Analysis of direct capture of CO₂ from ambient air via steam-assisted temperature–vacuum swing adsorption

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Abstract

In this work, direct air capture (DAC) via adsorption is studied through the design and analysis of two temperature–vacuum swing adsorption (TVSA) cycles. In the first part, a novel way of describing the adsorption of CO₂ in presence of water vapor is proposed for co-adsorption kinetic and thermodynamic data gathered from the literature. Secondly, two TVSA cycle designs are proposed: one with a desorption step via external heating, and one with a steam purge. A schematic method for the determination of the cycle step times is proposed and a parametric study on the operating conditions is performed via cycle simulations using a detailed, first principles model. Finally, the two cycles are compared in terms of CO₂ production and energy consumption. The parametric study on the desorption time shows that there is a desorption time yielding the highest CO₂ production at low energy consumptions. Low evacuation pressures are necessary to reach high CO₂ production, but higher evacuation pressures show to be always favorable in terms of specific electrical energy requirements. A steam purge requires an additional thermal energy cost, but it not only allows decreasing the specific electrical energy consumptions, it also enhances CO₂ desorption kinetics and allows reaching higher CO₂ productions at milder evacuation pressures. The results of this work present the possibility to directly relate the availability of power and heat to the design of the cycle.

Keywords Direct air capture · S-TVSA · Simulations · Adsorption · Carbon capture · Negative emissions technology

List of symbols

Greek symbols

α	Toth exponent (–)
β	Modified Toth isotherm parameter (kg mol ^{–1})
χ	Toth isotherm parameter (–)
η	Efficiency (–)
γ	Modified Toth isotherm parameter (kg mol ^{–1})
Φ	CO ₂ purity in product stream (–)
ρ_b	Adsorbent bed density (kg m ^{–3})
ρ_p	Particle density (kg m ^{–3})
ε_t	Bed void fraction (–)

Roman symbols

ΔH_0	Isosteric heat of adsorption (kJ mol ^{–1})
ΔH_v	Enthalpy of vaporization (kJ kg ^{–1})

$\dot{m}$	Mass flow rate (kg s ^{–1})
b	Toth affinity coefficient (kPa ^{–1})
b_0	Toth affinity coefficient at reference temperature (kPa ^{–1})
C	Heat capacity (J K ^{–1} mol ^{–1})
c	Gas phase concentration (mol m ^{–3})
c_G	GAB isotherm parameter (–)
c_m	GAB isotherm parameter (mol kg ^{–1})
d_p	Particle diameter (m)
F	Volumetric flow rate (m ³ s ^{–1})
h_L	Heat transfer coefficient column–column wall (J m ^{–2} s ^{–1} K ^{–1})
h_W	Heat transfer coefficient column wall–heat jacket (J m ^{–2} s ^{–1} K ^{–1})
k	Mass transfer coefficient (s ^{–1})
K_{ads}	GAB isotherm parameter (–)
L	Length of adsorbent bed (m)
m	Mass (kg)
n	Number of components (–)
n_{s0}	Toth maximum capacity at reference temperature (mol kg ^{–1})
n_s	Toth maximum capacity (mol kg ^{–1})
p	Pressure (Pa)

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Q	Heat (J)
q	Adsorbed phase concentration (mol kg ⁻¹)
q^*	Adsorbed phase concentration at equilibrium (mol kg ⁻¹)
R	Ideal gas constant (J mol ⁻¹ K ⁻¹)
R_{in}	Internal column radius (m)
R_{out}	External column radius (m)
T	Temperature (K)
t	Time (s)
t	Toth exponent (–)
T_0	Reference temperature (K)
t_0	Toth exponent at reference temperature (–)
t_{cycle}	Total cycle time (s)
u	Velocity (m s ⁻¹)
W	Electrical energy (J)
x	Relative humidity (–)
z	Space (m)

Subscripts and superscripts

ads	Adsorbed phase
amb	Ambient
CO ₂	Carbon dioxide
g	Gas phase
H	High
H ₂ O	Water
L	Low
P	Product stream
s	Solid
v	Water vapor
w	Column wall
wf	Working fluid of heat jacket

Acronyms

DAC	Direct air capture
PCC	Post-combustion capture
PDE	Partial differential equation
S-TVSA	Steam-assisted temperature vacuum swing adsorption

1 Introduction

A major cause of climate change is the increasing concentration of greenhouse gases, one of which being CO₂, which concentration has rapidly increased from 280 ppm in the pre-industrial era to 407 in 2018 (IEA 2019). As a consequence, the global temperature has increased, posing a threat to the environment, and in the effort of limiting this increase to 1.5–2 °C, a transition to net-zero CO₂ emissions by 2050 is necessary (IPCC 2018).

CO₂ emissions mitigation technologies have been widely studied and developed to tackle these issues; many of which focus on CO₂ capture technologies at the emission source. Assuming all of the emitted CO₂ coming from point sources,

such as power plants and industry, can be removed with these technologies or avoided altogether by using renewables as energy source, there is still the need to account for unavoidable residual emissions coming from sectors such as agriculture and aviation (IPCC 2018). These account for about one fourth of the global greenhouse gas emissions, and cannot be taken care of using conventional CO₂ capture systems. Direct air capture (DAC), a removal technology in which CO₂ is captured directly from ambient air, has the potential to deal with these residual emissions, and has the additional advantage of being able to address both present and past emissions. DAC technologies can contribute to net-negative CO₂ emissions, when the captured CO₂ is coupled to carbon storage systems (Fuss et al. 2018), or to net-zero CO₂ emissions, when it is used for the production of carbon-rich synthetic fuels that are powered by renewable energy sources (Davis et al. 2018; Sutter et al. 2018).

