Techno-economic analysis of the Ca-Cu process integrated in hydrogen plants with CO₂ capture

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Abstract

In this work, a techno-economic analysis of a hydrogen production plant based on the Ca-Cu process has been carried out. The simulation of the whole hydrogen production plant has been performed, including the calculation of the Ca-Cu fixed bed reactors system using a sharp front modelling approach. From the analyses carried out, it has been demonstrated that the optimal operation point from the energy performance point of view is reached when fuel needed for sorbent regeneration is entirely supplied by the off-gas from the PSA hydrogen purification unit, which corresponds to operating the plant with the minimum steam-to-carbon ratio in the reforming step. Moreover, lowering the operating pressure of the Ca-Cu system results beneficial from the hydrogen production efficiency, but the CO₂ emissions and the economics worsen.

The Ca-Cu based hydrogen production plant operating at a high pressure has been demonstrated to be cost efficient with respect to a benchmark hydrogen production plant based on conventional fired tubular reformer and CO₂ capture by MDEA absorption. A hydrogen production cost of 0.178 €/Nm³ and a CO₂ avoided cost of 30.96 €/ton have been calculated for this Ca-Cu hydrogen production plant, which are around 8% and 52% lower, respectively, than the corresponding costs of the benchmark.

Keywords: Sorption enhanced reforming; Calcium looping; Chemical looping; Fixed bed; hydrogen production; CO₂ capture

1 Introduction

Currently, 90% of the hydrogen produced worldwide is used as a raw material in the synthesis of ammonia and methanol and in the oil refining industry for the hydrocracking of the heavy feedstocks as well as for the desulphurization of diesel fuel [1]. Hydrogen consumption is expected to keep on rising in the future due to the increase in the need of ammonia-based fertilizers and liquid hydrocarbons as a result of a growing global

population and possibly due to the emerging economy based on the use of hydrogen as a clean fuel for transport and heating. Steam Methane Reforming (SMR) is the most widely used technology for hydrogen production at a commercial scale nowadays, being adopted in more than 50% of the hydrogen produced worldwide. This is a well-established technology with high hydrogen production efficiencies of 72-77 % and the lowest hydrogen production costs with respect to the other hydrogen production processes based on coal gasification, water electrolysis or biomass gasification [2]. Regarding the carbon footprint of a large scale SMR-based plant, 8.1 tons of CO₂ per ton of H₂ are produced in the reformer furnace where the energy needed for the endothermic reforming process is supplied by air-fired combustion [3]. Modern SMR plants may achieve up to 10% of reduction in the CO₂ emissions to the atmosphere thanks to improved efficiency, but if significant CO₂ emissions reduction has to be fulfilled, CO₂ Capture and Storage (CCS) technologies need to be implemented, with CO₂ avoidance cost between 40 and 85 €/t, largely depending on natural gas and electricity price [1].

Among the different emerging technologies for hydrogen production with inherent CO₂ capture, there is a strong need of processes with reduced energy penalties and costs. The Ca-Cu looping process is one of such emerging technologies, having shown a noticeably improved performance when focused on hydrogen production with respect to the commercial SMR systems [4]. This process performs SMR of methane in the presence of a CaO-based sorbent that reacts with the CO₂ produced by the water gas shift (WGS) reaction, forming solid CaCO₃. The subsequent calcination of the CaCO₃ is sustained by the exothermic reduction of a CuO-based material in the same solid bed. This process, which is carried out in a system of fixed bed reactors operating in parallel at different temperatures and pressures [5–7], consists of three main reacting stages, namely (i) sorption enhanced reforming (SER), (ii) Cu oxidation with diluted air, and (iii) CuO reduction and simultaneous CaCO₃ calcination using H₂, CO and CH₄ as fuel gas. Figure 1 shows a schematic of the fixed bed reactor system proposed in this work, which consists of four reactors operating in parallel. The hydrogen production stage through the SER process corresponds to stage A in this figure, where pre-reformed natural gas is the feed gas. This stage operates at a high pressure of 10-30 bar. The H₂-rich gas produced in stage A is cooled and sent to a PSA unit for separating the high purity hydrogen product. The PSA off-gas, containing the unreacted CH₄, H₂, CO and CO₂, constitutes the fuel gas used in the reduction/calcination stage C, which may be integrated with an input of additional natural gas. The Cu oxidation corresponds to the stage B of the process shown in Figure 1 and it is carried out at the same operating pressure of stage A. This reactor is fed with diluted air, which is obtained by mixing compressed air with a fraction of the N₂-rich gas recirculated from stage B outlet. Dilution with N₂ is needed to limit the maximum temperature reached within the solid bed during this oxidation stage. A heating stage B' is then needed for heating up the solid bed before the reduction/calcination stage C begins. This heating process is performed by means of a stream of recirculated N₂-rich gas from stage B outlet.

Figure 1 Simplified scheme of a H₂ production plant integrated with the Ca-Cu process

This process has experienced a significant development in the recent years, especially in the framework of the FP7 EU project ASCENT [8]. Regarding the functional materials needed in the Ca-Cu process, CaO-based CO₂ sorbents and high load Cu-based materials with the appropriate proportions of Ca and Cu have been prepared, characterized and tested under conditions relevant for SER and reduction/calcination stages of the Ca-Cu process at large scale [8-9]. Dynamic 1-D pseudo homogeneous models have been also developed for simulating the operation of the fixed bed reactors of the Ca-Cu process and determine the operational window of each reacting stage of the process, as well as the effect of the kinetics and the Cu-to-Ca ratio needed in the solid bed [10–14]. Moreover, such reactor models have been also used to evaluate the performance of alternative operation strategies that aim at increasing the CO₂ capture efficiency when the process is integrated in a power plant [16].

Mass and energy balances of a natural gas combined cycle power plant integrated with the Ca-Cu process have been calculated [17] considering the simple reactor model proposed by Fernández et al. [7]. Such integration work demonstrated that electric efficiency penalties similar to the lowest reported in the literature for alternative pre-combustion CO₂ capture technologies were possible. When focused on hydrogen production, equivalent hydrogen production efficiencies as high as 77% and CO₂ capture rate of the order of

94% were reported, which are significantly better (i.e. 6 and 10%-points above, respectively) than those reported for a benchmark ATR-based hydrogen production technology with CO₂ capture using MDEA [17-18]. Alternatively, the Ca-Cu process has shown also great potential when being part of a state-of-the-art ammonia production plant, reducing the primary energy consumption per unit of ammonia by 14% compared to the commercial technology for ammonia production and simplifying the ammonia synthesis loop [20].

In this work a techno-economic analysis of a hydrogen production plant based on the Ca-Cu process is carried out. Mass and energy balances of the whole hydrogen production plant have been calculated, including the results from a 1-D sharp-front reactor model (SFM) for predicting the behavior of the fixed bed reactors system comprising the Ca-Cu process. With respect to the previous process modelling works on hydrogen production through the Ca-Cu process, this paper includes a sensitivity analysis on the key design and process parameters such as the steam-to-carbon ratio, the reactors pressure and the CO₂ sorbent capacity. Moreover, an economic analysis has been performed to calculate the cost of the hydrogen produced and of the CO₂ avoided of the Ca-Cu hydrogen plant operating at two different pressures (i.e. 11 and 25 bar). A conventional hydrogen production plant based on a fired tubular reformer (FTR) is considered for the sake of comparison. The performance and economics of this benchmark plant without and with CO₂ capture with a MDEA process are also calculated and presented in this work.

2 Methodology

2.1 Reactors modelling and validation

In this work the simulation of the Ca-Cu process reactors is performed with a simplified sharp front model (SFM). The modelling approach is the same proposed by Noorman et al [21]. Main assumptions used for the development of the model are the following ones:

- Reactions kinetics are fast enough and gas-particle heat transfer coefficient is sufficiently high to generate sharp reaction and heat fronts.
- Packed beds reactors are adiabatic.
- Plug flow pattern model for the reactors: concentration/temperature gradients on the radial direction are neglected.
- Homogeneous solid composition.

