reaction stage, the CaO -based sorbent regeneration takes place through the calcination of the CaCO_3 formed during the SER thanks to the energy released by the reduction of CuO with a gaseous fuel (mixture of CH_4 , H_2 and CO). This process stage takes place at atmospheric pressure to moderate the temperature required for the regeneration of the sorbent. The energy balance to this process stage will determine the CuO/CaCO_3 molar ratio in the bed that allows the complete calcination of the CaCO_3 and the heating up the bed up to calcination temperature without any additional energy supply [9, 10]. This ratio will depend on the fuel gas composition. Due to the evolution of the gas and solid temperature profiles along the reactors in the three reaction stages described above, it is required to introduce intermediate stages those allow running the process in an adiabatic mode. As for example, stage B' in Figure 1b) that increases bed temperature to adequate it for the calcination/reduction stage exchanging sensible heat from the gas stream at high pressure that is recirculated to dilute the oxidant concentration at reactor inlet during the oxydation stage B. Also, different heat management strategies have been proposed to fulfill the fuel requirements in the calcination/reduction stage while achieving high CO_2 capture rates in the whole Ca/Cu process. Early in the design of the process it was proposed the inclusion of a steam reforming of additional methane (or natural gas) stage C' to take advantage of the sensible heat excess in bed producing a H_2/CO -rich syngas to be used directly in the calcination/reduction stage as a fuel gas, and lowering the bed temperature to adequate it to the following SER reaction stage [4]. A low S/C molar ratio of 1.5 was proposed to reduce the CO_2 produced during operation, and therefore minimize the carbonation of the sorbent before SER stage. A variation to this configuration proposed the use of the off-gas from the PSA H_2 purification unit together with a pre-reformed natural gas stream with an S/C of 1 in stage C'[11]. According to process simulations, reducing the natural gas fed to this process stage, would reduce its cooling potential, and an additional stage that would boost the conversion of the CH_4 at the SER exit was proposed.

Aiming for a reduction of the number of total reactors operating in a complete Ca/Cu H_2 production cycle an optimized process design was recently presented [5]. Among the main modification on process operation conditions, it was proposed to operate the SER stage at a moderate pressure of 10 bar, with a relatively low S/C molar ratio to avoid any possible hydration of the CaO sorbent; to recirculate the O_2 depleted gas stream fraction at higher temperature to heat up the bed in B' stage, and to mix a fraction of the PSA off-gas from the H_2 purification step with the H_2/CO -rich gas produced in the high temperature SMR stage (C') to be used as a fuel gas in Stage C. The use of a fraction of the PSA off gas allowed reducing the energy requirements for the calcination/reduction stage, and the composition of the gas stream entering the reactor (with high content of H_2 , and CO) allowed keeping the Cu/Ca molar ratio in the reactor as 2. A total number of five process stages: SER, Cu oxidation, solid/gas heat exchange, CuO reduction/ CaCO_3 calcination and SMR would allow the production of H_2 and/or power from natural gas while generating a CO_2 concentrated stream adequate for reuse and/or permanent storage. As a result of the important impulse to the development of the Ca/Cu process achieved within the recently finished FP7 ASCENT project [12], a complete techno economical analysis of the process has been recently published [13]. Within the process layout presented, the alternative of feeding an adiabatically pre-reformed natural gas stream to the calcination/reduction reactor that would be mixed with the off gas from the H_2 purification unit was evaluated [14, 15]. From the analysis performed within that work it was demonstrated that from the energy performance point of view the optimal operation was reached when the fuel required for sorbent regeneration was supplied by the off gas from the PSA hydrogen purification unit. This would imply operating the plant with the lowest S/C ratio in the SER stage [14]. In this work, a complete Ca/Cu cycle that includes the main reaction stages has been investigated in a lab scale fixed-bed reactor capable of operating under pressure. The aforementioned strategies described to perform the reduction/calcination stage have been experimentally explored. The objective of the work is to experimentally asses the good performance of the process in terms of H_2 production and CO_2 capture efficiencies.

