Validation of the H₂ production stage via SER under relevant conditions for the Ca/Cu reforming process practical application

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ABSTRACT

The joint performance of a CaO-based sorbent and a Ni-based commercial catalyst has been assessed under relevant conditions for the SER stage in the Ca/Cu H₂ production process. These conditions comprise processing CH₄ space velocities suitable for the scaling up of the process, operation of the system at pressure, and testing materials that had experienced up to 200 oxidation/reduction cycles. The system, catalyst and CaO-based sorbent, was able to fulfil the SER equilibrium composition up to 2.5 kg CH₄ h⁻¹ kg cat⁻¹, CH₄ space velocity that would allow the scaling up of the process. In this way, a gas stream containing up to 95 % vol. H₂ was obtained at 923 K, steam to carbon ratios of 3.2 and 4, sorbent to catalyst weight ratios from 4 to 15 and for operation pressures between 1 and 9 bar. The effect of oxidation/reduction cycles on catalyst performance was assessed, and the mixture sorbent and aged catalyst was able to

process up to $2.5 \text{ kg CH}_4 \text{ h}^{-1} \text{ kg cat}^{-1}$, corroborating the operational limit determined for the fresh materials.

The total operation pressure (from 1 to 9 bar) did not have an important influence on H_2 yield, and/or materials performance. Sorbent carbonation reaction rates up to $4.42 \cdot 10^{-2} \text{ kmol h}^{-1} \text{ kg sorb}^{-1}$ were determined in the experiments, being this parameter responsible of the limit in CH_4 space velocity that can be successfully converted through this sorbent/catalyst system. The experimental results have been successfully described by a pseudo-homogeneous reactor model that incorporates the main kinetic expressions of the reactions involved in the SER stage.

Keywords: Sorption Enhanced Steam Methane Reforming, H_2 production, pressurized fixed bed reactors, CO_2 capture, $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent, Ca/Cu process

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1. Introduction

It is expected that worldwide demand for H_2 increases progressively in the next decades firstly as a result of demand from petroleum refineries and chemical industries and secondly due to the use of H_2 as a clean source of energy in a near future [1]. Otherwise, the necessity for developing new CO_2 capture technologies to mitigate the emissions from large scale power plants and industrial processes will be an essential point to fulfil strict environmental regulations associated with climate change [2].

Under this background, there are emerging new chemical processes for large scale H_2 production from fossil fuels joined with CO_2 capture systems in order to reduce the costs and the energy penalty associated to close to commercial capture processes [3].

Steam Methane Reforming (SMR) is the most widely used technology to produce H₂ at commercial scale, producing around 50 % of the H₂ worldwide. [4, 5]. This process that is responsible of significant CO₂ emissions (9,1 - 8,9 kg CO₂/kg H₂), is followed by a two stages shift process to maximize CO conversion, and a pressure swing adsorption unit (PSA) when looking for H₂ purities greater than 95 % [4, 6].

Although there are well-established and efficient routes to capture diluted CO₂ from different gas streams to produce a concentrated stream suitable for geological storage, the development of new technologies that allow reducing even more the CO₂ capture cost is still needed. In this context, the sorption enhanced steam methane reforming (SER) arises as a novel intensified process that combines the H₂ production with inherent CO₂ capture in a single system.

In the SER process, the reforming water gas shift (WGS) reactions and the removal of CO₂ take place simultaneously in one single stage in presence of a catalyst and a CO₂ sorbent (Equation 1). The use of a CaO-based material allows the CO₂ to be removed from the gas phase as soon as it is produced, forming CaCO₃ [7]. According to thermodynamic predictions and experimental results, it is possible to obtain more than 95 % vol. H₂ (on a dry basis) using CaO as sorbent in the range of temperatures from 923 to 1023 K [7]. The CO₂ sorption reaction (i. e. the carbonation of CaO) is exothermic and supplies “in situ” the heat required for carrying out the endothermic reforming process.

As a product gas with almost pure H₂ is obtained directly from the reformer, the downstream purification process is simplified. The presence of sorbent minimizes the formation of coke allowing for a reduction of the steam excess in the reformer, and the

operation at lower temperature favours the use of cheaper materials in the reactor units [7-10].

The cyclic operation of the process requires the regeneration of the sorbent through the calcination of the CaCO_3 formed. This reaction is highly endothermic and it must be performed in a CO_2 -rich atmosphere if the process aims at zero emission by introducing the subsequent steps of CO_2 purification, compression and geological storage. Additional energy is required to reach the high calcination temperatures that equilibrium demands (above 1173 K in pure CO_2 at atmospheric pressure) [11]. Several process configurations, which include the use of interconnected fluidised bed reactors, have been proposed to solve the regeneration of the sorbent while the CO_2 capture is achieved. As for example, the oxy-combustion of additional CH_4 or off gas from a H_2 PSA unit in the calciner reactor [6, 12-14], the indirect heat transfer through high temperature surfaces [15-18], the heating by direct contact with hot solids from an air-blown combustion chamber [19, 20], or the use of chemical looping combustion (CLC) systems making use of the large heat-transfer capacity of NiO [21] that come from an oxidation stage at temperatures above 1273 K. In the recent years innovative processes have proposed the use of a redox-loop to provide the energy required to drive the regeneration of the sorbent as the Ca/Cu H_2 production process [22-24] that aims for pressurized H_2 production with reduced CO_2 emissions, or the SER-CLC where part of the energy required to drive the calcination of the sorbent comes from a Ni/NiO redox loop [25]. The present manuscript is focussed on the Ca/Cu looping process [22, 24], that it is based on a patent by Abanades and Murillo [23]. It incorporates a second chemical loop, Cu/CuO , to the CaO/CaCO_3 loop in the SER process. In this way, the exothermic reduction of CuO with H_2 , CO or CH_4 provides the energy to simultaneously drive the calcination of CaCO_3 . The coupling of both endothermic and

exothermic reactions in one single stage allows for higher integration as the heat is directly transferred without the need for intermediate heat exchange devices. The basic Ca/Cu looping process consists of a sequence of three main reaction steps (see Fig. 1a), 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 SER of methane in the presence of a reforming catalyst, a CaO-based sorbent and a Cu-based solid. This process stage has been designed to take place at 873-1023 K, steam-to-methane molar ratios (S/C) 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 [26]. These conditions are not far from those of the H_2 production stage in any other SER process operating in pressurized fixed bed reactors. In the next step, the Cu-based material is oxidized with diluted air at a high pressure. A low content of oxygen in the feed moderates the bed temperature increment during the oxidation of Cu to CuO, thereby avoiding the decomposition of $CaCO_3$ by partial calcination [27]. 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 [28-30]. A complete heat management strategy has been developed to allow the Ca/Cu process running in an adiabatic cycle (See Figure 1 b extracted from Fernández et al. [24]). In this way, the inclusion of intermediate stages in the process (B' and C' in Figure 1b) that would adequate the bed temperature for the subsequent process stage has been described in detail in the works by Fernández et al. [24] and Martinez et al. [31]. These works solved the complete mass and energy balances of the process for a H_2 production plant [24, 31], and a power production plant from natural gas reforming with

CO₂ capture [32]. The published works delimited the operational window for the Ca/Cu process and gave a complete description of the gas streams (temperature, pressure and composition) and bed of solids (temperature and composition).

Figure 1.

Regarding the operation and reactor design, dynamic reactor models have been developed to study the transient behavior of systems in fixed beds and to identify suitable operating conditions [33]. In a recent FP7 project, ASCENT [34], the viability of the critical reduction/calcination stage of the Ca/Cu process has been demonstrated at a laboratory scale under pseudo-adiabatic conditions [35]. From a process perspective, simulations integrating the Ca/Cu looping process to power systems [31, 36, 37] have shown that high CO₂ capture efficiencies are achievable with moderate efficiency penalties with respect to natural gas combined cycle (NGCC) systems without CO₂ capture.

