

Modelling of an integrated process for atmospheric carbon dioxide capture and methanation

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Abstract

Negative-emission technologies are largely investigated to better control atmospheric carbon dioxide concentration driving global warming. Calcium looping has been proposed in literature for direct air capture, but a comprehensive system analysis is still missing. Methanation of carbon dioxide can represent an alternative to geological storage, widely investigated within the power-to-gas framework. In this study, an integrated process considering the catalytic methanation of the concentrated carbon dioxide stream after capture from ambient air by a pure hydrogen stream from water electrolysis was proposed and numerically investigated. The system relies on packed bed reactors and uses calcium oxide as sorbent, and a nickel-based catalyst for methanation. A comprehensive study on the overall system performance was carried out, assuming a carbon dioxide capture target of 100 t y^{-1} . Model computations suggest that roughly 50-in-parallel reactors, 0.5 m diameter each, are required for a continuous operation. The overall energy demand of the integrated process ranges within 344–370 $\text{GJ t}_{\text{CH}_4}^{-1}$, or 215–293 $\text{GJ t}_{\text{CH}_4}^{-1}$ if neglecting the humidifier. The methanation process requires 3-in-series reactors and can yield a continuous gas stream with a flow rate of 5 kg h^{-1} and a methane molar fraction of nearly 91%. If this stream is exploited for heat generation, a return of energy index of 16%, or 23% if neglecting the humidifier, is foreseen. The proposed process stems as viable solution towards a circular carbon economy.

Keywords

calcium looping; carbon capture and utilization; direct air capture; limestone; power to gas; renewable energy

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1. Introduction

Reducing atmospheric carbon dioxide (CO₂) emissions is imperative to reduce global warming and mitigate serious climate change. Apart from a wider exploitation of renewable energies, carbon capture and sequestration (CCS) technologies may allow to use conventional fossil fuels in a “greener” way, by producing a concentrated CO₂ stream ready for subsequent sequestration. CCS is frequently considered for integration with power/cement industries. However, decarbonizing these sectors may be insufficient to limit global warming within 1.5 °C above pre-industrial levels and meet the Conference of Parties Agreement. Negative emission technologies, such as direct CO₂ capture from air, commonly referred to as direct air capture (DAC), stem as viable and required solutions to contribute to the target (Rogelj et al., 2015). The low atmospheric CO₂ concentration of about 415 ppm makes DAC a high energy-intensive process, though its development features some unquestionable advantages. DAC would be flexible in terms of plant location, allowing to save on land and/or CO₂ transport costs. Moreover, DAC could be useful in capturing CO₂ emissions from delocalized sources and hard-to-decarbonize sectors (e.g., transport field, domestic heating and cooking). Techno-economic assessments of DAC forecasted that cost may decrease below 50 € t_{CO₂}⁻¹ by 2040 (Fasihi et al., 2019).

Different DAC processes have been proposed in literature, always entailing a CO₂ capture and a sorbent regeneration step. The reactive materials considered include liquid and solid sorbents based on alkali/alkali-earth metal oxides and hydroxides, supported amines, and metal-organic frameworks (Sanz-Pérez et al., 2016). Among them, direct or indirect use of Ca-based sorbents is frequently considered because of a good balance of properties such as low toxicity, wide availability, low cost, and good reactivity. Zeman and Lackner (2004) proposed to use a sodium hydroxide solution for the CO₂ capture step. For its regeneration, the obtained carbonate solution is reacted with calcium hydroxide (Ca(OH)₂) to precipitate calcium carbonate (CaCO₃). CaCO₃ is eventually calcined at high temperature to produce a concentrated CO₂ stream and calcium oxide (CaO) which, upon hydration, regenerates Ca(OH)₂, closing the loop. This process scheme has been largely investigated in literature, with first commercial plants already in-operation (Carbon Engineering, 2019). Comprehensive material and energy balances performed by Baciocchi et al. (2006), revealed that the specific energy demand of this process is larger than the heat released to emit the same amount of CO₂ if coal is considered as energy source, but smaller if methane is considered. Mahmoudkhani and Keith (2009) proposed to use a different regeneration step, by precipitating sodium carbonate from the carbonate solution and reacting it with sodium tri-titanate to release CO₂. According to their results, the modified process requires lower temperature and reaction heat, at the expense of a more complex reaction scheme. Nikulshina and Steinfeld (2009) investigated instead the direct use of CaO as solid sorbent by performing experiments in fluidized bed reactors according to the Calcium Looping cycle (CaL). The effect of water vapor concentration in atmospheric air was deeply scrutinized, revealing that a concentration of at least 3%_v is required for a fast reaction kinetics. Moreover, they proposed integration of DAC with concentrating solar power systems to supply the energy required for calcination, exploiting the capability of fluidized beds of working simultaneously as chemical reactor and solar particle receiver (Tregambi et al., 2021c). A different approach

to reduce the burden of the endothermic limestone calcination was proposed by Hanak et al. (2017), who studied the integration of DAC with electricity generation from solid oxide fuel cells by means of model computations, finding positive synergies between these processes. First experimental demonstration of this integration was given by Nabavi et al. (2019), who performed tests using a kW scale solid oxide fuel cell, and by Erans et al. (2019), who performed pilot scale tests under high steam concentration to reduce the temperature required for the calcination. More recently, Samari et al. (2020) investigated CO₂ capture from air at ambient temperature using natural and pelletized limestone as sorbent. Experiments in a fixed bed reactor proved that carbonation proceeds up to high conversion degree, provided that inlet air has a relevant humidity content, and demonstrated that DAC using lime-based sorbent is technically feasible. Influence of the humidity content on material carbonation was previously inferred also by Dheilly et al. (2002), who exposed Ca(OH)₂ samples to controlled atmosphere of CO₂ under different relative humidity conditions. At ambient temperature and relative humidity values of 30% carbonation was not observed, whereas with relative humidity content of 100% a complete carbonation was obtained. Moreno et al. (2021) investigated CO₂ capture at ambient temperature in a fluidized bed of Ca(OH)₂, studying the influence of material storage under controlled humidity. It was found that pre-hydration under 100% relative humidity greatly enhances the CO₂ capture performance of the material. Finally, passive carbonation of CaO/Ca(OH)₂ is investigated in literature. Erans et al. (2020) experimentally demonstrated this concept by contacting a thin layer of material to the atmosphere, and proving that high carbonation degree can be obtained. Abanades et al. (2020) proposed to build large porous structures of Ca(OH)₂ and performed a basic cost analysis, estimating values within 140–340 \$ t_{CO₂}⁻¹. Even if air compression costs can be avoided, this approach is characterized by a lower productivity since the passive carbonation requires week-to-month reaction times.

