Hydrogen production through sorption enhanced steam reforming of natural gas: Thermodynamic plant assessment

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ABSTRACT

A detailed and comprehensive simulation model of a H_2 production plant based on the Sorption Enhanced Reforming (SER) process of natural gas has been developed in this work. Besides thermodynamic advantages related to the shift of reforming equilibrium, SER technology features an intrinsic CO_2 capture that can be of interest in environmentally constrained economies. The model comprises natural gas treatment, H_2 and CO_2 compression, as well as H_2 purification with an adsorption unit that has been integrated within the SER process by using the off-gas for sorbent regeneration. A complete thermal integration has been also performed between the available hot gas streams in the plant, so that high pressure steam is generated and used to generate power in a steam cycle.

A comprehensive comparison with conventional H_2 production technologies based on fired tubular reforming (FTR) has been made by defining a proper set of performance indexes. The investigation allowed to set the optimal design parameters and operating conditions of the SER plant and conclude that a better hydrogen production efficiency can be attained when reactors are designed for atmospheric pressure operations rather than pressurized (3 bar) conditions. The SER plant with optimized design parameters (reformer operating temperature at 923 K and a steam-to-carbon ratio in the initial charge around 2) shows considerable improvements on the carbon capture ratio (around 99% for the SER case vs. 85% for the FTR case) and on the natural gas to hydrogen conversion efficiency (by around 15 percentage points) in comparison to the FTR based process featuring CO_2 capture. On the whole, a higher natural gas to hydrogen conversion efficiency by 9–15 percentage points, or by 3–6 percentage points when considering credits for steam and electricity import/export, have resulted for the SER plant operating at atmospheric pressure in comparison to the conventional hydrogen production process.

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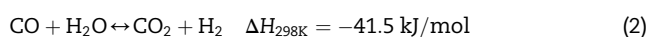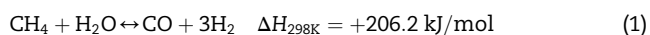
1. Introduction

Hydrogen main applications comprise ammonia and methanol synthesis, hydrocraking and hydroprocessing in refineries, hydrogenation of ethylene, metallurgical processes or glass production. Other recent applications of hydrogen as low emission fuel for gas turbines, fuel cells and combustion engines have also been proposed, which could result in large hydrogen demands in a medium-to-long term [1]. There is also global concern about reducing anthropogenic CO_2 emissions to the atmosphere to mitigate the problem of global warming. Among the different options to fulfil this objective in the energy sector at a large scale, carbon capture and storage arises as the only technology available to achieve this deep emission reduction from fossil fuels usage [2]. In this context, large scale hydrogen production processes including CO_2 capture at a reduced cost and more efficient than existing processes, constitute a great opportunity in the climate change mitigation route [3,4].

Steam Methane Reforming (SMR) is the most widely used technology to produce H_2 at commercial scale, responsible for around 50% of the H_2 produced worldwide [2,5]. First step entails the catalytic reforming of natural gas, NG, (reaction 1) at high temperatures and high pressure (typically 1073–1173 K and 15–30 bar). In the Fired Tubular Reforming (FTR) arrangement, reaction takes place within catalyst-filled alloy reactor tubes directly radiated by the flames of external burners. Additional NG is usually burnt with air in the furnace burners to supply the high temperature heat required to sustain the endothermic reaction. FTR is followed by a shift reaction stage (reaction 2) in the 623–673 K temperature range to improve CO conversion to CO_2 and enhance hydrogen yield [6,7]. In case CO_2 absorption is performed on the synthesis gas before the hydrogen purification unit, a second water gas shift reactor operating at a lower temperature (around 473 K) is usually introduced to increase CO_2 concentration in the gas and favour hydrogen yield. The final H_2 separation in a Pressure Swing Adsorption (PSA) unit allows removing other species in the product gas leading to hydrogen purity greater than 99.9%. SMR represents the most valuable, commercially proven technology for H_2 production on a mid to large scale compared to the alternative technologies which are the current choice for distributed (catalytic partial oxidation) or massive production (coal gasification or autothermal reforming).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{298K} = +206.2 \text{ kJ/mol} \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41.5 \text{ kJ/mol} \quad (2)$$

Despite its attractiveness, SMR presents important disadvantages [6] associated to expensive high alloy steels required in the tubes, complexity of the process (high number of stages with different catalysts) and thermodynamic constraints that force to operate SMR at high temperatures and relatively low pressure to enhance hydrogen yield [7–9].

To overcome the thermodynamic limitations of the SMR, the Sorption Enhanced Reforming (SER) process proposes the addition of a Ca-based CO_2 acceptor to the commercial SMR catalyst so that the reforming, shift and CO_2 removal processes (reactions 1, 2 and 3) take place simultaneously in the reactor [10–12]. Although this work is focused on employing a CaO-based material as CO_2 sorbent to perform the SER process, other natural and synthetic sorbents like dolomite or hydrotalcite have been proposed and experimentally tested in fixed bed and fluidised bed reactors to prove their suitability as CO_2 sorbents for carbon capture in SER applications [11–16]. The combination of chemical and separation reactions simplifies the process, improves efficiency and enhances conversion and hydrogen yield [9,11,12]. According to SER equilibrium, product gas with a hydrogen content around 96% vol. (dry basis) is possible in a wide range of temperatures from 923 K to 1023 K when using CaO-based sorbents, and no shift catalysts would be required at reaction conditions thanks to the CO_2 removal reaction [8,11]. Because of the reactions occurring in the same reactor vessel, energy released by exothermic shift and carbonation reactions balances that required in the endothermic reforming reaction, and no supplementary energy would be needed to drive the reforming process like in the SMR [8].

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad \Delta H_{298K} = -178.8 \text{ kJ/mol} \quad (3)$$
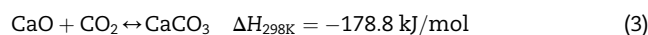
One of the main issues to consider in the SER process is the sorbent regeneration stage, needed to continuously regenerate the sorbent and allow cyclic operations. Commonly, energy for sorbent regeneration is supplied by direct combustion of a fuel, usually with pure O_2 to avoid dilution of the CO_2 generated during sorbent calcination [17,18]. In this configuration, temperatures around 1223 K are required in the regenerator-combustor to favour calcination reaction equilibrium, prevent Ca-sorbent from sintering and avoid large sorbent replenishment [19,20]. Higher calcination temperatures might be used if low sorbent capacity were accepted in the process, by using larger amounts of sorbent, or in case that high sinter-resistant synthetic sorbents were developed. Other alternatives have been proposed to avoid the large-electricity demanding O_2 production process that is required in the direct combustion option described above. In these solutions calciner is warmed up by sensible heat from hot gas/solid streams introduced in the calciner [21–23], by indirect heating from an external heat source [24,25] or by coupling an exothermic reduction reaction in the calciner using CH_4, CO or H_2 as reducing agent [26–29].

There is a large number of published works on Ca-based sorbent synthesis and performance, appropriate for SER operation because of their low inert content and high cycle stability [30–34], on experimental tests in fixed-bed reactors for SER operation using Ca-based sorbents [8,13,14] and on modelling fixed-bed or fluidized bed SER reactors that elucidate the best operating conditions from an equilibrium point of view [25,35–40]. Concerning process configuration, multiple fixed bed reactors switching from H_2 production and sorbent regeneration is the predominant reactor configuration both for experimental and modelling research on SER [13,25,39,40]. Ochoa-Fernandez et al. (2007) [17] and

Solieman et al. (2009) [41] assessed a complete plant for H_2 production based on a packed bed system with high pressure reforming and low pressure calcination for H_2 production and for electricity production in a combined cycle power plant, respectively. From an industrial scale production, this configuration of fixed bed reactors offers some restrictions from continuous regeneration of the sorbent, limited heat transfer and sorbent/catalyst separation, and this is why it is commonly relegated to small production scale [42]. Low pressure interconnected fluidized bed reactors have become a common option for SER operation since it allows sorbent circulation between reactors and easy adding/replenishment of solids in the system, and it enjoys good heat transfer characteristics and uniform temperature in each reactor [25,42]. Chen et al. (2011) [24] assessed only the reactor system and considered low pressure (2 bar) interconnected fluidized beds, with sorbent regeneration at 1173 K by oxy-fuel combustion. Romano et al. (2011) [18] considered the integration of an SER process into a combined cycle based power plant, by using two pressurized interconnected fluidized beds with high temperature (1473 K) calcination by oxy-fuel combustion, requiring improved sorbent and catalyst properties with respect to the current technology. Although this reactor configuration has already been demonstrated for other processes in pilot scale plants, its main disadvantage when used for reforming applications is that H_2 is delivered at low pressure. Considering that low pressure applications are rather uncommon, H_2 stream from this process requires cooling and compression to be taken to the proper pressure for its final utilization.

Although there is a wide database of published works about SER referred to sorbent characteristics, experimental tests and reactor modeling, there is still a gap of information about complete hydrogen production plants based on SER to analyze how the different operating conditions or assumptions considered influence plant performance. The main objective of this work is to fill this gap of knowledge by developing a complete simulation model of a hydrogen production plant based on the SER process that delivers H_2 at an adequate pressure to be compared with an SMR-based plant. The model developed in this work comprises NG treatment, H_2 and CO_2 compression, as well as H_2 purification with a PSA unit that has been integrated within the SER process by using the off-gas to be burnt with oxygen for sorbent regeneration. A complete thermal integration has been arranged between the available hot gas streams in the plant so that high pressure steam is raised and used to generate power in a steam cycle. Different performance indexes have been defined to assess the thermodynamic "quality" of the SER conversion process, set the main design parameters of the plant and make a comparative analysis with an FTR based plant.

2.   Process simulation description

The hydrogen production plant simulation model based on the SER process has been built up in Aspen Hysys. Performance of the different case studies analyzed have been

compared with a reference plant based on a commercial FTR arrangement, for a better assessment of the performance in terms of energy consumption and carbon capture rate.

2.1.   Reference plant: steam reforming of natural gas with CO_2 capture

The reference plant considered is based on conventional natural gas steam reforming in an FTR arrangement, as commonly installed in refineries [43–45]. A typical H_2 output of 30,000 Nm^3/h has been assumed as reference for all the plants considered in this work. A detailed layout of this reference plant featuring CO_2 capture by MDEA absorption is shown in Fig. 1.

After the desulphurization step, NG is mixed with steam and sent to an adiabatic pre-reformer operating at 32 bar. A steam-to-carbon (S/C) molar ratio of 4 has been assumed to ensure a satisfactory overall methane conversion in SMR and CO conversion in WGS, so as to make possible a high CO_2 capture ratio.[1] The pre-reformed charge is sent to the FTR, designed to achieve an outlet reformed gas temperature of 1163 K. At the FTR exit, the reformed syngas is cooled down by producing saturated high pressure steam (at 100 bar). This configuration avoids problems related to metal dusting, since the evaporating water keeps tubes below the critical temperature for its initiation. Syngas, once cooled to 603 K, is sent to a high temperature WGS reactor, where most of the CO is converted to CO_2, enhancing H_2 content in the syngas. After cooling to 473 K, CO is further converted to CO_2 in a low temperature WGS reactor, so that at the exit about 90% of the carbon in the natural gas input is present in the syngas as CO_2.

Syngas from WGS section is then cooled to nearly ambient temperature and sent to a chemical absorption section for CO_2 separation. CO_2 capture is performed by means of an MDEA chemical absorption process [46] that selectively removes about 95% of the CO_2 releasing a H_2-rich stream. The high-purity CO_2 released in the stripper (whose reboiler requires 0.88 MJth per kg of CO_2 captured from condensation of 2.7 bar steam) is then cooled, dried and compressed to the final pressure of 110 bar. The CO_2-lean H_2-rich stream from the MDEA process is then partly sent to the PSA unit for further purification. PSA separates 90% of the inlet hydrogen as high pressure, extremely pure stream. The PSA off-gas is mixed with the syngas fraction by-passing the PSA and used as carbon lean fuel in the burners of the FTR furnace leading to 85% of carbon capture ratio from the overall H_2 production process.