The Ca/Cu looping process requires functional materials, which must be able to be carbonated and calcined maintaining high CO₂ uptake (in the case of CaO-based sorbents), to be oxidized and reduced showing high O₂ carrying capacity (in the case of Cu-based solids) or exhibit sufficient catalytic activity (in the case of the reforming catalyst) over many cycles. In recent years, good progress has been made in the development of high-performance materials with direct application to the Ca/Cu looping process, as their characteristics are not very far from those of functional materials required in processes as CLC and conventional SER processes. Thus, CaO-based sorbents with stable CO₂ sorption capacity, and up to 30 % wt. active CaO, have been obtained through different synthesis routes [38-41]. Copper-based oxygen carriers with sufficient active content (Cu loads over 60 % wt.) have been developed [42], which are resistant to agglomeration and deactivation in the long term. Finally, some recent

works are oriented to the development of composite materials containing CaO and CuO [29, 30, 43, 44] and/or CaO and Ni acting as reforming catalyst [45, 46] that have been tested in TGA, and fixed bed reactors. However, in general these materials are still immature with respect to the use of individual pellets and important efforts on their development are required to experimentally prove the advantages of composite materials.

The present work evaluates the H₂ production via SER within conditions of the Ca/Cu looping process. These conditions include the operation of the process under pressure, at a relatively high S/C and moderate temperature [7, 26, 47]. In this H₂ production stage, the Cu-based material will act as inert, because although Cu is a well-known catalyst for the WGS reaction, it presents low activity at the temperature range of operation for the H₂ production stage [48] and the final product gas composition will be mainly determined by sorbent reactivity [26, 47]. The presence of Cu in the reactor would affect to the thermal ballast and to the total amount of sorbent material that can be allocated in a given reactor volume. This last fact will determine the duration of the H₂ production stage that will end when the sorbent saturates. For these reasons, the presence of Cu has been avoided during the experimental campaign, and the work has been focussed on proving the viability of the use of a commercial Ni catalyst (HiFUEL® R110) and a sorbent material, that has shown sufficient CO₂ carrying capacity and reaction kinetics to sustain the process [49, 50]. There are no significant number of papers in the literature evaluating the performance of materials those have experienced a relevant number of reaction cycles for the process. In this way, the main contribution of this work will be to assess the performance of materials with a lifetime representative for the process, and evaluate whether the operation limits of the system (sorbent and catalyst) in terms of CH₄ space velocity referred to the catalyst content in

bed are affected by the number of reaction cycles and/or operation under pressure. The experimental tests will comprise the operation of a fixed-bed reactor under pressure, in a range of MHSV (mass hourly space velocity of CH_4) expected for the process at higher scale, with an aged catalyst and along multiple oxidation/reduction/reforming cycles always looking for the highest CH_4 flow to be converted with the lowest amount of catalyst possible. The experimental values have been also validated through a dynamic reactor model that incorporates existing knowledge on kinetics and basic assumptions about gas flow and heat transfer.

2. Materials and methods

2.1. Description of the materials: Sorbent and catalyst.

A $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ material has been selected as CO_2 sorbent. Natural limestone and calcium aluminate cement were used as raw materials of the synthetic sorbent. The material was synthesised by mechanical mixing followed by an agglomeration process, and finally a calcination stage. First, natural limestone was milled ($d_p < 75 \mu\text{m}$) and later calcined in air for 2 h at 1173 K, producing 55.59 % wt. of solid residue. Main components of calcined limestone were 97.85 % wt. of CaO , 0.19 % wt. of MgO and 1.92 wt.% of Na_2O . Calcium aluminate cement is a commercial product from cement industry mainly composed of aluminium, iron and calcium oxides. The principle of this synthesis route is that the CaO reacts, at high temperature, with the Al_2O_3 from the aluminate cement to form $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, bringing chemical and mechanical stability to the sorbent material [40, 50]. The sorbent material was prepared by mixing in a shear agglomerator a 10 % wt. calcium aluminate cement with calcined natural limestone, while drop wise of a 10 % wt. poly-ethylene glycol aqueous solution addition. Two

fraction of different particle size cut of 100-200 μm and 600-1000 μm were used in the experimental test campaigns.

The catalyst used in this work (HiFUEL® R110) was a commercial reforming catalyst provided by the Johnson Matthey Company. It is a Ni based catalyst supported on CaAl_2O_4 for steam reforming of natural gas. This solid was available in pellet form and it was crushed and sieved to produce two different particle size cuts 100-200 μm and 600-1000 μm for the experimental tests. The Ni content in the material ranged from 15.9 to 20 % wt., as determined by element analysis within this current study.

Three experimental set-up have been used for the experimental work described in the paper: a TGA apparatus that allowed aging the catalyst and determining the evolution of CO_2 carrying capacity of the CaO-based sorbent, a micro-fixed bed reactor that allowed testing the catalyst together with the sorbent through oxidation/reduction/reforming cycles, and a bench-scale fixed bed reactor that allowed testing the materials in a wide range of CH_4 MHSV and pressure. Their descriptions are comprised in the following paragraphs.

2.2 TGA apparatus:

The catalyst was aged through oxidation/reduction cycles, in a TGA apparatus that consists of a quartz tube with a suspended platinum basket that is placed inside a furnace. The temperature and sample weight were continuously controlled and recorded on a computer. The reacting gas mixture was regulated by means of mass flow controllers and fed in through the bottom of the quartz tube. The routine for the TGA cycling was: heating up to 1123 K in N_2 (50 $\text{K}\cdot\text{min}^{-1}$ heating rate); a reduction stage at 1123 K with 10 % vol. H_2 in N_2 for 5 minutes; 1 minute in N_2 atmosphere; and a 5 minutes oxidizing stage with 20 % vol. O_2 in N_2 . The reduction/oxidation routine was

repeated up to 200 times. After cycling, the sample was cooled down to room temperature in N₂. 0.1 g of catalyst was loaded in the TGA. This TGA was also used to determine the evolution of CO₂ carrying capacity of the CaO-based sorbent with the number of reaction cycles at meaningful conditions for the process according to the following routine: 15 minutes of carbonation at 923 K, 15 % vol. CO₂/15 % vol. H₂O in air. The sorbent calcination was performed at 1123 K in a 70 % vol. CO₂ in air. Dedicated experiments were performed to determine sorbent apparent carbonation kinetics at 923 K and 10 % vol. CO₂ in air.

2.3. Micro-fixed bed reactor.

Mixtures of catalyst and CO₂ sorbent, were tested in a micro-fixed bed reactor capable of allocating up to 0.8 g of material, to assess the effect that the oxidation/reduction stages could have on materials performance. The reactor was a 300 mm long tubular quartz reactor, with an inner diameter of 6.8 mm. The different sorbent/catalyst weight ratios (Z) tested resulted in total bed lengths from 20 mm to 40 mm. The reactor was located in a cylindrical electrically heated oven whose temperature was controlled by a PID controller and a thermocouple placed in the centre of the bed of sample. The gas mixture that enters the reactor was generated by a set of mass flow controllers calibrated for CH₄, H₂, O₂, Ar and water. The water flow was mixed with Ar and CH₄ and evaporated in a stainless steel pipe heated at 673 K by a cylindrical electric furnace connected to a temperature controller. Different feeding mixtures were stabilized in a secondary line before passing through the reactor where the catalyst and sorbent were placed. After the reactor, a recovery system to condense water was disposed. Finally, aliquots of the gas stream were on line analysed using a quadrupole spectrometer (Omnistar, Pfeiffer Vacuum). The routine for the tests was as follows: the mixture sorbent/catalyst was heated in Ar, in situ oxidized and reduced at 1123 K in a 30 % vol.