In DAC processes, the goal is to separate CO₂ from the other components in the air, which are mainly N₂, O₂ and water vapor (Socolow et al. 2011). Due to the low concentration of CO₂ in the air, chemical sorbents with high affinity to CO₂ are good options for the separation. The diluted concentration presents an additional challenge in the process design and operation due to the fact that high volumes of air need to be processed to extract a significant amount of CO₂; in a process with 100% recovery, approximately 1400 m³ of air at normal conditions need to be processed in order to capture 1 kg of CO₂, thereby making it more of a CO₂ extraction technology than an air purification technology. On the other hand, advantages might include that with respect to point-source CO₂ capture systems, such as post-combustion capture from flue gases, there is no requirement that the capture unit be located at the source of CO₂ emission. This does not mean, however, that a DAC unit can be placed anywhere, since both its functioning and cost will highly depend on the availability and type of energy sources, on the availability of CO₂ storage and/or transportation and on the atmospheric conditions of the chosen location.

Today, most DAC applications capture CO₂ either via absorption in aqueous solutions or via adsorption on amine-functionalized solid sorbents. In both processes, the CO₂ in the air is uptaken by the sorbent, leaving the CO₂-reduced air components to exit the column in gaseous form (Bacocchi et al. 2006; Keith et al. 2018). In absorption processes, CO₂ reacts with the aqueous sorbent, for instance KOH, forming H₂O and K₂CO₃. In a second step, calcium hydroxide is added to K₂CO₃, forming a solid calcium carbonate with the CO₂ in solution and regenerating the aqueous solvent. To then release CO₂ from the carbonate via calcination, temperatures of around 900 °C and a pure-oxygen atmosphere are required (Mazzotti et al. 2013; Zeman 2007). In amine-functionalized adsorption processes, CO₂ binds to the amines forming a carbamate.

The removal of CO₂ and sorbent regeneration differ greatly with respect to absorption processes, as CO₂ is typically removed by vacuum and heating at regeneration temperatures under 110 °C (Darunte et al. 2016; Gebald et al. 2011; Serna-Guerrero and Sayari 2010). Although absorption is used as the benchmark technology for various CO₂-gas separations, the high-quality heat required for the solvent regeneration makes studying adsorption-based DAC processes, where the low-grade heat could be eventually provided by waste heat, very promising and interesting.

A great part of the research on adsorption-based DAC is focused on novel materials that have high CO₂ capacities in DAC-relevant conditions. Gebald et al. (2011) and Serna-Guerrero et al. (2010) developed amine-based solid silica particles and experimentally tested the material's stability on adsorption-desorption cycles. Darunte et al. (2016) showed how using metal organic frameworks as solid supports for amines could have an advantage over the silica-based sorbents due to their high specific surface area. Whilst the research on the potential of novel materials continues, there is a growing need for a study of the direct air capture process as a whole in order to acquire a better understanding of DAC process performance in terms of capture, regeneration, selectivity, pressure drop and energy requirements. Detailed reviews and technoeconomic assessments of DAC processes can be found in the literature (Fasihi et al. 2019; Sanz-Pérez et al. 2016), where existing DAC processes are compared in terms of type of process, materials used, CO₂ productivities, energy consumptions and costs. What is lacking is a detailed understanding of the impact that the process design and operation has on the performance. To address this caveat, this work sets out to simulate a cyclic DAC adsorption process, based on a detailed representation of the adsorption phenomena, to inform optimal DAC process design. A detailed, first principles, in-house model is used. For the process simulations, the equilibrium and kinetic data on the binary adsorption of CO₂ and H₂O on the amine-functionalized solid sorbent developed by Gebald et al. (2014) are used. As using steam as a purge has proven to be feasible on amine-supported sorbents (Bos et al. 2019; Li et al. 2010), and given its potential to enhance CO₂ desorption during regeneration, cycle designs with and without steam purge are presented and compared in terms of their CO₂ production and energetic requirements. With the aim of understanding how to minimize the energy consumption, a parametric study on the desorption time, evacuation pressure and on the steam purge velocity allows the determination of the crucial elements that influence the electrical and thermal energy requirements of a direct air capture process.

2 Modeling

In this work, we use a standard one dimensional model for gas adsorption in fixed beds (Casas et al. 2012). The model is described in detail in Sect. 2.1. The constitutive equations are chosen to describe an amine-appended nano fibrillated cellulose material that has been specifically studied and developed for DAC applications (Gebald et al. 2014; Wurzbacher et al. 2012, 2016). Using the data from the three experimental works cited, we have determined the adsorption isotherms and transport parameters, as described in Sect. 2.2. The adsorbent used in the three papers mentioned is always the same, but the amine content, and therefore, the adsorbent's maximum uptake capacity differs. As a consequence we have been able to determine model parameters that are plausible, but not necessarily accurate in describing any of the three specific adsorbents. This choice is consistent with the scope of this work, where the focus is on the effect of operating conditions on DAC performance, hence plausibility of the model parameters is more important than accuracy.

2.1 Column model

The model here proposed is a detailed first principles model of a transient, one-dimensional cylindrical column of length L . The model consists of energy and material balances involving the gas phase, the solid phase and the column wall. The balances form a set of partial differential equations (PDE) that are solved transiently until a cyclic steady-state is reached. The following assumptions are made:

- One-dimensional model in the axial direction, therefore there are no concentration, temperature or velocity radial gradients;
- The solid and gas phases are in thermal equilibrium;
- The mass transfer rate is described using a linear driving force model (LDF);
- Axial dispersion and axial conductivity are assumed to be negligible under the conditions of the simulations and in the scope of the analysis presented in this work;
- The pressure drop is described using the Ergun equation;
- The heat capacities, the viscosity, the isosteric heat of adsorption and the heat and mass transfer coefficients are constant.