2. Experimental

Three functional materials for the Ca/Cu H_2 production process those were deeply characterized and tested within the umbrella of the FP7 project ASCENT [12] have been selected to perform the series of tests presented in this work. A co-precipitated Cu-based material was prepared by the Johnson Matthey Company. The material that had 72 % wt. CuO on to Al_2O_3 , was highly stable along redox cycles performed in a differential thermogravimetric analyser. It was able to transport 0.149 mg O/mg oxidized material with minimum losses in oxygen transport capacity (lower than 1 %) after more than 100 reaction cycles at 870°C (See Figure 2 a). The material was pelletized and the final particle size used in these tests was in the range 600-2000 μm . The CaO-based material was a $CaO-Ca_{12}Al_{14}O_{33}$ sorbent that has been prepared through mechanical mixing of the precursors, followed by an agglomeration process and a calcination stage to form the mayenite [16]. This material presented a stable CO_2 carrying capacity of 0.2 g/g calcined sorbent along more than 100 calcination/carbonation cycles performed in TGA under representative conditions for the process (Represented in Figure 2 b). A particle size cut of 600-1000 μm was used in the test. Finally, the catalyst was a commercial reforming catalyst, Ni- $CaAl_2O_4$, provided by the Johnson Matthey Company (HiFUEL® R110) in the framework of the ASCENT project. This material has been grinded down to a particle size cut of 600-1000 μm . The Ni content of the catalyst was determined by ICP elemental analysis as 18 % wt. average. According to a recent study carried out with this material by our research group [17], the HiFUEL catalytic activity for the steam methane reforming reaction was maintained after multiple redox cycles as the operation limits determined for the fresh catalyst were still valid for a mixture catalyst sorbent that had experienced hundred redox cycles. A detailed study has been performed to determine the materials kinetic parameters those govern the oxidation and reduction reactions of the Cu-based material [18, 19], the carbonation reaction of the CO_2 sorbent [16], and the reforming kinetics of the catalyst. According to the results obtained during the materials testing, they presented sufficient reactivity and stability to be used for the process proof of concept that took place within the project. Batches of several kg of materials were prepared and sent for testing along the project for the different research groups involved. In this work, a mixture of the three materials (with a total weight of 90 g of calcined and reduced materials) has been introduced in a fixed bed reactor to form a bed of solids with 43.3 % wt. CuO, 25.6 % wt. CaO and 1.7 % wt. Ni, being the rest inert species for the reactions involved. The bed mixture resulted in a sorbent to catalyst weight ratio of 3 and the Cu/Ca molar ratio was approximately 2.

Figure 2. a) Cu-based material oxygen transport capacity (OTC) along redox cycles performed at 870 °C in the TGA apparatus. Reduction with a 10 % vol. H_2 in N_2 ; oxidation in air. b) CaO-based material CO_2 carrying capacity with the number of calcination/carbonation cycles performed in a TGA apparatus. Calcination at 870 °C, 70 % CO_2 in air, carbonation at 650 °C and 15 % vol. CO_2 .

The fixed bed reactor is an 18 mm inner diameter stainless steel tube, that it heated externally by an electric heating wire. The maximum power input to the bed is 1.25 kW, and it is externally insulated by a quartz wool layer that covers the reactor and heating wire. A serie of thermocouples are located along the bed length, being seven of them immersed in the bed of solids (that has a total length of about 0.2 m). The gas flows downwards in the reactor and the control of the temperature in the system is ruled by the thermocouple placed in the bottom part of the bed, which is the last part of bed being affected by the heat exchange or reaction fronts. The experimental rig is equipped with gas mass flow controllers (CH_4 , N_2 , CO_2 , H_2 , CO and O_2) and also a liquid mass flow controller that allows introducing water when is required. The mixture of gases (and water in some process steps) is introduced in a

tubular pre-heater that heats up the stream up to 400 °C before entering the reactor. The system is capable of operating at pressure (up to 10 bar have been successfully reached) thanks to an end-valve that regulates and controls the pressure in the reactor. The gas product (after condensation of the steam) is online characterized with an extractive analyser SICK GMS810 (IR-analysis and heat conductivity analysis) that takes a fraction of the gas product stream. To determine the total gas production, a known flow of N₂ is introduced with the gas fed (i.e. about 5 to 7 % vol. N₂ is introduced together with the reacting gases). The overall heat transfer coefficient has been experimentally determined as 9.5 W/m²K, considering a reference ambient temperature of 25 °C [20].