More complex Ca-Cu reactor models have been proposed in the literature, such as the Pseudo Homogeneous Model (PHM) developed by Martini et al. [14] and Fernandez et. al. [10-12]. These models, validated on experimental data for the CaCu process [9,13,14,22] and chemical looping processes [23–25], account for axial mass and heat dispersion and for reaction kinetics and can therefore predict more realistic temperature and concentration profiles in the bed. In this work, the use of the SFM has been preferred for the process simulations due to the fast convergence time of a complete cycle (order of seconds), which allowed to perform a wide sensitivity analysis, to be compared with the much longer convergence time (order of days)

needed with the PHM. The high computational time of the PHM in this plant is due to the dependency of the composition and flow rate of the gas fed to stage C on the results of stage A simulation. Because of this, the S/C ratio at stage A inlet has to be tuned to obtain the same duration of all the stages, as shown in Figure 2. This computational time issue is not present in Ca-Cu process integrated in power plants, where flow rate and composition of fuel fed to stage C is independent of heat and mass balances of stage A.

Figure 2 Conceptual scheme used for the simulation

The SFM for Ca-Cu process has already been used by Martinez et al. [20] in a previous work. An improvement has been implemented to consider the partial re-carbonation of the sorbent during stage C. From the more accurate PHM [14], it was found that as the reduction-calcination front advances during stage C, the bed is progressively left calcined and reduced. In these conditions, carbonation is favoured since reforming of the fuel, which is continuously fed to stage C, cools the bed and generates CO₂ with a partial pressure higher than the carbonation-calcination equilibrium one. Therefore, sorbent in the initial part of the bed is partly recarbonated after it is calcined. The updated SFM has been validated against the PHM in each stage of the process. The assumptions used for the validation of stages A and C (the stages with the most complex reactions) are reported in Table 1.

Table 1 Main assumptions used for the validation of stage A and stage C

Stage A	
Pre-reformer inlet temperature	490°C
S/C at pre-reformer inlet	1.93
Pressure at stage A inlet	11 bar
$T_{g,in,A}$	700°C
Gas inlet composition [kmol _i /kmol _{tot}]	
H ₂	0.0836
N ₂	0.0027
CO	0.0005
CO ₂	0.0322
CH ₄	0.2969
H ₂ O	0.5841
Stage C	
$T_{g,in,C}$	700 °C
Pressure at stage C inlet	1.8 bar
Cu/CaO _{active}	1.92
S/C	1
Gas inlet composition [kmol _i /kmol _{tot}]	
H ₂	0.2171
N ₂	0.0064
CO	0.1856
CO ₂	0.0407
CH ₄	0.1620
H ₂ O	0.3883

In Figure 3, the gas composition profiles obtained for stage A with the SFM and the PHM are reported for an operating pressure of 11 bar. In Figure 4, temperature profiles of stages A and C obtained with the two models are shown. In Table 2, average molar concentration of the gas generated during stage A and stage C, average gas outlet temperature, fraction of bed carbonated (X_{carb}) and carbon capture of stage A (defined as ratio between the molar flow rate of carbon species separated by the sorbent in stage A and the molar flow rate of carbon species entering the same stage) are summarized for two operating pressures (11 and 25 bar), which are latterly analysed. As can be noticed, differences between the predictions made by the two models can be considered acceptable for the scope of this work.

Figure 3 Gas composition profiles for an intermediate time of stage A obtained with the sharp front model (up) and with the pseudo homogeneous model (bottom) with the operating conditions summarized in Table 1

Figure 4 Temperature profiles at intermediate time of stage A (a-b) and stage C (c-d) obtained with the SFM (a-c) and PHM (b-d) with the operating conditions summarized in Table 1

Table 2 Stage A and stage C average outlet composition and calculated parameters

y_i [kmol _i /kmol _{tot}]	Stage A pressure=11 bar				Stage A pressure =25 bar			
	Stage A		Stage C		Stage A		Stage C	
	SFM	PHM	SFM	PHM	SFM	PHM	SFM	PHM
H ₂	0.7115	0.6833	0.0000	0.0078	0.6406	0.6204	0.0000	0.0089
N ₂	0.0021	0.0021	0.0039	0.0039	0.0020	0.0072	0.0037	0.0037
CO	0.0608	0.0532	0.0000	0.0049	0.0406	0.0351	0.0000	0.0050
CO ₂	0.0133	0.0150	0.4307	0.4214	0.0139	0.0146	0.4279	0.4180
CH ₄	0.0531	0.0671	0.0000	0.0000	0.0630	0.0712	0.0000	0.0000
H ₂ O	0.1591	0.1793	0.5655	0.5620	0.2400	0.2515	0.5684	0.5644
T _{out} [°C]	828.3	801.0	699.0	702.7	836.5	825.0	715.4	736.2
X _{carb} [%]	-	-	22.42	23.29	-	-	23.67	25.14
CCR _A [%]	50.13	48.00	-	-	51.44	50.82	-	-

2.2 Process integration

The Ca-Cu process studied in this work has been integrated in a medium scale hydrogen plant producing 30'000 Nm³/h of high purity hydrogen. The tool employed for process simulations is the commercial software Aspen Plus. Gas properties have been evaluated with the cubic equation of state of Peng Robinson [26] for the exception of the CO₂ compression section where the Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules has been used [27]. Pure water and steam thermodynamic properties have been evaluated through STEAMNBS.

In Figure 5 the complete plant flowsheet of the Ca-Cu based plant with stages A, B and B' operating at 25 bar is shown. For the case study with a lower operating pressure in these stages, inlet pressure of the natural input to the plant is adjusted according to the process assumptions given in Table 3 for reaching 11 bar at stage A inlet. Natural gas (stream #1) entering the system is mixed with part of the hydrogen produced (#23) to reach a hydrogen molar concentration around 2%. This stream (#2) is then pre-heated until a temperature

of 365 °C before entering the hydrogen sulphide removal section. Here sulphur compounds are firstly converted into H₂S, which is afterwards adsorbed in a system of ZnO beds. The desulfurized natural gas is then heated and mixed with high-pressure steam (#65) bled from a steam turbine at 26.5 bar to reach the S/C required by stage A. This stream is then sent to an adiabatic pre-reformer where carbon species higher than CH₄ are converted, preventing the risk of coke formation in the Ca-Cu bed. The pre-reformed natural gas is then heated in HX4 and HX5 to the target temperature of 700°C needed at stage A inlet (#10).

The H₂-rich gas produced in stage A (#11) is cooled down to 40°C. Part of the heat recovered is used to preheat the feed of stage A and stage C and the natural gas entering the adiabatic pre-reformer. Part of the thermal power is also used to produce high pressure steam at 100 bar and 485 °C. After final cooling by cooling water, condensed water is separated and the resulting gas (#20) is sent to a Pressure Swing Adsorption (PSA) unit where the purity of the hydrogen recovered achieves 99.999%. It is assumed that 90% of the inlet hydrogen is recovered as high purity hydrogen in the PSA unit and it is then compressed to the final delivery pressure of 29 bar. In the cases where the Ca-Cu reactors are operated at 11 bar, the hydrogen-rich syngas is compressed up to 25 bar before the PSA unit, in order to keep a sufficiently high feed pressure allowing to achieve the 90% of hydrogen recovery factor [28]. It must be observed that the assumed PSA hydrogen recovery factor is the same in the CaCu and in the benchmark hydrogen plants. This is therefore a conservative assumption for the CaCu plant, which may take advantage of the higher hydrogen content in the PSA feed and achieve a higher recovery factor after proper PSA optimization.

The carbon-rich PSA off-gas (#24) is heated to 200°C against the N₂-rich gas from the turbine and mixed with the low-pressure steam (#64) to reach a S/C around 1. This stream is then further heated up in HX10 and HX6 to around 700°C with the CO₂-H₂O mixture from stage C and with the hot syngas from stage A and then fed to stage C for bed regeneration. As discussed further on, the best plant performance is obtained when the S/C ratio in stage A is tuned to generate a PSA off-gas flow rate that matches the fuel requirement in stage C. This condition is that represented in Figure 5. For higher S/C in stage A, the PSA off-gas would not be sufficient for bed regeneration and additional natural gas should be fed to stage C, as shown in Figure 1. The CO₂-rich gas stream leaving step C (#29) is cooled down to 40°C to be compressed after water removal for CO₂ storage (#36).

Air needed in stage B is delivered by an adiabatic compressor and then mixed with part of the N₂-rich stream recycled from stage B outlet. Recycle flow rate is tuned to achieve an oxygen concentration of around 3% at stage B inlet (#39) to limit the maximum temperature inside stage B to values around 830-850°C. Working below such temperatures would avoid Cu agglomeration and decomposition [29], as well as minimize the unwanted calcination of the CaCO₃ present in the solid bed which would lead to a decrease of the overall carbon capture efficiency. The oxygen-depleted stream produced by stage B (#40) is partly sent to a turbine (#41) and partly recycled (#44). Part of this recycle is used for bed heating in stage B' (#45) as indicated in Figure 5.