O₂ and 20 %vol. H₂ for 30 min, respectively. The total flow was set as 1.8 Nl·h⁻¹. The system was cooled down to 923 K and the SER test was performed at a fixed S/C ratio of 4 and at a set of MHSV. The MHSVs tested ranged from 0.75 kg CH₄·h⁻¹·kg cat⁻¹ to 2.5 kg CH₄·h⁻¹·kg cat⁻¹, with and without inert Ar. Between SER tests, steps of oxidation/reduction under conditions described above were carried out to calcine the sorbent and to reduce the catalyst simulating the steps of the SER coupled to the Ca/Cu looping process. The changes in temperature between reaction stages took place at a heating rate of 40 K·min⁻¹.

2.4. Bench-scale fixed bed reactor.

A tubular stainless steel fixed bed reactor with an internal diameter of 16.4 mm was used to explore the operational limits in terms of CH₄ space velocity (expressed as MSHV) and to determine the effect of total operation pressure on the SER stage, for the fresh materials. The reactor was placed inside a tubular electrically heated oven controlled by a PID controller and a thermocouple on the surface of the bed [50]. This reactor allowed testing mixtures of catalyst and sorbent up to 30 g, resulting in bed heights of 0.15 m. The system allowed feeding CH₄, N₂, CO₂ and H₂ by means of the corresponding mass flow controllers. Water was fed from a pressurized vessel through a mass flow controller. The water flow was evaporated and steam was then mixed with the N₂ and CH₄ flows before entering the reactor. Downstream the fixed bed, the product gas passes through a condenser to remove moisture before analysis. The system has also a valve that regulates and controls the pressure, allowing operation up to 10 bars. Finally, aliquots of the gas stream were on line analysed (IR-analysis and heat conductivity analysis, with an extractive analyser SICK GMS810), in this way the concentration of H₂, CH₄, CO and CO₂ in the gas product stream was determined and N₂ was used as an internal standard to quantify the total gas production. In this rig, the

effect of CH_4 space velocity from 1.78 to 4 $\text{kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$ (at 1 bar) and the effect of total pressure from 1 to 9 bar (at 2.5 $\text{kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$) on product gas composition was analysed at a given temperature of 923 K and a S/C molar ratio of 3.2. The routine for the tests included a catalyst pre-reduction and simultaneous sorbent calcination stage performed at 1148 K in a 15 % vol. H_2 in N_2 gas stream (total flow 77 $\text{Nl} \cdot \text{h}^{-1}$). The duration of this stage was extended until CO_2 release, and H_2 consumption were not observed. In this way, two batches of materials have been used in the tests performed in this rig: the first batch was used for the experiments at atmospheric pressure, and the second batch was used for the experimentation under pressure. In between the SER tests, the bed material was calcined always avoiding catalyst oxidation, as the influence of the oxidation/reduction cycles was evaluated in the micro-fixed bed reactor described above. Heating and/or cooling rates in between reaction stages at different temperature was set at 40 $\text{K} \cdot \text{min}^{-1}$. See Table 1 that compiles the experimental conditions of the SER tests performed in this work.

Figure 2

Table 1

2.5. Characterization.

The catalyst has been characterized by TPR analysis to determine the main temperatures of reducible species present in the material, fresh and aged. The analysis has been performed in a PulseChemisorb 700 of Micromeritics within a measuring range from 318 K to 1173 K. XRD analysis was performed to determine the crystalline phases and mean crystallite sizes for the fresh and used materials in an X-ray diffractometer Bruker AXS D8ADVANCE using $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) coupled to energy dispersive X-ray (EDX) using a Hitachi S-3400 N was applied in

order to determine the morphology and nickel distribution in the surface of the samples. The fresh samples (sorbent and catalyst) were also texturally characterized, though Hg porosimetry to determine the total pore volume and the pore size distribution, N₂ adsorption to determine its BET surface, and He pycnometry to determine its true (or skeleton) density.

3. Model description

A pseudo-homogeneous fixed-bed reactor model has been used to describe the performance of the reactor during the SER stage. This operation has been simulated by means of a dynamic model, since the sorption enhanced reforming is time-dependent, being the CO₂-sorbent gradually converted in the course of the process. A multi-component system with overall mass and energy balances with pressure drop was employed in the simulation, adopting the following assumptions: plug flow with mass and thermal dispersion in the axial direction, negligible radial temperature and radial concentration gradients, negligible inter-particle concentrations and temperature gradients at the scale of millimeters, ideal gas behavior, a constant bed void fraction, perfect mixing of the solids and a uniform particle size. An overview of the mass and energy balances is given in Table 2. The axial mass and heat dispersion coefficients are calculated by the equations listed in Table 3.

Table 2

Table 3

Table 4

The high value of the wall-bed heat transfer coefficient (h_w) calculated assuming the operating conditions of this work indicates that the system performs under pseudo-isothermal conditions. The kinetics of steam reforming and water gas shift reactions have been extensively studied in the literature [51, 52]. On the basis of previous works

about SER [8, 9, 53, 54], the kinetics reported by Xu and Froment [55, 56] were assumed in this work. The expressions for the calculation of these kinetics and equilibrium parameters are listed in Table 4. The carbonation of calcium oxide is described using the empirical equation obtained by Rodriguez et al. [57] to interpret the pilot results from the capture of CO₂ by CaO, which is consistent with earlier studies published on carbonation of CaO [58-60]. The effect of the operation at a high pressure on carbonation kinetics is also incorporated in the model (q factor), as it is assumed in a recent work on SER in pressurized fixed beds [33]. A factor (η) has been assumed in the model to tackle the mass transfer resistances at particle level, and also to describe the possible reduction of catalyst activity with respect to the kinetics obtained by Xu and Froment [55], simplification that has been adopted by different authors in the literature [8, 60]. An equal value of η of 0.3 has been considered in this work for all the reactions involved in the SER stage. The volume fraction of CO₂ in the equilibrium is estimated using the equation obtained by Baker [11]. The equations used to calculate the carbonation kinetics and the CaCO₃/CaO/CO₂ equilibrium are also listed in Table 4. The mathematical model is mainly composed of partial differential equations, algebraic equations, and initial and boundary conditions. The model was implemented and solved by MATLAB programming software. The partial differential equations for each gas component (i. e. CH₄, H₂O, H₂, CO, CO₂) were converted to a set of ordinary differential equations with initial conditions by discretizing the spatial derivative in axial direction (z) using finite differences both for the first and for the second order. For finite differences, the reactor length was divided into 50 sections with 51 nodes, which allows a reasonable speed calculation to be achieved together with good accuracy in the simulations. The initial and boundary conditions in the equations listed in Table 2 are as follows:

$$C_i = C_{i,0} \quad T = T_{s_0} \quad \text{at } t = 0 \quad (35)$$

$$C_i = C_{i,n} \quad T = T_{g_{in}} \quad P = P_{in} \quad \text{at } z = 0 \quad (36)$$

The system formed by the differential and algebraic equations was simultaneously solved using a MATLAB tool called “ode15s.m”, which is a function implemented to calculate initial value problems in stiff differential equations. It must be highlighted that the model has been previously validated against experimental data taken from previous works on SER in fixed-bed reactors [8, 60, 61].