The component and overall mass balances are therefore the following:

$$\epsilon_t \frac{\partial c_i}{\partial t} + \frac{\partial(uc_i)}{\partial z} + \rho_b \frac{\partial q_i}{\partial t} = 0 \quad i = 1, \dots, n, \quad (1)$$

$$\varepsilon_t \frac{\partial c}{\partial t} + \frac{\partial(uc)}{\partial z} + \rho_b \sum_{j=1}^n \frac{\partial q_j}{\partial t} = 0, \quad (2)$$

where z and t are the independent variables of space and time; c and q are the total fluid and adsorbed phase concentration, y_i is the molar fraction of each component i ; u is the superficial gas velocity; ε_t is the total void fraction; ρ_b is the adsorbent bed density, and n is the total number of components, three in our case. The mass transfer for each component is calculated using a linear driving force:

$$\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i) \quad i = 1, \dots, n, \quad (3)$$

where k_i is the lumped mass transfer coefficient and q_i^* is the adsorbed phase concentration of each component at equilibrium, calculated based on the isotherm models described in Sect. 2.2.1. Two energy balances describing the heat transfer between the fluid phase, solid phase, column wall and outside (heating/cooling jacket) are needed:

$$(\varepsilon_t C_g + \rho_b C_s + \rho_b C_{ads}) \frac{\partial T}{\partial t} - \varepsilon_t \frac{\partial p}{\partial t} + u C_g \frac{\partial T}{\partial z} + \rho_b \sum_{j=1}^n \Delta H_j \frac{\partial q_j}{\partial t} = -\frac{2h_L}{R_{in}}(T - T_w), \quad (4)$$

$$\frac{\partial T_w}{\partial t} = \frac{2}{C_w(R_{out}^2 - R_{in}^2)} [h_L R_{in}(T - T_w) - h_w R_{out}(T_w - T_{wf})], \quad (5)$$

where T , T_w and T_{wf} are the column, column wall and working fluid temperature; p is the total pressure in the column; C_g , C_s , C_{ads} and C_w are the fluid, solid, adsorbed phase and wall heat capacities; ΔH_j is the heat of adsorption for component j ; h_L and h_w are the heat transfer coefficients from the column to the column wall and from the column wall to the environment respectively; R_{in} and R_{out} are the inner and outer wall radius. The model parameters are reported in Table 1. The low values of the mass transfer coefficients and the large heat capacity of the adsorbent lead to conditions where neglecting axial dispersion and axial conductivity (see fourth bullet at the beginning of this section) is a reasonable assumption.

The energy and material balances are solved in Fortran using the finite volume method, where the PDEs are discretized along the space coordinate into equally-spaced cells. The values at the cell boundaries are calculated using the Total Variation Diminishing (TVD) scheme with a Van Leer flux limiter to avoid oscillations (LeVeque 2002). The PDEs are solved in time using the LSODES solver on Fortran. The boundary conditions for each step of the process are

Table 1 Model parameters used for the simulation: column sizing, adsorbent properties and fluid characteristics

Column	
Column length L (m)	0.01
Inner column diameter R_{in} (m)	0.08
Outer column diameter R_{out} (m)	0.082
Particle density ρ_p (kg m ⁻³)	61
Bed density ρ_b (kg m ⁻³)	55.4
Material density ρ_{mat} (kg m ⁻³)	1590
Particle size d_p (m)	0.0075
Wall heat capacity C_w (J K ⁻¹ m ⁻³)	4×10^6
Solid heat capacity C_s (J K ⁻¹ kg ⁻¹)	2070
Heat transfer	
Heat transfer coefficient h_L (W m ⁻² K ⁻¹)	3
Heat transfer coefficient h_w (W m ⁻² K ⁻¹)	26
CO ₂	
Heat of adsorption ΔH_{CO_2} (kJ mol ⁻¹)	-57
Heat capacity C_{CO_2} (J K ⁻¹ mol ⁻¹)	42.46
Mass transfer coefficient k_{CO_2} (s ⁻¹)	0.0002
H ₂ O	
Heat of adsorption ΔH_{H_2O} (kJ mol ⁻¹)	-49
Heat capacity C_{H_2O} (J K ⁻¹ mol ⁻¹)	73.1
Mass transfer coefficient k_{H_2O} (s ⁻¹)	0.002

described in Table 3 and explained in Sect. 2.3. For more information on the model used, a detailed description of it can be found in previous works (Casas et al. 2012).

2.2 System characterization

The main criterion for selecting the adsorbent used for the process simulations in this work is the availability of equilibrium and kinetic data on the binary adsorption of CO₂ and H₂O in DAC-relevant conditions. For this study, the adsorption equilibrium and kinetic data of CO₂ and H₂O on APDES-NFC, that has been experimentally obtained by Gebald et al. and Wurzbacher et al. (Gebald et al. 2014; Wurzbacher et al. 2012, 2016), is used. APDES-NFC is an amine-functionalized nanofibrillated cellulose that binds to CO₂, leading to the formation of a carbamate when in a dry gas and to ammonium bicarbonate when in the presence of water vapor.

2.2.1 Adsorption isotherms

The single and binary equilibrium data of H₂O and CO₂ on APDES-NFC have been extracted from Figs. 3 and S2 (Gebald et al. 2014) and the isotherm fitting has been done in this work.

Figure 1a shows the water equilibrium data both in the case of a single-component equilibrium experiment ($p_{CO_2} = 0$ kPa,

solid markers) and in the case of co-adsorption of CO₂ and H₂O ($p_{\text{CO}_2} = 0.045$ kPa, open markers) on APDES-NFC (Gebald et al. 2014). In their work, Gebald et al. postulate that H₂O physisorbs to a silanol group, a cellulose hydroxyl group or an unreacted amine group when CO₂ is absent, or via zwitterion deprotonation when CO₂ is present and already adsorbed on the solid. The equilibrium data exhibits a type II isotherm, which is typical for adsorption on cellulose-based materials (Thommes et al. 2015); as commonly used to describe H₂O adsorption on such materials (Bratasz et al.

2011), the Guggenheim–Anderson de Boer (GAB) was used to model the water uptake $q_{\text{H}_2\text{O}}$, as a function of the relative humidity, x :

$$q_{\text{H}_2\text{O}}(x) = c_m \frac{c_G K_{\text{ads}} x}{(1 - K_{\text{ads}} x)(1 + (c_G - 1)K_{\text{ads}} x)}, \quad (6)$$

where c_m , c_G and K_{ads} are the three GAB parameters. The GAB parameters were estimated using a nonlinear least-squares function and are represented in Table 2. The open markers, showing data from equilibrium experiments of a binary mixture in which CO₂ is present, fall right on the GAB isotherm, which suggests that the water uptake is barely influenced by the presence of CO₂. This is confirmed by other results reported in the literature (Veneman et al. 2014). Therefore for the process simulations, H₂O equilibrium loading is modeled using the single-component GAB isotherm for both single and binary mixtures.