Assumptions for the calculation of the plant are reported in Table 3. Properties of the streams shown in Figure 5 for the operating pressure of 25 bar and an S/C at pre-reformer inlet equal to 2.27 are reported in Table A1 in the appendix. Temperature-heat diagrams obtained for the Ca-Cu plant operated with these conditions are shown in Figure A1 in the appendix. Most of the heat from the Ca-Cu process is recovered from the H_2 -rich and N_2 -rich gas from stages A and B, respectively. The energy recovered from the N_2 -rich gas recirculated from stage B outlet in SH1, EVA1 and ECO1B represents a great heat source in the Ca-Cu process since it allows generating 9.43 kg/s of superheated steam (#55) sent to the steam turbine for power production, which corresponds to 87% of the total superheated steam produced. A minor fraction of the steam sent to the steam turbine is produced in the heat exchanger EVA2 situated in the cooling line of the H_2 -rich gas, which is mainly used for pre-heating the feed gas to stages A and C.

Figure 5 Scheme of a full-scale H_2 production plant integrated with the Ca-Cu process-case at 25 bar

Table 3 Main process assumptions for the calculation of the H₂ production plant integrated with the Ca-Cu process

* values subject to sensitivity analysis.

Natural gas	
Composition [vol%]: CH ₄ 89.00, C ₂ H ₆ 7.00, C ₃ H ₈ 1.00, C ₄ H ₁₀ 0.11, CO ₂ 2.00, N ₂ 0.89	
LHV [MJ/kg]: 46.51 MJ/kg	
NG supply temperature [°C]: 15°C	
Natural Gas pre-treatment	
Operating temperature of the desulphurization unit [°C]	365
Pressure loss in the desulphurization unit [bar]	0.36
Adiabatic pre-reformer inlet temperature [°C]	490
Pressure loss in the pre-reformer [bar]	0.36
S/C molar ratio at stage A pre-reformer inlet	2.27-3*
S/C molar ratio at stage C inlet	1
Ca-Cu process	
Feed gas temperature to stages A and C [°C]	700
Feed gas temperature to stage B [°C]	300
Operating pressure of stage A [bar]	11-25*
Operating pressure of stage B [bar]	11-25*
Operating pressure of stage C [bar]	1.8
Heat recovery system	
Evaporation pressure [bar]	100
Superheated steam temperature [°C]	485
Minimum ΔT in gas-gas heat exchangers [°C]	20
Minimum ΔT in gas-liquid water heat exchangers [°C]	10
Minimum ΔT in gas-evaporating water heat exchanger [°C]	10
Water subcooling ΔT at evaporator drum inlet [°C]	5
Pressure loss in gas heating/cooling line [% of the inlet pressure of each heat exchanger]	1
Heat losses in each heat exchanger [% of the heat transferred]	0.7
Pressure of the steam export [bar]	6
Steam turbine isentropic efficiency [%]	85
Steam turbine mechanical-electric efficiency [%]	94
N ₂ turbine	
Isentropic efficiency [%]	85
Mechanical-electric efficiency [%]	96
Air compressor	
Polytropic efficiency [%]	80
Mechanical-electric efficiency [%]	96
Recirculating fan and H ₂ compressor	

Polytropic efficiency [%]	80
Mechanical-electric efficiency [%]	94
Inter-cooled CO ₂ compressor	
Number of intercooled compression stages	3
Intercooling temperature [°C]	28
Intercooling pressure loss [% of inlet pressure]	1%
Outlet pressure after compression stages [bar]	79.2
Final CO ₂ storage pressure [bar]	110
Polytropic efficiency of compression stages [%]	80/80/75
Pump hydraulic efficiency [%]	75
Other assumptions	
PSA feed pressure in the HP/LP stage A cases [bar]	23.3/25
PSA hydrogen recovery efficiency [%]	90
Heat rejection auxiliaries power consumption [% of heat transferred]	0.8

2.3 *Economic model*

The methodology used to perform the economic analysis follows a “bottom-up” approach. Firstly, capital costs of each installed plant item are estimated by means of cost scaling techniques, cost functions and single point data. All costs are referred to the same year 2017 by means of the CEPCI coefficients [30].

With the aim of working with a reduced reactor volume and pressure drop, each reactor of the Ca-Cu process has been assumed to be divided into four “sub-reactors” sharing the same set of valves, as depicted in Figure 1. This allows reducing the steel thickness and the reactor length and volume while keeping a proper length to diameter ratio of 2, ultimately reducing the vessel cost and the amount of functional material. Larger number of sub-reactors would further reduce the reactors volume and the Capex. However, this would also lead to more frequent valve opening-closing cycles as well as to less stable gas composition at reactors outlet due to variable concentration profiles during breakthrough, which have an economic impact difficult to consider. For this reason, the number of sub-reactors has not been optimized from the economic point of view.

Reactors diameter, both in the high-pressure case and in the low-pressure case, have been chosen imposing a maximum superficial velocity in stage A equal to 0.25 m/s, resulting in the geometry shown in Table 4. Each reactor is provided with 4 switching valves on the inlet duct and 4 switching valves on the outlet one. Reactors have been provided with an internal insulation with a thickness of 300 mm, which allows to have a reactor outer wall temperature of about 70 °C. Thickness of the steel and costing of the vessels has been performed thanks to inputs received from an industrial technology provider within Ascent project [8].

Table 4 Reactors dimensions and assumptions

	<i>25 bar</i>	<i>11 bar</i>
Diameter of each sub-reactor [m]	1.8	2.5
length of each sub-reactor [m]	3.5	4.9
Total number of reactors [-]	4	4
Total reactors inner volume [m ³]	34.5	94.1

Sizing and costing of heat exchangers have been performed with the commercial software Aspen Exchanger Design & Rating. The installed cost of other plant units is computed with scaling functions (1-2) with the parameters summarized in Tables A2 and A3 in the Appendix. For units not reported in the table, single point cost data have been provided by industrial partners of the Ascent project [8].

$$C = C_0 \cdot \left(\frac{S}{S_0}\right)^f \quad (1)$$

$$C = F_{bm} \cdot 10^{[k_1 + k_2 \cdot \text{Log}_{10}(S) + k_3 \cdot (\text{Log}_{10}(S))^2]} \quad (2)$$

The sum of the installed costs of all the plant units gives the total direct plant cost (TDPC). Indirect costs, related to yard improvement, service facilities, buildings and engineering costs have been assumed equal to 14% of the TDPC [31] and summed to the TDPC to obtain the Engineering, Procurement and Construction Costs (EPC). The total plant cost (TPC) is then obtained by increasing the EPC by 14% to include owner's costs and contingencies.

As for the labor cost, the same number of employees per shift of [31] has been considered, with a cost of the personnel equal to 40.24 €/hr. Yearly maintenance costs are calculated as % of the TDPC (with different values depending on the section of the plant), as summarized in Table A4 in the Appendix..

Consumable costs assumptions are detailed in Table A5. The lifetime of the functional material is not supported by experimental data, since long run tests of the CaCu process have not been performed yet. Therefore, the assumed value represents a reasonable target for the material in a commercial plant. For the steam exported from the plant, a revenue has been assumed corresponding to the avoided cost of the natural gas burnt in a boiler with 90% of efficiency, producing the same amount of LP steam.

In Table A6 assumptions for the long-run profitability analysis have been reported. The availability of the plant has been assumed equal to 7500 hours. However, for the first year of operation the number of hours has been reduced to 5700 hours [31] due to unforeseen circumstances, typical of newly built plants.

2.4 Key performance indicators

Main plant performance indexes are introduced to evaluate the behaviour of the Ca-Cu plant when varying plant configuration and process parameters. For the definition of these indexes it is considered the same approach of Martínez et al. [32], considering that the hydrogen production plant has natural gas as main input, and CO₂ for storage, vented gas and steam exported as main outputs. In addition, there may be an exchange of electricity with the grid, since it can be exported from the plant or imported when the turbine output is not enough for fulfilling the consumption of the auxiliaries. The definitions of the key performance indicators employed in the analysis of the plant are reported below.