Reuse of the concentrated CO₂ stream in methanation processes, rather than geological storage, is a hot topic in current literature, widely investigated within the Power-to-Gas (PtG) framework. Renewable energy can be used to drive water electrolysis and produce hydrogen (H₂) which, after mixing with CO₂, may be reacted in catalytic reactors to produce methane (CH₄) following the Sabatier reaction. An extensive survey on reactor technologies for methanation and current commercial/pilot scale plants has been performed by Rönsch et al. (2016). Ni-based catalyst are frequently considered for the methanation as they exhibit good performance in terms of CO₂ conversion and CH₄ selectivity within 300–500 °C (Lazaroiu et al., 2020). Moreover, Huynh et al. (2020) demonstrated the possibility to produce Ni-Fe based catalysts for CO₂ methanation on a large-scale. Integration of CO₂ capture and methanation is assessed in literature with different approaches and by considering different CO₂ sources. Jo et al. (2020) synthesized a Ni/CaO sorbent/catalyst via the sol-gel route, and tested it in fixed bed reactors for CO₂ capture from concentrated stream and methanation, finding an optimum reaction temperature of 500 °C. Leonzio (2017) considered methanation of CO₂ from an anaerobic digester, estimating a levelized cost of energy of 260 € MWh⁻¹ by using 100% renewable energy. Integration of DAC and methanation was experimentally investigated by Veselovskaya et al. using K₂CO₃/Al₂O₃ as sorbent for CO₂ capture, and a nickel- (Veselovskaya et al., 2017) or ruthenium-based (Veselovskaya et al., 2018) catalyst for the methanation reaction. Experimental tests proved that desorbed CO₂ can be converted to

CH₄ with conversions of 98–99%. Jeong-Potter and Farrauto (2021) synthesized instead a dual function material embodying Ru/Na₂O as catalyst/adsorbent. The material was tested under isothermal conditions at 320 °C and proved to be able to capture CO₂ at atmospheric concentration and produce CH₄ with a yield of 150 μmol g_{material}⁻¹. Drechsler and Agar (2020) performed a process analysis on a DAC-PtG integrated scheme, finding that several synergies between the two processes may be exploited. Finally, Peters et al. (2019) performed a techno-economic analysis on PtG, estimating a cost of 5.5 € kg_{CH₄}⁻¹ for its integration with DAC. In this study, an integrated process in which CO₂ is captured from air using the CaL cycle, and then mixed with a pure H₂ stream from water electrolysis to eventually produce CH₄, is proposed and numerically investigated. Research studies on the CaL for DAC have already been performed in literature, but a comprehensive system analysis is still missing. Moreover, the performance of an integrated system exploiting CaL for DAC and subsequent methanation of the captured CO₂ has never been investigated. The system considered in this study relies on packed bed reactors for both CO₂ capture and methanation. CaO was considered as sorbent for CO₂ capture, while Ni supported on Al₂O₃ was considered as catalyst for the methanation. The aim of this study is to develop a mathematical model and establish the related overall mass/energy balances required to predict the performance of this integrated system under different scale or process conditions. Upon validation, the model was solved to give first insights about the potentiality of this integrated system by considering a realistic scale for the DAC unit, and realistic process parameters for the CaL cycle and for the methanation unit according to established literature data.

2. Methodology

In this section, the process scheme of the integrated process is presented. Then, modelling and kinetic equations are thoroughly described, and model validation against published experimental data is performed. Finally, the model is applied to estimate the process viability and energy requirements of the integrated process under conditions suitable for an industrial application of the technology.

Chemical reactions involved in the considered process are the reversible CaO carbonation/calcination for DAC (R₁) and the Sabatier reaction for CO₂ methanation (R₂):



2.1 Process description

Figure 1-A depicts the process scheme during the carbonation step, namely CO₂ capture. Ambient air is first compressed (C₁) and then sent into a humidifier (H₁) to increase the water content up to a volumetric concentration of 3%_v. Air humidification is essential to promote CaO carbonation under low CO₂ concentration. A value of 3%_v was proven to be sufficient to guarantee satisfactory reaction kinetics in the 573–673 K temperature range (Nikulshina and Steinfeld, 2009). Humidified air is then sent into a heat exchanger (HX₁), where it is preheated by the purified air leaving the reactors. Lastly, an electric gas heater

(GH₁) adjusts the temperature of the humidified air up to the input value selected for the process. In the packed beds, CO₂ reacts with CaO to produce CaCO₃ according to chemical reaction R₁. Exhaust gas, consisting of purified air, is then sent to the heat exchanger (HX₁) for heat recovery before being vented to the atmosphere. Calcination step, namely regeneration of the sorbent, is performed according to the process scheme depicted in Figure 1-B. A stream of pure CO₂ from a vessel (V₁) is sent to a compressor (C₂) and then preheated in a heat exchanger (HX₂) by the exhaust gas leaving the reactors. Then, it is further heated by an electric gas heater (GH₂) to match the inlet temperature value chosen for the regeneration process. In the packed bed reactors, the hot CO₂ stream heats the solid sorbent driving the calcination reaction: additional CO₂ is released, and the initial sorbent is progressively regenerated. Exhaust gas, consisting in a CO₂ stream with a larger mass flow rate, is sent to the heat exchanger (HX₂) for heat recovery, further cooled to ambient temperature in a different heat exchanger (HX₃), and then split in two streams: one recirculated to the initial vessel (V₁), to be eventually recycled as process gas for the calcination process, the other sent to a compressor (C₃) and then mixed with H₂ from water electrolysis for the methanation unit. According to the flow rate of air that is treated, either a single, or multiple in-parallel packed bed reactors, may be used.