Table 1 compiles the experimental conditions for the main stages of the tests performed in the experimental rig according to the process configuration depicted in Figure 1 b). The total pressure, initial bed temperature, gas composition and gas space velocity are shown. Five consecutive cycles of the main reaction stages for the Ca/Cu process have been performed: Sorption Enhanced Reforming (Stage A), Cu oxidation (Stage B), CuO reduction and CaCO₃ calcination (Stage C) and Steam Methane Reforming (Stage C'). This process configuration considers that the energy required to calcine the CaCO₃ formed during the Sorption Enhanced Reforming is provided by the reduction of CuO with a gas stream whose composition corresponds to the mixing of the syn-gas produced by a Methane Steam Reforming Stage at high temperature (Stage C') and the off gas of the PSA H₂ purification unit (see Figure 1 b for the simplified process scheme). In this way, Stage C' would have two functions: to provide the suitable gas composition to fulfill the energy balance of the calcination/reduction and to cool down the bed for the SER stage in the following cycle [5]. Additionally two more cycles have been performed, with a different gas composition for stage C, (C_{option2}). In this case, and according to the simplified process scheme presented in Figure 5 a), within the same process step would take place the CuO (and NiO) reduction, the CaCO₃ calcination and a Methane Reforming Step that would take place behind the reduction reaction front and that would serve to cool down part of the bed [13, 15]. See Table 1 for detailed composition for C_{option 2} and Figure 5 a).

Figure 3. a) Scheme of the experimental fixed bed reactor ; b) Photograph of the experimental rig, with the detail of the set-up of thermocouples.

Table 1. Process stage operation conditions in the Ca/Cu cycle.

	A: H ₂ production stage	B: Oxidation stage	C _{option1} : Reduction/ Calcination stage	C': SMR cooling stage	C _{option 2} : Reduction/ Calcination/ SMR
P (bar)	10	10	1	1	1
T_{initial bed} (°C)	675	700	820	820	820
Gas comp. (% vol.)	23 CH ₄ , 72 H ₂ O and 5 N ₂	5 O ₂ , 95 N ₂	54 H ₂ , 27 CH ₄ , 12 CO, 7 N ₂	47 CH ₄ , 47 H ₂ O, 6 N ₂	21 CH ₄ , 39 H ₂ O, 21.2 H ₂ , 13.5 CO, 5CO ₂ , 5 N ₂
Gas spatial velocity (h⁻¹)	7950	8188	4300	1815	2413

Once the materials were introduced in the reactor, to assure that there was not CuO, neither CaCO₃ and that the commercial reforming catalyst was active for the CH₄ reforming, the reactor was heated up to 875 °C in a 10 % vol. H₂ in N₂ gas stream. In every cycle, after each reaction stage, it was needed to accommodate the temperature of the bed and the total pressure in the system to those required in the following reaction stage. These steps are not included in Table 1 for simplicity. They consisted in a pressurization step from atmospheric to operation pressure in a 10 % vol. H₂ stream in N₂ before the SER stage; a heating up step in N₂ at pressure up to oxidation bed Temperature before the oxidation stage and finally a heating up, depressurization step performed in a rich CO₂ stream in N₂. This last step served to assure that any possible CaO decomposed during the oxidation period is carbonated again, and also to assure that the system is over the calcination equilibrium and calcination reaction will only take place due to the energy released by the CuO reduction with the fuel gas introduced in Stage C. In this work, the complete break-through of the gases has been allowed in every process stage, trying to elucidate the presence of any side reaction reflected in the product gas composition once the materials in the bed have been completely converted.