- *Equivalent natural gas* ($\dot{m}_{NG,eq}$) represents the actual NG dedicated for hydrogen production, subtracting to the real NG input the NG that is saved from producing the steam exported ($\dot{Q}_{th}$) and the electricity exported to the grid ($\dot{W}_{el}$):

$$\dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{\dot{Q}_{th}}{\eta_{th,ref} \cdot LHV_{NG}} - \frac{\dot{W}_{el}}{\eta_{el,ref} \cdot LHV_{NG}} \quad (3)$$

The primary energy consumption of NG associated to $\dot{Q}_{th}$, which represents the heat associated to the steam exported from the plant at 6 bar, is calculated through the thermal efficiency $\eta_{th,ref}$, which is considered equal to 90% and represents the reference thermal efficiency to produce steam in a conventional boiler [33]. Similarly, the energy consumption associated to the net electricity exported from the grid is calculated through $\eta_{el,ref}$, which is the electric efficiency of a natural gas combined cycle, considered equal to 58.3% [31]. In case there is an import of electricity to the plant, $\dot{W}_{el} < 0$ and the term associated to the electricity export would turn out positive in Eq. (3), making the equivalent primary energy consumption to increase.

- *Equivalent hydrogen production efficiency* ($\eta_{H2,eq}$) is the hydrogen production efficiency calculated according to Eq. (4), considering the equivalent NG consumption. This equivalent efficiency allows comparing homogeneously different hydrogen production plants working with different outputs of electricity and heat since the use of the equivalent NG consumption neutralises these outputs.

$$\eta_{H2,eq} = \frac{\dot{m}_{H2} \cdot LHV_{H2}}{\dot{m}_{eq,NG} \cdot LHV_{NG}} \quad (4)$$

- *Equivalent CO₂ emissions* (given in kg_{CO2}/s) are the CO₂ emissions associated to the equivalent NG consumption and are calculated according to Eq. (5). The calculation of these emissions includes the specific emission factor of the NG (e_{NG}), which corresponds to 2.65 kg_{CO2}/kg_{NG} according to the NG composition given in Table 3.

$$E_{eq} = \dot{m}_{NG,eq} \cdot e_{NG} \quad (5)$$

- *Equivalent Carbon Capture Ratio (CCR_{eq})* accounts for the CCR of the process based on the CO₂ emissions associated to the equivalent NG input. It can be calculated according to Eq. (6)

$$CCR_{eq} = \frac{\dot{m}_{CO_2, captured}}{\dot{m}_{NG, eq} \cdot e_{NG}} \quad (6)$$

- *Equivalent specific primary energy consumption for CO₂ avoided ($SPECCA_{eq}$)* index (given in MJ/kg_{CO₂}), which accounts for the equivalent primary energy that is needed for avoiding the emission of 1 kg of CO₂ to the atmosphere with respect to the reference hydrogen production process without CO₂ capture. It is calculated using Eq. (7), where $\eta_{H_2-ref, eq}$ and E_{eq-ref} are the equivalent H₂ production efficiency and the equivalent CO₂ emissions of the reference FTR plant without capture:

$$SPECCA_{eq} = \frac{\left(\frac{1}{\eta_{H_2, eq}} - \frac{1}{\eta_{H_2-ref, eq}} \right)}{E_{eq-ref} - E_{eq}} \quad (7)$$

- *Cost of CO₂ avoided (CCA)* measures the additional cost that a plant with CO₂ capture has when compared to a plant without CO₂ capture. Its definition for hydrogen production plants is expressed with Eq. (8):

$$CCA = \frac{C_{H_2} - C_{H_2, ref}}{E_{eq, ref} - E_{eq}} \quad (8)$$

where C_{H_2} and $C_{H_2, ref}$ correspond to the hydrogen production costs (€/Nm³) for the plant with CO₂ capture and the plant without CO₂ capture.

3 Results

3.1 Heat and mass balances

3.1.1 Base case discussion

Results of the simulation of the complete hydrogen plant integrated with the Ca-Cu process are reported Table 5. As a basis for the comparison, a hydrogen production of 30'000 Nm³/h has been kept for all the cases analysed in this work. In this table, the energy balance and the KPIs of the benchmark FTR hydrogen production plants without CO₂ capture and with CO₂ capture by Methyl Diethanolamine (MDEA) (originally developed in [32] and updated in Ascent project [8]) are also shown in the last two columns.

Results of the Ca-Cu plant operated at 25 bar with a S/C ratio of 2.27 at the inlet of stage A pre-reformer are included in the first column of Table 5. This S/C value is such that the PSA off-gas matches the amount of fuel gas needed for sorbent regeneration in stage C. The hydrogen production efficiency (η_{H_2}) obtained for the Ca-Cu plant (74.1%) is higher than the efficiency of both the FTR with and without CO₂ capture (+0.7

and +1.5% points, respectively). The equivalent hydrogen production efficiency ($\eta_{H_2,eq}$) of the Ca-Cu plant is also significantly higher (+3.7% points) than the efficiency of the FTR plant with CO₂ capture. The reason of the increased difference in $\eta_{H_2,eq}$ is the higher export of LP steam, which compensates the higher net electric absorption.

After CO₂ compression, the second main electric consumption of the Ca-Cu plant is associated to the air compressor-N₂ turbine group, since the gas flow rate expanded in the turbine is less than the one compressed by the compressor because of the uptake of O₂ from the air flow in stage B. Moreover, this relatively high power absorption is due to the low thermodynamic efficiency of this gas cycle, which is related to the low turbine inlet temperature combined with a high compressor pressure ratio (about 25). Non-negligible power absorption is also associated to the stage B recycle fan, which recirculates a significant gas flow rate.

As for CO₂ capture efficiency, the Ca-Cu plant achieves a CCR of 95.6% and a CCR_{eq} of 98.7%. The higher value for the CCR_{eq} is due again to the CO₂ credits associated to LP steam export. Compared to the benchmark, the CCR is significantly higher than in the FTR plant with CO₂ capture (~75%), where CO₂ is absorbed from the syngas by MDEA process, but CO₂ generated in the FTR burners is emitted. By combining the equivalent hydrogen production efficiency and the CCR , a $SPECCA_{eq}$ of 1.54 MJ_{LHV}/kgCO₂ is calculated for the Ca-Cu process, which is less than halved the $SPECCA_{eq}$ of 3.48 MJ/kgCO₂ calculated for the benchmark plant with CO₂ capture.

In Figure 6, the Sankey diagram of the energy flows of the base case Ca-Cu hydrogen plant is shown. As can be observed, most of the energy penalty (about 20% of the inlet natural gas heating value) is associated to the heat released in the stage B recycle cooler (i.e. cooling of stream #47 to #49 in Figure 5).

Figure 6 Sankey diagram of the energy flows (LHV basis for fuels) of the base case Ca-Cu hydrogen plant

Table 5 Energy balance and performance comparison of the benchmark hydrogen production plants (FTR with and w/o CO₂ capture) and the hydrogen production plants including a Ca-Cu process

	Ca-Cu plants					Benchmark plants	
	25 bar	11 bar	25 bar	25 bar	25 bar	FTR w/o capture	FTR with capture
Pressure at stage A and B inlet							
Active CaO in bed [%]	30	30	30	20	40		
Steam-to-carbon ratio at pre-reformer inlet [-]	2.27	1.93	3	2.38	2.17	3	4
Natural gas input [kg/s]	2.61	2.48	2.60	2.57	2.63	2.62	2.64
Natural gas thermal input [MW]	121.4	115.3	121.1	119.3	122.3	121.7	122.9
Equivalent natural gas input [MW]	117.6	115.0	121.1	120.1	113.5	107.5	122.7
Hydrogen thermal output [MW]	89.9	89.9	89.9	89.9	89.9	89.3	89.2
Thermal power output (as LP steam) [MW]	6.33	3.94	3.28	3.58	8.00	9.56	2.15
Electric power output [MW]							
Steam turbine	4.28	3.52	3.28	3.71	4.59	3.80	3.30
MDEA process	--	--	--	--	--	--	-0.70
CO ₂ compressors	-2.41	-2.17	-2.40	-2.38	-2.43	--	-2.10
Air compressor-N ₂ turbine group	-2.27	-0.20	-2.26	-2.13	-2.34	--	--
Recycle fan (stage B)	-0.90	-0.91	-0.87	-0.98	-0.84	--	--
Hydrogen compressor	-0.30	-0.20	-0.31	-0.30	-0.30	--	--
Syngas compressor	--	-1.76	--	--	--	--	--
Natural gas expander	--	--	0.22	--	--	--	--
Other auxiliaries (pumps, heat rejection, H ₂ recycle compressor)	-0.31	-0.24	-0.34	-0.31	-0.30	-1.70	-1.70
Net electric power output [MW]	-1.90	-1.97	-2.11	-2.39	-1.62	2.13	-1.25
η_{H_2} [% _{LHV}]	74.07	77.99	74.26	75.35	73.49	73.33	72.56
$\eta_{H_2,eq}$ [% _{LHV}]	76.44	78.68	74.27	75.28	77.36	83.07	72.70
CCR [%]	95.61	90.82	95.63	95.73	95.56	--	75.18
CCR _{eq} [%]	98.68	91.62	95.64	95.64	101.00	--	75.34
E_{eq} [gCO ₂ /MJ _{LHV,H₂}]	0.99	6.07	3.34	3.30	-0.44	68.62	19.34
SPECCA _{eq} [MJ _{LHV} /kgCO ₂]	1.54	1.07	2.32	1.90	1.29	--	3.48