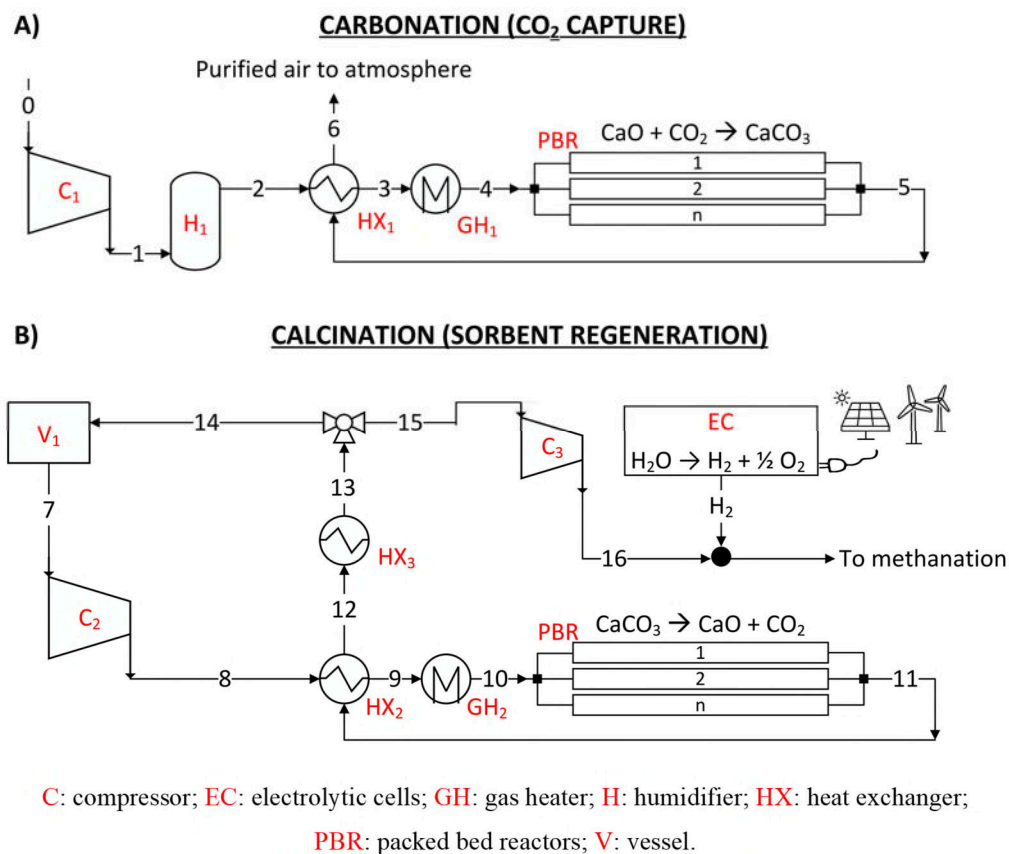


Figure 1. Process flow diagram for the carbonation (A: CO₂ capture) and calcination (B: sorbent regeneration) steps.

2.2 Overall energy/mass balance on the system

The following section describes the equations used to perform the global mass/energy balances on the system. Following the process scheme presented in Figure 1, the power required by the compressors, gas heaters, and humidifier was estimated. Symbols are described when first introduced, and further summarized in a dedicated

Nomenclature section reported in Supplementary Material. In all the equations, the “ k ” index refers to the properties of the stream in the position reported in Figure 1.

The power (P) required by the compressors was evaluated as:

$$P_{C_i} = \frac{W_k}{PM_k} (h_{k+1} - h_k) \frac{1}{\eta_{comp}} \quad (1)$$

where i is an index ($i=1,2,3$), W the mass flow rate, PM the molecular weight, h the specific molar enthalpy, η_{comp} the efficiency of the compressor. For C_1 and C_2 , outlet pressure depends on the pressure drop established within the packed bed, as inferred from the Ergun equation, whereas for C_3 the outlet pressure is dictated by the process parameters of the methanation reaction. Compressor outlet temperature was computed by referring to a single stage isentropic process. If a lower outlet temperature is obtained, a slightly higher energy consumption of the humidifier should be expected.

For C_1 , the mass flow rate depends on the CO_2 removal:

$$W_0 = \frac{M_{CO_2}}{t_{work} PM_{CO_2} v_{CO_2}} PM_{air} \quad (2)$$

where M_{CO_2} is the mass of CO_2 removed from the atmosphere in 1 year of operation, t_{work} the effective carbonation operating time in 1 year, PM_{CO_2} and PM_{air} the molecular weight of CO_2 and of atmospheric air, respectively, and v_{CO_2} the volumetric fraction of CO_2 in atmospheric air (415 ppm).

For C_2 , the mass flow rate was chosen by setting the superficial gas velocity in the packed bed so that the pressure drop through the reactor does not exceed a threshold value. It should be noted that higher working pressure will penalize the calcination reaction due to thermodynamic constraints, bringing to the need for higher process temperatures, which in turn will increase the sintering of the sorbent and reduce its reactivity and cyclability (Di Lauro et al., 2021).

The power required by the gas heaters was evaluated as:

$$P_{GH_i} = \frac{W_k}{PM_k} \bar{C}_{p,k} (T_{k+1} - T_k) \quad (3)$$

where $\bar{C}_{p,k}$ is the average molar heat capacity and T the temperature.

The power required by the humidifier was estimated under the hypothesis that air leaving the humidifier is at the dew point, as:

$$P_H = \frac{W_1}{PM_1} (v_{H_2O}^f - v_{H_2O}^{init}) [\bar{C}_{p,H_2O} (T_{sat,H_2O} - T_{H_2O}^{init}) + \Delta H_{vap}] - \frac{W_1}{PM_1} \bar{C}_{p,air} (T_1 - T_2) \quad (4)$$

where $v_{H_2O}^f$ and $v_{H_2O}^{init}$ is the final and initial volumetric fraction of H_2O , respectively, \bar{C}_{p,H_2O} the average molar heat capacity of liquid water, T_{sat,H_2O} the dew point temperature at $v_{H_2O}^f$, also equal to T_2 , $T_{H_2O}^{init}$ the initial temperature of the water used in the humidifier, ΔH_{vap} the latent heat of vaporization at T_{sat,H_2O} , $\bar{C}_{p,air}$ the average molar heat capacity of atmospheric air.

Finally, for the methanation reaction, a molar flow rate of H₂ equal to 4 times that of CO₂ is required according to the stoichiometry of the Sabatier reaction (R₂). The power required by the electrolytic cells was computed as:

$$P_{H_2} = 4 \frac{W_{15}}{PM_{CO_2}} \eta_{elcz} \quad (5)$$

where η_{elcz} is the specific energy consumption of the electrolyzer, equal to 3.87×10^5 J mol_{H₂}⁻¹ (Carmo et al., 2013).

2.3 Detailed modelling of carbonation and calcination reactors

A model of the packed bed reactor was developed to investigate the evolution of the carbonation degree, and of the emitted/trapped CO₂ molar flow, during the reactor operation. Moreover, the solution of the mathematical model provides the total duration of the carbonation and calcination steps and the change of the exhaust gas temperature in time, required to compute the power demands of the gas heaters.

Packed bed reactors were modelled with a 1D pseudo-homogenous model. Therefore, it is assumed the absence of radial temperature and concentration gradients, and the lack of both intra-particle and interphase temperature and concentration gradients.