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4. Results and discussion

4.1. Materials characterization

Textural characterization of the catalyst and CaO based sorbent are summarised in Table 5. The mean pore size value was calculated with the BJH method from the desorption branch. It is observed that while the Ni catalyst is a meso-porous material, the sorbent is a macroporous material with a lower surface area. Figure 3 a) shows the XRD pattern of the reduced and cycled catalyst (200 oxidation/reduction cycles) where the characteristic peaks of reduced Ni, Al_2O_3 and $\text{CaO}(\text{Al}_2\text{O}_3)_2$ phases are observed for both samples. From this pattern, the initial Ni crystallite size was calculated by Rietveld method as 9 nm, and it increased up to 55 nm for the aged catalyst (material that had experienced 200 oxidation/reduction cycles). Figure 3 b) illustrates the presence of CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as main phases in the fresh sorbent structure.

Table 5

Figure 3

Figure 4 includes SEM micrographs of the fresh and aged catalyst, both in reduced form. Simultaneously, EDX analysis determined a similar amount of Ni in both catalyst samples that was concentrated in the brightest spots detected in the micrographs. As it

can be observed, the initial good dispersion of Ni on to the inert support typical of the reduced catalyst is altered for the aged sample that presents an increment in the number and size of Ni aggregates (brightest spots). The increase of the crystal size and formation of surface aggregates are facts known to reduce active surface and, therefore, might affect to catalyst activity.

Figure 4

Figure 5 presents the H₂-TPRs of the fresh and aged catalyst samples. It enables to identify the different Ni phases present in the fresh catalyst and how the structure of the materials has evolved due to the oxidation/reduction cycles experienced. In this figure, three main peaks are observed for the fresh catalyst. The peak at about 613 K is ascribed to the reduction of weakly bound NiO species, commonly known as “free nickel” [62]. The peak placed around 853 K can be attributed to bidimensional NiO monolayer [63, 64]. The peak present at the highest temperature of 973 K can be assumed to be produced by the reduction of NiO in moderate interaction with the support forming amorphous Ni-Ca-Al [63, 64]. The data correspondent to the cycled sample, indicate that the reducibility of the material has improved because there is only one H₂ consumption peak comparable in area to the fresh sample (62.9 cm³·g⁻¹ and 67.2 cm³·g⁻¹, respectively) that has shifted to 687 K, close to the typical temperature of weakly bound NiO species. The ease of NiO reduction indicates the presence of larger metallic Ni that could be also coherent with the increment on the Ni crystallite size determined for the cycled sample through XRD analysis [62].

Figure 5

With respect to the sorbent material its textural properties (Table 5) do not differ in great extent from CaO of natural limestone in terms of porosity, BET surface and material density [65]. Two aspects related to sorbent that need to be proved to be

sufficient to sustain the process, are its CO₂ carrying capacity and reactivity towards the carbonation reaction. Figure 6a) shows the evolution of sorbent CO₂ carrying capacity with the number of reaction cycles obtained in the TGA apparatus under reference conditions meaningful for the process described in the experimental section. Up to 100 reaction cycles were performed to determine the stability of the materials, and the results showed that the material is able to capture up to 0.2 g. CO₂/g. calcined material in the long term. This is approximately 3.5 times the CO₂ carrying capacity that presents an standard CaO from natural limestone [39]. Figure 6a) also includes the theoretical curve that fitted the experimental data according to Equation 37 and serves to estimate the evolution of CO₂ carrying capacity of the material (X, expressed as g CO₂/g calcined sorbent) along the number of reaction cycles (N), with two parameters: k=0.5 that is defined as sorbent deactivation constant and X_r=0.17 that would correspond to the sorbent residual capacity for an infinite number of cycles [66].

$$X = \frac{1}{\frac{1}{(1-X_r)} + kN} + X_r \quad (37)$$

Figure 6

Figure 6b) shows the evolution of CaO molar conversion with time (2nd cycle as an example), at 923 K and 0.1 bar CO₂ in air. From the experimental conversion curve, the carbonation constant (k_{carb} h⁻¹) has been determined according to Equation (29) in Table 4 [57] as 2160 h⁻¹. According to the experimental results, data from the literature [49], and the modeling results presented by Fernández et al. [26] the sorbent material would allow for sharp breakthrough curves.

4.2. Sorption enhanced reforming tests

a) Effect of MHSV

437 According to published work on the modelling of H₂ production via SER process, CH₄
438 space velocities in the SER stage between 0.75-1 kg CH₄ h⁻¹ kg cat⁻¹ would be sufficient
439 to sustain the process [26, 47, 53, 67]. In this way, aiming to explore the operational
440 limits in terms of CH₄ mass hourly space velocity (expressed as kg CH₄ h⁻¹ kg cat⁻¹) for
441 the materials selected, an initial set of experiments has been performed in the bench-
442 scale fixed bed reactor at atmospheric pressure. The main operational variables as
443 reforming temperature, S/C and Z have been set as fixed conditions in this batch of
444 experiments. The operation conditions have been extracted from the modelling and
445 simulation results presented by Fernandez et al. [26, 47] that developed a mathematical
446 model capable of determining the operational window for a large scale H₂ production
447 facility via Ca/Cu reforming process. The fixed bed reactor has been design as an
448 isothermal reactor. In this way, both gas and bed are supposed to be at the same
449 temperature at the bed inlet (923 K), and the control system of the rig works to maintain
450 the temperature during the test. The S/C molar ratio in the feeding gas stream has been
451 set as 3.2, which according to thermodynamic predictions allows at 923 K and
452 atmospheric pressure a 95 % vol. H₂ (dry basis) gas product. The S/C molar ratio has an
453 important impact on the SER performance, especially for values below 3. At these
454 conditions, the increase in steam in the feed highly improves the H₂ yield and methane
455 conversion. However, S/C molar ratios higher than 4, barely enhance the H₂ purity in
456 the product gas, especially at moderate pressures [7, 49, 50, 53, 68]. Finally, Z has been
457 fixed as 5. This ratio will determine, for a given sorbent and a given reactor volume, the
458 duration of the H₂ production stage (pre-break trough period) at a certain CH₄ space
459 velocity. According to the modeling work performed by Fernández et al. [26], and
460 considering a conventional Ni (9 % wt.)/Al₂O₃ reforming catalyst, a ratio Z =3 would be
461 sufficient to yield H₂ purities of about 92 % vol. The effect of this operational variable

was experimentally analyzed by García-Lario et al. [49] for mixtures of CaO-Ca₁₂Al₁₄O₃₃ and a synthesized Ni/NiAl₂O₄ reforming catalyst in a range from 3.1 to 11.7. The experimental results showed that the system of solids was capable to produce a gas stream close to SER equilibrium for Z=7 and a CH₄ space velocity up to 2.3 kg CH₄ h⁻¹ kg cat⁻¹ (this is 6.62 kg CH₄ h⁻¹ kg Ni⁻¹ when referred to the Ni content in the material). A total Ni in bed close to 3 % wt. was sufficient for a good gas-sorbent-catalyst contact in the reactor and for a good performance of the combination of materials. The CH₄ flow that can be reformed in the reactor will depend on both catalyst activity and sorbent carbonation kinetics [12, 26, 47, 49]. In this way the variables kg CH₄ h⁻¹ kg cat⁻¹ together with the sorbent carbonation rate that can be expressed as kmol CO₂ h⁻¹kg sorbent⁻¹, will be the parameters that will serve to determine the operational window of a combination of materials. Referring the CH₄ space velocity to the Ni content of the catalyst, will allow comparing the performance of materials with different active phase content. Considering the Ni load of the HiFUEL® R110 catalyst tested in this work, a Z of 5 was selected (3.1 % wt. Ni in bed), introducing in the reactor a total weight of solids of 26.4 g with a particle size cut of 600-1000 µm. Under the described conditions, the effect of CH₄ space velocity on gas product composition has been assessed testing CH₄ MHSV between 1.78 and 4 kg CH₄ h⁻¹ kg cat⁻¹ respectively. The MHSVs tested, correspond to linear gas velocities (at the reaction conditions of 923 K, S/C 3.2, and 5 % vol. N₂ as standard) ranging from 0.21 to 0.53 m s⁻¹ respectively. The experiments have been performed consecutively, in this way the materials experienced four consecutive reforming/carbonation and calcination cycles. Figure 7 a) shows examples of the experimental results obtained and compiles the effect of CH₄ space velocity on product gas composition (H₂ and CO₂ evolution with time on dry basis and free of N₂ are represented). The Figure also incorporates the thermodynamic