3.1.1 Effect of stage A and stage B pressure

In this section, the effects of a reduction in the operating pressure of stages A and B are evaluated. As shown in Table 5, operating at a reduced pressure of 11 bar (second column) leads to an increased CO₂ loss in stage B. As a result, compared to the higher pressure case (first column) discussed in the previous section, a lower amount of sorbent has to be regenerated in stage C, less fuel is therefore needed in this stage and a lower amount of air is needed in the oxidation of stage B per unit of natural gas fed to stage A ($\dot{m}_{\text{air}}/\dot{m}_{\text{NG,inA}}$).

Table 6 Results obtained for the reactors simulation with the sharp front model

Stage A and B pressure	[bar]	25	11	25	25	25
X _{CaO}	[%]	30	30	30	20	40
S/C	[-]	2.27	1.93	3	2.38	2.17
Relative step duration (fixed reactor size)	[-]	1	0.40	1.02	0.78	1.21
Relative reactor size (given step duration)	[-]	1	2.53	0.98	1.28	0.83
T _{max,A}	[°C]	839.5	794.6	848.0	854.9	828.3
T _{max,B}	[°C]	830.0	830.0	830.0	830.0	830.0
y _{O2,inB}	[%mol.]	2.99	2.95	2.99	2.73	3.16
CCR _A	[%]	51.44	50.13	57.73	44.58	56.04
Cu/Ca	(molar)	0.60	0.57	0.60	0.42	0.79
Cu/Ca _{active}	(molar)	2.02	1.92	2.01	2.12	1.97
$\dot{m}_{\text{air}}/\dot{m}_{\text{NG,inA}}$	[-]	6.12	5.60	6.10	5.95	6.20
$\dot{m}_{\text{N2,turbine}}/\dot{m}_{\text{NG,inA}}$	[-]	4.62	4.23	4.60	4.48	4.67
$\dot{m}_{\text{N2,inB}}/\dot{m}_{\text{NG,inA}}$	[-]	19.19	17.03	19.13	23.84	16.38
$\dot{m}_{\text{N2,recyclebypass}}/\dot{m}_{\text{NG,inA}}$	[-]	15.52	13.29	15.45	13.67	16.50
$\dot{m}_{\text{N2,outB}}/\dot{m}_{\text{NG,inA}}$	[-]	44.90	37.10	44.19	48.03	42.81
Carbon loss in B	[%]	4.28	9.09	4.27	4.17	4.34

As for the electric balance (Table 5), the compressor-turbine group absorbs less electric power when stage A and stage B are operated at a lower pressure. This is a consequence of the lower pressure ratio, which is preferable from a thermodynamic efficiency point of view for moderate maximum temperatures of the gas cycle. The CO₂ compression train has a slightly lower consumption in the low-pressure case due to the lower amount of CO₂ captured by the process. On the other hand, a syngas compressor is needed to raise the stage A syngas pressure up to the PSA pressure of 25 bar.

When comparing the KPIs between the two cases case, lower pressure leads to higher η_{H2} and a lower CCR. The higher η_{H2} is mainly due to the lower air flow rate and N₂ recycle in stage B, leading to lower thermal power transferred to the gas and the steam cycles and lower stack loss. The resulting $SPECCA_{eq}$ of the 11 bar case is 1.07 MJ_{LHV}/kg_{CO2}, i.e. 30% less than for the 25 bar base case.

3.1.2 Effect of S/C in stage A

The effect of S/C ratio in the stage A pre-reformer has been investigated by increasing it up to 3, starting from the base case at 25 bar (third column of Table 5 and Table 6). The effect of higher S/C is a higher H_2 production in stage A, leading to a reduced amount of PSA off-gas which becomes insufficient to sustain sorbent regeneration in stage C. Therefore, part of the inlet natural gas (about 12% of the total) is introduced in the system to feed stage C and an additional pre-reformer is employed to treat this NG stream, as depicted using dotted lines in Figure 1.

Results of the simulations show that higher S/C ratio favours CH_4 conversion and CO_2 capture in stage A (CCR_A increases from 51.4% in the base case to 57.7% in the high S/C case). However, CCR of the plant is barely dependent on the S/C because carbon slipping from stage A is not emitted but recovered in the downstream PSA unit. The η_{H_2} is only 0.2% points higher in the high S/C case than in the base case. Because of the higher steam used in the process, the case with higher S/C features lower LP steam export and lower steam turbine power output, leading to lower $\eta_{H_2,eq}$, lower CCR_{eq} and ultimately to a higher $SPECCA_{eq}$ (i.e. 2.32 MJ/kg CO_2) than in the base case.

3.1.3 Effect of sorbent capacity

The effect of the CO_2 sorbent capacity has been assessed by changing the fraction of active CaO between 20% and 40% (fourth and fifth columns of Table 5 and Table 6) in order to analyse the impact of this parameter into the global performance. Typical active CaO contents achieved in the literature for this functional material are close to 30% [34,35], as considered for the base case. The value of 20% of active CaO has been chosen as a possible residual capacity of a highly cycled sorbent after many years of operation subjected to mechanical and thermal stress. As shown in Table 6, a higher sorbent capacity leads to an increase of CCR_A . When CaO capacity is increased, more energy is needed for bed regeneration (see the Cu/Ca ratio increasing from 0.42 to 0.79 when CaO capacity increases from 20% to 40%) because the % of $CaCO_3$ in the bed at the beginning of stage C is increased. Therefore, a higher amount of PSA off-gas fuel is needed in stage C. In case no natural gas wants to be fed to stage C (justified by the better performance results discussed in the previous section), the S/C ratio at stage A inlet needs to be such that the PSA off-gas fulfils the energy consumption in stage C. Therefore, in order to increase the amount of energy in the PSA off-gas, the S/C ratio at stage A inlet should be reduced, as shown in Table 6 for this case. The use of a lower S/C ratio results in a lower CH_4 conversion in the initial part of the bed during stage A, where CaO is fully carbonated and CH_4 is converted according to the equilibrium of conventional adiabatic SMR. Consequently, when S/C is reduced, a higher amount of unreacted CH_4 remains at the carbonation reaction front. This additional methane is reformed at the carbonation reaction front, balancing the exothermic carbonation

reaction heat and reducing the temperature increase at this reaction front, favouring in this way CO₂ absorption in this stage and so CCR_A .

When CaO capacity is increased, the Cu/Ca ratio needed in the solid bed is also higher since the amount of CaCO₃ to be calcined is raised. As a result, a higher air flow rate has to be fed to stage B ($\dot{m}_{air}/\dot{m}_{NG,inA}$) to oxidize the Cu present in the solid bed, which turns into a higher N₂ flow rate sent to the N₂ turbine ($\dot{m}_{N2,turbine}/\dot{m}_{NG,inA}$) and a larger flow rate of the stage B' recycle bypass ($\dot{m}_{N2,recyclebypass}/\dot{m}_{NG,inA}$) per kg of NG to stage A. The increase of these two N₂ flow rates leads to higher thermal power transferred to the steam cycle in the N₂ recycle heat exchanger and in the N₂ turbine off-gas, leading to a lower cold gas efficiency and therefore to lower η_{H2} , which reduces from 75.35 to 73.49% when sorbent capacity is increased from 20 to 40%. The higher N₂-rich gas flow rate from B to the N₂ turbine also causes a small increase of the CO₂ loss from B for the case with higher sorbent capacity, and so makes the CCR slightly reduced.