The energy balance equation reads ($j=calc, carb$):

$$\frac{d[u_{g,j} \rho_{g,j} C_{pg,j} T]}{dz} + [(1 - \varepsilon) \rho_{s,j} C_{ps,j} + \varepsilon \rho_{g,j} C_{pg,j}] \frac{dT}{dt} = \varepsilon \frac{d}{dz} \left(\lambda_{ax} \frac{dT}{dz} \right) + r_j (-\Delta H_j) \quad (6)$$

where z is the axial coordinate of the reactor, u_g the gas superficial velocity, ρ_g and ρ_s the gas and solid mass density, respectively, C_{ps} and C_{pg} the specific heat of the solid and gas phase, respectively, t the time, ε the bed void fraction, λ_{ax} the axial heat dispersion coefficient, computed according to Han et al. (2013), r_j the velocity of the chemical reaction, ΔH the reaction enthalpy. The mass balance equations on the gas and solid phase read:

$$\frac{d[u_{g,j} C_{CO_2,j}]}{dz} + \varepsilon \frac{dC_{CO_2,j}}{dt} = \varepsilon \frac{d}{dz} \left(D_{ax,j} \frac{dC_{CO_2,j}}{dz} \right) + \zeta_j r_j \quad (7)$$

$$r_j = \frac{dX_j}{dt} \rho_M (1 - \varepsilon) \quad (8)$$

where C_{CO_2} is the concentration of CO₂ in the gas phase, D_{ax} the effective axial dispersion coefficient (Han et al., 2013), ζ the stoichiometric coefficient of CO₂, X the conversion degree, ρ_M the molar density of the sorbent. The kinetic equation for the calcination reaction is obtained from Fan et al. (2009), that of the carbonation reaction from Nikulshina and Steinfeld (2009) and Shih et al. (1999):

$$\frac{dX_{calc}}{dt} = k_{calc} \left(1 - \frac{X_{calc}}{X_{max}} \right)^{2/3} \left(C_{CO_2,eq} - C_{CO_2} \right) \quad (9)$$

$$\frac{dX_{carb}}{dt} = k_{carb} \left(1 - \frac{X_{carb}}{X_{max}} \right) \quad (10)$$

where k_{calc} and k_{carb} are the kinetic constants of the calcination and carbonation reaction, respectively, evaluated according to the Arrhenius equation, with pre-exponential factor (k_0) and activation energy (E_a) summarized in Table 1, X_{max} the maximum conversion degree of the sorbent and $C_{CO_2,eq}$ the equilibrium concentration of CO₂ (Tregambi et al., 2021b). It is interesting to observe that, for carbonation under low CO₂ concentration, the reaction appears to be of zero order with respect to CO₂.

Table 1. Reaction parameters for the carbonation and calcination reactions.

Reaction	k_0		E_a	
calc	23,797	$m^3 mol^{-1} s^{-1}$	150	kJ mol ⁻¹
carb (3% _v H ₂ O)	1.55×10^{-3}	s^{-1}	9.9	

2.4 Modelling of methanation unit

The methanation of CO₂ is characterized by a significant heat release and a volumetric contraction of the reacting gas by 40%. To obtain a high methane yield, use of low temperatures and high pressures is dictated by thermodynamic constraints (Rönsch et al., 2016). In the present study, the methanation process is performed in a series of adiabatic fixed bed reactors featuring inter-cooling between each stage and using Ni supported on Al₂O₃ as catalyst. The model implemented is presented and described in a previous research paper (Bareschino et al., 2021).

2.5 Model validation and application

The described model was validated against experimental data of Samari et al. (2020) with reference to the carbonation stage. Reactor dimensions and process parameters required for model computations were tuned to meet the specifications of the tests performed in the referenced work. Experimental data of dimensionless CO₂ concentration (i.e., ratio between outlet and inlet value) were compared to modelling predictions. The comparison, shown in Figure 2, reveals a satisfactory match between the experimental data of pelletized limestone and the predicted modelling curve, supporting the validity of the proposed model.

Once validated, the model was solved by considering a realistic scale for the DAC system, and realistic process parameters for the CaL/methanation reactors according to literature data, so as to provide insights about the potentiality of the proposed integrated system. Model parameters are thoroughly described in the following, and further summarized in Table S1. The temperature of the gas phase fed to the reactor during the air capture stage (T_4) was set at 573 K (Nikulshina and Steinfeld, 2009), whereas during the sorbent regeneration (T_{10}) it was set at 1,223 K (Di Lauro et al., 2021). For the packed bed reactors, a diameter of 0.5 m and a length of 1.0 m were chosen, similar to typical dimensions considered in literature (Mancusi et al., 2020). Bed void fraction was set at 0.4, particle diameter was kept at 2.5 mm. Inlet gas velocity was set at 1.0 m s⁻¹ during calcination. For carbonation, two different values were used: 0.5 m s⁻¹ during the initial operation of the reactor and 1.0 m s⁻¹ during subsequent operation. Such values of velocity were chosen from preliminary estimation of the pressure drop through the reactor, for which a threshold value of about 0.1 atm was selected. Therefore,

outlet pressure of C_1 and C_2 equals 1.1 atm. The outlet pressure of C_3 was instead set at 20 bar to favour the course of the methanation reaction (Tregambi et al., 2021b). The efficiency of the compressor was set at 88% (Tregambi et al., 2021a). Outlet water vapor fraction ($v_{H_2O}^f$) was set at 3%; correspondingly, T_2 equals 297.5 K. For ambient air, it was considered an initial temperature (T_0) of 293 K and an initial water vapor content ($v_{H_2O}^{init}$) of 1.15%, corresponding to a relative humidity of 50%. Initial water temperature in the humidifier ($T_{H_2O}^{init}$) was set at 288 K. Temperature profile of the packed bed at the end of the calcination stage dictates the initial one for the carbonation stage, and vice versa. Concerning the heat exchangers, it was assumed that the temperature difference between the entering hot gas stream and the exiting cold gas stream is 15 K. Maximum carbonation degree (X_{max}) was set at 0.20 (Di Lauro et al., 2021). Mass density of the solid phase (ρ_s) was set at 1,650 kg m⁻³ for CaO (Scala et al., 1997); correspondingly, mass density of the solid phase equals 1,909 kg m⁻³ for the carbonated material, and sorbent molar density (ρ_M) equals 29.5 kmol m⁻³. All the required thermodynamic properties were retrieved from Green and Perry (2008). Moreover, it was assumed that ideal gas state assumption holds. The CO₂ capture target was set at 100 t y⁻¹. Process parameters relevant to the methanation system can be found in Bareschino et al. (2021).