The reference FTR plant without CO_2 capture differentiates from the configuration shown in Fig. 1 because it lacks of the low temperature WGS reactor and the CO_2 absorption section, and NG is used as fuel in the FTR burners instead of

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[1] Avoiding carbon deposition and ensuring enough steam-to-dry gas ratio at high temperature WGS inlet are additional constraints calling for an adequate S/C ratio in the reforming charge. An S/C of at least 2.7 has been selected to comply with all those limits. This value has been adopted for the reference plant without CO_2 capture later introduced.
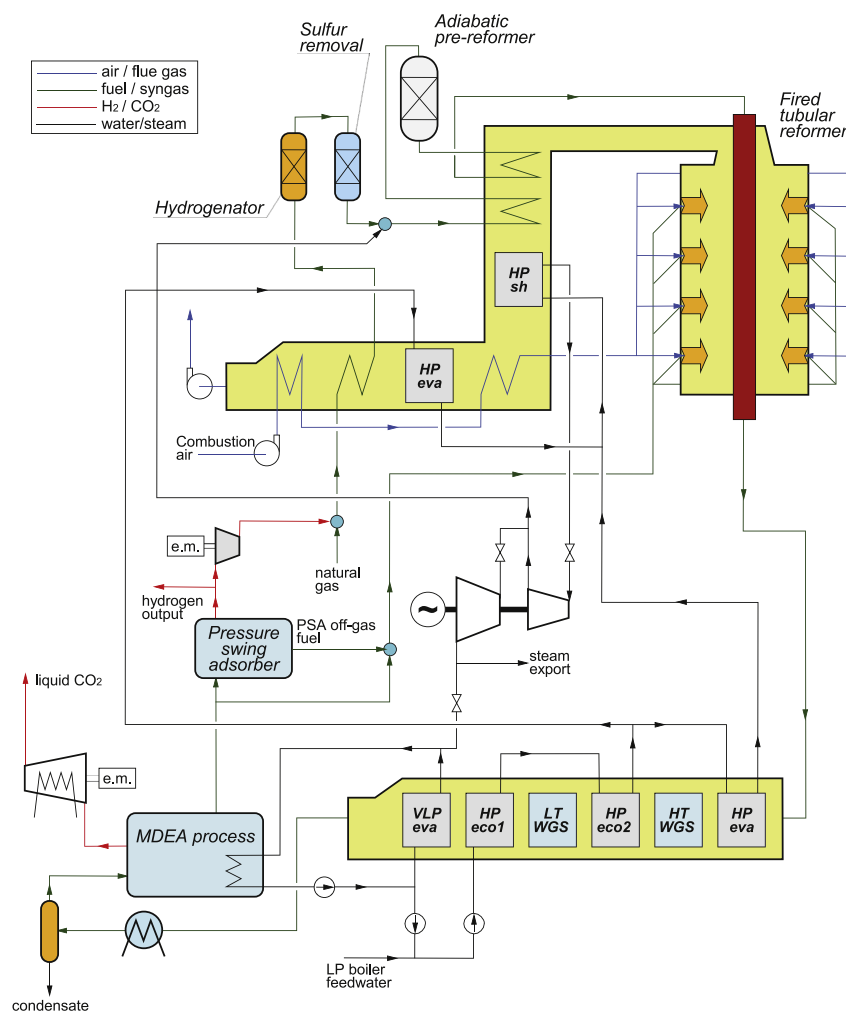
Fig. 1 − **Layout of the H₂ production plant based on a Fired Tubular Reformer (FTR) used as a comparison.**

low purity hydrogen. Syngas at the exit of the high temperature WGS is hence cooled to nearly ambient temperature and sent to the PSA purification unit, where high pressure pure hydrogen is separated. The resulting low pressure off-gas stream from the PSA is rich in CO_2 but still contains significant fractions of combustible species (CH_4 and CO, along with H_2). It is therefore mixed with additional untreated NG and burned in the FTR furnace. Since high carbon to CO_2 conversion is not essential in plants without CO_2 capture, S/C ratio in the initial charge has been reduced to 2.7 just to comply with the requirements summarized in footnote 1. These changes allow a plant simplification and an improvement of the overall NG to H_2 conversion efficiency provided that unconverted methane and CO included in the syngas stream are effectively exploited afterwards as fuel in the FTR furnace.

In both plants, excess heat is available from syngas and furnace flue gas cooling, with respect to the amount required to guarantee the selected S/C ratio in the reformer. Thus, heat is mainly recovered by producing high pressure steam (100 bar) and a backpressure steam turbine is propelled by expanding steam, in order to improve efficiency of

the overall process. Steam is first expanded to an intermediate pressure of 40 bar, where part of the steam is extracted to form the reforming charge. The extra steam available is further expanded to 6 bar and is partly used for CO_2 stripping (when the CO_2 absorption unit is used) and partly exported from the SMR plant. It should be noted that the high pressure evaporation level of 100 bar is higher than typically adopted in current hydrogen plants. However, this was considered a better assumption for benchmark plants, for a fair comparison with mid-long term plants, adopting advanced technologies and aiming at low emissions and high efficiencies.

2.2.   Sorption enhanced reforming of natural gas

Fig. 2 shows the layout of the hydrogen production plant based on the SER process assessed in this work. Reformer and calciner are circulating fluidized bed reactors operating at the same low pressure and at different temperatures, so that the $CaO-CaCO_3$ system is conveniently favoured in each reactor. Temperature in the reformer has been varied in the range between 873 K and 948 K, which lead to the
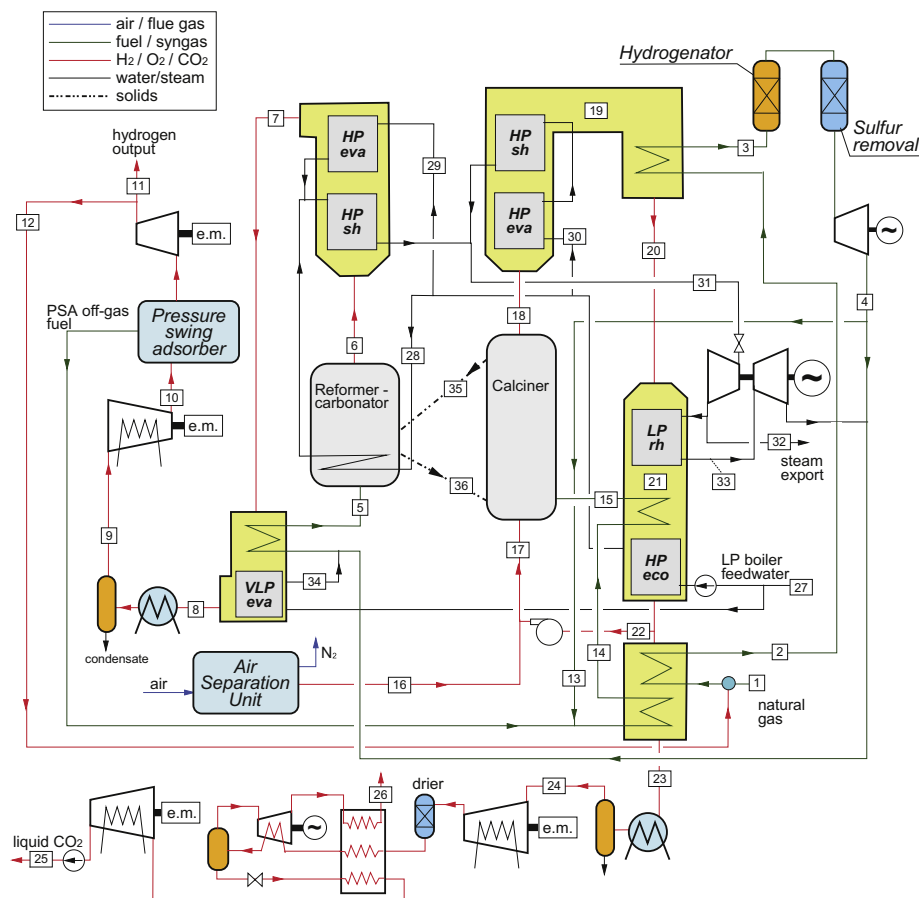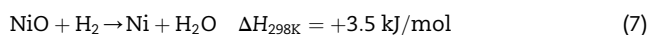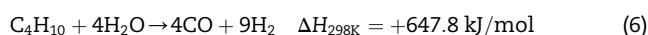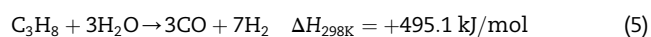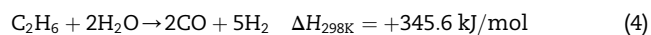
Fig. 2 – Layout of the assessed hydrogen production plant based on SER process.

maximum hydrogen yield in the SER equilibrium (reactions 1, 2 and 3) [8]. Reactions considered in the reformer-carbonator are: (1) Reforming of the higher hydrocarbons fed with the NG into CO and H_2 (reactions 4, 5 and 6), which is considered as irreversible for all higher hydrocarbons provided that enough catalyst activity exits [47]; (2) Activation of the Ni-based catalyst (in the form of NiO when coming from the calciner) by reduction with the H_2 present in the reactor (reaction 7); (3) Equilibrium between reforming, water gas shift and carbonation reactions, responsible for the improved CH_4 conversion in the SER process (reactions 1, 2 and 3). Charge fed into the reformer is usually pre-heated to around 573 K, although at high reformer temperatures (i.e. 923 K or 948 K) slightly higher reformer inlet temperatures of 623–648 K are needed to keep the reactor thermally neutral. Although reforming of hydrocarbons is strongly endothermic, there is generally a heat excess in the reformer reactor because of the high temperature and flow rate of solids coming from calciner, and due to the heat released by CaO carbonation.

$$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2 \quad \Delta H_{298K} = +345.6 \text{ kJ/mol} \quad (4)$$

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \quad \Delta H_{298K} = +495.1 \text{ kJ/mol} \quad (5)$$

$$C_4H_{10} + 4H_2O \rightarrow 4CO + 9H_2 \quad \Delta H_{298K} = +647.8 \text{ kJ/mol} \quad (6)$$

$$NiO + H_2 \rightarrow Ni + H_2O \quad \Delta H_{298K} = +3.5 \text{ kJ/mol} \quad (7)$$

CaO-based sorbent composition assumed in the simulation model is 85% wt. of CaO over an Al-based support (considered as Al_2O_3 in the model for energy balance calculations), leading to a CaO-based sorbent with residual 40% of active CaO after repeated carbonation–calcination cycles, based on the literature published on high stability Ca-based sorbents for CO_2 capture [30–33,48]. According to the activity of the Ca-based sorbent assumed in this work, a minimum solid circulation of 2.5 mol of Ca per mol of C at the entrance of the reformer would be needed to fully adsorb all the CO_2 producible in the reformer-carbonator. Thus, it has been chosen a solid circulation of 3 mol of Ca per mol of C to have some excess of circulating sorbent. As presented further on, the actual sorbent conversion in the carbonator will vary between 23 and 32%, as determined by the chemical equilibrium established at the different operating conditions explored for the reformer-carbonator (S/C, temperature and pressure). According to literature data, the resulting amount of active sorbent should lead to a highly reactive solid population in the carbonator, allowing the reactor to operate very close to the equilibrium with reasonable solid inventories [49–51].

In addition, a typical commercial reforming catalyst of 18% wt. of Ni supported over Al_2O_3 has been considered in the simulations, using a reasonable catalyst-to-sorbent mass ratio of 0.3 in the solid stream from the calciner to the reformer (calculated as mass of active catalyst, including the Al_2O_3 support, with respect to the total amount of CaO in the Ca-based sorbent) [36]. Steam-to-carbon ratio, S/C, in the gas stream fed to the reformer-carbonator is usually in the 3—5 range to ensure high hydrogen yield [42] and therefore high overall CO_2 capture rate. In this work, the S/C molar ratio in the reformer charge has been varied within all the range that complies with feasible plant operations.

Contrary to post-combustion Ca-looping processes, where ash and $CaSO_4$ can accumulate in the circulating solids, in principle no purge is required in this application since an ash and sulphur-free fuel is burned in the calciner. Sorbent and catalyst make-up is hence needed to compensate the material loss due to attrition and entrainment from the fluidized beds, which should be limited as much as possible. Therefore it seems reasonable to assume low make-up values leading to negligible effects on plant mass and energy balances. On the other hand, the impact of even small sorbent and catalyst losses might be important on the operating costs, and therefore, experimental tests focused on sorbent and catalyst mechanical resistances would be needed to have reliable estimations on solids losses to be introduced in the simulation model. In this work, a minimum sorbent make-up flow of 0.001 mol of Ca per mol of C fed into the reformer has been considered in the SER plant to compensate for these losses [52,53] (not depicted in the plant layout in Fig. 2 for the sake of simplicity).

After cooling and heat recovery, gas from the reformer is conditioned for compression by removing water in a condenser at 304 K. After condensation, a H_2-rich gas stream is obtained (purity close to 97% for the highest S/C molar ratio) and it is compressed up to 20 bar to be purified in a PSA unit. H_2 compressor has been simulated as a 5-stage intercooled compressor, with intermediate condensate removal. PSA technique for hydrogen purification is based on adsorbing selectively gas species different from hydrogen on a solid surface of a microporous adsorbent such as zeolites or activated carbons. It operates close to ambient temperature and produces a nearly pure H_2 gas stream (>99.9% of purity) at a pressure slightly lower than feed pressure and an off-gas at low pressure, containing the hydrogen not separated and the rest of impurities (CH_4, CO, CO_2, N_2). H_2 recovery factor (HRF) usually ranges from 75 to 90%, greatly influenced by the off-gas to feed pressure ratio. The lower the off-gas pressure, which can range between atmospheric and about 10 bar, the higher the HRF and, therefore, the lower the investment and the operating costs [54]. For a PSA feed gas pressure of 20 bar, a 90% of HRF is possible if PSA off-gas pressure is near atmospheric, but this recovery factor is reduced to 85% if off-gas pressure goes up to 2 bar [54]. Since comparison with the conventional steam reforming plant sets hydrogen output pressure at 29 bar, additional hydrogen compression obtained from the PSA working at 20 bar is needed, as depicted in the plant layout in Fig. 2.