Figure 1b shows the CO₂ uptake on APDES-NFC under dry ($p_{\text{H}_2\text{O}} = 0$ kPa, solid markers) and wet ($p_{\text{H}_2\text{O}} = 2.55$ kPa, open markers) conditions at temperatures ranging between 296 and 343 K. The dry gas containing CO₂ shows a favorable isotherm that can be accurately described by the Toth isotherm, where the loading is a function of both CO₂ partial pressure and temperature as given by:

$$q_{\text{CO}_2}(T, p_{\text{CO}_2}) = n_s(T) \frac{b(T)p_{\text{CO}_2}}{[1 + (b(T)p_{\text{CO}_2})^{1/t(T)}]}, \quad (7)$$

Table 2 GAB, Toth and modified Toth isotherm fitted parameters

GAB	
c_G (–)	0.1489
K_{ads} (–)	0.5751
c_m (mol kg ^{–1})	36.48
Toth	
T_0 (K)	296
n_{s0} (mol kg ^{–1})	2.38
b_0 (kPa ^{–1})	70.74×10^4
t_0 (–)	0.4148
ΔH_0 (kJ mol ^{–1})	–57.047
α (–)	–1.606
χ (–)	0
Modified Toth	
γ (kg mol ^{–1})	0.0061
β (kg mol ^{–1})	28.907

Fig. 1 **a** Equilibrium data of H₂O on APDES-NFC (Gebald et al. 2014) in single (solid markers) and binary adsorption with $p_{\text{CO}_2} = 0.045$ kPa (open markers) and GAB fit; **b** equilibrium data of CO₂ on APDES-NFC (Gebald et al. 2014) in dry (solid markers) and

humid adsorption with $p_{\text{H}_2\text{O}} = 2.55$ kPa (open markers), Toth fit in dry conditions (solid line) and Modified Toth fit in binary conditions (dotted line)

$$n_s(T) = n_{s0} \exp \left[\chi \left(1 - \frac{T}{T_0} \right) \right], \quad (8)$$

$$b(T) = b_0 \exp \left[\frac{\Delta H_0}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right], \quad (9)$$

$$t(T) = t_0 + \alpha \left(1 - \frac{T_0}{T} \right), \quad (10)$$

where n_s , b and t are the temperature-dependent Toth parameters. Here, the reference temperature was set to 296 K and n_{s0} , b_0 and t_0 were estimated by fitting the corresponding data points. Data at 296, 323 and 343 K were then used to estimate α , χ and the isosteric heat of adsorption, ΔH_0 , which are reported in Table 2. Although all parameters were re-estimated in this work, ΔH_0 was found to be in the same range as that in Gebald et al.'s work. Contrary to what was observed for water adsorption in the presence of CO₂, the CO₂ uptake is indeed influenced by the presence of water vapor in the gas. Results show that the CO₂ uptake is enhanced when water is present; for a given temperature, the shape of the isotherm becomes slightly steeper (= higher affinity) and the uptake at higher partial pressures increases (Serna-Guerrero et al. 2008). To describe the co-operative adsorption of CO₂ in humid conditions, Wurzbacher et al. used an empirical approach, by introducing an enhancement factor that takes into account the presence of water (Wurzbacher et al. 2016). Although the relation holds for some data points, it fails to describe the behavior of others. Similar to a recent work (Hefti and Mazzotti 2018), a new isotherm model, accounting for the dependence on the water loading, is proposed in this work to describe CO₂ uptake in binary conditions. Using the Toth isotherm as a basis, the new isotherm model proposed in the following equation accounts for the water uptake dependence in the maximum uptake term, n_s , and in the affinity coefficient, b :

$$q_{\text{CO}_2}(T, p_{\text{CO}_2}, q_{\text{H}_2\text{O}}), \quad (11)$$

$$= n_s(T, q_{\text{H}_2\text{O}}) \frac{b(T, q_{\text{H}_2\text{O}}) p_{\text{CO}_2}}{[1 + (b(T, q_{\text{H}_2\text{O}}) p_{\text{CO}_2})^{t(T)}]^{1/t(T)}}, \quad (12)$$

$$n_s(T, q_{\text{H}_2\text{O}}) = n_s(T) \left[\frac{1}{1 - \gamma q_{\text{H}_2\text{O}}} \right] \quad \gamma > 0, \quad (13)$$

$$b(T, q_{\text{H}_2\text{O}}) = b(T)(1 + \beta q_{\text{H}_2\text{O}}) \quad \beta > 0. \quad (14)$$

The water dependence is introduced in such a way that when water vapor is present in the gas, both the isotherm affinity and the maximum uptake increase, whereas when absent,

the model reduces to the single-component Toth isotherm of Eq. 7. The available equilibrium data shown in Fig. 1 was used to estimate the parameters γ and β , so as the modified Toth isotherm was determined, as shown by the dashed curves. The isotherm parameters are presented in Table 2.

2.2.2 Heat and mass transfer

The heat and mass transfer coefficients were estimated by fitting the model equations to dynamic experiments of CO₂ and H₂O coadsorption on APDES-NFC (Wurzbacher et al. 2012, 2016).

The mass transfer coefficients were estimated by a linear square fitting of the one dimensional mass balances and the linear driving force assumption of Eq. 3 to the experimental breakthrough curves. The mass transfer coefficient for CO₂ has been estimated to be $2 \times 10^{-4} \text{ s}^{-1}$, which is in line with the values found in a recent work on the same material and those on an amine-functionalized MOF under DAC conditions (Darunte et al. 2019; Ng et al. 2018); that of water has been found to be $2 \times 10^{-3} \text{ s}^{-1}$. A calibration of the maximum CO₂ and H₂O uptake was necessary in order to compensate for the difference in amine content between the paper reporting the breakthrough experiments (Wurzbacher et al. 2012) and that used for the determination of the adsorption isotherms (Gebald et al. 2014). Experimental breakthrough curves of CO₂ and H₂O respectively at ca. 400 ppm and a relative humidity of 40% are shown in Fig. 2a together with the simulation results obtained using the estimated parameters (Wurzbacher et al. 2012). The comparison between measurements and simulations shows a good fitting.