487 equilibrium predictions according to the software HSC Chemistry (dashed lines), and
488 the reactor model predictions (black solid lines). The Figure 7 a) shows, for every
489 experiment represented, the three typical reaction periods in a SER reforming process:
490 the pre-breakthrough period, where the sorbent is reacting with CO₂ and the global
491 reaction shifts the equilibrium towards H₂ production (SER equilibrium), the transition
492 period where the sorbent in the bed is approaching its total conversion and the H₂
493 content in the product gas gradually decreases (while CO₂ concentration increases), and
494 finally the third stage where the sorbent is no longer active and typical Steam Methane
495 Reforming gas composition is achieved [7]. The results from Figure 7a) indicate that up
496 to 2.5 kg CH₄ h⁻¹ kg cat⁻¹ the system is able to reach the theoretical equilibrium
497 composition at both the pre-breakthrough period and the post-breakthrough. At the
498 highest space velocity tested (4 kg h⁻¹ kg cat⁻¹), it has been experimentally observed that
499 although there is a clear breakthrough curve for the CO₂, the system is not able to reach
500 the SER equilibrium during the pre-breakthrough period of the bed. The % vol. H₂ is
501 clearly below the equilibrium predictions, and this might indicate that the sorbent
502 carbonation rate is not sufficient to sustain the SER reaction. Once the sorbent is
503 saturated, the product gas composition is slightly below the SMR composition, this
504 might indicate that the CH₄ space velocity tested is close to the operational limits of the
505 catalyst (those are 1123-1173 K reforming temperature for near equilibrium operation
506 and MSHV < 3.9 kg CH₄ h⁻¹ kg cat⁻¹). The maximum sorbent carbonation rate in bed
507 determined from the experiments was 4.42*10⁻² kmol h⁻¹kg sorb⁻¹ and corresponds to
508 the experiment performed at 4 kg CH₄ h⁻¹ kg cat⁻¹ and a gas linear velocity of 0.53 m s⁻¹.
509 It falls in the range of expected carbonation rate for materials with the average CO₂
510 carrying capacity and carbonation kinetics reported in Figure 6 [26, 47]. As described in
511 the experimental section, the calcination in this series of tests was performed in N₂ and

H₂ to prevent the oxidation of the catalyst. The mass balance to the C in the system allowed determining the sorbent CO₂-carrying capacity that was 0.75 g CO₂/g calcined material in the first cycle, and 0.58 g CO₂/g calcined material in the fourth cycle. The pre-breakthrough period length diminished along cycling due to the decrease in CO₂ carrying capacity of the sorbent that can be observed in Figure 6 a), and also to the increase on CH₄ space velocity. The H₂ purity and CO₂ capture efficiency was 93 % vol. and 92 % respectively during the pre-break period for MHSV up to 2.5 kg CH₄ h⁻¹ kg cat⁻¹. These ratios were decreased down to 88 % vol. H₂ concentration, and CO₂ capture efficiency of 80 % for the experiment at 4 kg CH₄ h⁻¹ kg cat⁻¹. As it can be seen in Figure 7 a) that includes the modelling results, the reactor model is able to describe the main features of the experimental curves as they are: the pre-breakthrough length, the slope of the breakthrough curve and the product gas composition. This indicates that the assumptions and the kinetic expressions incorporated in the model were suitable to describe the evolution of SER reaction in the fixed bed reactor. Still, it is necessary to highlight that the effectiveness factor (η) was reduced to 0.1 to obtain an accurate fit for the lowest MHSV tested. The reason for this was an operational limitation in the experimental rig, as the condenser located after the reactor in the system, added additional dispersion to the gas analysis system. In the case for the other two MHSV tested no additional dispersion was observed and the model predicted accurately the breakthrough curve through the effectiveness factor ($\eta=0.3$ for all the reactions involved as shown in Table 4). Finally the discrepancies between experimental and predicted values during the pre-breakthrough period for the highest space velocity tested indicate that this operational condition is over the limit for the Z tested. Figure 7 b) shows the average product gas composition (% vol.) during the pre and post-breakthrough periods respectively for the experiment performed at 2.5 kg CH₄ h⁻¹ kg cat⁻¹.

Figure 7

b) Effect of total operating pressure

The CH₄ MSHV space velocity of 2.5 kg CH₄·h⁻¹·kg cat⁻¹ (or 13.5 kg CH₄·h⁻¹·kgNi⁻¹ using an average Ni content of 18 % wt.) was selected to perform the experiments under pressure. This CH₄ MSHV was considered to be close to the operational limit for the combination of materials, as this was the highest space velocity that allowed the bed mixture to reach the gas composition given by the thermodynamics at atmospheric pressure. Then, for this space velocity and maintaining the S/C ratio, Z ratio and reforming temperature as for the tests at atmospheric pressure, a series of tests has been performed varying the total pressure of the system between 1 to 9 bar. As for the previous tests, the starting materials were fresh, and the calcination was performed in the presence of H₂ to avoid catalyst oxidation. Figure 8 shows the evolution of product gas composition, referred to H₂ and CO₂, with time (d.b. and free of N₂) at different pressures (3 to 9 bar), those correspond to gas linear velocities of 0.1 m/s, 0.06 m/s, 0.042 m/s and 0.033 m/s respectively. According to the thermodynamic predictions, the SER reaction is favoured at low pressures [7] as the progression of the reaction results in an increment on the number of moles in the gas phase (Reaction 1). Modelling and simulation results confirm this trend of increasing H₂ purity and CH₄ conversion at lower pressure for a given temperature and S/C ratio [47], although this effect is more prominent under SMR conditions. The experimental results plotted in Figure 8 show, that the total pressure in the reactor (in the range of pressures evaluated) has a low impact on the gas product composition during SER pre-breakthrough period once the reforming temperature, the S/C ratio and CH₄ MSHV are fixed. It can be also seen that the bed of solids is able to fulfil the equilibrium composition during the pre-breakthrough period. This might indicate that the sorbent carbonation reaction that is

reported to be negatively affected by the total operation pressure [33] was still fast enough for the SER reaction to proceed. It is however necessary to highlight that the linear gas velocity in these experiments was in every case lower than the gas linear velocity tested during operation at atmospheric pressure. The mass balance to the C in the experiments showed that the CO₂ carrying capacity of the sorbent was 0.73 g CO₂/g calcined material in the first cycle and was progressively decreasing down to 0.65 g CO₂/g calcined material in the fourth cycle. The pre-breakthrough period length was in agreement with these results, and the shorter duration of the SER reaction at 3 bar is related with the slightly higher CH₄ conversion, and lower CO and CO₂ in product gas stream (due to equilibrium) that led to the sorbent saturation in a shorter period of time. The H₂ concentration in the gas stream was over 93 % vol. up to 9 bars with CO₂ capture efficiencies of 95 % during the pre-breakthrough period. The H₂ concentration during the post-break trough period decreased from 75 % H₂ vol. at 1 bar (this is 2 percentage points, p.p. below thermodynamic equilibrium) down to 63.1 % vol. at 9 bars. As can be seen in Figure 8, the dynamic model used in this work (solid lines in the Figure) gives a good description of SER operation for the conditions tested. During the pre-breakthrough and post-breakthrough periods, the model predicts the gas composition according to SER and SMR equilibriums, respectively. Moreover, the kinetics assumed for steam reforming, water gas shift and carbonation reactions, together with the efficiency factor (η) and the pressure factor (q) (see Table 4) incorporated to the model in order to tackle mass transfer resistances and the effect of pressure on the reactions allow an accurate description of the breakthrough curves.