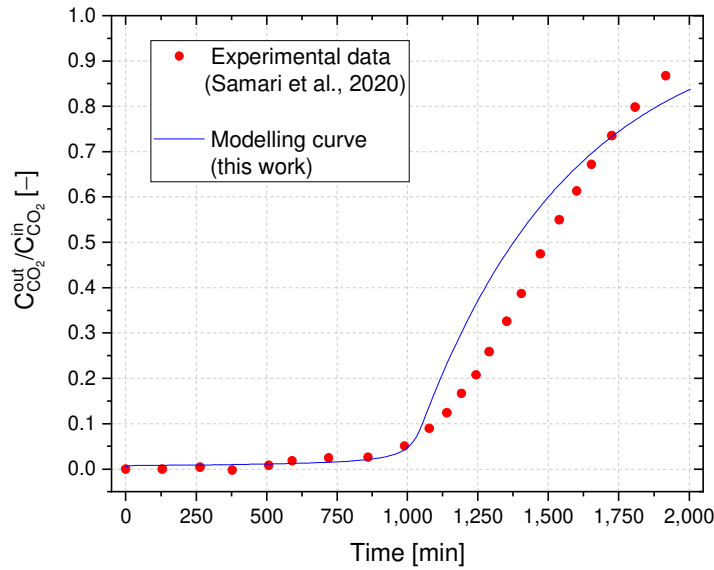


Figure 2. Comparison between experimental and predicted modelling curve.

The mathematical model was solved with COMSOL Multiphysics using the BDF solver. Axial coordinate of the reactor was divided in 4,000 elements, and a relative tolerance of 1.0×10^{-6} was set for convergence of the solution.

3. Results

This section describes the results inferred from model computations. First, specific results related to carbonation, calcination, and methanation steps are discussed. Then, the overall mass and energy balance of the system is discussed, and a sensitivity analysis of the different process parameters is performed.

3.1 Packed bed reactors model

Figure 3 displays the model results for the carbonation stage. Figure 3-A shows the evolution of the carbonation degree of the sorbent along the axial coordinate of the reactor, parametric in time. It is noticed that the carbonation degree front shifts almost rigidly with time. Altogether, about 103 h of continuous operation can be achieved before sorbent saturation. This is evident from Figure 3-B, which shows the CO₂ captured by a single packed bed reactor vs. the operating time. Integration of the CO₂ profile over total time returns the maximum amount of CO₂ that can be trapped by the sorbent.

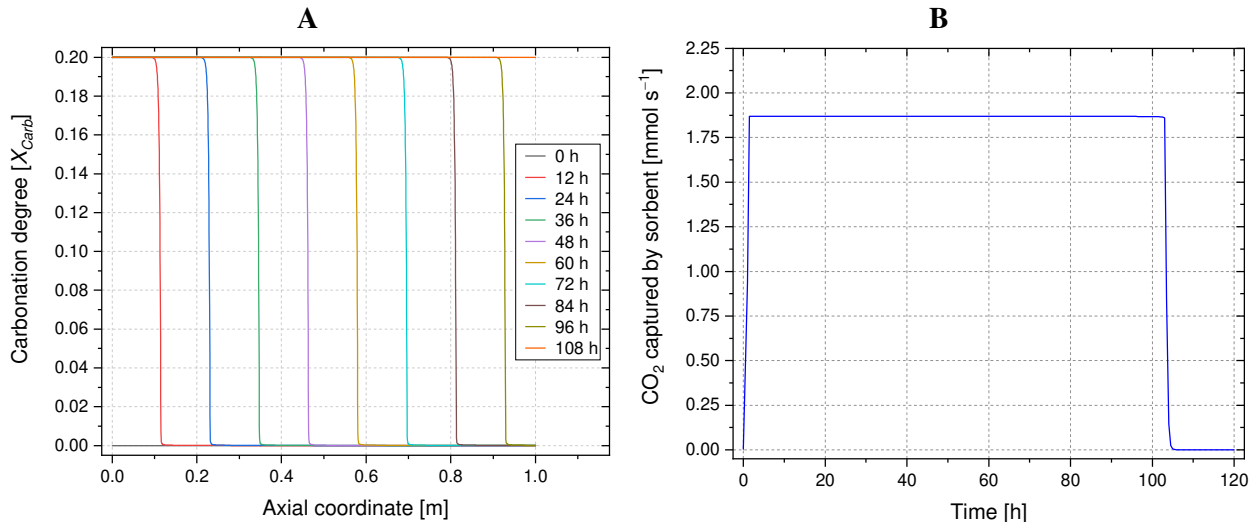


Figure 3. Carbonation degree vs. axial coordinate (A); CO₂ captured vs. time (B).

Figure 4 displays the model results for the calcination stage. Figure 4-A refers to the calcination degree of the sorbent vs. the axial coordinate of the reactor. The step shape of the different parametric curves is a direct consequence of the pressure gradient established within the packed bed. As the axial coordinate increases, the absolute pressure decreases almost linearly, favouring the course of the calcination reaction. Complete calcination of the sorbent is achieved after about 11 h of continuous operation. This is even more evident in Figure 4-B, which shows the CO₂ emitted by a single packed bed reactor vs. the operating time. Integration of the CO₂ profile over total time returns the amount of CO₂ previously trapped by the sorbent.

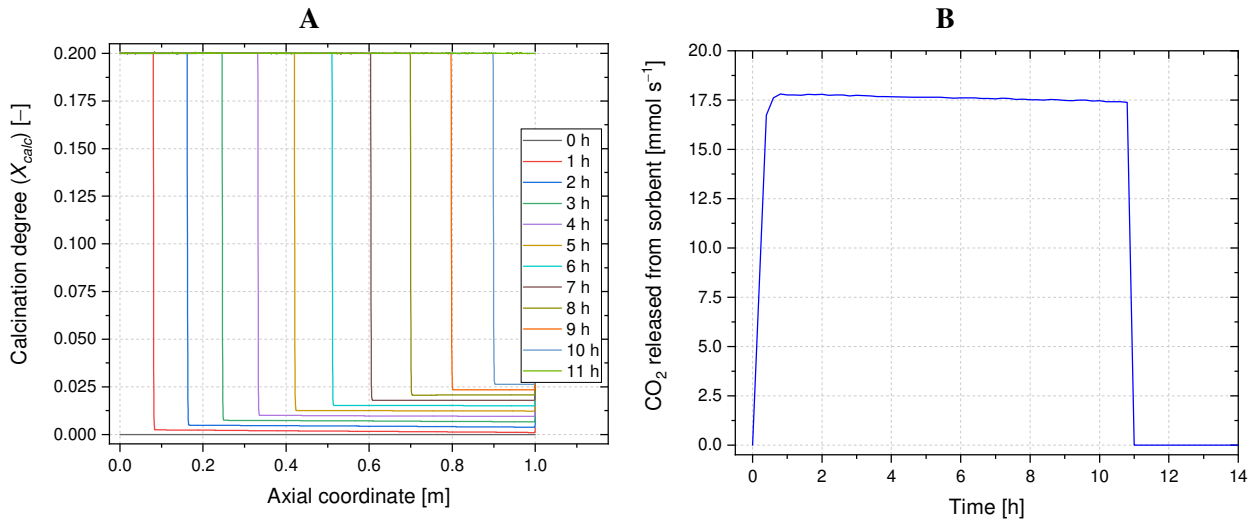


Figure 4. Calcination degree vs. axial coordinate (A); CO₂ emitted vs. time (B).