Similarly, the energy balances of Eqs. 4–5 were used to estimate the heat transfer coefficients h_L and h_W from experimental data of the desorption of an inert gas, namely the wall and gas temperature plotted for both experiments and simulations in Fig. 2b (Wurzbacher et al. 2016). Using the heat transfer coefficients reported in Table 1, the agreement between the two is satisfactory.

2.3 Cycle design

In this work, a steam-assisted temperature–vacuum swing adsorption (S-TVSA) cycle is presented, as shown in Fig. 3. The cycle is made up of four steps; (1) adsorption, (2) blow-down, (3) heating and (4) desorption. In the adsorption step, a fan is used to blow air at atmospheric temperature T_L and pressure p_H through the packed column until the bed reaches almost complete saturation of CO₂ in the bed. Atmospheric air is modeled as a ternary mixture of CO₂, H₂O and air at a constant composition of 400 ppm of CO₂, with a relative humidity of 50% and air composition of 98.8%. Air is made up of mainly N₂ and O₂, which have low affinity to the material. For this reason, air is modeled as an inert compound made

Fig. 2 **a** CO₂ (orange) and H₂O (blue) experimental breakthrough curves (markers) on APDES-NFC (Wurzbacher et al. 2012) and model simulation results (solid curves); **b** wall (black) and inert gas (red) temperature during desorption experiment (markers) on APDES-NFC (Wurzbacher et al. 2016) and model simulation results (solid curves) (Color figure online)

entirely up of N₂. At the end of the adsorption step, CO₂ and H₂O are both in gas and solid phase. After the adsorption step, the blowdown step takes place, where the air inlet is closed and the column is brought down to the evacuation pressure, p_L , with a vacuum pump at the column outlet. In this short step, air is partially removed from the gas phase in the column and released back into the atmosphere. In the following heating step, heat is transferred to the column through the external heating jacket at the desorption temperature T_H . Like in the blowdown step, the stream exiting the column during heating is mainly composed of air and is therefore released back into the atmosphere. The desorption step is modeled with two variants; in one case, it is modeled as a heating step, where the two driving forces for desorption, heat and low pressure, are provided by the external jacket and by the vacuum pump (cycle B). The second alternative is to use a steam purge, that not only gives an additional temperature swing through direct contact with the adsorbent material, but also adds to the pressure swing-driven desorption through purge by displacement (cycle A). Superheated steam enters the column at the desorption temperature, T_H , and evacuation pressure p_L . During CO₂ and H₂O desorption, to reduce the electrical energy requirements and to avoid problems in the pump due to the formation of liquid water among compression, a water trap is added before the compressor, where H₂O is condensed out of the hot stream.

The boundary conditions for each step are reported in Table 3. During the blowdown step, the pressure at the outlet is assumed to decrease with an exponential decay $p(t)$ that takes into account small flow resistances in the experimental setup (Casas et al. 2013). During the other steps, it is assumed to be kept constant using a back pressure regulator at either ambient pressure, i.e. $p(t) = p_H$, or under vacuum, i.e. $p(t) = p_L$.

Fig. 3 Four step temperature–vacuum swing adsorption cycle with (Cycle A) and without (Cycle B) steam purge; A adsorption step, BD blowdown step, H heating step, D desorption step

2.4 Performance indicators

To be able to accurately describe the performance of direct air capture cycles, some performance indicators must be defined and consequently evaluated. The purity of the product stream, Φ , depends on the mass content of the recovered CO_2 with respect to the air components that need to be separated:

$$\Phi = \frac{m_{\text{CO}_2}^{\text{P}}}{m_{\text{CO}_2}^{\text{P}} + m_{\text{Air}}^{\text{P}}}, \quad (15)$$

where m^{P} is the mass of each component in the product stream. Water is not included in this calculation because it is condensed out of the CO_2 – H_2O stream. The CO_2 production rate is defined as a function of the mass of recovered CO_2 per cycle time, t_{cycle} :

$$\dot{m}_{\text{CO}_2} = \frac{m_{\text{CO}_2}^{\text{P}}}{t_{\text{cycle}}}. \quad (16)$$

In this work the energy requirements are divided into thermal energy consumption, Q , and the mechanical energy consumption, W . The thermal energy consumption is defined as the sum of energy required for the external heating and for the purge steam.

$$Q = \max(0, Q_{\text{ext}}) + Q_{\text{steam}}, \quad (17)$$

$$Q_{\text{ext}} = h_{\text{w}} 2\pi R_{\text{out}} (T_{\text{wf}} - T_{\text{w}}) + h_{\text{L}} 2\pi R_{\text{in}} (T_{\text{w}} - T), \quad (18)$$

$$Q_{\text{steam}} = m_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} (T_{\text{v}} - T_{\text{amb}}) + m_{\text{H}_2\text{O}} \Delta H_{\text{v}} + m_{\text{H}_2\text{O}} C_{\text{v}} (T_{\text{H}} - T_{\text{b}}), \quad (19)$$

where T_{amb} is the ambient temperature, $m_{\text{H}_2\text{O}}$ is the total mass flow of steam being produced, $C_{\text{H}_2\text{O}}$ and C_{v} are the heat capacities of liquid water and water vapor, ΔH_{v} is the enthalpy of vaporization, T_{H} is the desorption temperature at which the steam enters the column and $T_{\text{v}} = f(p_{\text{L}})$ is the water boiling point at the desorption pressure. The heat requirements for the external heating bed include the heat transfer from the jacket to the wall and from the wall to the bed; those for the steam production include heating liquid water from ambient temperature to boiling point, that for water vaporization, and that to heat the saturated steam from boiling point to the desorption temperature. The mechanical energy consumption is the sum of the energy needed for the fan and for the vacuum pump, that is described as an isothermal compression:

Table 3 Boundary conditions for the DAC process

Adsorption	$p _{z=L} = p_{\text{H}}$ $u _{z=0} = u_{\text{air}}$ $T _{z=0} = T_{\text{air}}$ $y_i _{z=0} = y_{i,\text{air}}$
Blowdown	$p _{z=L} = p(t)$ $u _{z=0} = 0$ $\frac{\partial T}{\partial z} _{z=0} = 0$ $\frac{\partial y_i}{\partial z} _{z=0} = 0$
Heating	$p _{z=L} = p_{\text{L}}$ $u _{z=0} = 0$ $\frac{\partial T}{\partial z} _{z=0} = 0$ $\frac{\partial y_i}{\partial z} _{z=0} = 0$
Desorption: cycle A	$p _{z=L} = p_{\text{L}}$ $u _{z=0} = u_{\text{steam}}$ $T _{z=0} = T_{\text{steam}}$ $y_i _{z=0} = y_{i,\text{steam}}$
Desorption: cycle B	$p _{z=L} = p_{\text{L}}$ $u _{z=0} = 0$ $\frac{\partial T}{\partial z} _{z=0} = 0$ $\frac{\partial y_i}{\partial z} _{z=0} = 0$

$$W = \int_0^{t_{\text{cycle}}} [\dot{W}_{\text{fan}} + \dot{W}_{\text{comp}}] dt, \quad (20)$$

$$\dot{W}_{\text{fan}} = \frac{1}{\eta_{\text{fan}}} F(p_{\text{in}} - p_{\text{out}}), \quad (21)$$

$$\dot{W}_{\text{comp}} = \frac{1}{\eta_{\text{comp}}} \dot{n} R T \ln \left(\frac{p_{\text{H}}}{p_{\text{L}}} \right), \quad (22)$$

where F is the volumetric flow rate entering the column during a step, p_{in} and p_{out} are the inlet and outlet pressures of the gases entering and exiting the column, $\dot{n}$ is the molar flow rate being processed in the compressor, R is the ideal gas constant, p_{H} and p_{L} are the high (ambient) and low (vacuum) pressures of the compressor and η are the fan and vacuum pump efficiencies, reported in Table 4.

3 Results and discussions

The column design is a very important step of the direct air capture process design. Processing such high volumes of air means that the pressure drop in the adsorption step could significantly contribute to the electrical energy consumptions. To lower pressure drops, shorter columns (of around 0.5–2 cm (Climeworks 2019; Gebald et al. 2012; Yu and Brilman 2017)) are preferred to longer columns, typically

used in post-combustion capture. For the sake of adsorbing significant amounts of CO_2 , the short bed length often leads to pancake-like designs. In this work, an adsorbent bed of 1 cm in length and 8 cm in diameter is used. The length of the bed allows for pressure drops of under 1 mbar for all simulations. The diameter was specifically chosen to match the cross-sectional area of heat transfer experiments setup (Wurzbacher et al. 2016), so that heat transfer is modeled as precisely as possible, given the lumped heat transfer coefficients in the model.

The determination of the optimal operating conditions is done via parametric studies on the design variables, which can range from the stream flow rates and compositions, working fluid temperatures, evacuation pressure, step times and so on. To reduce computational cost, the degree of freedom of the design variables can be reduced by establishing rigorous criteria to determine the step times of steps 1–3, respectively t_1 , t_2 and t_3 . In this section, these criteria will be introduced and applied to the cycle (Fig. 4), in order to perform effectively the sensitivity analyses on the desorption time t_4 , the evacuation pressure p_L and the steam flow rate F_s (Figs. 5, 6, 7). The operating conditions used for all simulations in this work are summarized in Table 5.

3.1 Step time determination

For all simulations shown in this work, the times of steps 1–3 are set using criteria that are based on physical arguments related to the purpose of each step of the cycle. In the adsorption step, the goal is to maximize the bed's capacity to adsorb CO_2 hence to fully saturate the column with CO_2 . This is done because, contrarily to post-combustion capture (PCC), the CO_2 recovery, defined as the ratio between the CO_2 captured in the product stream over the amount of CO_2 fed with ambient air during one cycle, is not a limiting factor. When the column is saturated, the CO_2 in the air flows through the column and back into the atmosphere, therefore not contributing to net-positive emissions like in the case of PCC. However, the CO_2 mass transfer rate is slow, which entails that adsorption times are very long, as shown in Fig. 2a. Therefore, the adsorption time has been defined as the time at which the last gridpoint of the bed reaches 90% saturation starting from a fully regenerated column, therefore

ensuring CO_2 saturation even when the bed is initially not entirely regenerated. The adsorption time is therefore maintained constant for all simulations. Once the CO_2 is captured, blowdown occurs with the goal of bringing the column down to evacuation pressure p_L . For such a column, the time it takes to do so is very short and is almost independent of the chosen evacuation pressure, therefore it is also maintained constant for all simulations. In the heating step, the goal is to prepare the column for CO_2 desorption, and this differs based on the cycle design and evacuation pressure. In cycle B, where there is no steam purge in the desorption step, the only condition that must be satisfied is the removal of air ($y_{\text{Air}} < 20\%$) from the column so as to always ensure CO_2 purity in the product stream during desorption (> 0.996 for all simulations). The time it takes to satisfy this condition is a function of the chosen evacuation pressure. In cycle A, to avoid condensation of the water vapor in the steam purge, the column must also reach a minimum temperature T_M ; we have chosen 5°C above the boiling point, which also is a function of p_L . Therefore, the minimum time it takes to fulfill both conditions corresponds to the heating step time t_3 , which, as expected, increases with the evacuation pressure.