As for the overall energy balance reported in Table 5, the main effect of the variation of the CaO capacity is related to the variation of the S/C at stage A. As discussed previously, an increase of the sorbent capacity brings about a reduction of the S/C ratio and an increase of the heat recovered in the N₂ recycle, which lead to an increase of the steam turbine power output and of the exported steam. As a result, $\eta_{H2,eq}$ and CCR_{eq} increase with the sorbent capacity and $SPECCA_{eq}$ reduces to 1.29 MJ_{LHV}/kg_{CO2} in the case with 40% of active CaO (i.e. ~16% less than in the Ca-Cu base case).

According to these results, for a plant intended to maximize the hydrogen production efficiency η_{H2} , it seems better to operate with low sorbent conversion. In a few words, this is because the higher CO₂ capture ratio in stage A is not beneficial from the point of view of the heat balance. As a matter of fact, carbon slipping from stage A is separated with no significant energy penalty in the PSA, while CO₂ captured in stage A leads to higher gas flow rates in stage B-B' for supporting sorbent calcination and higher energy losses associated to the N₂ recycle. On the other side, when considering the net electric input and the thermal power exported, higher sorbent conversion appears advantageous, since it allows achieving better equivalent indexes $\eta_{H2,eq}$, CCR_{eq} and $SPECCA_{eq}$. Moreover, higher sorbent conversion leads to longer cycle durations (see Table 6) and therefore to longer expected lifetime of the valves (or alternatively to smaller and cheaper reactors for given cycle duration).

3.2 Economic analysis

Results of the economic analysis of the Ca-Cu hydrogen plants are presented and compared with the benchmark hydrogen plants. In Table 7 the installed capital cost breakdown of the different plants analyzed is shown. The highest cost item in the Ca-Cu plant is the reactors system, including vessels, valves and initial fill (IF) (see Table 8 for the breakdown of the cost of the reactors). The capital cost is significantly influenced by the operating pressure since when lower pressure of the Ca-Cu reactors is selected, reactors

volume and so their cost increase. High costs are also obtained for the air compressor and N₂ turbine group, which are higher in the high pressure case due to the net higher power absorbed.

As for the final TPC, the low pressure Ca-Cu plant features a ~7% higher TPC+IF cost than the high pressure Ca-Cu plant. Compared to the benchmark, the 25 bar Ca-Cu plant features ~16% lower TPC+IF cost than the benchmark FTR plant with CO₂ capture, mainly because of the avoided cost for the FTR reactor and the MDEA-based CO₂ separation process.

Table 7 Installed capital costs and initial fill cost of the assessed hydrogen plants

Cost Item	Ca-Cu 25 bar	Ca-Cu 11 bar	FTR w/o capture	FTR with capture
	M€			
NG pre-treatment and pre-reforming	0.20	0.28	0.20	0.23
Ca-Cu reactors and valves	10.63	12.47	-	-
FTR	-	-	19.33	24.08
HT WGS	-	-	0.13	0.18
LT WGS	-	-	-	0.12
Syngas Cooling	3.67	5.24	2.52	2.78
	<i>Hydrogen-rich gas cooling line</i>	0.77	0.58	
	<i>CO₂-rich gas cooling line</i>	0.91	0.96	
	<i>Stage B' recycle gas cooling line</i>	1.43	3.67	
	<i>Turbine heat exchanger</i>	0.55	0.03	
MDEA process	-	-	-	12.73
CO ₂ compression	5.11	4.78	-	4.70
Steam turbine & generator	2.31	2.01	2.13	1.90
Feedwater, cooling water system & miscellaneous BOP	11.22	10.22	4.04	7.08
Accessory electric plant	9.11	10.49	5.47	8.10
PSA unit	4.41	4.10	3.87	4.08
Other blowers and compressors	0.13	-	0.10	0.10
Air compressor-N ₂ turbine group and electric motor	5.97	3.71	-	-
Recirculating fan	0.73	0.74	-	-
Hydrogen compressor	1.10	0.52	-	-
Syngas compressor	-	1.43	-	-
TDPC	54.58	55.98	37.81	66.07
Yard improvement	0.82	0.84	0.57	0.99
Service facilities	1.09	1.12	0.76	1.32
Engineering & consultancy	2.46	2.52	1.70	2.97
Building	2.18	2.24	1.51	2.64
Miscellaneous	1.09	1.12	0.76	1.32
EPC	62.22	63.82	43.10	75.32
Other Owner's costs	9.33	9.57	6.46	11.30
TPC	71.56	73.39	49.56	86.61
Initial fills				
Hydrodesulphurization catalyst	0.04	0.04	0.04	0.04

ZnO absorbent	0.10	0.09	0.10	0.10
Pre-reformer catalyst	0.52	0.65	0.52	0.53
MDEA solvent	-	-	-	0.04
FTR reforming catalyst	-	-	0.31	0.32
Ca-Cu functional materials	2.02	5.48	-	-
High temperature shift catalyst	-	-	0.16	0.26
Low temperature shift catalyst	-	-	-	0.26
TPC+IF	74.25	79.65	50.70	88.17

Table 8 Breakdown of the Ca-Cu reactor cost

	25 bar	11 bar
	M€	M€
Costs for each reactor		
Insulation	0.13	0.23
Steel (including head, shell, nozzle)	1.30	1.32
Valves	0.35	0.52
Ca-based sorbent	0.07	0.20
Cu-based oxygen carrier	0.25	0.67
Ni-based catalyst	0.18	0.50
Total material cost of each reactor	1.42	1.56
Total cost of each reactor	1.77	2.08
Total installed reactors cost (all reactors)	10.63	12.47
Cost of functional material per reactor	0.51	1.37
Total cost of functional material (all reactors)	2.02	5.48

The O&M costs are reported in Table 9, referred to an availability of the plant of 7500 hours. The most important expense is related to the purchase of the natural gas. Since the size of the plant is determined on the target hydrogen production of 30'000 Nm³/h, the cost associated to the purchase of natural gas is lower in those cases with higher hydrogen production efficiency. Labor cost is the prevalent fixed O&M cost. For calculating the cost for the replacement of the functional material, materials lifetime has been assumed equal to 5 years. This cost is higher in the 11 bar case because of the higher reactors volume and the consequently higher amount of functional material needed in the system, accounting for 1.10 M€ (i.e. almost 10.5 % of the total fixed O&M cost) in this case.

Table 9 O&M costs of the assessed hydrogen plants

	Ca-Cu 25 bar	Ca- Cu 11 bar	FTR w/o capture	FTR with capture
Variable O&M	M€/y	M€/y	M€/y	M€/y

Natural gas	21.88	20.78	21.94	22.15
Raw water	0.12	0.11	0.01	0.03
Process water	0.25	0.28	0.61	0.56
Steam Export Revenues	-1.24	-0.79	-1.91	-0.43
Electricity Purchase	0.83	0.86	-0.93	0.55
Total	21.85	21.24	19.73	22.86
Fixed O&M				
Operating labor	5.29	5.29	5.29	5.29
Property taxes and insurance	1.43	1.47	0.99	1.73
Maintenance labor	0.38	0.38	0.24	0.48
Maintenance materials	0.56	0.57	0.36	0.72
Administrative & support labor	1.42	1.42	1.38	1.44
Chemicals and replacements				
<i>MDEA solvent</i>	-	-	-	0.25
<i>FTR reforming catalyst</i>	-	-	0.05	0.05
<i>Ca-Cu reactors filling</i>	0.40	1.10	-	-
<i>High temperature shift catalyst</i>	-	-	0.03	0.04
<i>Low temperature shift catalyst</i>	-	-	-	0.04
<i>Pre-reformer catalyst</i>	0.13	0.16	0.13	0.13
<i>Hydrodesulphurization catalyst</i>	0.004	0.004	0.004	0.004
<i>ZnO absorbent</i>	0.06	0.06	0.06	0.06
Total	9.67	10.45	8.54	10.26

The resulting cost of hydrogen and of CO₂ avoided are reported in Table 10. The lowest cost of hydrogen is obtained for the FTR without capture. The calculated cost of hydrogen for the benchmark FTR plant of 0.153 €/Nm³ is higher than 0.114 €/Nm³ reported in [1], where however 8% lower natural gas price was assumed and a significantly larger plant was considered (100'000 vs. 30'000 Nm³/h), leading to lower Capital and fixed O&M costs. Both hydrogen plants integrated with the Ca-Cu process result in lower hydrogen production costs than the FTR plant with CO₂ capture. For the high-pressure Ca-Cu case, the hydrogen cost results 0.178 €/Nm³, i.e. ~2% less than the low pressure Ca-Cu case and ~8% less than the benchmark FTR plant with capture. This high pressure Ca-Cu plant also achieves the lowest CO₂ avoided cost (30.96 €/ton), which is ~16% less than the 11 bar case and ~52% less than the benchmark FTR plant with CO₂ capture.