Finally, Figure 5 shows the outlet temperature of the gas stream vs. the operating time for carbonation (T_5) and calcination (T_{11}). At the beginning of the carbonation stage, the temperature of the sorbent is 1,223 K, as resulting upon completion of the previous calcination stage. Therefore, during the initial operation, the air stream is progressively heated to this temperature as it moves through the packed bed. The sorbent is completely “cooled” in about 65 min: after this period, the outlet temperature equals 576 K for the whole carbonation step. This value is slightly higher than that of the entering air stream (573 K) due to the exothermic carbonation reaction. The increase in temperature is however modest because of the very low atmospheric CO₂ concentration.

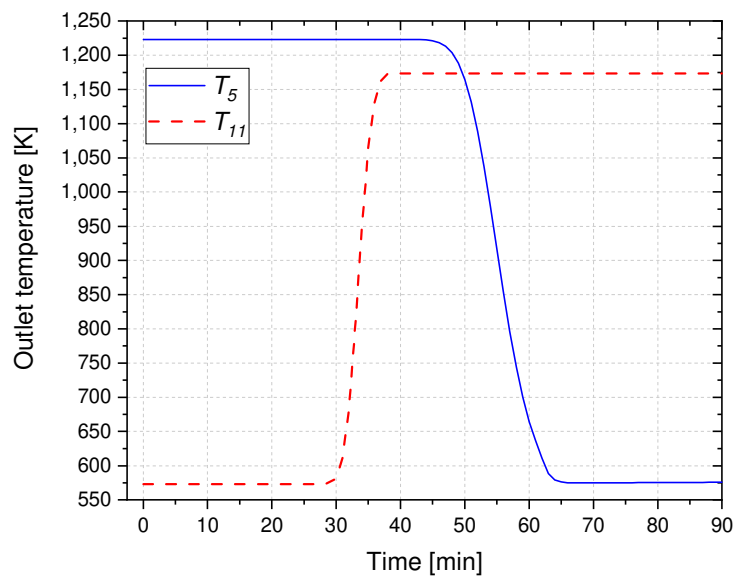


Figure 5. Exhaust gas temperature during initial carbonation (T_5) and calcination (T_{11}) stage.

When performing the calcination stage, the initial temperature of the sorbent is 573 K, as resulting upon completion of the previous carbonation step. Consequently, the hot gas stream entering the reactor at 1,223 K is progressively cooled to this temperature as it moves through the packed bed, while at the same time the

sorbent is progressively heated. This period lasts about 30 min, then the outlet temperature rapidly increases up to about 1,173 K and remains stable until the end of the calcination stage. Interestingly, this value differs from the inlet temperature of 1,223 K: the calcination reaction indeed withdraws heat from the hot gas stream up to the equilibrium temperature, which is of about 1,173 K at the end of packed bed reactor, where the absolute pressure almost equals the atmospheric value. Comparison of curves in Figure 5 also highlights that a different time is needed to completely cool or heat the sorbent. This is mostly because, during the initial period of carbonation, the inlet gas velocity is kept at the lower value of 0.5 m s^{-1} to limit the pressure drop through the packed bed. The actual velocity within the reactor, indeed, increases during the initial carbonation period due to the heating of the gas stream.

3.2 Methanation unit

Methanation can occur either in phase with calcination (“pwc”) or, alternatively, it can be decoupled from the calcination and conceived as a continuous process (“cont”) by using an intermediate tank for CO₂ storage. The methanation unit was modelled under both scenarios by using as input flow either the cumulative stream of CO₂ produced during the calcination, or a CO₂ stream distributed to have a continuous flow, plus the stoichiometric H₂ required for the methanation reaction. The total molar flow equals 15.7 kmol h^{-1} (pwc) or 1.5 kmol h^{-1} (cont). Model solution revealed that, to obtain a sufficiently high conversion degree of CO₂, three in-series methanation reactors are required. The first reactor is operated with a recycle ratio of 3, to limit the adiabatic temperature increase. The optimal inlet gas temperature to the three in-series reactors is 553 K, 573 K and 573 K, respectively, and the energy required to heat the feed stream is guaranteed by the exothermic methanation reaction. Under these parameters, the model returns a volume of 0.9 m^3 , 2.7 m^3 and 7.8 m^3 for the first, second and third reactor, respectively, if methanation is phased with calcination, and of 0.1 m^3 , 0.3 m^3 and 0.8 m^3 for the first, second and third reactor, respectively, if methanation occurs as a continuous process. The main results concerning the methanation unit are summarized in Table 2. Upon water condensation, the stream exiting the network of adiabatic reactors features a total mass flow rate of about 52.4 kg h^{-1} (pwc) or 5.0 kg h^{-1} (cont), with a molar fraction of methane of nearly 91%. Depending on the legislation of the specific country, this stream can be injected into the natural gas grid, burnt for energy production, or used in other chemical/physical processes.

Table 2. Results concerning the methanation unit.

Parameter (outlet value)	Value (pwc)	Value (cont)
CO ₂ molar fraction, dry basis [%]	1.77	
H ₂ molar fraction, dry basis [%]	7.06	
CH ₄ molar fraction, dry basis [%]	91.17	
CO ₂ conversion degree [%]	98.1	
CH ₄ mass flow rate [kg h ⁻¹]	49.29	4.71
CO ₂ mass flow rate [kg h ⁻¹]	2.63	0.25
H ₂ mass flow rate [kg h ⁻¹]	0.48	0.05

3.3 Overall balance on the direct air capture system

Solution of the mathematical model revealed that the duration of a complete carbonation and calcination cycle is of about 114 h, 103 h of which related to CO₂ capture and 11 h of which to sorbent regeneration. Considering a capacity factor for the plant of 85%, the mass stream of air that needs to be treated by the array of packed reactors is 6.5 kg s⁻¹. Accounting for the slight increase after air humidification and dividing by the mass flow rate entering a single reactor under the set pressure and temperature values, the use of about 50 in-parallel packed bed reactors is required. Figure 6 summarizes the power requirement of the main components of the system.