In a large scale Ca/Cu looping process, there are also intermediate stages as pressurization, despressurization and rinse stages to make the transition from a reducing atmosphere to oxidation conditions, those would be required for a safe and adequate process operation. It is out of the scope of this work to reproduce and to evaluate the impact of these intermediate stages on process efficiency. Also, given the limitations of the experimental rig, it is out of the scope of this work to replicate the intermediate non-reactive stages needed for heating the solid bed before the reduction/calcination stage, which uses some of the process gas streams involved. The transition between reaction stages has been done through the accommodation stages described in the paragraph above.

3. Results

In general highly reproducible results have been obtained in the consecutive cycles performed in the system in terms of product gas composition, reaction time and temperature profiles registered along bed reactor, indicating that the stability of the materials is in agreement with TGA results for the number of cycles tested. The upper row in Figure 4 shows an example of the obtained results in terms of gas composition at reactor exit along five reaction cycles (stages A, C and C' from left to right) and the lower row shows the evolution of temperature profile along bed length with time during these process stages (only one cycle is shown for simplicity). As it can be seen in the Figure 4 a) the system was able to fulfill the SER equilibrium during the pre-breakthrough period (black line) under the conditions of Table 1, those corresponded to a CH₄ space velocity of 2.5 kg CH₄/h kg catalyst at an S/C of 3 and at 10 bars producing a gas stream containing 94.0 % vol. H₂ (dry basis). During this process stage, the temperature set-point of the bed has been maintained at 650 °C, and it has been possible to observe the evolution of the SER reaction front along bed length. As soon as the CO₂ is formed due to the reforming and WGS reactions, it is captured by the sorbent in a narrow reaction front, the temperature of the bed slice increases and the heat exchange front (hot gas) moves forward in the bed. Once the CaO in this portion of the bed is saturated, only the CH₄ reforming takes place and progressively cools down the saturated bed. The maximum temperature measured was reached in the middle part of the bed. As the system was not completely adiabatic, it was not observed the temperature plateau described through modeling work on SER in fixed bed reactors in the literature [7, 14]. Still it is important to highlight that the product gas composition during the pre-break through of the system was barely affected by the temperatures reached inside the bed in agreement with modeling results. The sorbent presented a CO₂ capture rate of $4.5 \cdot 10^{-2}$ kg CO₂/h kg calcined sorbent, and the mass balances to the process stage at the break-through determined that the material presented a CO₂ carrying capacity in the first cycle tested of 0.4 g/g calcined sorbent that decreased slightly with the cycles being estimated 0.35 g/g calcined sorbent at the fifth cycle. These data are in agreement with the evolution of sorbent CO₂ carrying capacity along calcination/carbonation cycles determined in the TGA apparatus. As it can be observed a slight decrease in the H₂ % vol. was obtained in the fifth cycle, this could be explained to some segregation that took place in the bed as the catalyst, that had been crushed to produced a homogeneous bed with the sorbent and Cu-based material, tend to lose mechanical stability. As a

consequence an important fraction of the Ni present in the mixture of solids was found in a particle fraction below 200 μm after discharging the bed.

The second reaction stage performed was the Cu Oxidation Stage, whose operation conditions are reported in Table 1. It is not represented in Figure 4 to simplify the number of figures. The initial bed temperature was set at 725 $^{\circ}\text{C}$, the power input to the reactor was cut off while a 5 % O_2 in N_2 stream was introduced in the reactor at 10 bar and a linear gas velocity of 0.045 m/s. The O_2 was reacting in a relatively narrow front as indicated by the temperature profiles measured in the bed. A maximum bed temperature of 775 $^{\circ}\text{C}$ was registered in the middle part of the bed. An almost pure N_2 stream gas obtained during the pre-breakthrough period of the oxidation stage, being CO_2 the only impurity measured in the reactor exit, at concentration slightly over to equilibrium. According to the mass balances at this process stage all the Cu and Ni present in the bed were oxidized. Once the oxidation stage has ended, the reactor is depressurized in a 40 % vol. CO_2 in N_2 stream and heated up to 825 $^{\circ}\text{C}$. The purpose of this conditioning was to avoid any prompt CaCO_3 decomposition while the heating up of the bed.