Solids leaving the reformer are sent to the calciner reactor that operates at a temperature high enough to ensure complete calcination. This temperature is set by complying with a number of conflicting requirements that can be summarized as follows:

- the lower limit of the calciner operating temperature is the equilibrium temperature of reaction (3) calculated (according to Baker [55]) for the given CO_2 partial pressure in the gas exiting the calciner (synthetic Ca-based sorbents can show discrepancies with natural sorbents in the equilibrium data for reaction (3). However, this effect has been neglected since no information about equilibrium data of the synthetic sorbent used is available and, in the absence of better information, information for natural sorbent from Baker [55] has been used);
- a suitable temperature margin over the previous limit has to be kept in order to provide enough driving force for reaction completion;
- on the other hand, as reported in the literature, temperature difference between carbonator and calciner influences to a large extent fuel consumption in the calciner [56]. Thus, the higher the temperature margin, the lower the process conversion efficiency. A 15 K temperature margin between calciner temperature and equilibrium temperature of reaction (3) has been assumed as an acceptable value to meet these needs [57];
- although commercial steam reforming catalyst can face temperatures up to 1273 K, Ca-based sorbent capacity is dramatically affected when going above 1223 K [19,20]. By keeping the calcination temperature at this value and taking into account the assumptions of previous bullets, the maximum operating pressure of the two reactor system is limited to about 3 bar.

Energy for sorbent calcination is supplied by burning additional NG and the PSA off-gas under oxy-combustion conditions. 95% purity oxygen (with 2% of N_2 and 3% of Ar in mixture) comes from an Air Separation Unit (ASU), whose energy consumption has been assumed equal to 250 kWh/ton of O_2 produced [58]. To mitigate hot spots in the calciner, the oxygen stream is diluted to 35% vol. O_2 content by recycling part of the outlet gas stream from the reactor (stream 22 in Fig. 2). An oxygen excess of about 7% has been taken into account to ensure complete fuel combustion that results in 1.5% vol. oxygen content in the calciner outlet stream (wet basis, equivalent to ~2.6% dry basis). Moreover, due to the oxidant reaction atmosphere and the high temperatures in the calciner, full oxidation of the catalyst has been assumed in this reactor. The catalyst is then reduced in the reformer, where reducing conditions exist, by oxidizing a fraction of the reformer feed as in a chemical looping combustion mechanism.

Gas from calciner is cooled down to 573 K before being split into the stream recycled to the calciner and the one going to purification and compression. A blower is needed in the recycled gas line to compensate for the pressure losses in the calciner and in the heat recovery system. After further cooling and heat recovery, the stream, having a CO_2 content of 93—94% vol. (dry basis), is purified from the non-

condensable gases by means of a single stage auto-refrigerated cryogenic process. The impure CO_2-rich stream is initially compressed by a three-stage intercooled compression. The CO_2 knock out drum pressure was set to obtain the required purity specification of 96% mol., resulting to be about 20 bar. CO_2 stream at the intermediate pressure is then dried, cooled down to 219 K and sent to a knockout drum, where the liquid stream is separated from the non-condensable gas-rich stream. CO_2 rich stream is further dehydrated with a circulating triethylene glycol desiccant and/or molecular sieve to prevent plugging due to ice formation in the cold section. The purified liquid CO_2 is then throttled in a valve in order to reduce its temperature and ensure a minimum internal ΔT of 2 K in the cryogenic heat exchanger. The gaseous flow exiting the knockout drum is also expanded to nearly atmospheric pressure in a three-stage inter-heated cryogenic expander, recovering part of the compression energy and contributing to the total chilling power by further cooling the impure CO_2 stream before entering the knockout drum. The CO_2-rich gas stream obtained goes through a second two-stage compression section with intermediate cooling/condensation at 89 bar, and it is finally pumped to 110 bar.

Heat recovered from cooling gas streams is used to pre-heat calciner and reformer feed streams, and to generate superheated steam at 100 bar and 758 K that is expanded in a steam turbine and supplies the steam required in the reformer. To properly arrange the layout of the different heat exchangers, composite curves (Temperature vs. Heat transferred) of gas stream from reformer (Fig. 3(a, b)) and from calciner (Fig. 3(c)) have been drawn. High pressure econo-miser (HP ECO) delivers water at 573 K close to saturation to the evaporator that produces steam at 585 K. High pressure steam can be generated thanks to the heat released from the reactions inside the reformer (horizontal line in Fig. 3(a)) and to the heat recovered from the outlet gas. Steam generated in this way may reach half of the total amount of steam produced in the process when the reformer operates at 873 K, the lowest reformer temperature analyzed in this study. When the reformer operates at a higher temperature, more energy is required to warm the inlet charge up to the reaction temperature. Therefore, the energy available for steam production in the reformer-carbonator diminishes or even reduces to zero when temperature exceeds 923 K, as explained in Section 3.2.1. In Fig. 3(b) that refers to a case with a reformer operating temperature of 923 K, the horizontal stroke of the heat transfer composite curve is virtually negligible. Additional low pressure steam is produced with the remaining low temperature heat before the PSA purification unit.

Fig. 3(c) depicts the heat recovery system associated to the calciner outlet stream at a higher temperature than the reformer. To reduce the maximum metal temperatures and allow using cheaper materials, high pressure superheater (HP Sh) has been placed after the evaporator at a lower temperature without affecting plant performance. It should be highlighted that no CO-rich syngas stream with high carbon activity is generated in the system, allowing rising superheated steam with no risk of incurring in metal dust-ing corrosion. The total amount of steam produced from
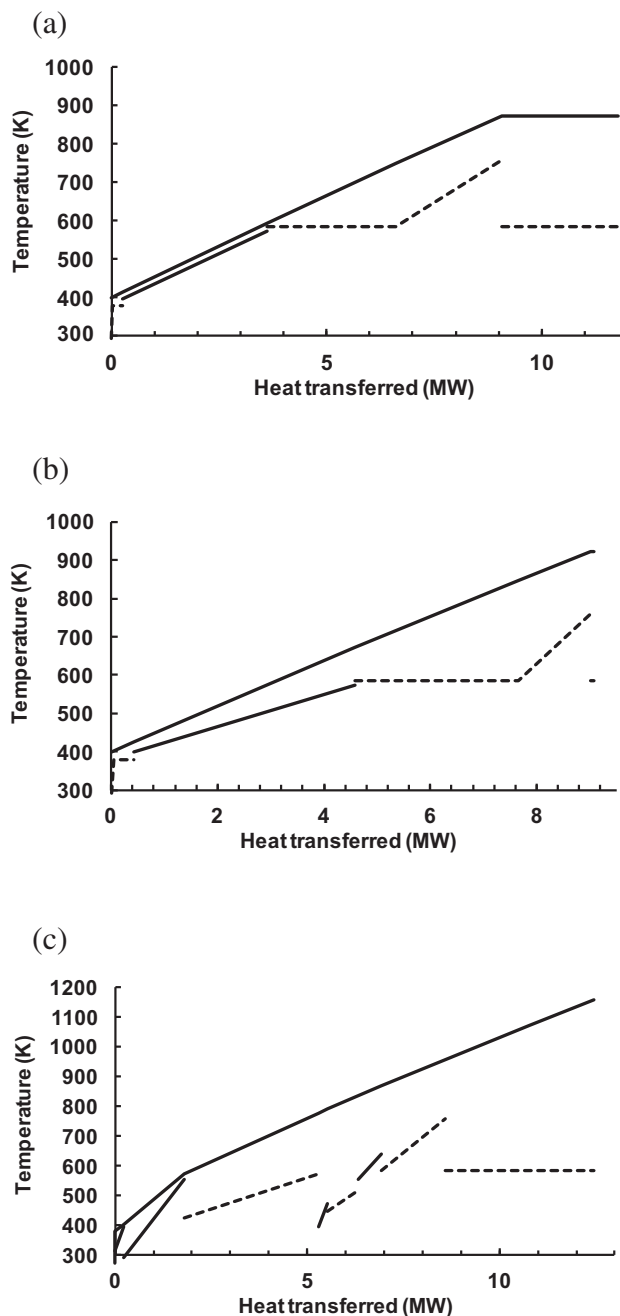

Fig. 3 — Composite curves (temperature vs. heat transferred) of: (a) Gas from the reformer at 873 K and at maximum feasible S/C (3.2), (b) Gas from the reformer at 923 K at maximum feasible S/C (2.2), (c) Gas from the calciner at 1158 K (referring to reformer in (b) case) (dashed lines refer to water/steam, and continuous lines to gas).

heat recovery is expanded to 6 bar to fit the steam export conditions as in the reference case. Steam required in the reformer is drawn at 6 bar and expanded in an additional turbine section to the required 1.27 bar reformer pressure. Eventually, at high S/C ratio, the reformer reactor needs the total amount of steam generated in the process and no steam is therefore left for export. It has been also assumed that boiler feed water is available at 6 bar and 423 K, partly as returning condensate from heat utilities and from low temperature waste heat recovery from the process and from other units which can be available for example in a refinery. The main assumptions made for the system evaluation are summarized in Table 1.

3. Simulation results

3.1. Plant performance indexes

Different performance indexes have been defined to analyze global performance of the assessed plant based on the SER process, and to compare it with that of the plant based on conventional steam methane reforming taken as a reference. Fig. 4 shows a simplified diagram of the inputs and products of the H_2 production plant assessed to help in the definition of these performance indexes.

Hydrogen production efficiency, η_{H2}, defined according to Eq. (8), is the ratio between the energy of the hydrogen output and the energy of the NG fuelled into the plant (both based on LHV).

$$\eta_{H2} = \frac{\dot{m}_{H2} \cdot LHV_{H2}}{\dot{m}_{NG} \cdot LHV_{NG}} \tag{8}$$

Reference FTR based plant produces 30,000 Nm³/h of hydrogen at 29 bar, common size for hydrogen plants installed in refineries. Thus, H_2 production in the simulated plant based on the SER process has been adjusted to this value as in the reference case, and the energy of the H_2 output would be about 90 MW in all the cases.

As mentioned before, SER plant layout has been designed to have a 6 bar slightly superheated steam export as in the reference plant design. The heat associated to this steam export has been calculated assuming that steam at 6 bar is condensed to saturated liquid (Q_{th}). Electric consumption in the reference FTR plant with CO_2 capture comes mainly from the CO_2 compression and purification unit (CPU), which represents more than half of the total power output of the steam cycle. Heat is required for stripping the solvent in the MDEA process. In the SER plant, significant additional electric power is required to run the H_2 compressor and the ASU. As a result, electricity from the grid is required in the SER plant, which exhibit a net electricity import in every case analyzed ($W_{el} < 0$).

To consider the contribution of the electricity and heat flows exchanged with the exterior, an equivalent NG thermal input has been defined according to Eq. (9). It represents the NG actually dedicated to H_2 production and is calculated by subtracting from the actual NG input the NG flow rate associated to Q_{th} and W_{el}:

$$\dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{Q_{th}}{\eta_{th} \cdot LHV_{NG}} - \frac{W_{el}}{\eta_{el} \cdot LHV_{NG}} \tag{9}$$

η_{th} is the reference thermal efficiency considered to produce steam in a conventional industrial boiler (assumed as 90%), and η_{el} is the electric efficiency of an NG fired power plant (assumed as 58.3% [59]). Based on this equivalent NG input, an equivalent hydrogen production efficiency ($\eta_{eq,H2}$) has been defined according to Eq. (10):

$$\eta_{eq,H2} = \frac{\dot{m}_{H2} \cdot LHV_{H2}}{\dot{m}_{NG,eq} \cdot LHV_{NG}} \tag{10}$$

$\eta_{eq,H2}$ allows comparing homogenously the thermal performance of plants that produce different amounts of the three final products, properly accounting for the additional production or consumption of utilities. This approach is justified by considering, for example, that the hydrogen plant can be located in a refinery, where steam production is considered a valuable benefit. However, there could be some situations where steam export is useless, and therefore, an alternative performance index would be preferable to evaluate the hydrogen production efficiency. So as to account for these cases, an equivalent hydrogen production efficiency ($\eta'_{eq,H2}$) has been defined according to Eq. (11).

$$\eta'_{eq,H2} = \frac{\dot{m}_{H2} \cdot LHV_{H2}}{\dot{m}_{NG} \cdot LHV_{NG} - \dfrac{W'_{el}}{\eta_{el}}} \tag{11}$$

It includes an equivalent power generation W'_{el} defined as sum of the electricity output in the plant, W_{el}, and the electricity that could be produced by expanding to 0.05 bar the steam available for export at 6 bar. A Q_{th} to W_{el} conversion factor of 0.25 MJ$_e$/MJ$_{th}$ was assumed.