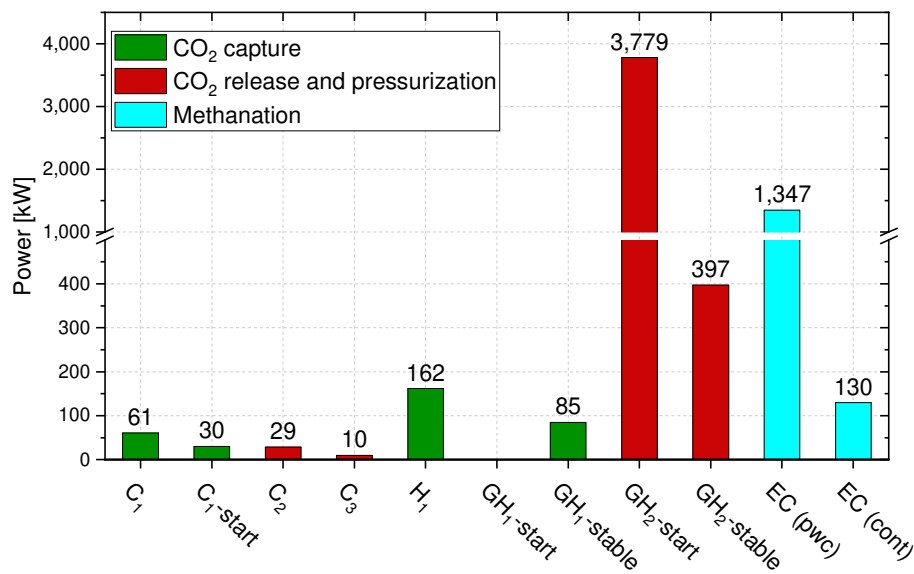
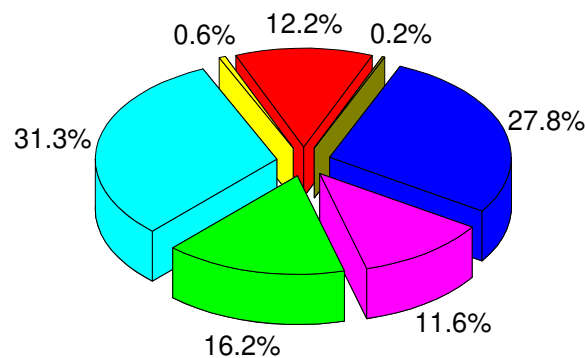
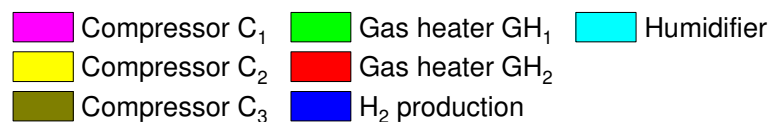


Figure 6. Power demand of the main components of the system.

During the carbonation stage, the power required to drive the air compressor is about 61 kW, except during the start-up period, namely the time required to cool the sorbent from 1,223 K to 576 K, because of the lower inlet gas velocity. The power required by the humidifier is more than double than that of the air compressor and values about 162 kW, but this energy is required at quite low temperature. Concerning the gas heater, no power is required during the start-up period, as the temperature of the gas stream exiting the packed bed reactor (T_5) is much higher than that required for the inlet gas stream as detailed in Figure 5: the thermal duty can be completely satisfied by the heat exchanger. Differently, once the heat previously accumulated by the sorbent is dissipated, the gas heater demands about 85 kW to heat the air stream to the desired inlet temperature value. During the calcination stage, the power consumption of the compressors is slightly lower compared to the carbonation stage, and equals 29 kW for C₂ and 10 kW for C₃. On the other hand, the power required by the gas heater is significantly higher. It amounts to about 3.78 MW during the start-up period, namely when the sorbent is initially heated from 573 K to 1,173 K, and eventually decreases to about 397 kW, a value still higher than those for the other components. Finally, for the methanation stage, the power required by the electrolyzers is of about 1.35 MW if the process occurs in phase with the calcination, and of about 130 kW if the operation is performed continuously by buffering the released CO₂ stream with an intermediate storage

tank. Overall, under steady-state operation, a power of about 307 kW, 436 kW and 1.35 MW (pwc) or 130 kW (cont) is required for CO₂ capture, CO₂ release with pressurization, and methanation, respectively.

Figure 7 shows the overall energy demand of each component and of the whole integrated process, computed by considering the individual power demands and the period length of the different stages. The proposed process requires about 355 GJ t_{CH₄}⁻¹ (5,672 kJ mol_{CH₄}⁻¹) to capture CO₂ directly from atmospheric air and convert it to CH₄. Humidification of air is the most energy intensive operation, but it should be underlined that this process requires thermal energy at very low temperature, which could be provided from waste heat recovered from other industrial processes or from integration with low temperature renewable energies (e.g., geothermal). If the power consumption of the humidifier is ruled out, the overall energy consumption reduces to about 243 GJ t_{CH₄}⁻¹ (3,896 kJ mol_{CH₄}⁻¹). H₂ production is the second most energy intensive operation, demanding about 28% of the overall energy consumption, followed by air/CO₂ heating, demanding the 12–16% each, and air compression, demanding the 12%. Compression of CO₂ for the calcination and methanation steps merely accounts for less than 1% of the overall energy consumption. Previous research papers report an estimated energy consumption within 207–45,000 (Krekel et al., 2018) and 10,600 (Nikulshina and Steinfeld, 2009) kJ mol_{CO₂}⁻¹ for CaO/Ca(OH)₂ sorbents, in agreement with results of the present work. When the CH₄-rich stream produced is exploited for heat generation, it is possible to compute a return of energy index as the ratio between the energy produced by the CH₄-rich stream and the overall energy input to the process. With the given data, about 912 kJ_{th} are produced by accounting for the higher heating values, vs. an overall energy input of 5,672 kJ if considering all the system components, and of 3,896 kJ if neglecting the humidifier, corresponding to a return of energy index of 16.1% and 23.4%, respectively.



OVERALL ENERGY DEMAND = 355 GJ t_{CH₄}⁻¹

Figure 7. Energy demand of the different components and of the whole integrated process.

3.4 Effect of the operating parameters

Key operating parameters of the system are represented by the process temperature during chemical reactions, and by the inlet gas velocity in the packed bed reactors. The influence of these variables was scrutinized and main differences with respect to the base case are summarized in Table 3.

The process temperature during carbonation is changed by varying the temperature of the air stream fed to the reactor (T_4), while keeping constant the inlet gas velocity. The value is increased up to 623 K and, in order to keep constant the inlet gas velocity, the mass stream of air fed to each reactor is accordingly reduced. When increasing T_4 , the carbonation period increases to 112 h. Thus, even at the low temperature of the base case, the process is not limited by the kinetics of the chemical reaction, as the prevailing effect is that of the mass stream reduction. Accordingly, the number of required reactors increases to 54. The power demand of the different components for the CO₂ capture step is only marginally affected, whereas that of CO₂ release and methanation (pwc) increases by 32 kW and 100 kW, respectively. The overall energy demand of the process is unchanged, while the power demand of the methanation under continuous operation is never affected by the change in the investigated parameters. Likewise, the process temperature during calcination is changed by varying the temperature of the CO₂ stream fed to the reactor (T_{10}). Again, the inlet mass stream is modified to keep constant the inlet gas velocity. When T_{10} is reduced to 1,203 K, the calcination period increases to 18 h and the number of reactors to 53, because of the slower reaction kinetics. Consequently, a smaller stream of CO₂ is released from the sorbent, inducing a decrease of the power demand of the compressor C₃ and of H₂ production. Conversely, the power demand of all the other components slightly increases. Altogether, under stable operation, the power demand of the CO₂ capture step increases by 18 kW, whereas that of CO₂ release and methanation decreases by 105 kW and 470 kW, respectively. Interestingly, the power demand of carbonation and calcination stages is quite similar under this process condition, which can ease the design of the energy supply, but the overall energy demand is increased by 5 GJ t_{CH₄}⁻¹. The scenario completely reverts when T_{10} is increased to 1,243 K.