A concentrated CO_2 stream was generated during the reduction /calcination stage (Figure 4 b) with a fuel gas composition that would result from the mixture of a SMR at high temperature (Figure 4 c) and the off gas of the H_2 purification PSA unit (process scheme from Figure 1b). The initial bed Temperature was set at about 825 $^{\circ}\text{C}$, and once the fuel gas was introduced in the system the temperature set-point of the reactor was lowered to avoid any power input to the system. As it can be seen in Figure 4 b, all the reducing gases were converted within the bed being CO_2 the only gas measured at reactor exit during the pre-breakthrough. Figure 4 e) shows how the temperature in the bed is increasing due to the exothermic reduction reactions taking place, and how the heat exchange front is moving forward in the reactor. Maximum temperatures of about 855 $^{\circ}\text{C}$ were registered in the middle part of the bed. Inlet gas velocity to the reactor was 0.24 m/s, but as a result of the reactions involved the number of moles in the gas phase increased together with the CO_2 released by the calcination of the sorbent. As a consequence a gas stream with a maximum CO_2 concentration of 50 % vol. in steam was produced. The reaction front reaches last portion of the bed in about five minutes, (see Figure 4 e) and at the same time the break-through of the reducing gases takes place (see Figure 4 b). As it can be observed the break-through of the CH_4 is slower than for CO and H_2 , in agreement with results presented in the literature [21]. It is also observed that the CO concentration in the break-through of the gases exceeds the concentration introduced in the system for a few minutes, this might indicate that side reactions as CH_4 thermal decomposition together with water gas reaction could be taking place while there is steam in the reactor produced by the oxidation reactions of H_2 , and CH_4 . According to the mass balances to the cycle 1 process stage 0.47 moles of CuO have been reduced and 0.21 moles of CaCO_3 have been calcined at CO and H_2 break-through resulting in a 85 % calcination efficiency in molar basis. 95 % of the mol of CO_2 have exited the reactor at the CH_4 break-through. As it can be observed in the Figure 1e), although the reactor is not completely adiabatic, the bed temperature at the end of the calcination/reduction stage is close to 800 $^{\circ}\text{C}$ in an important fraction of the bed. According to the process modeling published in the literature, at the end of the calcination/reduction stage an important fraction of the bed would be at temperatures close to 900 $^{\circ}\text{C}$, and a cooling step will be required to adequate the reactor for starting a new cycle [5]. Therefore, in some process configurations it has been proposed the inclusion of a SMR stage with a low S/C molar ratio not only for producing the fuel gas for the calcination/reduction stage, but also to cool down the bed to start a new H_2 production stage [5].

In this work to emulate this process stage, operation conditions included in Table 1 for Stage C' have been adopted. In this way a total flow in the reactor of 40 IN/hr, with an S/C molar ratio of 1 has been introduced in the bed in which the materials are in calcined and reduced form. The initial bed temperature has been set as 800 $^{\circ}\text{C}$, and the set point of the bed has been maintained constant during the SMR stage, to compensate the heat losses to the atmosphere, and to assure that the endothermicity of the reforming reaction was responsible of the cooling down of the bed. As it can be seen in Figure 1 c), the gas composition obtained in the consecutive cycle those included the SMR stage is highly reproducible. A gas product stream with an average H_2 content (d.b., N_2 free) of 73 % vol. has been produced, with a calculated CH_4 conversion of 93 % molar basis. All the gases are at equilibrium concentration as calculated with HSC chemistry and the average CO is 20 % vol. given the fact that the WGS reaction is not favored at this high temperature. The CO_2 concentration measured (d.b. free of N_2) at reactor exit is below the CaO

carbonation equilibrium that is 3.47 % vol. at 700 °C [22]. As it can be observed in the temperature profile of this process stage, the CH_4 is being converted in the first part of the bed, cooling down quickly the solids, this would allow removing from the bed the sensible heat cumulated during the calcination/reduction step as well as producing a syngas at high temperature suitable for the reduction/calcination of the CaCO_3 . After 20 minutes of Stage C', the composition of the gas entering the reactor was set at 10 % H_2 in N_2 to start a new cycle. The temperature of the reactor was increased up to 875 °C, and no H_2 consumption neither CO_2 emissions were detected indicating that the bed was completely calcined and reduced for the new SER stage.