Considering the simplified diagram of the assessed plant in Fig. 4, the carbon capture ratio (CCR) can be calculated with Eq. (12) as the ratio between the mass flow rate of CO_2 sent to storage arising from the CPU, and the mass flow rate of CO_2 associated to the NG fed into the plant:

$$CCR = \frac{\dot{m}_S \cdot y_{CO2,S}}{\dot{m}_{NG} \cdot LHV_{NG} \cdot E_{NG}} \tag{12}$$

where $y_{CO2,S}$ is the mass fraction of CO_2 in the liquid stream sent to storage (stream 25 in Fig. 2), and E_{NG} is the specific CO_2 emission per unit of energy input of NG (57.0 g of CO_2 per MJ$_{LHV}$, according to the assumed NG composition in Table 1). Since the non-converted carbon in the NG fed into the reformer is used as fuel in the calciner, where it is transformed into CO_2 for its storage, CO_2 emissions from the plant come exclusively from the gas vented to the atmosphere in the CPU (stream 26 in Fig. 2), and CCR values around 98% can be attained. For the FTR reference plant, a larger quantity of CO_2 is emitted to the atmosphere with the combustion flue gas from the furnace and lower values of CCR are therefore expected.

Specific CO_2 emissions (expressed as gCO_2 per MJ of H_2 output) in the hydrogen plant are given by Eq. (13):

Table 1 − Base assumptions made to construct the simulation model of the hydrogen production plant based on the SER process.

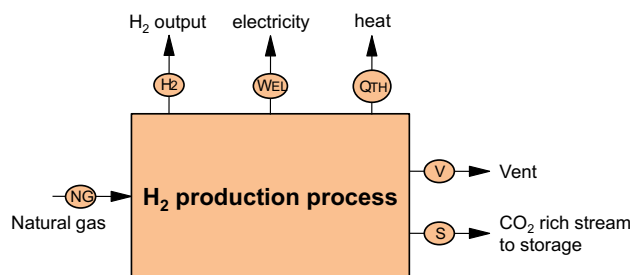|	
Natural gas properties	
Composition (% volume)	89% CH_4; 7% C_2H_6; 1% C_3H_8; 0.11% C_4H_{10}; 2% CO_2; 0.89% N_2
LHV (MJ/kg)	46.482 MJ/kg
S-removal unit	
Operating temperature	638 K
NG pressure loss before S-removal	3 bar
SER loop	
Ca-to-C molar ratio at the reformer inlet	3
Catalyst-to-sorbent mass ratio into the reformer	0.3
Ca-to-C molar sorbent make-up flow	0.001
Reformer inlet temperature	573−648 K
Reformer temperature	873−948 K
Calciner temperature	1158−1223 K
O_2 content in the oxidant stream fed into the calciner	35% vol.
O_2 content in the calciner flue gas	1.5% vol.
Pressure loss in reformer/calciner	0.1 bar
Heat recovery system	
Minimum temperature difference in gas−gas exchangers	20 K
Minimum temperature difference in gas−liquid exchangers	10 K
Minimum temperature difference in gas−boiling liquid exchangers	10 K
Total pressure loss in a gas cooling line	9% of the initial pressure
Heat losses in each heat exchanger	0.7% of the heat transferred
Calciner recycle blower	
Polytropic efficiency	80%
Mechanical−electric efficiency	94%
Steam cycle parameters	
Live steam conditions	100 bar/758 K
Steam export pressure	6 bar
Steam turbine polytropic efficiency	80%
Steam turbine mechanical-electric efficiency	94%
H_2 compressor	
Intermediate pressure for PSA separation	20 bar
Number of intercooled compression stages	5
Final H_2 pressure for plant export	29 bar
Additional compression stages	1
Inter-cooling temperature	304 K
Inter-cooling pressure loss	1%
Polytropic efficiency for compression stages	80%
Mechanical−electric efficiency	94%
CO_2 compression and purification	
Number of intercooled compression stages (before/after CO_2 purification)	3 + 2
Inter-cooling temperature	301 K
Inter-cooling pressure loss	1%
Pressure at knockout drum	20 bar
Temperature at knockout drum	219 K
Minimum ΔT in cryogenic heat exchanger	2 K
Final CO_2 purity	96 %mol
Isentropic efficiency for cryogenic expander stages	82%
Mechanical-electric efficiency of cryogenic expander	90%
Outlet pressure after compression stages	89 bar
Final CO_2 pressure	110 bar
Isentropic efficiency of compression stages	84%
Pump hydraulic efficiency	80%
Mechanical−electric efficiency of compressors and pump	94%
NG expander	
Polytropic efficiency	80%
Mechanical−electric efficiency	94%

Fig. 4 – Simplified diagram of the main inputs and products of the H_2 production plant in Fig. 2.

$$E = \frac{\dot{m}_V \cdot y_{CO2,V}}{\dot{m}_{H2} \cdot LHV_{H2}} \tag{13}$$

Accordingly to Eqs. (9) and (12), an equivalent CCR has been also defined by Eq. (14) to account for the specific emissions associated to the equivalent NG thermal input:

$$CCR_{eq} = \frac{\dot{m}_S \cdot y_{CO2,S}}{\dot{m}_{NG} \cdot LHV_{NG} \cdot E_{NG} - Q_{th} \cdot E_{th} - W_{el} \cdot E_{el}} \tag{14}$$

where E_{th} and E_{el} represent the equivalent specific CO_2 emissions per unit of heat and electricity, respectively. They can be defined according to NG composition and their

respective conversion efficiency resulting in $E_{th} = 63.3$ gCO_2/ MJ_{th} and $E_{el} = 97.7$ gCO_2/MW_{el}. Based on this definition, CCR_{eq} higher than 100% will be obtained if the net emission credits associated to steam and electricity export compensate the CO_2 released to atmosphere. In the SER plant described in this work, where $W_{el} < 0$ and almost all the CO_2 produced in the reformer-carbonator is eventually captured in the calciner, this can occur when CO_2 emissions (from a conventional boiler) associated to steam export exceed those CO_2 emissions (from a combined cycle) associated to the electricity import.

The equivalent specific CO_2 emissions (gCO_2 per MJ of H_2 output) can be estimated according to Eq. (15), including the specific CO_2 emissions associated to the heat and electricity produced (Q_{th} and W_{el}):

$$E_{eq} = \frac{\dot{m}_V \cdot y_{CO2,V} - W_{el} \cdot E_{el} - Q_{th} \cdot E_{th}}{\dot{m}_{H2} \cdot LHV_{H2}} \tag{15}$$

From this definition, negative equivalent specific CO_2 emissions ($E_{eq} < 0$) are attained in case CCR_{eq} is higher than 100%.

Equivalent CCR'_{eq} and E'_{eq} can be also defined, based on Eqs. (14) and (15) respectively, by considering no steam export and an equivalent power generated W'_{el}, accounting for the additional power producible by expanding the 6 bar steam in analogy to η'_{eq} defined by Eq. (11).

Finally, an estimation of the thermal energy required to avoid the emission of one kg of CO_2, compared with the reference plant without CO_2 capture, has been done through the equivalent specific primary energy consumption for CO_2 avoided ($SPECCA_{eq}$) index, according to Eq. (16):

Table 2 – Performance parameters associated to the reference plant with and without CO_2 capture.		
	Reference FTR based plant	Reference FTR based plant with CO_2 capture
S/C at reformer inlet	2.70	4.00
NG thermal input (MW)	121.94	130.79
Steam turbine electric output (MW)	3.34	3.84
CO_2 compressor electric consumption (MW)	–	2.15
Other plant auxiliaries (MW)	0.96	1.35
Net electric plant output (MW)	2.39	0.34
Heat Output (MW)	8.62	4.06
Equivalent NG thermal input (MW)	108.27	125.69
H_2 yield in the reformer (moles of H_2 obtained in the reformer/equivalent CH_4 fed to the reformer[a])	3.08	3.60
Overall H_2 yield (moles of H_2 output/moles of equivalent CH_4[a])	2.46	2.29
η_{H2} (%)	73.98	68.78
$\eta_{eq,H2}$ (%)	83.33	71.57
$\eta'_{eq,H2}$ (%)	79.03	70.03
CCR (%)	–	84.92
CCR_{eq} (%)	–	88.37
CCR'_{eq} (%)	–	86.47
E (gCO_2/MJ of H_2)	77.02	12.49
E_{eq} (gCO_2/MJ of H_2)	68.39	9.26
E'_{eq} (gCO_2/MJ of H_2)	72.10	11.01
$SPECCA_{eq}$ (MJ/kg CO_2)	–	3.33
$SPECCA'_{eq}$ (MJ/kg CO_2)	–	2.66

[a] Equivalent CH_4 of a mixture of hydrocarbons is the amount of CH_4 that has the same capacity of generating H_2 by SMR and WGS reactions. Therefore, the molar flow rate of equivalent CH_4 is defined as: $\dot{M}_{CH4,eq} = \dot{M}_{CH4} + 7/4 \cdot \dot{M}_{C2H6} + 5/2 \cdot \dot{M}_{C3H8} + 13/4 \cdot \dot{M}_{C4H10}$.

$$\text{SPECCA}_{eq} = \frac{\frac{1}{\eta_{eq,H2}} - \frac{1}{\eta_{eq,H2}|_{ref}}}{E_{eq,ref} - E_{eq}} \cdot 1000 \qquad (16)$$

where $\eta_{eq,H2}|_{ref}$ is the equivalent hydrogen efficiency of the reference plant without CO_2 capture, and E_{eq} and $E_{ref,eq}$ are the equivalent specific CO_2 emission, in gCO_2 per MJ of H_2 output, in the assessed plant and in the reference one without CO_2 capture, respectively. For those cases where no steam utilisation is present, an SPECCA'_{eq} could be estimated by substituting in Eq. (16) $\eta'_{eq,H2}$ and E'_{eq} instead of $\eta_{eq,H2}$ and E_{eq} for both the reference and the assessed plants.

Operating parameters associated to the reference FTR plant with and without CO_2 capture are reported in Table 2. As seen from these results, CCR for the reference plant is near 85% with a modest η_{H2} of 68.78%, well below η_{H2} for the reference plant without CO_2 capture (73.98%) mainly due to the inefficiencies resulting from using H_2 as fuel in the FTR-furnace.

3.2. Sensitivity analysis

A sensitivity analysis has been carried out to appreciate the effect of the main operating parameters on the SER plant performance. Basis for calculation has been kept at 30,000 Nm^3/h of pure H_2 output at 29 bar so that results can be directly compared to those given for the reference cases in Table 2.

3.2.1. Reforming temperature and S/C molar ratio
This section analyzes the effect of a variation of the reformer-carbonator temperature and the S/C molar ratio on the performance of the SER plant operating at around atmospheric pressure. When the reformer-carbonator reactor of Fig. 2 operates at 873 K, the sensible heat provided by cooling solids from the calciner and by the equilibrium of the SER reactions is higher than heat required to heat up gaseous reactants. This excess heat is therefore balanced by supposing to raise HP steam at 100 bar in the reactor water-walls or immersed tubes. As long as the reactor working temperature increases, the excess heat reduces due to the simultaneous reduction of the heat available from cooling the solids and the increase of heat required to heat up gaseous reactants. At 923 K operating temperature, the excess heat virtually diminishes to zero so that higher operating temperature could be achieved either by providing additional heat from an external source or by supplying hotter gaseous reactants. None of these alternatives have been considered in the present analysis and, as a result, the operating temperature of the reformer-carbonator is limited in the range 873−923 K.

Since the PSA off-gas is used as fuel in the calciner, the PSA regeneration pressure is actually constrained by the calciner pressure so as to avoid an intermediate compressor. In case the calciner is operated at atmospheric pressure, a PSA feed pressure of 20 bar is suitable to reach an HRF of 90% [54]. Burning the PSA off-gas and additional NG in oxygen brings about CO_2 contents in the range of 55−59% at the calciner outlet (stream 18 of Fig. 2). For a bed operated at atmospheric pressure, 1158 K is the temperature required to

achieve complete calcination under the assumptions listed in Section 2.2.

A variation range for the S/C ratio has been identified for each temperature of the reformer-carbonator considered in the analysis. The upper limit of this range corresponds to that configuration where the total amount of steam generated by heat recovery is used in the reformer-carbonator and, consequently, there is no steam export at 6 bar. Under this condition, NG-to-hydrogen conversion increases provided that steam excess favours reforming and WGS reactions. Therefore, this configuration requires the lowest NG input to the reformer to produce the assigned hydrogen output. On the other hand, the high conversion results in a low heating value of the PSA off-gas and, therefore, a larger NG flow rate is sent directly to the calciner as shown in Table 3. Results in this table also show that the higher the reformer temperature, the lower the upper bound of the S/C ratio variation range. As mentioned before, as reforming temperature increases, temperature difference between reactors decreases so that less heat is available from cooling the solids. As a consequence, steam generated in the plant reduces and lower S/C ratios are achievable in the reformer.