Figure 8

At this point, the performance of the system composed of sorbent and catalyst has been evaluated and the limits on terms of CH₄ space velocity and the effect of total operating

pressure on the fresh materials has been evaluated. As described on the introduction section one intrinsic characteristic of the Ca/Cu reforming process is the existence of process stages that alternate oxidation and reducing conditions. And it is of crucial importance to corroborate the experimental results obtained, with materials that have experienced a high number of oxidation/reduction cycles. To do so, a series of tests were performed in the second experimental set up described in the experimental section, the micro-fixed bed reactor that allowed testing the materials aged in the TGA apparatus and also bed mixtures with very low catalyst content through oxidation/reduction/reforming cycles.

c) Effect of the sorbent to catalyst weight ratio (ratio Z).

The effect that ratio Z, that refers to the catalyst present in bed (and therefore the Ni content), had on the SER stage was evaluated for a fixed set of experimental conditions. Those were: CH₄ space velocity of 0.75 kg CH₄·h⁻¹·kg cat⁻¹, S/C molar ratio of 4 and 923 K as reforming temperature. The different proportions (those ranged from Z=4 to 15) were obtained reducing the amount of fresh catalyst in the isothermal reactor length of 40 mm. The CH₄ inlet flow was adjusted on each experiment, in order to keep constant the MHSV. The results in Figure 9 show that the sorbent to catalyst ratios studied were sufficient to yield a H₂ purity (d.b. free of Ar) in the product gas of about 92%, close to the maximum permitted by the SER equilibrium. The carbon balance for the experiments indicated that the material presented a CO₂ carrying capacity higher than 0.50 g CO₂/g sorbent along the first two cycles compared to the 0.39 g CO₂/g sorbent calculated for Z equal to 4 in the 7th cycle. The experimental results show that the mixture of fresh materials is able to operate successfully under SER conditions for Ni contents in bed as low as 1 % Ni wt. in bed. This corresponds to Z equal to 15, at a CH₄ space velocity of 0.75 kg CH₄·h⁻¹·kg cat⁻¹ (or 5.3 kg CH₄·h⁻¹·kg Ni⁻¹).

Figure 9

d) Effect of oxidation/reduction cycles in materials performance.

To evaluate the effect of oxidation/reduction cycles on catalyst performance, the material aged in the TGA apparatus (200 oxidation/reduction cycles) was mixed with fresh sorbent to build a bed of approximately 20 mm in length with a sorbent to catalyst weight ratio of 4. Up to 20 cycles that consisted on reduction stage/SER stage/calcination-oxidation stage according to the conditions described in the experimental section, were performed to evaluate the stability of the mixture aged catalyst and sorbent at 923 K, S/C ratio of 4 and MHSV $0.75 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$. Figure 10 shows the experimental results obtained for cycles 3, 4, 11 and 20, in terms of evolution of the product gas composition with time. In this figure the big dotted and dashed lines represent the experimental data and the small dotted horizontal lines indicate theoretical equilibrium composition at both the pre-breakthrough and the post-breakthrough periods. The experimental results show that, in both pre and post-breakthrough periods the composition obtained in every experiment closely reproduced the values calculated for thermodynamic equilibrium. As it is expected, the breakthrough period, that starts when the sorbent approaches saturation, is shortened with the increasing number of cycles due to the reduction in CO_2 sorption capacity reported in Figure 6a). The calculated CO_2 -carrying capacity decreases in these experiments from 0.62 grs. CO_2/gr . calcined material in the third cycle to 0.53 in the fourth cycle and 0.4 in the twentieth cycle. The H_2 purity was 92% vol. and methane conversion was higher than 95% producing only traces of this gas in the product.

Figure 10

e) Effect of CH_4 MHSV on aged materials performance.

Finally, a series of test was performed to corroborate the operational window that had been previously determined for the fresh materials. Figure 11 includes the results of experiments carried out at increasing MHSV. The experiments at $0.75 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$ and $1.11 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$ were performed with the same bed used for the stability tests, but increasing the CH_4 flow. The experimental results show that the system of solids, the catalyst cycled 200 times and the $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent, was able to produce a gas stream close to the thermodynamic predictions for $Z=4$, temperature 923 K and S/C 4. To allow further increasing the CH_4 space velocity, some fresh sorbent (300 mg) was mixed with the used bed to increase the average CO_2 carrying capacity of the mixture up to $0.5 \text{ g CO}_2/\text{g calcined sorbent}$. The Z parameter of the bed was varied in this way from 4 to 7 (and consequently, the Ni content in bed was decreased from 3.5% wt. Ni to 2.1 % wt. Ni). The experimental results at $2.5 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$ ($13.5 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg Ni}^{-1}$) are incorporated to Figure 11. According to the results obtained at these conditions the gas product composition reaches thermodynamic values of equilibrium. This result agrees with the results obtained in the bench-scale fixed reactor with fresh materials. In this way, the mixture sorbent/catalyst is able to reach equilibrium at space velocity of $2.5 \text{ kg CH}_4 \cdot \text{h}^{-1} \cdot \text{kg cat}^{-1}$ for up to 9 bar total pressure, with aged materials, and Ni loads in bed as low as 2.1 % wt. Ni.

Figure 11

4. Conclusions

The joint performance of a commercial Ni-based catalyst (HiFUEL® R110) and a CaO- based sorbent on to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ has been assessed in an operational window suitable for the SER stage in the Ca/Cu H_2 production process. The effect of CH_4 space velocity on gas product composition was evaluated and the operational limits for the system were experimentally found at atmospheric pressure and for the fresh materials. The criteria to

select the operational limits of a combined pair of sorbent-catalyst was determined by the CH_4 space velocity in terms of $\text{kg CH}_4 \text{ h}^{-1} \text{kg cat}^{-1}$ (or $\text{kg CH}_4 \text{ h}^{-1} \text{kg Ni}^{-1}$ when referred to the Ni content of the catalyst), and the sorbent carbonation rate in terms of $\text{kmol CO}_2 \text{ h}^{-1} \text{kg sorbent}^{-1}$ that the system is able to process achieving the SER thermodynamic equilibrium. Expressing the CH_4 space velocity referred to the Ni content of the catalyst allowed comparing the performance of catalyst with different Ni load. In this way the HiFUEL® R110 catalyst was able to successfully treat up to $13.5 \text{ kg CH}_4 \text{ h}^{-1} \text{kg Ni}^{-1}$ at 923 K, and S/C of 3 and up to 9 bar total pressure, being this figure suitable for the scaling up of the SER process. The sorbent material was able to operate up to a gas linear velocity of 0.53 m/s, and presented a maximum reaction rate of $4.42 \cdot 10^{-2} \text{ kmol h}^{-1} \text{kg sorbent}^{-1}$. The operational limits detected for the fresh materials have been confirmed when the catalyst is aged, in this way, the catalyst cycled 200 times under oxidizing/reducing conditions was able to process $13.5 \text{ kg CH}_4 \text{ h}^{-1} \text{kg Ni}^{-1}$ within a bed containing a total Ni content as low as 2.1 % wt. The dynamic reactor model developed gives a good description of the transient performance of the SER reaction in a fixed-bed reactor. The duration of both pre-breakthrough and breakthrough periods and the product gas composition were accurately predicted.