Finally, the inlet gas velocity is varied within ± 0.5 m s⁻¹. Correspondingly, the outlet pressure of C₁ and C₂ is changed to 1.05 atm for $u_g=0.5$ m s⁻¹ and 1.20 atm for $u_g=1.5$ m s⁻¹ to account for the different pressure drop through the packed bed. When u_g is increased to 1.5 m s⁻¹, the carbonation and calcination period decreases to 63 h and 7 h, respectively, because of the higher mass stream fed to the reactors. Accordingly, the number of reactors reduces to 31. The power required by the compressors C₁ and C₂ is however almost doubled because of the higher pressure drop. Altogether, under stable operation, the power consumption during both carbonation and calcination stages increases, whereas that during the methanation step slightly decreases. The overall energy demand increases by about 15 GJ t_{CH₄}⁻¹, but it must be underlined that the increase in the high-quality energy is even more pronounced and equal to 50 GJ t_{CH₄}⁻¹ because of the higher energy consumption of the compressors. The scenario completely reverts when u_g is reduced to 0.5 m s⁻¹. The carbonation and calcination periods increase, together with the number of required reactors, while the power demand of the compressors reduces due to the lower pressure drop. On the whole, the overall energy demand reduces by about 11 GJ

$t_{\text{CH}_4}^{-1}$, but the reduction in the high-quality energy is even more pronounced and equal to 28 GJ $t_{\text{CH}_4}^{-1}$, because of the lower energy consumption of the compressors.

Overall, analysis of Table 3 suggests that varying the process conditions may have different effects on the design of the integrated system. A further techno-economic optimization will have to be performed to disclose the best operating parameters.

Table 3. Effect of the key operating parameters.

Parameter	Base case	Difference with respect to base case*				
		T_4 [K]	T_{10} [K]		u_g [m s^{-1}]	
		↑623	↓1,203	↑1,243	↓0.5	↑1.5
Carbonation period [h]	103	↑112	n.c.		↑217	↓63
Calcination period [h]	11	n.c.	↑18	↓8.2	↑23	↓7
Reactors, number [-]	50	↑54	↑53	↓49	↑105	↓31
C ₁ , power [kW]	61	↓60	↑64	↓59	↓31	↑117
C ₂ , power [kW]	29	↑31	↑31	↓27	↓15	↑55
C ₃ , power [kW]	10	↑11	↓6	↑13	10	10
H ₁ , power [kW]	162	↓161	↑172	↓158	↑188	↓112
GH ₁ -stable, power [kW]	85	n.c.	↑90	↓82	n.c.	
GH ₂ -start, power [MW]	3.78	↑3.80	↑3.94	↓3.75	n.c.	
GH ₂ -stable, power [kW]	397	↑426	↓294	↑497	n.c.	
H ₂ production, power [MW]	1.35	↑1.45	↓1.21	↑1.76	n.c.	↓1.33
CO ₂ capture, power** [kW]	307	↓306	↑325	↓299	↓303	↑314
CO ₂ release plus pressurization, power** [kW]	436	↑468	↓331	↑537	↓421	↑463
Methanation (pwc), power [MW]	1.35	↑1.45	↓0.88	↑1.76	n.c.	↓1.33
Methanation (cont), power [kW]			130			
Overall energy [GJ $t_{\text{CH}_4}^{-1}$]	355	n.c.	↑360	↓352	↓344	↑370
(w/o humidifier)	(243)		↑(249)	↓(241)	↓(215)	↑(293)
Return of energy index [%]	16.1	n.c.	↓15.8	↑16.2	↑16.6	↓15.4
(w/o humidifier)	(23.4)		↓(22.9)	↑(23.6)	↑(26.5)	↓(19.5)

* n.c.: not appreciably changed

** stable operation

4. Conclusions

An integrated process embodying direct capture of CO₂ from atmospheric air and its subsequent methanation was proposed and numerically investigated. Packed bed were considered as multiphase chemical reactors. CaO was selected as sorbent for CO₂ capture, while Ni-supported on alumina was considered as catalyst for the methanation. Model computations disclosed that, to remove 100 t y⁻¹ of CO₂, about 50 in-parallel reactors, 0.5 m diameter each, are necessary under the investigated process conditions. The carbonation stage features a first transient period, during which the bed is cooled after the previous calcination stage, and a subsequent almost steady-state operation, during which CaO reacts with atmospheric CO₂ at nearly constant temperature. The transient operation lasts 60 min and demands 111 kW, the subsequent stationary step lasts 102 h and demands 307 kW. The calcination stage features shorter characteristic times but higher power requirements. The initial transient operation, during which the bed is heated after the previous carbonation, requires 35 min and a power of 3,819 kW, while the subsequent stable operation lasts 10.5 h and demands 436 kW. Methanation demands 1,350 kW if performed in phase with calcination, or 130 kW if performed continuously by means of an intermediate CO₂ storage tank. An array of three in-series packed bed reactors is required, with a volume of about 0.1 m³, 0.3 m³ and 0.8 m³ if methanation occurs continuously. A stream with a mass flow rate of 5.0 kg h⁻¹ is produced in the methanation unit under the continuous operation scenario, with a methane molar fraction of nearly 91%. Overall, the energy consumption of the integrated process is estimated in about 355 GJ t_{CH₄}⁻¹ (5,672 kJ mol_{CH₄}⁻¹), with an index of energy return of 16% if the CH₄-rich stream is exploited for heat generation.

Considering the promising outcomes of this study, the proposed process may be seen as a viable solution towards a circular carbon economy, allowing for a stronger penetration of renewable energy sources. However, the low atmospheric CO₂ concentration makes direct air capture a high energy intensive process, accounting for about 70% or 50% of the overall energy demand if considering or neglecting the humidifier, respectively. This could represent a limitation for this technology, if compared to point source CO₂ capture. Future work will be targeted at performing a comprehensive techno-economic analysis and optimization of the process to assess the capital costs, the CO₂ capture cost and the price of the CH₄ produced, so as to establish its competitiveness against alternative technologies.

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