Since a reduction of the S/C ratio enhances the off-gas heating value, the lower bound of the S/C variation range is set by the case where the calcination is sustained by exclusively burning the PSA off-gas (i.e. no additional NG input in the calciner is required). This solution leads to maximize the 6 bar steam export.

The results of the complete sensitivity analysis are plotted in Fig. 5, where hydrogen production efficiencies and specific CO_2 emissions are reported according to the different definitions presented previously. Fig. 5(a) presents the curves of the performance indexes, η_{H2} and E, obtained by varying the S/C ratio within the allowed range for different temperatures in the reformer-carbonator. Both reformer temperature and S/C ratio significantly affect parameters analyzed, with better performances at higher S/C ratios and higher SER temperatures on both H_2 efficiency and specific emission. Higher value of S/C ratio implies larger CH_4 conversion in the reformer-carbonator and, therefore, lower NG flow rate needed to accomplish the H_2 production established for comparison. Moreover, increasing reformer temperature translates into a reduced temperature difference between reactors and, as a result, lower heat input in the calciner for solid preheating. Both tendencies cause NG thermal input to the plant to decrease, making η_{H2} increase as observed in Fig. 5(a). When credits associated to steam export and power input are accounted for the overall picture changes, as shown in Fig. 5(b). According to this scenario, operating at low reforming temperature and low S/C ratio is preferable from a specific emissions point of view, mainly thanks to the credits associated to steam export. Under these conditions, a larger heat input is required in the calciner due to the higher ΔT of the solids to be heated up to the calciner temperature and the higher circulation rate between the reactors. In these cases, despite the higher electric consumption for O_2 production and H_2 compression (containing a larger amount of impurities in cases with lower S/C), the effect of the higher heat

Table 3 – Sensitivity analysis results for the maximum and minimum values of S/C in the reformer at atmospheric pressure for different temperatures (for these cases, calciner operates at 1158 K).

Reformer temperature	873 K		893 K		923 K	
S/C at reformer inlet	3.23	1.82	2.93	1.86	2.16	1.98
NG thermal input to the plant (MW)	112.6	115.8	111.0	113.1	107.6	107.7
% of NG sent to reformer	81.04	100.0	83.77	100.0	96.37	100.0
CaO to $CaCO_3$ conversion in the reformer, %	30.92	24.60	29.68	24.37	24.58	23.35
Total thermal input to the calciner, H_{calc} (MW)	35.90	38.17	34.41	35.79	31.22	31.28
PSA off-gas thermal input to calciner (MW)	14.42	38.17	16.28	35.79	26.78	31.28
Heat extracted from reformer-carbonator (MW)	2.69	5.87	1.42	3.48	0.05	0.18
Steam turbine electric output (MW)	5.09	5.30	4.69	4.78	3.78	3.76
NG expansion (MW)	1.40	1.44	1.38	1.40	1.34	1.34
ASU electric consumption (MW)	2.98	3.23	2.86	3.02	2.59	2.60
H_2 compressor electric consumption (MW)	5.45	5.80	5.50	5.80	5.75	5.83
CO_2 compression and purification (MW)	2.54	2.62	2.51	2.55	2.43	2.43
Other plant auxiliaries (MW)	0.51	0.52	0.48	0.48	0.39	0.40
Net electric plant output (MW)	−4.99	−5.43	−5.28	−5.67	−6.04	−6.16
Heat output (MW)	0.00	6.93	0.00	4.86	0.00	0.62
Equivalent NG thermal input (MW)	121.2	117.5	120.1	117.4	117.9	117.5
H_2 yield in the reformer (moles of H_2 obtained in the reformer/equivalent CH_4 fed to the reformer)	3.64	2.87	3.58	2.94	3.21	3.09
Overall H_2 yield (moles of H_2 output/moles of equivalent CH_4 fed to the plant)	2.66	2.58	2.70	2.65	2.78	2.78
η_{H2} (%)	79.90	77.67	81.03	79.56	83.67	83.56
$\eta_{eq,H2}$ (%)	74.25	76.60	74.92	76.63	76.31	76.55
$\eta'_{eq,H2}$ (%)	74.25	73.64	74.92	74.53	76.31	76.27
CCR (%)	98.51	98.37	98.56	98.51	98.72	98.72
CCR_{eq} (%)	91.54	97.01	91.14	94.90	90.04	90.44
CCR'_{eq} (%)	91.54	93.26	91.14	92.29	90.04	90.12
E (gCO_2/MJ of H_2)	1.06	1.17	1.01	1.07	0.87	0.87
E_{eq} (gCO_2/MJ of H_2)	6.49	2.22	6.74	3.80	7.43	7.12
E'_{eq} (gCO_2/MJ of H_2)	6.49	5.22	6.74	5.89	7.43	7.38
$SPECCA_{eq}$ (MJ/kg CO_2)	2.37	1.59	2.18	1.62	1.81	1.73
$SPECCA'_{eq}$ (MJ/kg CO_2)	1.24	1.39	1.06	1.15	0.70	0.71

recovered and delivered as low pressure steam prevails. In case steam is useless for export (Fig. 5(c)), configurations with higher S/C and higher SER temperatures show better H_2 production efficiencies (a smooth optimum S/C value can actually exist), while differences in specific emissions become smaller.

The maximum η_{H2} obtained in the analysis is 83.7%, attained by the configuration featuring the highest reformer-carbonator operating temperature (923 K) and highest possible S/C ratio (2.16). Moreover, under these conditions, $\eta_{eq,H2}$ and $\eta'_{eq,H2}$ obtained are also among the highest values from the cases analysed (76.3% both of them). Temperature, pressure, flow rate and composition of the main gas streams (referred to Fig. 2) of this case are reported in Table 4.

When compared to the reference FTR technology, despite the high energy demand in the calciner reactor, it is noticed that between 10 and 20% less additional fuel is required in the SER plant in comparison with the FTR plant including CO_2 capture, as already assessed in the literature [8,10,17]. As a consequence of this fact, and due to the higher CH_4 conversion in the reformer, further favoured by operating at atmospheric pressure, the SER plant achieves higher η_{H2} than the FTR case with CO_2 capture. As seen from Fig. 5(a), the lowest η_{H2} obtained for the SER plant is about 77.7% (operating at 873 K in the reformer and with minimum S/C ratio in the reformer-carbonator), which is about 9 percentage points above the η_{H2} assessed for the FTR plant featuring CO_2 capture. When equivalent H_2 production efficiencies are considered, differences reduce but are still significant, with improvements of about 3–6 percentage points for the SER cases.

Also about specific emissions, SER cases show significantly better results than FTR plants, thanks to the high carbon capture rates. CCR and CCR_{eq} higher than 98 and 90% respectively can be obtained, due to the fact that almost all the carbon fed to the plant with NG is recovered as CO_2 for storage in the calciner. In comparison, CCR and CCR_{eq} evaluated for the FTR case just limit to 84.9 and 88.4% respectively. Correspondingly, specific emissions of the SER plants are significantly reduced with respect to FTR. A 53% reduction in equivalent emission E'_{eq} (from 11.01 to 5.22 g_{CO2}/MJ$_{H2}$) is achieved by SER plant with 873 K reforming temperature and minimum S/C ratio. Even higher reductions ensue for E and E_{eq} indexes.

By combining energy consumption and emissions, it is observed that $SPECCA_{eq}$ and $SPECCA'_{eq}$ values of 1.59–2.37 MJ/kg$_{CO2}$ (vs. 3.33 MJ/kg$_{CO2}$ of the FTR case) and 0.70–1.39 MJ/kg$_{CO2}$ (vs. 2.66 MJ/kg$_{CO2}$) are obtained respectively, induced by both the high H_2 production efficiencies and the nearly complete carbon capture achieved in the SER plant. As commonly obtained in hydrogen production plants
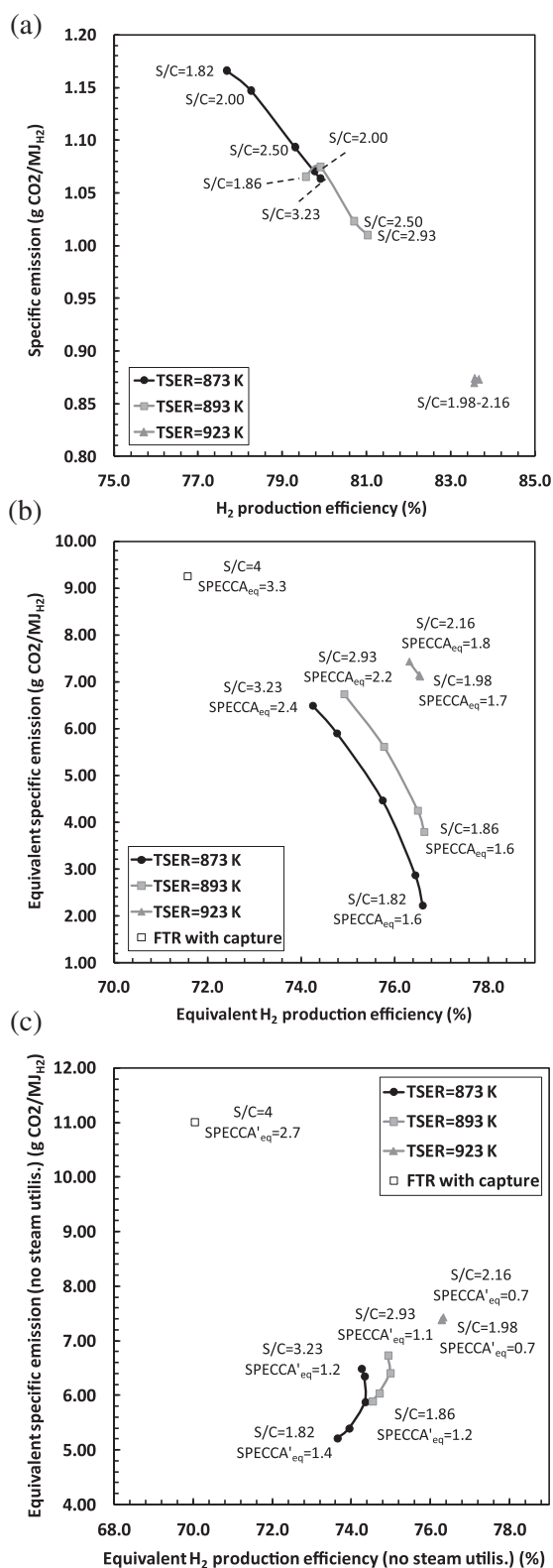
(a)

(b)

(c)

Fig. 5 – (a) η_{H2} vs. E, (b) $\eta_{eq,H2}$ vs. E_{eq} and (c) $\eta'_{eq,H2}$ vs. E'_{eq} for different reformer-carbonator temperatures and S/C ratios at atmospheric pressure.

with CO_2 capture, it is confirmed that $SPECCA_{eq}$ values obtained in this work for the SER plant are well below those reported for power generation plants that, in the case of an SER plant coupled with a gas turbine combined cycle, have been estimated at 3.4 MJ/kg CO_2 avoided [18]. Certainly, this is also a consequence of the intrinsic lower invasiveness of including pre-combustion CO_2 capture in a plant producing H_2 than in a power plant.

3.2.2. Operating pressure and PSA H_2 recovery factor
An elevated pressure for calciner and reformer reduces the energy consumption to run the H_2 and CO_2 compressors necessary to take the streams to the desired final values of 29 bar and 110 bar, respectively. However, lower CH_4 conversions in the reformer than those at atmospheric pressure are achieved due to the negative effect of pressure on the thermodynamic equilibrium of the SER reactions. Given the maximum calciner temperature of 1223 K stated in Section 2.2 and according to the CO_2 partial pressure that results from burning NG and PSA off-gas in the calciner, 3 bar is the highest pressure limit for operating the calciner ensuring a difference between equilibrium pressure of reaction (3) and CO_2 partial pressure high enough to drive the reaction. Such a difference is about 0.4 bar (around 0.1 in terms of CO_2 molar fraction) and corresponds to a temperature difference of around 20 K between equilibrium temperature and calciner temperature.

In order to evaluate the effects of operating at 3 bar in the reformer and in the calciner, a sensitivity analysis, similar to that performed at atmospheric pressure, has been carried out by modifying the temperature of the reformer-carbonator and testing the range of feasible S/C ratios in the reformer. Since the HRF in the PSA unit is dramatically affected by the operating pressure ratio, feed gas pressure in the PSA unit has been raised to 30 bar in this analysis to avoid excessively reducing HRF. Doing so, the HRF remains at a proper value of 85% for an off-gas pressure of around 3 bar [54]. Consequently, additional H_2 compression after the PSA unit is not needed in these cases to reach the pressure of 29 bar set for hydrogen output and PSA off-gas can be directly used as fuel in the calciner with no need of compression. In addition to these cases, a set of simulations has also been performed considering the release of PSA off-gas at lower pressure (1.27 bar) in order to re-establish an HRF in the PSA unit of 90% (maintaining feed gas pressure in the PSA unit at 20 bar as in the cases in Section 3.2.1). In these cases, a compressor has been added to pressurize the PSA off-gas up to the calciner pressure, and additional compression would be needed to reach the pressure of 29 bar set for hydrogen output.