Figure 4 shows profiles that are obtained in a cyclic steady-state with fixed operating conditions on a cycle operating at a 50 mbar evacuation pressure and a steam flow rate of $25\text{ cm}^3/\text{s}$: in pink, the adsorption step; in dark gray, the blowdown step; in light gray, the heating step; in blue, the desorption step. Figure 4a shows the adsorbed CO_2 profile at the exit of the column, showing how 90% of its adsorption capacity in that point is reached, which is 2.02 mmol/g . It also shows that very little CO_2 is lost during blowdown and heating due to their short step times and temperatures. At these conditions, full regeneration is obtained at desorption times that are approximately two times longer than the adsorption time. The pressure profile shows that the transition from ambient pressure, p_H , to the evacuation pressure p_L , occurs almost instantly. During blowdown, only part of the air in the column is removed, as seen in Fig. 4c. The remaining air is removed in the heating step, where the minimum temperature to avoid steam condensation, calculated as a function of p_L using Antoine's equation, is also reached. Figure 4f shows the relative humidity of the gas exiting the column. The decrease in relative humidity in the blowdown step is due to the little desorption of H_2O in this step, which consequently decreases by very little the temperature. The relative humidity profile in the cycle shows that, although steam only contains water vapor, it enters the column at such high temperature and low pressure, that the relative humidity decreases during desorption, meaning that water is actually desorbing from the adsorbent and not adsorbing, as seen in Fig. 4e.

Table 4 Fan and compressor electrical efficiencies (Krishnamurthy et al. 2014)

	Efficiency, η
Fan	0.5
Vacuum pump, $p_L \leq 0.01\text{ bar}$	0.3
Vacuum pump, $p_L \geq 0.1\text{ bar}$	0.7
Vacuum pump, $p_L: 0.01\text{--}0.1\text{ bar}$	0.3–0.7

Fig. 4 Evolution of cyclic steady-state profiles during the adsorption step (pink), blow-down (dark gray), heating (light gray) and desorption (blue) of a cycle with steam purge. **a** CO_2 loading at the column exit, **b** pressure profile at column exit, **c** molar fraction of air in the outlet stream, **d** fluid temperature at the column exit, **e** H_2O loading at the column exit and **f** relative humidity of stream exiting column (Color figure online)

Fig. 5 Effect of evacuation pressure, p_L , and desorption time, t_4 , for simulations of cycle A and fixed steam flow rate ($F_s = 25 \text{ cm}^3/\text{s}$) on the CO₂ production rate (a) and specific energy consumptions (b). p_L : 30, 50, 80, 100, 200 mbar; t_4 : 500–6100 s, where the direction of the arrow indicates increasing desorption time

3.2 Effect of evacuation pressure

Figure 5 compares the CO₂ production rate to the specific electrical and thermal energy requirements for different process designs. Each curve represents a different evacuation pressure in the range 30 mbar to 200 mbar, and each point on the curve represents a different desorption time, t_4 , ranging from 2000 to 50,000 s, where 30,000 s is long enough for full regeneration to occur. The arrow on each curve shows the direction of increasing t_4 . The curves exhibit similar trends, showing that there is a desorption time yielding

Fig. 6 Effect of steam flow rate, F_s , and desorption time, t_4 , for fixed evacuation pressure ($p_L = 50 \text{ mbar}$) on the CO₂ production rate (a) and specific energy consumptions (b). F_s : 0 (cycle B), 5, 10, 17.5, 25 cm³/s (cycle A); t_4 : 500–6100 s, where the direction of the arrow indicates increasing desorption time

highest CO₂ production rate corresponding to an energy consumption close to the lowest values. Lower evacuation pressures yield higher driving forces for CO₂ desorption, which explains the difference in peak in CO₂ production between the curves. In Fig. 5a, the direction of t_4 suggests that operating at low desorption times is not convenient in terms of specific electrical energy consumptions because similar production rates are achieved at lower specific electrical energy consumptions when desorption is long. However, working

Fig. 7 Electrical vs. thermal energy consumption for CO₂ production rate isolines of 1.9 (circles), 2.2 (squares) and 2.45×10^{-5} kg/h (triangles) and evacuation pressures of p_L : 30 (solid), 50 (dashed) 100 mbar (dotted). The color scheme corresponds to the steam flow rate, increasing from left to right: F_s : 0 (gray), 5 (purple), 10 (yellow), 17.5 (orange), 25 cm³/s (blue) (Color figure online)

at desorption times longer than the peak in production is not convenient either, because in all cases the specific electrical energy consumption reaches a minimum, under which it is not possible to operate. At long t_4 , the components in the gas and solid phase reach equilibrium and the outlet stream exits the column at constant composition and continuously decreasing flow rate. The CO₂ in the product stream therefore almost ceases to increase, as does the electrical energy consumption of the vacuum pump due to the continuously decreasing molar flow rate of the product stream. On the other hand, the thermal energy consumption does not cease to increase, as seen in Fig. 5b, since the heat requirements for steam production are constant throughout desorption. Therefore, although the denominator of the specific thermal energy reaches a constant value, the numerator continues to increase, which explains why the direction of t_4 in Fig. 5b is inverted with respect to Fig. 5a. This result suggests that, thermal energetically speaking, lower desorption times are favorable.

The overall trend of the electrical energy curves show a slight trade-off between high CO₂ production rates and low energy consumptions. A similar trade-off is not observed in the thermal energy curves. Instead, the peak in CO₂ production increases with decreasing specific thermal energy, suggesting that it would be always best to operate at low evacuation pressures.

3.3 Effect of steam flow rate

The effect of the steam flow rate has been studied for $p_L = 50$ mbar at desorption times between 2000 and 50,000 s. For constant p_L , the cyclic capacity increases with the steam flow rate, yielding higher amounts of CO₂ extracted from equally-saturated adsorbent beds. For each curve in Fig. 6a, the electrical energy contribution of the first three steps of the cycle is equal due to the identical operating conditions. As increasing F_s in the desorption step enhances CO₂ desorption, the molar flow rate that the compressor must process is higher. Therefore, the total electrical energy increases with F_s , but at high t_4 , the specific electrical energy decreases because it is compensated by the higher production of CO₂ (in the denominator). This is why no trade-off is observed, like in the case of Fig. 5a, and why the minimum in specific electrical energy is fundamentally constant for all F_s .