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Nomenclature

C_i concentration of component i in the reactor, kmol m^{-3}

687	$C_{i,in}$	concentration of component i in the feed, kmol m^{-3}
688	$C_{i,0}$	initial concentration of component i, kmol m^{-3}
689	C_{pg}	specific heat capacity of the gas, $\text{kJ kg}^{-1} \text{K}^{-1}$
690	C_{ps}	specific heat capacity of the solid, $\text{kJ kg}^{-1} \text{K}^{-1}$
691	D_{eff}	axial mass dispersion coefficient, $\text{m}^2 \text{h}^{-1}$
692		
693	d_p	particle diameter, m
694	D_r	inner diameter of the reactor, m
695	h_{fs}	fluid-gas heat transfer coefficient, $\text{kJ h}^{-1} \text{m}^{-2} \text{K}^{-1}$
696	H_{ri}	heat of reaction, kJ kmol^{-1}
697	h_w	heat transfer coefficient through the reactor wall, $\text{kJ h}^{-1} \text{m}^{-2} \text{K}^{-1}$
698	k_{carb}	rate constant of CaO carbonation, h^{-1}
699	k_g	thermal gas conductivity, $\text{kJ h}^{-1} \text{m}^{-1} \text{K}^{-1}$
700	k_j	rate constant of reaction j (j= I, II, III), $\text{kmol bar}^{0.5} \text{kg}^{-1} \text{h}^{-1}$
701	K_i	adsorption constant of component i, $i=\text{CO}, \text{H}_2, \text{CH}_4 \text{ bar}^{-1}$; $i=\text{H}_2\text{O}$ dimensionless
702	K_j	equilibrium constant of reaction j, $j=\text{I, II bar}^2$; $j=3$ dimensionless
703	k_{fs}	fluid-gas mass transfer coefficient, m h^{-1}
704	L	reactor length, m
705	M_{CaO}	molecular weight of CaO, kg kmol^{-1}
706	M_g	molecular weight of the gas, kg kmol^{-1}
707	P	total pressure, bar
708	Pe_{az}	Peclet number, dimensionless
709	P_i	partial pressure of component i, bar
710	P_{in}	pressure at the reactor entrance, bar
711	Pr	Prandtl number, dimensionless
712	r_{carb}	rate of CaO carbonation, $\text{kmol kg}_{cat}^{-1} \text{h}^{-1}$
713	Re	Reynolds number, dimensionless
714	r_i	rate of formation/consumption of component i, $\text{kmol kg}^{-1} \text{h}^{-1}$
715	R	ideal gas constant, $\text{kJ kmol}^{-1} \text{K}^{-1}$

716	R_j	rate of reaction j ($j=I, II, III$), $\text{kmol kg}^{-1} \text{ h}^{-1}$
717	S_c	Schmidt number, dimensionless
718	t	time, h
719	T	temperature, K
720	T_w	reactor wall temperature, K
721	T_{gin}	feed gas temperature, K
722	T_{in}	feed gas temperature, K
723	T_0	initial temperature of the solids in the reactor, K
724	T_{s0}	initial solid temperature, K
725	u	superficial velocity of gas, m/h
726	x_i	gas-phase mole fraction of component i , dimensionless
727	X	fractional carbonation conversion of CaO, dimensionless
728	X_{max}	maximum fractional carbonation conversion of CaO, dimensionless
729	z	axial coordinate in bed, m
730	Greek letters	
731	ε	bed void fraction, dimensionless
732	φ_{ij}	stoichiometric coefficient of component i , dimensionless
733	ρ_{CaO}	apparent density of CaO-based material, kg m^{-3}
734	ρ_{cat}	apparent density of reforming catalyst, kg m^{-3}
735	ρ_g	gas phase density, kg m^{-3}
736	ρ_s	apparent density of the two mixed solids in the reactor, kg m^{-3}
737	η	effectiveness factor, dimensionless
738	v_{CO_2}	gas-phase mole fraction of CO_2 , dimensionless
739	$v_{\text{CO}_2, \text{eq}}$	gas-phase equilibrium mole fraction of CO_2 , dimensionless
740	μ_g	viscosity of gas, bar h

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Table 1: SER tests experimental conditions.

Experimental set-up	particle size cut (μm)	Bed length (m)	MHSV (kg CH ₄ h ⁻¹ kg cat ⁻¹)	Z	S/C	Total operation pressure (bar)
Micro-fixed bed	100-200	0.02-0.04	0.75-2.5	4-15	4	1
Bench-scale fixed bed	600-1000	0.15	1.78-4.0	5	3.2	1
Bench-scale fixed bed	600-1000	0.15	2.5	5	3.2	1-9

Table 2: Mass and energy balances used in the model.

Component molar balances

$$\varepsilon \frac{\partial C_i}{\partial t} = -u_g \frac{\partial C_i}{\partial Z} + \frac{\partial}{\partial Z} (D_{eff} \frac{\partial C_i}{\partial Z}) + \eta(1 - \varepsilon)r_i \rho_i \quad (2)$$

Energy balance

$$\left((1 - \varepsilon)\rho_s C_{ps} + \varepsilon \rho_g C_{pg} \right) \frac{\partial T}{\partial t} = -u_g \rho_g C_{pg} \frac{\partial T}{\partial Z} + \frac{\partial}{\partial Z} (\lambda_{eff} \frac{\partial T}{\partial Z}) - \Sigma \eta_i (1 - \varepsilon) H_{ri} + h_w (T_w - T) \frac{4}{Dr} \quad (3)$$

Where h_w is the wall-bed heat transfer coefficient calculated according to [69]

$$h_w = 2.03 \frac{kg}{Dr} Re^{0.8} \exp\left(-\frac{6}{Dr}\right) ; Re = \frac{u_g \varepsilon \rho_g Dr}{\mu} \quad (4)$$

Momentum balance, Ergun equation

$$\frac{dP}{dZ} = -150 \frac{\rho_g u_g^2 (1 - \varepsilon)^2}{d_p^2 \varepsilon^3} + 1.75 \frac{\rho_g u_g^2 (1 - \varepsilon)}{d_p \varepsilon^3} \quad (5)$$

Table 3: The axial mass and heat dispersion coefficients.

Axial mass dispersion coefficient [70]

$$D_{eff} = \left[\frac{0.73}{ReSc} + \frac{0.5}{\varepsilon + \frac{9.7\varepsilon^2}{ReSc}} \right] u_g d_p \quad (6)$$

Effective axial heat dispersion [71]

$$\lambda_{eff} = \lambda_{0bed} + \frac{RePrk_g}{Pe_{az}} + \frac{Re^2Pr^2k_g^2}{6(1-\varepsilon)Nu} \quad (7)$$

Where λ_{0bed} is calculated according to [72]

$$\lambda_{0bed} = \left(\frac{k_s}{k_g} \right)^{0.28 - 0.757 \log(\varepsilon) - 0.057 \log \left(\frac{k_s}{k_g} \right)} \quad (8)$$

In which Pe_{az} is calculated according to [73]

$$Pe_{az} = \frac{2p}{1-p} ; p = 0.17 + 0.29e^{\left[\frac{-24}{Re} \right]} \quad (9)$$

Gas-to-particle heat transfer coefficient [74]

$$Nu = 2 + 1.8Re^{0.5}Pr^{0.33}$$

Table 4. Equations, kinetic and equilibrium parameters in SMR [55-57].