Table 5 reports plant performance obtained for maximum and minimum S/C ratios at the different reformer temperatures analysed. Compared with the results at atmospheric pressure in Fig. 6(a) for a reformer temperature of 873 and 923 K, noticeably lower η_{H2} values and higher specific CO_2 emissions result when operating at 3 bar. This is mainly due to the higher temperature difference between two reactors, which translates into a higher heat input in the calciner and higher total NG thermal input to get the established hydrogen output. Another reason of the lower η_{H2} is the negative effect

Table 4 – Temperature, pressure, mass flow rate and composition of the main gas streams in Fig. 2, for reformer at 923 K and atmospheric pressure, with the maximum S/C ratio of 2.16.

Stream	T (K)	P (bar)	G (kg/s)	M (kmol/s)	Molar composition (%)								
					CH_4	CO	CO_2	C_{2+}	H_2	H_2O	N_2	O_2	Ar
1	288.0	30.40	2.31	0.128	89.00	–	2.00	8.11	–	–	0.89	–	–
2	553.0	28.88	2.32	0.131	87.12	–	1.96	7.94	2.11	–	0.87	–	–
3	638.0	27.36	2.32	0.131	87.12	–	1.96	7.94	2.11	–	0.87	–	–
4	421.7	1.27	2.32	0.131	87.12	–	1.96	7.94	2.11	–	0.87	–	–
5	648.0	1.27	7.43	0.415	26.44	–	0.59	2.41	0.64	69.65	0.26	–	–
6	923.0	1.17	3.42	0.546	2.99	2.40	1.04	–	76.35	17.02	0.20	–	–
7	673.0	1.09	3.42	0.546	2.99	2.40	1.04	–	76.35	17.02	0.20	–	–
8	399.0	1.01	3.42	0.546	2.99	2.40	1.04	–	76.35	17.02	0.20	–	–
9	304.0	1.01	2.12	0.473	3.44	2.76	1.20	–	87.97	4.39	0.23	–	–
10	311.0	20.0	1.78	0.455	3.59	2.88	1.25	–	91.62	0.42	0.24	–	–
11	311.0	29.0	0.75	0.372	–	–	–	–	100.0	–	–	–	–
13	421.7	1.27	0.10	0.005	87.12	–	1.96	7.94	2.11	–	0.87	–	–
15	473.0	1.27	1.12	0.085	24.67	15.36	6.81	0.50	49.05	2.27	1.34	–	–
16	298.0	1.27	2.87	0.089	–	–	–	–	–	–	1.91	95.00	3.09
17	517.0	1.27	8.30	0.249	–	–	37.92	–	–	23.70	1.46	35.06	1.86
18	1158.0	1.17	13.42	0.395	–	–	59.14	–	–	36.97	1.21	1.50	1.17
19	825.4	1.11	13.42	0.395	–	–	59.14	–	–	36.97	1.21	1.50	1.17
20	790.9	1.09	13.42	0.395	–	–	59.14	–	–	36.97	1.21	1.50	1.17
21	745.0	1.06	13.42	0.395	–	–	59.14	–	–	36.97	1.21	1.50	1.17
22	573.0	1.01	5.42	0.160	–	–	59.14	–	–	36.97	1.21	1.50	1.17
24	304.0	1.01	6.55	0.155	–	–	89.68	–	–	4.43	1.84	2.28	1.78
25	302.7	110.0	6.24	0.143	–	–	96.00	–	–	0.00–	0.97	1.72	1.31
26	293.0	1.01	0.19	0.005	–	–	33.85	–	–	–	28.27	20.80	17.07
27	423.0	6.00	5.03	0.279	–	–	–	–	–	100.0	–	–	–
28	573.0	100.0	0.03	0.002	–	–	–	–	–	100.0	–	–	–
29	573.0	100.0	2.05	0.114	–	–	–	–	–	100.0	–	–	–
31	758.0	100.0	5.03	0.279	–	–	–	–	–	100.0	–	–	–
32	444.8	6.0	–	–	–	–	–	–	–	100.0	–	–	–

of pressure on steam reforming equilibrium, leading to reduced CH_4 conversions at a given temperature and S/C ratio. As a result, the η_{H2} obtained when operating at 3 bar at the same SER temperature is around 6–8 percentage points lower than the corresponding case at atmospheric pressure. However, η_{H2} obtained at 3 bar is still above that obtained for the FTR reference plant featuring CO_2 capture, and an advantage of at least 3 percentage points has been obtained for every case in Fig. 6(a) with respect to the FTR case. From results in Table 5, it can be appreciated that the maximum S/C ratio achievable at the different temperatures analysed at 3 bar is higher than the maximum S/C ratio feasible at atmospheric pressure, mainly because the higher temperature in the calciner allows for a larger heat recovery, and therefore a larger steam production. From an $\eta_{eq,H2}$ point of view, results are pretty similar for both pressures analysed when S/C ratio in the reformer is minimized as depicted in Fig. 6(b). When the operating pressure increases, there is a trade-off between the benefit reported by a reduced electric consumption of H_2 and CO_2 compressors together with the increased steam production, and the disadvantage associated to a higher NG thermal input and a higher ASU electric consumption. As a consequence of these effects, in the best cases $\eta_{eq,H2}$ results in almost the same values when operating at 3 bar, while specific emissions averagely reduce and turn even negative in some cases, due to the emission credits

associated to steam export. However, if there is no steam utilisation, $\eta'_{eq,H2}$ values at 3 bar are below those at atmospheric pressure and differences of around 2–3 percentage points can be observed for a given S/C molar ratio and SER temperature, according to Fig. 6(c). With respect to the FTR reference plant, pressurized SER plants show better $\eta'_{eq,H2}$ efficiency with a minimum advantage of around one percentage point. On the other hand, advantages of the high pressure cases in terms of specific emissions are maintained when no steam utilization is considered.

From the same figures, it can be observed that when HRF of 90% is re-established by reducing the pressure of the PSA off-gas, an improvement of about 1 percentage point of η_{H2} and $\eta'_{eq,H2}$ is obtained with respect to the corresponding cases with reforming reactor at 873 K, as well as for the maximum $\eta_{eq,H2}$ that raises up to around 77.5% if reformer is operated at the minimum S/C ratio. Conversely, equivalent emissions slightly reduce mainly due to the larger steam export. On the whole, a moderate effect can be obtained by improving the HRF in the PSA unit.

According to the results obtained for the performance indexes at different pressures, operating at atmospheric pressure is preferable from a hydrogen efficiency point of view (either when there is external steam utilisation or not), while pressurized cases shows lower specific emissions. From an operation and economic point of view, pressurized reactors

Table 5 – Sensitivity analysis results for the maximum and minimum values of S/C in the reformer at 3 bar for different temperatures and two different HRF in the PSA unit (for these cases, calciner operates at 1223 K).

Reformer temperature	873 K		923 K		948 K		873 K	
S/C at reformer inlet	4.30	2.02	3.67	2.12	3.24	2.21	4.34	1.86
PSA off-gas pressure (bar)	3.14	3.14	3.14	3.14	3.14	3.14	1.27	1.27
HRF in PSA (%)	85	85	85	85	85	85	90	90
NG thermal input (MW)	119.6	125.2	116.0	119.2	113.7	115.3	118.2	124.7
% of NG sent to reformer	79.8	100.0	83.8	100.0	87.7	100.0	76.2	100.0
CaO to $CaCO_3$ conversion in the reformer, %	31.84	24.82	30.39	25.01	28.62	24.68	31.87	23.65
Total thermal input to the calciner, H_{calc} (MW)	43.60	47.89	40.11	42.45	37.94	39.06	41.48	46.42
PSA off-gas thermal input to calciner (MW)	19.35	47.89	21.26	42.45	23.90	39.06	13.14	46.42
Heat extracted from reformer-carbonator (MW)	4.17	9.98	1.12	4.72	0.45	1.38	3.87	10.28
Steam turbine electric output (MW)	5.78	6.53	5.01	5.41	4.53	4.68	5.51	6.41
NG expansion (MW)	1.10	1.15	1.07	1.10	1.05	1.06	1.09	1.15
ASU electric consumption (MW)	3.53	3.97	3.25	3.50	3.07	3.19	3.42	3.92
H_2 compressor electric consumption (MW)	4.16	4.48	4.21	4.46	4.27	4.46	3.75	4.07
CO_2 compression and purification (MW)	2.06	2.15	2.00	2.05	1.96	1.99	2.03	2.14
Other plant auxiliaries (MW)	0.64	0.64	0.57	0.56	0.52	0.50	0.80	0.96
Net electric plant output (MW)	−3.51	−3.56	−3.95	−4.06	−4.24	−4.40	−3.40	−3.53
Heat output (MW)	0.00	12.35	0.00	7.82	0.00	4.73	0.00	13.15
Equivalent NG thermal input (MW)	125.6	117.6	122.8	117.5	121.0	117.6	124.1	116.1
H_2 yield in the reformer (moles of H_2 obtained in the reformer/equivalent CH_4 fed to the reformer)	3.69	2.81	3.62	2.95	3.53	3.05	3.69	2.67
Overall H_2 yield (moles of H_2 output/moles of equivalent CH_4 fed to the plant)	2.50	2.39	2.58	2.51	2.63	2.60	2.53	2.40
η_{H2} (%)	75.23	71.85	77.54	75.47	79.12	78.03	76.10	72.14
$\eta_{eq,H2}$ (%)	71.63	76.51	73.28	76.59	74.36	76.51	72.51	77.46
$\eta'_{eq,H2}$ (%)	71.63	71.39	73.28	73.26	74.36	74.46	72.51	71.90
CCR (%)	98.13	97.95	98.26	98.16	98.36	98.31	98.23	98.06
CCR_{eq} (%)	93.44	104.31	92.86	99.62	92.44	96.40	93.61	105.29
CCR'_{eq} (%)	93.44	97.33	92.86	95.28	92.44	93.82	93.61	97.73
E (gCO_2/MJ of H_2)	1.42	1.63	1.28	1.39	1.18	1.23	1.32	1.54
E_{eq} (gCO_2/MJ of H_2)	5.22	−3.21	5.55	0.29	5.79	2.68	5.02	−3.89
E'_{eq} (gCO_2/MJ of H_2)	5.22	2.13	5.55	3.67	5.79	4.73	5.02	1.80
$SPECCA_{eq}$ (MJ/kg CO_2)	3.10	1.49	2.62	1.55	2.31	1.63	2.82	1.26
$SPECCA'_{eq}$ (MJ/kg CO_2)	1.95	1.94	1.49	1.46	1.20	1.15	1.69	1.78

would lead to compact vessels and less compression requirements, which would turn into lower investment costs expected, with possible lower cost of hydrogen produced and CO_2 avoided.

3.2.3. Effect of Ca-to-C molar ratio in the reformer

The Ca-to-C molar ratio chosen at the reformer inlet determines the solid circulation between reactors and, therefore, the energy balance in the system. So far, the Ca-to-C molar ratio in the reformer has been set to 3, leading to CaO to $CaCO_3$ conversions between 23 and 32% in the cases assessed (meaning 58–80% conversion of the active CaO). For a given operating temperature of reformer-carbonator and calciner, the higher the Ca-to-C molar ratio, the higher the fuel thermal power required in the calciner (H_{calc}) to heat the incoming solids up to the calcination temperature. Correspondingly higher sensible heat of the solids is released in the reformer leading to a larger steam production. The increase of fuel input to the calciner and the amount of steam exported for a given S/C ratio, have opposite effects on $\eta_{eq,H2}$ and $\eta'_{eq,H2}$. In the equilibrium reactor model assumed for the reformer-carbonator reactor, any other effect associated to changes in the Ca-to-C molar ratio (e.g. gas–solid contact time, reaction kinetics) cannot

be observed. More detailed reactor models (including reaction kinetics, gas–solid mixing model or reactor dimensioning) would be needed to evaluate these effects. Therefore, considerations shown in this work are consistent with the equilibrium calculations assumed for the reformer-carbonator reactor.

To analyze the overall effect of the Ca-to-C molar ratio in the plant performance a sensitivity analysis has been carried out with reference to the case with atmospheric reformer operating at 873 K and 2.5 S/C ratio. The temperature chosen allows wide variability of the S/C ratio to the reformer while the S/C ratio optimises $\eta'_{eq,H2}$, whereas η_{H2} and $\eta_{eq,H2}$ show small improvements for higher S/C ratio. Under these reference conditions, setting the Ca-to-C ratio equal to 3 brings about a 28.8% conversion of CaO to $CaCO_3$ in the reformer (corresponding to a conversion of around 72% of the active CaO) and heat fuel input required in the calciner H_{calc} is equal to 36.5 MW_{LHV} (of which 21.0 MW_{LHV} supplied by the PSA off-gas).