Table 10 Cost of hydrogen and cost of CO₂ avoided of the assessed hydrogen plants

		Ca-Cu	Ca-Cu	FTR	FTR
		25 bar	11 bar	w/o capture	with capture
Natural Gas	[€/Nm ³]	0.097	0.092	0.098	0.099
Steam Export	[€/Nm ³]	-0.006	-0.004	-0.009	-0.002
Electricity	[€/Nm ³]	0.004	0.004	-0.004	0.002

Purchase					
Other variable	[€/Nm ³]	0.002	0.002	0.003	0.003
O&M					
Fixed O&M	[€/Nm ³]	0.043	0.046	0.038	0.046
Capital cost	[€/Nm ³]	0.038	0.041	0.027	0.045
Cost of Hydrogen	[€/Nm ³]	0.178	0.181	0.153	0.194
CCA	[€/ton]	30.96	36.79	-	64.07

Finally, in Figure 7, the effect of the Ca-Cu system costs (i.e. reactors and valves, and functional materials costs) on the CCA and on the hydrogen cost is shown for the 25 bar Ca-Cu hydrogen plant and compared with the benchmark FTR plant with CO₂ capture. The point where Ca-Cu and FTR lines cross indicate the maximum admissible cost for the Ca-Cu reactors (a) and materials (b) to be competitive with the benchmark. Considering the CCA, the maximum cost for the reactors and valves of the Ca-Cu system is about 43 M€ for this process to be competitive with respect to the FTR plant with CO₂ capture, which implies more than three times the cost calculated in this work (the cost of the Ca-Cu functional materials for this analysis has been kept unaltered and equal to 2.02 M€ as indicated in Table 8). Regarding the initial fill cost, this maximum cost for the initial fill would be about 20 M€, which would imply an increase of almost 10 times the cost calculated in this work, maintaining constant the reactors and valves cost. Considering the cost of hydrogen, the breakeven point lies at about 30 M€ for the vessels and valves system (considering the baseline costs of the functional material) and to about 13 M€ for the initial fill (considering the baseline vessels and valves cost). As demonstrated with this analysis, there is still margin for competitiveness for the Ca-Cu system with respect to the FTR-based technology if deviations from the assumptions made in this work regarding the functional materials and reactors & valves costs of the Ca-Cu system, which would make these costs to be raised.

Figure 7 CCA and hydrogen production cost for the hydrogen plant integrated with the Ca-Cu process as a function of (a) the reactors investment cost (reactors and valves) and (b) the initial fill cost. The horizontal dotted lines represent the CCA and the Hydrogen cost of the benchmark FTR plant with CO₂ capture. The vertical line represents the calculated cost for the 25 bar Ca-Cu plant

Conclusions

In this work, the performance of a Ca-Cu based hydrogen production plant operating under different conditions has been assessed and compared from a thermo-economic point of view with a benchmark hydrogen plant based on conventional SMR technology. From the analyses carried out, the following conclusions can be drawn:

- The operating conditions of the Ca-Cu process minimizing the specific primary energy consumption for CO₂ avoided ($SPECCA_{eq}$) correspond to those where the off-gas from the PSA hydrogen purification unit fulfils the energy needed in the sorbent regeneration step of the Ca-Cu process. Such operating conditions correspond to the minimum S/C ratio in the sorption enhanced reforming stage A of the Ca-Cu process.
- Increasing up to 40% the CO₂ sorption capacity of the Ca-based sorbent is not advantageous from the point of view of the hydrogen production efficiency and of the CO₂ capture ratio. High sorbent capacity involves higher CO₂ separation in stage A and therefore higher energy losses associated to sorbent regeneration. Low CO₂ separation in stage A is not penalizing from the energy balance point of view because of the small energy penalty for removing the carbon species downstream stage A, in the PSA hydrogen purification unit. On the other hand, high sorbent capacity leads to higher equivalent hydrogen production efficiency and higher equivalent carbon capture ratio (i.e. accounting for the credits associated to the net electricity consumption and the heat export), but also lower $SPECCA_{eq}$.
- Operating the Ca-Cu system at moderate pressure (11 bar) is beneficial from the energy efficiency point of view because it leads to higher hydrogen production efficiency and lower $SPECCA$ than in the base case operating at 25 bar. However, from an environmental point of view, lower pressure leads to higher CO₂ loss in stage B and therefore to lower CO₂ capture efficiency. Moreover, from the economic point of view, lower Ca-Cu pressure brings about larger vessels and therefore higher capital cost expenditure, leading to higher cost of hydrogen and higher cost of CO₂ avoided.
- The hydrogen production plant based on the Ca-Cu process integrated results to be economically competitive with respect to a benchmark fired tubular reforming (FTR) plant with CO₂ capture as far as hydrogen production costs (~8% less) and CO₂ avoided cost (~52% less) are concerned.

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Appendix

Table A1 Properties of the main streams for the H₂ production plant integrated with the Ca-Cu process: Case at 25 bar and S/C at pre-reformer inlet of 2.27.

Stream	T [°C]	P [bar]	G [kg/s]	Q [kmol/s]	G*LHV [MW]	Composition [%mol]										
						Ar	CH ₄	CO	CO ₂	H ₂	H ₂ O	N ₂	O ₂	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
1	15.0	27.03	2.61	0.145	121.4	0.00	89.00	0.00	2.00	0.00	0.00	0.89	0.00	7.00	1.00	0.11
2	15.4	27.03	2.62	0.148	122.2	0.00	87.25	0.00	1.96	1.96	0.00	0.87	0.00	6.86	0.98	0.11
3	297.6	26.76	2.62	0.148	122.2	0.00	87.25	0.00	1.96	1.96	0.00	0.87	0.00	6.86	0.98	0.11
4	365.0	26.49	2.62	0.148	122.2	0.00	87.25	0.00	1.96	1.96	0.00	0.87	0.00	6.86	0.98	0.11
5	365.0	26.13	2.62	0.148	122.2	0.00	87.25	0.00	1.96	1.96	0.00	0.87	0.00	6.86	0.98	0.11
6	320.7	26.13	9.04	0.504	122.2	0.00	25.59	0.00	0.58	0.58	70.67	0.26	0.00	2.01	0.29	0.03
7	490.0	25.87	9.04	0.504	122.2	0.00	25.59	0.00	0.58	0.58	70.67	0.26	0.00	2.01	0.29	0.03
8	437.2	25.51	9.04	0.527	123.1	0.00	27.04	0.04	2.72	6.79	63.17	0.24	0.00	0.00	0.00	0.00
9	592.1	25.25	9.04	0.527	123.1	0.00	27.04	0.04	2.72	6.79	63.17	0.24	0.00	0.00	0.00	0.00
10	700.0	25.00	9.04	0.527	123.1	0.00	27.04	0.04	2.72	6.79	63.17	0.24	0.00	0.00	0.00	0.00
11	836.5	25.00	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
12	720.0	24.75	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
13	620.0	24.50	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
14	582.7	24.25	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
15	407.6	24.01	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
16	321.0	23.77	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
17	278.2	23.53	5.48	0.650	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
18	137.3	23.30	5.48	0.578	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
19	40.0	23.30	5.48	0.578	141.0	0.00	6.30	4.06	1.39	64.06	24.00	0.20	0.00	0.00	0.00	0.00
20	40.0	23.30	0.76	0.375	90.6	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
21	30.9	29.00	0.75	0.372	89.9	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
22	40.0	23.30	0.01	0.003	0.7	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
23	59.3	27.50	0.01	0.003	0.7	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
24	40.0	1.86	1.94	0.121	50.4	0.00	33.93	21.86	7.46	34.50	1.19	1.07	0.00	0.00	0.00	0.00
25	200.0	1.84	1.94	0.121	50.4	0.00	33.93	21.86	7.46	34.50	1.19	1.07	0.00	0.00	0.00	0.00
26	174.2	1.84	3.29	0.196	50.4	0.00	20.94	13.49	4.61	21.29	39.02	0.66	0.00	0.00	0.00	0.00