$$R_1 = \frac{1}{(DEN)^2} \frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1} \right) \quad (10)$$

$$R_2 = \frac{1}{(DEN)^2} \frac{k_2}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_2} \right) \quad (11)$$

$$R_3 = \frac{1}{(DEN)^2} \frac{k_3}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_3} \right) \quad (12)$$

$$DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}} \quad (13)$$

$$r_{CH_4} = -R_1 - R_2 \quad (14)$$

$$r_{H_2O} = -R_1 - 2R_2 - R_3 \quad (15)$$

$$r_{H_2} = 3R_1 + 4R_2 + R_3 \quad (16)$$

$$r_{CO_2} = R_2 + R_3 \quad (17)$$

$$r_{CO} = R_1 - R_3 \quad (18)$$

$$r_i = \sum_{j=1}^3 \varphi_{ij} R_j \quad (i=1-5 \text{ component: CH}_4, \text{H}_2\text{O, H}_2, \text{CO}_2, \text{CO, } j=1-3) \quad (19)$$

$$K_1 = \frac{1}{\exp(0.2513 Z^4 - 0.3665 Z^3 - 0.58101 Z^2 + 27.1337 Z - 3.2770)} \text{ bar}^2 \quad (20)$$

$$Z = 1000/T - 1; \quad K_2 = K_1 K_3 \quad (21)$$

$$k_1 = 1.842 \cdot 10^{-4} \exp \left[\frac{240100}{R} \left(\frac{1}{T} - \frac{1}{648} \right) \right] \text{ kmol bar}^{0.5} \text{ kg}^{-1} \text{ cat h}^{-1} \quad (22)$$

$$k_2 = 2.193 \cdot 10^{-5} \exp \left[\frac{243900}{R} \left(\frac{1}{T} - \frac{1}{648} \right) \right] \text{ kmol bar}^{0.5} \text{ kg}^{-1} \text{ cat h}^{-1} \quad (23)$$

$$k_3 = 7.558 \exp \left[\frac{67130}{R} \left(\frac{1}{T} - \frac{1}{648} \right) \right] \text{ kmol kg}^{-1} \text{ cat h}^{-1} \text{ bar}^{-1} \quad (24)$$

$$K_{\text{CH}_4} = 0.179 \exp \left[\frac{38280}{R} \left(\frac{1}{T} - \frac{1}{823} \right) \right] \text{ bar}^{-1} \quad (25)$$

$$K_{\text{H}_2\text{O}} = 0.4152 \exp \left[\frac{88680}{R} \left(\frac{1}{T} - \frac{1}{823} \right) \right] \text{ bar}^{-1} \quad (26)$$

$$K_{\text{H}_2} = 0.0296 \exp \left[\frac{82900}{R} \left(\frac{1}{T} - \frac{1}{648} \right) \right] \text{ bar}^{-1} \quad (27)$$

$$K_{\text{CO}} = 40.91 \exp \left[\frac{70650}{R} \left(\frac{1}{T} - \frac{1}{648} \right) \right] \text{ bar}^{-1} \quad (28)$$

$$\frac{dX_{\text{carb}}}{dt} = \frac{k_{\text{carb}}}{p^q} (X_{\text{max}} - X) (u_{\text{CO}_2} - u_{\text{CO}_2, \text{eq}}) \quad (29)$$

$$r_{\text{carb}} = \frac{1}{M_{\text{CaO}}} \left(\frac{dX_{\text{carb}}}{dt} \right) \quad (30)$$

$$C_{\text{CO}_2, \text{eq}} = \frac{5.045 \times 10^{11}}{T} \exp \left(\frac{-20.474}{T} \right) \quad (31)$$

$$k_{\text{carb}} = 2160 \text{ h}^{-1} \quad (32)$$

$$\eta = 0.3 \quad (33)$$

$$q = 0.3 \quad (34)$$

Table 5. Main textural properties of the fresh materials.

	$\rho \text{ g/cm}^3$	$\epsilon_{\text{particle}}$	$S_{\text{BET}} \text{ m}^2/\text{g}$	Mean pore size (nm)
Ni catalyst	3.4	0.41	25	14
CaO-Ca₁₂Al₁₄O₃₃	2.71	0.48	16	80

CAPTIONS FOR FIGURES

Figure 1. a) H₂ production Ca/Cu looping process concept. b) Example of complete Ca/Cu looping cycle configuration extracted from Fernández et al. [24].

Figure 2. Experimental set ups. a) bench-scale fixed bed reactor, b) micro-fixed bed reactor.

Figure 3. XRD patterns of a) reduced Ni Catalyst after different number of oxidation/reduction cycles and b) calcined CaO/ Ca₁₂Al₁₄O₃₃ sorbent.

Figure 4. SEM images of reduced Ni Catalyst after different number of oxidation/reduction cycles.

Figure 5. H₂-TPR profiles of Ni Catalyst, fresh and aged.

Figure 6. a) Evolution of sorbent CO₂ carrying capacity with the number of reaction cycles. Carbonation: 15 minutes at 923 K, 15 % vol. CO₂/15 % vol. H₂O in air. Calcination: 1173 K in a 70 % vol. CO₂ in air. b) Evolution of CaO molar conversion with time (2nd cycle), at 923 K and 10 % vol. CO₂ in air. The figure includes the predictions by Equation (29) in Table 4.

Figure 7. a) Effect of CH₄ space velocity expressed as kg CH₄ h⁻¹ kg cat⁻¹ on gas product composition with time. Evolution of H₂ and CO₂ % vol. (d.b. free of N₂) are plotted. Experimental conditions: S/C 3.2, Z=5 and 923K. Space velocities from 1.78 kg CH₄ h⁻¹ kg cat⁻¹ to 4 kg CH₄ h⁻¹ kg cat⁻¹ were evaluated. The figure includes model predictions in solid lines. b) % vol. of the meaningful species for the reaction during the pre-break, and post-break through periods for the experiment performed at 2.5 kg CH₄ h⁻¹ kg cat⁻¹.

Figure 8. Effect of total pressure of operation on the evolution of product gas composition with time, H₂ and CO₂ % vol. (d.b. free of N₂) plotted. Experimental conditions: S/C 3.2, Z=5 and 923K Space velocity 2.5 kg CH₄ h⁻¹ kg cat⁻¹; a) 3 bars total pressure ; b) 5 bars total pressure; c) 7 bars total pressure; d) 9 bars total pressure.

Figure 9. Evolution of product gas composition with time and Z, H₂ and CO₂ % vol. (d.b.) plotted. Experimental conditions: S/C 4, Z=4-15 and 923K, Space velocity 0.75 kg CH₄ h⁻¹ kg cat⁻¹.

Figure 10 Evolution of product gas composition for experiments that include HiFUEL® R110 catalyst cycled 200 times with time and cycle number, H₂ and CO₂ % vol. (d.b. free of Ar) plotted. Experimental conditions: S/C 4, Z=4 and 923 K, Space velocity 0.75 kg CH₄ h⁻¹ kg cat⁻¹.

Figure 11. Evolution of product gas composition obtained for HiFUEL® R110 cycled 200 times with time and space velocity, H₂ and CO₂ % vol. (d.b.) plotted. Experimental conditions: S/C 4, Z=4-7 and 923K, Space velocity 0.75-2.5 kg CH₄ h⁻¹ kg cat⁻¹.

Figure 1.

Figure 2.

Figure 3.

a)

b)

Figure 4.

Reduced

Reduced after 200 c

Figure 5.

Figure 6.

a)

b)

Figure 7.

a)

b)

Figure 8.

Figure 9.

Figure 10.

Figure 11.