Figure 4. Upper row: Product gas composition with time. a) H_2 production stage, b) Calcination/Reduction stage, c) SMR cooling stage. Operation conditions from Table 1. Lower row: Evolution of bed temperature with time and bed length. c) H_2 production stage, d) Calcination/Reduction stage, e) SMR cooling stage. Operation conditions from Table 1.

Finally, as described in the introduction section, different process schemes have been proposed in the literature for the Ca/Cu H_2 process. In this work the second alternative evaluated for the A recent paper by Riva et al. [13] proposed to perform the reduction/calcination stage with a gas stream produced by mixing the Off-gas of the PSA H_2 purification unit mixed with the gas coming out from a heated natural gas pre-reformer. According to the simulation results, the best case in terms of energy efficiency was obtained for the case in which the Off-gas from the PSA H_2 purification unit was sufficient to fulfill the energy requirements for the calcination/reduction stage. In this way, a CH_4 and CO rich stream (approximately 33 % vol. CH_4 , 20 % vol. CO and 33 % vol. H_2) would be mixed with low pressure steam in an S/C molar ratio of approximately 1.5 and fed to the oxidized and carbonated bed. See Table 1 for the final gas composition used in this process stage. As it has been described before for Stage C (option 1), the bed of solids was heated up in a 40 % vol. CO_2 in N_2 after the oxidation stage. Once the bed was at temperature and the desired gas composition was fed to the system, the temperature setpoint was lowered at 750 °C to avoid any external input of power to the system. Figure 5 b) shows the evolution of gas composition with time at reactor exit (once the steam is condensed). As it can be observed only CO_2 is measured for about 8 minutes at reactor exit, indicating that the fuel gas is being totally converted in the bed. Only the CO_2 coming from the oxidation reaction of the fuel gas and the calcination of the CaCO_3 is measured, and it would correspond to a maximum concentration of 40 % vol. inside the reactor. As it can be observed in Figures 5 b and c) the break-through of the gases and the arrival of the reduction reaction front to the last portion of the bed are coincident in time. A maximum temperature of 850 °C was measured in the first half of the bed. After the break-through of the

Figure 1 consists of two parts: (a) a schematic diagram of the experimental setup and (b) two graphs showing gas composition and temperature profiles.

(a) Schematic diagram of the experimental setup. The process involves four vertical columns labeled A, B, B', and C. Column A is a PSA (Pressure Swing Adsorption) unit. Column B is an Adiabatic Pre-reformer. Column B' is a reactor. Column C is a reactor. The feed gas is $\text{NG} + \text{H}_2\text{O}$, which enters Column A. The output of Column A is H_2 , which enters Column B. The output of Column B is $\text{N}_2 + \text{CO}_2$, which enters Column B'. The output of Column B' is $\text{N}_2 + \text{CO}_2$, which enters Column C. The output of Column C is CO_2 , which enters Column B. The output of Column B is H_2O , which enters Column C. The output of Column C is H_2 , which enters Column A. The output of Column A is Off-gas , which enters Column B.

(b) Two graphs showing gas composition and temperature profiles. The top graph shows Gas composition % vol. (d.b.) free of N_2 versus time (min). The bottom graph shows Temperature T ($^{\circ}\text{C}$) versus axial distance L (cm).

The top graph shows the gas composition profiles for CO_2 (green), H_2 (red), CH_4 (blue), and CO (purple) over time. The bottom graph shows the temperature profiles for different axial distances L (cm) and a setpoint (black line).

4. Conclusions

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