Different values have been assigned to the Ca-to-C ratio (2.5, 2.75, 3, 3.5 and 4) as depicted in Fig. 7. By modifying this ratio, the amount of catalyst circulating between the reactors is accordingly changed to maintain the given catalyst-to-sorbent mass ratio of 0.3. Despite the H_2
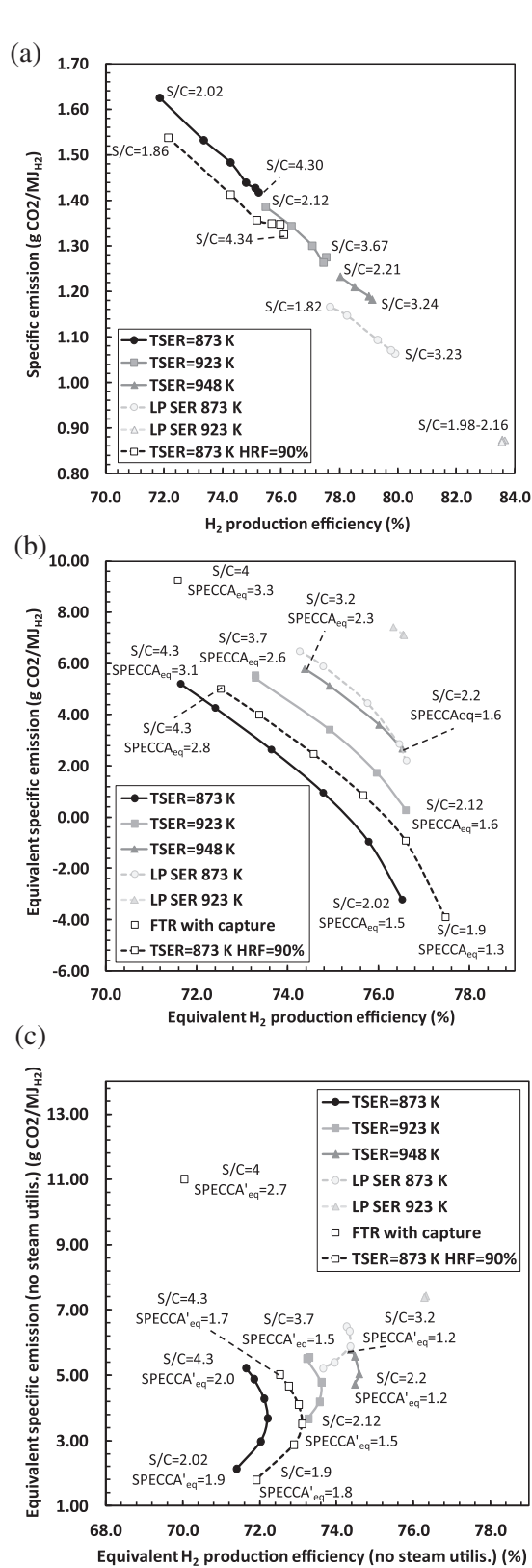
Fig. 6 – (a) η_{H2} vs. E, (b) $\eta_{eq,H2}$ vs. E_{eq} and (c) $\eta'_{eq,H2}$ vs. E'_{eq} for different reformer-carbonator temperatures and S/C ratios at 3 bar, compared with the atmospheric pressure cases at 873 and 923 K in the reformer-carbonator (already depicted in Fig. 5).
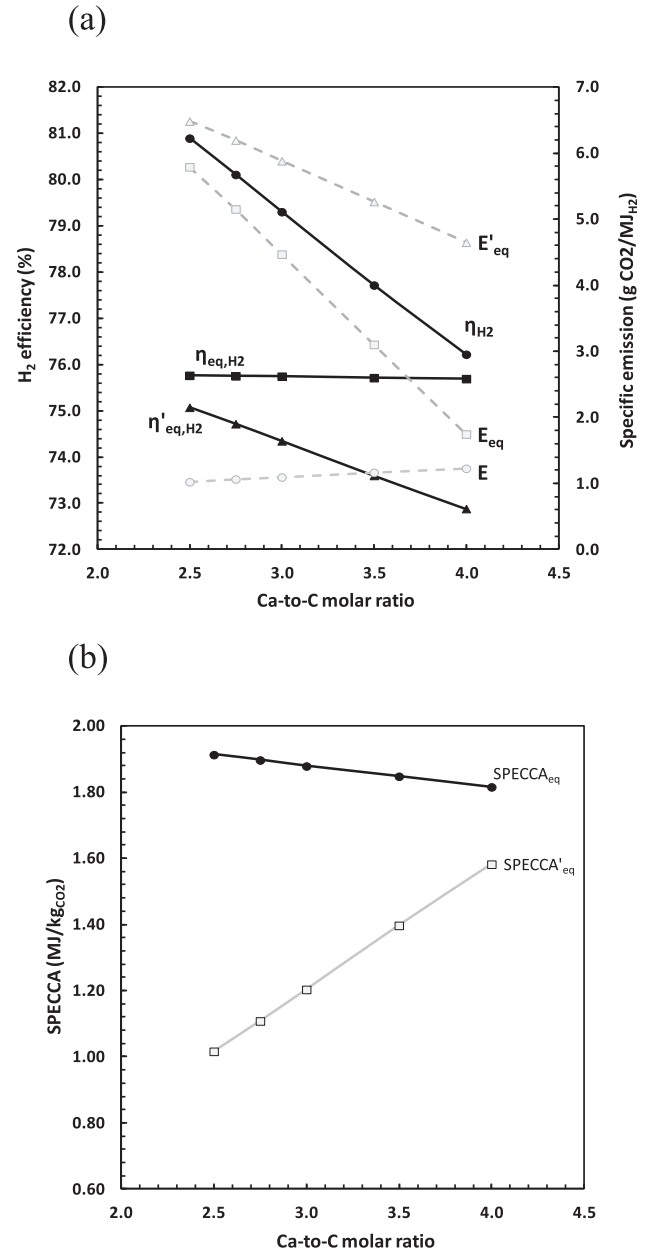

Fig. 7 – (a) H_2 production efficiencies, specific emissions and (b) $SPECCA_{eq}$, $SPECCA'_{eq}$ vs. Ca-to-C molar ratio for reformer-carbonator at 873 K and atmospheric pressure.

consumed in the reformer-carbonator by catalyst activation (according to Eq. (7)), H_2 yield in the reformer (mol of H_2/mol equivalent CH_4 as defined in Table 2) is almost constant between 3.37 and 3.40 when modifying the Ca-to-C ratio since the S/C ratio remains invariable at 2.5. However, it can be noticed in Fig. 7(a) that η_{H2} decreases substantially from around 81% to almost 76% when increasing Ca-to-C ratio from 2.5 to 4, due to an increase in H_{calc} (from 34.9 MW_{LHV} to 39.7 MW_{LHV}). On the contrary, negligible effect of the Ca-to-C ratio is observed on $\eta_{eq,H2}$ (constant at around 75.7%) because of the credits associated to the higher steam export

(up to around 7 MW at Ca-to-C of 4), which compensate the larger NG thermal input into the process. If steam export is not possible and steam produced can only be used for electricity production, $\eta'_{eq,H2}$ decreases from 75.1% to 72.9% with the Ca-to-C molar ratio. This reduction is not as pronounced as for η_{H2}, since the additional electricity produced reduces the net electricity import and moderates the effect on $\eta'_{eq,H2}$.

As far as specific emissions are concerned, it is observed that higher Ca-to-C ratios have practically no effect on E, since CCR in the plant is nearly independent on H_{calc}, while E_{eq} and E'_{eq} reduce due to the benefits on the avoided emissions associated to heat and power export.

As a result of the combined effects of H_2 production efficiency and emissions, a slight reduction of around 0.10 MJ/kg CO_2 and a more pronounced increase of around 0.60 MJ/kg CO_2 avoided are observed for the $SPECCA_{eq}$ and $SPECCA'_{eq}$ indexes, respectively, when increasing the Ca-to-C from of 2.5–4.0 (Fig. 7(b)).

4. Conclusions

A detailed and complete simulation model of a H_2 production plant based on the Sorption Enhanced Reforming (SER) process has been developed to analyse how the different operating conditions or assumptions considered influence plant performance. A complete thermal integration has been also performed between the available hot gas streams in the plant so that high pressure steam is generated and used to generate power in a steam cycle.

The sensitivity analysis showed that operating parameters of the SER plant (reformer temperature, S/C ratio and operating pressure) fairly affect the mix of products (hydrogen, electricity, heat) and proper performance indexes were introduced to compare the different conditions considered. Comparison is further influenced by the specific installation site, since credits for steam/electricity export/import depend on the respective generation technologies in the specific site considered.

When credits for steam export are considered, low S/C ratios are preferable for both equivalent H_2 efficiency and CO_2 emissions, since the positive effect of steam export becomes important. However, in case steam export is useless, an optimal S/C ratio exists for each temperature and pressure analyzed that maximises the equivalent H_2 efficiency, although the higher the reformer temperature, the higher the equivalent hydrogen efficiency obtained in every case. The analysis also showed that a slight pressurization of the plant (from atmospheric to 3 bar), negatively affects plant efficiency although it can provide an advantage in terms of investment costs because of more compact reactor vessels and smaller requirements concerning H_2 and CO_2 compression. Moreover, it has been observed that higher pressure cases have lower specific emissions than operation at atmospheric pressure. Thus, an economic analysis would be decisive to determine the optimum set of operating conditions, especially, with respect to operating pressure.

From a hydrogen efficiency point of view, operating at atmospheric pressure and at the highest reformer temperature of 923 K is preferable (either when there is outer steam utilisation or not), and η_{H2}, $\eta_{eq,H2}$ and $\eta'_{eq,H2}$ as high as 83.7%, 76.3% and 76.3%, respectively, can be obtained for the maximum S/C ratio of 2.16.

Comparing the results obtained with a conventional SMR based plant using commercially available amine absorption for CO_2 capture, it was observed that hydrogen efficiencies for SER plant at atmospheric pressure were well above those for the SMR plant. Looking at the lowest η_{H2} of 77.7% obtained for the SER plant, when operating at 873 K in the reformer with minimum S/C ratio of 1.82, it is around 9 percentage points higher than the η_{H2} assessed for the FTR plant featuring CO_2 capture. When equivalent H_2 production efficiencies are considered, differences reduce but are still significant, with improvements of about 3–6 percentage points for the SER cases. However, differences in hydrogen efficiencies between SER and SMR plants become smaller when high pressure operation is considered for the SER plant. The thermodynamic benefit highlighted could even be a minor advantage offered by the SER plant compared to the significantly lower reformer operating temperature and the intrinsic plant simplicity characteristic of SER process (with respect to conventional FTR technology).

Finally, it was analysed the effect of the solid circulation rate between reformer and calciner into plant performance indexes, and it was observed that, generally, the lower the solid circulation assumed (low Ca-to-C molar ratio), the higher the hydrogen efficiencies reported for the SER plant, for a given operating temperature and pressure. Thus, the development of highly active sorbents would allow reducing the solid circulation rate and therefore, increase the efficiency of the process. The effect on the equivalent specific emissions is opposite to that observed for the efficiency, and the higher the circulation rate between reactors, the lower the specific emissions. This is due to the positive effects of exporting steam and electricity, produced with much lower emission than the reference plants without CO_2 capture. Of course, this result is strictly linked to the performance of the reference technologies and it would partly change in case a carbon constrained world scenario is assumed, with lower efficiency and low emission reference power plants and boilers. In this case, credits for steam and electricity export/import would be different and, for example, much smoother effects on specific emission would be expected.

Nomenclature

E	specific CO_2 emissions in the hydrogen plant, gCO_2/ MJ of H_2 output
E_{el}	equivalent specific CO_2 emissions per unit of electricity, 97.7 gCO_2/MW_{el}
E_{eq}	equivalent specific CO_2 emissions in the assessed SER plant, gCO_2/MJ of H_2 output
E_{NG}	specific CO_2 emissions per unit of energy input of NG, 57.0 gCO_2/MJ of NG
$E_{eq,ref}$	equivalent specific CO_2 emissions in the reference plant without CO_2 capture, gCO_2/MJ of H_2 output
E_{th}	equivalent specific CO_2 emissions per unit of heat, 63.3 gCO_2/MW_{th}
H_{calc}	fuel thermal input to the calciner, MW_{LHV}
$\dot{m}_{H2}$	mass flow rate of the H_2 output, kg/s
$\dot{M}_i$	molar flow rate of component i, kmol/s
$\dot{m}_{NG}$	mass flow rate of the natural gas input to the plant, kg/s
$\dot{m}_{NG,eq}$	mass flow rate of the equivalent natural gas input, kg/s
$\dot{m}_S$	Mass flow of the liquid stream sent to storage, kg/s
$\dot{m}_V$	mass flow of the gas vented to the atmosphere, kg/s
Q_{th}	thermal power output of the steam export, MW
W_{el}	electricity power output of the plant, MW
W'_{el}	equivalent power generation including electricity from expanding the available steam export, MW
$y_{CO2,S}$	mass fraction of CO_2 in the liquid stream sent to storage
$y_{CO2,V}$	mass fraction of CO_2 in the gas vented to the atmosphere

Acronyms

ASU	Air Separation Unit
CCR	carbon capture ratio
CCR_{eq}	equivalent carbon capture ratio
ECO	economiser
EVA	evaporator
FTR	fired tubular reformer
HP	high pressure
HRF	hydrogen recovery factor in PSA
LHV	lower heating value
NG	natural gas
PSA	pressure swing adsorption
SER	sorption enhanced reforming
SH	superheater
SMR	steam methane reforming
$SPECCA_{eq}$	equivalent specific primary energy consumption for CO_2 avoided
$SPECCA'_{eq}$	equivalent specific primary energy consumption for CO_2 Avoided (for those cases with no steam utilisation)
VLP	very low pressure
WGS	water gas shift

Greek letters

η_{el}	electric efficiency of a conventional natural gas combined cycle
$\eta_{eq,H2}$	equivalent H_2 production efficiency
$\eta'_{eq,H2}$	equivalent H_2 production efficiency (when there is no steam utilisation)
$\eta_{eq,H2}\big|_{ref}$	equivalent H_2 production efficiency of the reference plant without capture
η_{H2}	hydrogen production efficiency
η_{th}	reference thermal efficiency of a conventional industrial boiler

REFERENCES

[1] Rostrup-Nielsen T. Manufacture of hydrogen. Catal Today 2005;106:293–6.