27	421.2	1.82	3.29	0.196	50.4	0.00	20.94	13.49	4.61	21.29	39.02	0.66	0.00	0.00	0.00	0.00
28	700.0	1.80	3.29	0.196	50.4	0.00	20.94	13.49	4.61	21.29	39.02	0.66	0.00	0.00	0.00	0.00
29	715.4	1.76	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
30	478.3	1.75	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
31	441.2	1.729	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
32	317.6	1.712	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
33	178.8	1.69	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
34	117.6	1.68	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
35	40.0	1.68	10.26	0.352		0.00	0.00	0.00	42.79	0.00	56.84	0.37	0.00	0.00	0.00	0.00
36	25.0	110.00	6.65	0.000		0.00	0.00	0.00	99.15	0.00	0.00	0.85	0.00	0.00	0.00	0.00
37	15.0	1.01	15.99	0.552		1.00	0.00	0.00	0.00	0.00	0.00	78.00	21.00	0.00	0.00	0.00
38	544.0	25.00	15.99	0.552		1.00	0.00	0.00	0.00	0.00	0.00	78.00	21.00	0.00	0.00	0.00
39	300.0	25.00	110.55	3.881		1.21	0.00	0.00	1.30	0.00	0.00	94.50	2.99	0.00	0.00	0.00
40	715.4	24.61	107.14	3.772		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
41	715.4	24.61	12.58	0.443		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
42	234.8	1.02	12.58	0.443		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
43	184.4	1.01	12.58	0.443		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
44	715.4	24.61	94.56	3.329		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
45	715.4	24.61	52.28	1.840		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
46	300.0	24.04	52.28	1.840		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
47	715.4	24.61	42.28	1.489		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
48	321.0	24.12	42.28	1.489		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
49	187.3	23.88	42.28	1.489		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
50	249.8	23.88	94.56	3.329		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
51	258.2	25.00	94.56	3.329		1.25	0.00	0.00	1.52	0.00	0.00	97.23	0.00	0.00	0.00	0.00
52	28.0	1.01	9.43	0.523		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
53	174.6	100.00	9.43	0.523		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
54	306.0	100.00	9.43	0.523		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
55	485.0	100.00	9.43	0.523		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
56	28.0	1.01	1.38	0.077		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
57	168.8	100.00	1.38	0.077		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
58	306.0	100.00	1.38	0.077		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
59	311.0	100.00	1.38	0.077		0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00

60	485.0	100.00	1.38	0.077	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
61	485.0	100.00	10.81	0.600	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
62	158.9	6.00	4.39	0.244	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
63	158.9	6.00	3.04	0.169	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
64	158.9	6.00	1.35	0.075	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
65	307.9	26.50	6.42	0.356	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00

Figure A1. Temperature-heat curve of the H₂-rich gas (a), N₂ stream (b) and CO₂-rich gas (c) cooling lines for the case at 25 bar and S/C at pre-reformer inlet of 2.27

Table A2 Scaling function parameters for calculating the installed cost of the hydrogen plants units according to Eq. (1)

Item	C_0 [M€ ₂₀₁₇]	Scale Parameter	S_0	f	Ref
PSA unit	36.56	Inlet flow rate	4.63 m ³ /s	1.00	[36]
MDEA plant	92.23	CO ₂ captured	62.59 kg/s	0.80	[37]
Syngas Cooling	2.67	UA	1.00 MW/K	0.22	*
Feedwater and BOP	65.20	Thermal power rejected to ambient	470 MW	0.67	[31]
Cooling water system	25.84	Thermal power rejected to ambient	470 MW	0.67	[31]
CO ₂ compression and drying	15.81	Compressor power	13 MW	0.67	[31]
Steam turbine and generator	1.16	Turbine power	1.65 MW	0.72	*
Station service equipment	111.43	Net auxiliary load	11 MW	0.51	[37]
Switchgear & motor control	1.90	Net auxiliary load	11 MW	0.51	[37]
Conduit & cable tray	3.29	Net auxiliary load	11 MW	0.51	[37]
Wire & cable	4.28	Net auxiliary load	11 MW	0.51	[37]
Protective equipment	2.78	Net auxiliary load	11 MW	0.58	[37]
Standby equipment	0.21	Gross total power	641 MW	0.47	[37]
Main Power transformers	10.92	Apparent total power	712.2 MVA	0.62	[37]
Electrical foundations	0.50	Gross total power	641 MW	0.70	[37]

Table A3 Scaling function parameters for calculating the installed cost of the hydrogen plants units according to Eq. (2)

Item	Type	Scale parameter	k_1	k_2	k_3	F_{bm}	Ref
H ₂ compressors	Rotary compressor	Fluid Power	5.035	-1.8002	0.8253	2.4	[38]
Syngas compressor/ recirculating fan (Ca-Cu)	Centrifugal compressor	Fluid Power	2.2897	1.3604	-0.1027	2.4	[38]
Air/flue gas blower (benchmark plants)	Centrifugal fan	Flow Rate	3.591	-0.3533	0.4477	2.7	[38]
Electric driver	Explosion proof	Shaft Power	2.4604	1.4191	-0.1798	1.5	[38]

* Internal database built on data from costing software and industries.

Table A4 Maintenance costs assumptions

Plant section	% of TDPC/year
Chemical island and syngas cooling	1.5
Power island, CO ₂ compression, WGS	2.5
Steam Turbine & Generator	2
Balance of plant	1.7

Table A5 Consumables cost assumptions

Consumable	Cost	Lifetime	Reference
Natural gas	6.5 €/GJ	-	
Raw water	0.35 €/m ³	-	[31]
Process water	6.04 €/m ³	-	[31]
MDEA solvent	1892 €/m ³	2 months	[37]
Ni catalyst (Ca-Cu)	50 €/kg	5 years	-
Cu carrier (Ca-Cu)	20 €/kg	5 years	-
Ca sorbent (Ca-Cu)	5 €/kg	5 years	-
Cost of electricity purchased	58.52 €/MWh	-	-
Steam Export Revenues	26.1 €/MWh	-	-

Table A6 Long-run profitability analysis assumptions

		Availability	7500	hours
		Operational life	25	years
Capital expenditure during construction		Construction time	3	years
		Tax rate	Pre-taxation	
		Depreciation time	No depreciation	
Year -3	40%	Inflation rate	0	%
Year -2	30%	Construction inflation	0	%
Year -1	30%	Interest rate	8	%

Nomenclature

Acronyms

BOP	Balance of Plants
CEPCI	Chemical Engineering Plant Cost Index
CCA	Cost of CO ₂ avoided
CCR	Carbon Capture Ratio
CCS	CO ₂ capture and Storage
ECO	Economizer
EPC	Engineering Procurement & Construction
EVA	Evaporator
FTR	Fired Tubular Reformer
HP	High Pressure
HT	High Temperature
HX	Heat Exchanger
IF	Initial Fill
KPI	Key Performance Indicators
LHV	Lower Heating Value
LP	Low Pressure
LT	Low Temperature
MDEA	Methyl Diethanolamine
NG	Natural Gas
O&M	Operating and Maintenance
PHM	Pseudo Homogenous Model
PSA	Pressure Swing Adsorption
SER	Sorption Enhanced Reforming
SH	Superheater

SFM	Sharp Front Model
SMR	Steam Methane Reforming
SPECCA	Equivalent Specific Primary Energy Consumption for CO ₂ avoided
TDPC	Total Direct Plant Cost
TPC	Total Plant Cost
WGS	Water Gas Shift

Symbols

C	[€]	Cost of equipment with size S
C_0	[€]	Reference cost of equipment with reference size S_0
e_{NG}	[kg _{CO2} /kg _{NG}]	CO ₂ emission factor of natural gas
E	[kg _{CO2} /MJ _{H2}]	Specific CO ₂ emissions of the hydrogen plant
f		Exponent in scaling cost function (Eq.(1))
F_{bm}		Bare module factor in scaling cost function (Eq.(2))
$k_{1,2,3}$		Scaling parameters in cost function (Eq.(2))
$\dot{m}$	[kg/s]	Mass flow rate
p	[bar]	Pressure
S		Scaling parameter in cost functions
S_0		Size parameter of the equipment with reference cost C_0
S/C	[-]	Steam-to-carbon ratio
T	[°C]	Temperature
X_{carb}	[-]	Fraction of bed re-carbonated at the end of stage C
y_i	[kmol _i /kmol _{tot}]	Molar fraction
η	[%]	Hydrogen Production Efficiency

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