[2] IEA. Energy technology analysis. CO_2 capture and storage – a key carbon abatement option; 2008.

[3] Metz B, Davidson O, de Coninck H, Loos M, Meyer L. IPCC special report on carbon dioxide capture and storage. Prepared by working Group III of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2005. p. 442.

[4] IEA. Hydrogen production and storage – R&D priorities and gaps; 2006.

[5] Meerman JC, Hamborg ES, van Keulen T, Ramírez A, Turkenburg WC, Faaij APC. Techno-economic assessment of CO_2 capture at steam methane reforming facilities using commercially available technology. Int J Greenhouse Gas Control 2012;9:160–71.

[6] Rostrup-Nielsen JR. Production of synthesis gas. Catal Today 1993;18:305–24.

[7] Rostrup-Nielsen JR, Sehested J, Nørskov JK. Hydrogen and synthesis gas by steam- and CO_2 reforming. Adv Catal 2002:65–139. Academic Press.

[8] Balasubramanian B, Lopez Ortiz A, Kaytakoglu S, Harrison DP. Hydrogen from methane in a single-step process. Chem Eng Sci 1999;54:3543–52.

[9] Lopez Ortiz A, Harrison DP. Hydrogen production using sorption-enhanced reaction. Ind Eng Chem Res 2001;40:5102–9.

[10] Brun-Tsekhovoi AR, Zadorin AN, Katsobashvili YR, Kourdyumov SS. The process of catalytic steam reforming of hydrocarbons in the presence of carbon dioxide acceptor. In: Press P, editor. Hydrocarbon energy progress VII. Moscow 1988. p. 885.

[11] Han C, Harrison DP. Simultaneous shift reaction and carbon dioxide separation for the direct production of hydrogen. Chem Eng Sci 1994;49:5875–83.

[12] Hufton JR, Mayorga S, Sircar S. Sorption-enhanced reaction process for hydrogen production. AIChE J 1999;45:248–56.

[13] Yi KB, Harrison DP. Low-pressure sorption-enhanced hydrogen production. Ind Eng Chem Res 2005;44:1665–9.

[14] Johnsen K, Ryu HJ, Grace JR, Lim CJ. Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as-acceptor. Chem Eng Sci 2006;61:1195–202.

[15] Reijers HTJ, Valster-Schiermeier SEA, Cobden PD, van den Brink RW. Hydrotalcite as CO_2 sorbent for sorption-enhanced steam reforming of methane. Ind Eng Chem Res 2005;45:2522–30.

[16] Cobden PD, van Beurden P, Reijers HTJ, Elzinga GD, Kluiters SCA, Dijkstra JW, et al. Sorption-enhanced hydrogen production for pre-combustion CO_2 capture: thermodynamic analysis and experimental results. Int J Greenhouse Gas Control 2007;1:170–9.

[17] Ochoa-Fernandez E, Haugen G, Zhao T, Ronning M, Aartun I, Borresen B, et al. Process design simulation of H_2 production by sorption enhanced steam methane

reforming: evaluation of potential CO_2 acceptors. Green Chem 2007;9:654—62.

[18] Romano MC, Cassotti EN, Chiesa P, Meyer J, Mastin J. Application of the sorption enhanced-steam reforming process in combined cycle-based power plants. Energy Procedia 2011;4:1125—32.

[19] Grasa GS, Abanades JC. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. Ind Eng Chem Res 2006;45:8846—51.

[20] González B, Grasa G, Alonso M, Abanades JC. Modeling of the deactivation of CaO in a carbonate loop at high temperatures of calcination. Ind Eng Chem Res 2008;47:9256—62.

[21] Meyer J, Mastin J, Bjørnebøle T-K, Ryberg T, Eldrup N. Techno-economical study of the zero emission gas power concept. Energy Procedia 2011;4:1949—56.

[22] Martínez I, Murillo R, Grasa G, Rodríguez N, Abanades JC. Conceptual design of a three fluidised beds combustion system capturing CO_2 with CaO. Int J Greenhouse Gas Control 2011;5:498—504.

[23] Rydén M, Ramos P. H_2 production with CO_2 capture by sorption enhanced chemical-looping reforming using NiO as oxygen carrier and CaO as CO_2 sorbent. Fuel Process Technol 2012;96:27—36.

[24] Chen Z, Grace JR, Lim CJ. CO_2 capture and hydrogen production in an integrated fluidized bed reformer-regenerator system. Ind Eng Chem Res 2011;50:4716—21.

[25] Johnsen K, Grace JR, Elnashaie SSEH, Kolbeinsen L, Eriksen D. Modeling of sorption-enhanced steam reforming in a dual fluidized bubbling bed reactor. Ind Eng Chem Res 2006;45:4133—44.

[26] Kumar RV, Cole JA, Lyon RK. Unmixed reforming: an advanced steam reforming process. In: 218th ACS National meeting. New Orleans, LA: American Chemical Society, division of fuel chemistry 1999. p. 894—8.

[27] Kumar RV, Lyon RK, Cole JA. Unmixed Reforming: a novel autothermal cyclic steam reforming process. In: Gregoire Padro CEa, LF, editor. Adv hydrogen energy. New York, Boston, Dordrecht, London, Moscow: Kluwer Academic Publishers; 2002. p. 31—46.

[28] Dupont V, Ross AB, Knight E, Hanley I, Twigg MV. Production of hydrogen by unmixed steam reforming of methane. Chem Eng Sci 2008;63:2966—79.

[29] Fernández JR, Abanades JC, Murillo R, Grasa G. Conceptual design of a hydrogen production process from natural gas with CO_2 capture using a Ca—Cu chemical loop. Int J Greenhouse Gas Control 2012;6:126—41.

[30] Stevens JF, Krishnamurthy B, Atanassova P, Spilker K. Development of 50 kW fuel processor for stationary fuel cell applications; 2007.

[31] Li Z-S, Cai N-S, Huang Y-Y, Han H-J. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide absorbent. Energy Fuels 2005;19:1447—52.

[32] Martavaltzi CS, Lemonidou AA. Parametric study of the $CaO-Ca_{12}Al_{14}O_{33}$ synthesis with respect to high CO_2 sorption capacity and stability on multicycle operation. Ind Eng Chem Res 2008;47:9537—43.

[33] Broda M, Müller CR. Synthesis of highly efficient, Ca-based, Al_2O_3-stabilized, carbon Gel-templated CO_2 sorbents. Adv Mater 2012;24:3059—64.

[34] Manovic V, Anthony EJ. CO_2 carrying behavior of calcium aluminate pellets under high-temperature/high-CO_2 concentration calcination conditions. Ind Eng Chem Res 2010;49:6916—22.

[35] Li Z-S, Cai N-S. Modeling of multiple cycles for sorption-enhanced steam methane reforming and sorbent regeneration in fixed bed reactor. Energy Fuels 2007;21:2909—18.

[36] Wang Y, Chao Z, Jakobsen HA. 3D simulation of bubbling fluidized bed reactors for sorption enhanced steam methane reforming processes. J Nat Gas Sci Eng 2010;2:105—13.

[37] Li Z-S, Cai N-S, Yang J-B. Continuous production of hydrogen from sorption-enhanced steam methane reforming in two parallel fixed-bed reactors operated in a cyclic manner. Ind Eng Chem Res 2006;45:8788—93.

[38] Wang Y, Chao Z, Chen D, Jakobsen HA. SE-SMR process performance in CFB reactors: simulation of the CO_2 adsorption/desorption processes with CaO based sorbents. Int J Greenhouse Gas Control 2011;5:489—97.

[39] Lee DK, Baek IH, Yoon WL. Modeling and simulation for the methane steam reforming enhanced by in situ CO_2 removal utilizing the CaO carbonation for H_2 production. Chem Eng Sci 2004;59:931—42.

[40] Fernández JR, Abanades JC, Murillo R. Modeling of sorption enhanced steam methane reforming in an adiabatic fixed bed reactor. Chem Eng Sci 2012;84:1—11.

[41] Solieman AAA, Dijkstra JW, Haije WG, Cobden PD, van den Brink RW. Calcium oxide for CO_2 capture: operational window and efficiency penalty in sorption-enhanced steam methane reforming. Int J Greenhouse Gas Control 2009;3:393—400.

[42] Harrison DP. Sorption-enhanced hydrogen production: a review. Ind Eng Chem Res 2008;47:6486—501.

[43] Aasberg-Petersen K, Bak Hansen JH, Christensen TS, Dybkjaer I, Christensen PS, Stub Nielsen C, et al. Technologies for large-scale gas conversion. Appl Catal A: Gen 2001;221:379—87.

[44] Dybkjaer I, Rostrup-Nielsen JR, Aasberg-Petersen K. Hydrogen and synthesis gas. Encyclopedia of hydrocarbons. Rome: Treccani; 2007. p. 469—500.

[45] Chiesa P. Advanced technologies for syngas and hydrogen (H2) production from fossil fuel feedstocks in power plants. In: Roddy D, editor. Advanced power plant materials, design and technology. Cambridge, United Kingdom: Woodhead Publishing Limited; 2010. p. 383—410.

[46] Romano MC, Chiesa P, Lozza G. Pre-combustion CO_2 capture from natural gas power plants, with ATR and MDEA processes. Int J Greenhouse Gas Control 2010;4:785—97.

[47] Christensen TS. Adiabatic prereforming of hydrocarbons — an important step in syngas production. Appl Catal A: Gen 1996;138:285—309.

[48] Qin C, Liu W, An H, Yin J, Feng B. Fabrication of CaO-based sorbents for CO_2 capture by a mixing method. Environ Sci Technol 2012;46:1932—9.

[49] Alonso M, Rodríguez N, Grasa G, Abanades JC. Modelling of a fluidized bed carbonator reactor to capture CO_2 from a combustion flue gas. Chem Eng Sci 2009;64:883—91.

[50] Abanades JC, Anthony EJ, Lu DY, Salvador C, Alvarez D. Capture of CO_2 from combustion gases in a fluidized bed of CaO. AIChE J 2004;50:1614—22.

[51] Rodríguez N, Alonso M, Abanades JC. Average activity of CaO particles in a calcium looping system. Chem Eng J 2010;156:388—94.

[52] González B, Alonso M, Abanades JC. Sorbent attrition in a carbonation/calcination pilot plant for capturing CO_2 from flue gases. Fuel 2010;89:2918—24.

[53] Jia L, Hughes R, Lu D, Anthony EJ, Lau I. Attrition of calcining limestones in circulating fluidized-bed systems. Ind Eng Chem Res 2007;46:5199—209.

[54] Stöcker J, Whysale M, Miller GQ. 30 Years of PSA technology for hydrogen production. http://www.uop.com/objects/30yrsPSATechHydPurif.pdf.

[55] Barker R. The reversibility of the reaction $CaCO_3 \rightleftarrows CaO + CO_2$. J Appl Chem Biotechnol 1973;23:733—42.

[56] Rodriguez N, Alonso M, Grasa G, Abanades JC. Heat requirements in a calciner of $CaCO_3$ integrated in a CO_2 capture system using CaO. Chem Eng J 2008;138:148—54.

[57] Martínez I, Grasa G, Murillo R, Arias B, Abanades JC. Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO_2 capture. Energy Fuels 2012;26:1432—40.

[58] Queneau P, Marcuson S. Oxygen pyrometallurgy at copper cliff—a half century of progress. J Organomet Chem 1996;48:14—21.

[59] Franco F, Anantharaman R, Bolland O, Booth N, van Dorst E, Ekstrom C, et al. European best practice guidelines for assessment of CO_2 capture technologies; 2011.