Figure 6b shows a CO₂-thermal energy trade-off when varying the amount of steam purge. The increase in thermal energy consumption with F_s is a direct consequence of the need for higher steam production. The gray curve, corresponding to the profile of cycle B with no steam, and the purple, which corresponds to low steam flow rates, exhibit an inversion in the direction of t_4 with respect to the higher steam flow rates. In the lower range, the direction is similar to that of the electrical energy, where higher desorption times yield lower specific energy consumptions for the same CO₂ production. Cycle B even reaches a minimum, similar to Fig. 6a. When steam is absent, in fact, the thermal energy entirely goes into externally heating the adsorbent bed through the wall. When the entire bed has reached desorption temperature, assuming that there are no heat losses, no thermal energy needs to be additionally provided and the total thermal energy consumption also ceases to increase. When steam is added, its production rate needs to be accounted for throughout desorption. For higher steam flow rates, the specific thermal energy consumption for high t_4 exceeds that of low desorption times, showing that low desorption times are favorable. Overall, the peak in production rate in cycle B with no steam yields a decrease in production of 9% and in specific thermal energy consumptions of 70% with respect to the peak at flow rates of $F_s = 25$ cm³/s.

3.4 Electrical vs. thermal energy consumption

Figure 7 shows productivity–evacuation pressure isolines for different steam flow rates. The circle, square and triangle markers correspond to CO₂ production rates of 1.9×10^{-5} , 2.2×10^{-5} and 2.45×10^{-5} kg/h, respectively. The solid, dashed and dotted lines correspond to evacuation pressures of 30, 50, and 100 mbar, respectively. The colors of the markers represent the steam flow rate, as in Fig. 6.

Table 5 Fixed and variable operating conditions used for all simulations

		Base case	Sensitivity 1	Sensitivity 2	Sensitivity 3
Adsorption					
Feed	y_{H_2O} (–)	0.0115			
	y_{CO_2} (–)	0.0004			
	y_{N_2} (–)	0.9881			
	$T_{air} = T_L$ (°C)	20			
	$p_{air} = p_H$ (bar)	1			
	F_{air} (cm ³ s ^{–1})	50			
Column press.	p_H (bar)	1			
Jacket temp.	T_L (°C)	20			
Step time	t_1 (s)	13,772			
Blowdown					
Column press.	p_L (mbar)	50	[30, 50, 80, 100, 200]		[30, 50, 100]
Jacket temp.	T_L (°C)	20			
Step time	t_2 (s)	30			
Heating					
Minimum temp.	$T_M = T_M(p_L)$ (°C)	42	[33, 42, 51, 56, 70]		[33, 42, 56]
Column press.	p_L (mbar)	50	[30, 50, 80, 100, 200]		[30, 50, 100]
Jacket temp.	T_H (°C)	95			
Step time	$t_3 = t_3(p_L)$ (s)	704	[477, 704, 969, 1120, 1732]		[477, 704, 1120]
Desorption					
Column press.	p_L (mbar)	50	[30, 50, 80, 100, 200]		[30, 50, 100]
Jacket temp.	T_H (°C)	95			
Steam purge	F_s (cm ³ s ^{–1})	25		[0, 5, 10, 17.5, 25]	[0, 5, 10, 17.5, 25]
	$p_s = p_L$ (mbar)	50	[30, 50, 80, 100, 200]		[30, 50, 100]
	$T_b = T_b(p_L)$ (°C)	37	[28, 37, 46, 51, 65]		[28, 37, 51]
	$T_s = T_H$ (°C)	95			
Step time	t_4 (s)	30,000	2000–50,000	2000–50,000	2000–50,000
Figures		Figure 4	Figure 5	Figure 6	Figure 7

The decision variables of the sensitivity analyses are p_L , t_4 , F_s , and all other parameters either vary as functions of the decision variables or are fixed and equal to the base case (empty cells)

This figure is a good illustration of the importance of the cycle design. By looking at the different curves at equal evacuation pressure, one can immediately notice that for low CO₂ production rates, such as 1.9×10^{-5} kg/h in the figure, it is favorable to operate at high evacuation pressures so as to reduce electrical energy consumptions. At constant levels of vacuum, the different steam purge flow rates result in an electrical–thermal energy trade-off. Higher steam flow rates indeed decrease the specific electrical energy consumption. However, this decrease is minimal with respect to the significant increase in the associated thermal energy consumption, suggesting that a steam purge might not be convenient. However, it is also clear that not all CO₂ production rates can be achieved at high p_L , which is clearly indicated by the absence of the 2.45×10^{-5} kg/h productivity isoline at 100 mbar. Such a rate can be produced at lower evacuation pressures, as demonstrated by the triangle curves at 50 and 100 mbar. However, even at such low pressures, it is not possible

to reach such production rate without steam (as indicated by the absence of the gray triangular markers). To increase CO₂ production, one must *either* decrease the evacuation pressure *or* increase the amount of steam purge. Steam could therefore become a valuable option, when low vacuums are not industrially feasible and when there is low-quality waste heat available. This is an important result because it shows how the availability and type of energy source highly influences how the optimal cycle is designed.

4 Conclusions

In this work, direct air capture via adsorption is studied through the design and analysis of two temperature–vacuum swing cycles. A novel way of describing the CO₂–H₂O co-adsorption, a rigorous way of designing a cycle, and

a parametric study on various operating conditions are presented.

It is well known, and our simulations confirm it, that direct air capture comes at the cost of a substantial energy penalty. Part of it (the larger fraction) is thermal energy for column regeneration, and part is electrical energy for air blowing and column evacuation. The trade-off between the two forms of energy is quantified by our model and well illustrated by the maps of Fig. 7. Results show how it is energetically favorable to operate at high evacuation pressures and low steam purge rates (or no steam at all) to obtain low CO₂ production rates. High CO₂ production can instead be achieved at deep vacuum levels or alternatively by increasing the steam purge; the choice will depend on the availability of power and heat.

In fact, where and how direct air capture is deployed will depend strongly on the absolute and relative availability of affordable and low-carbon power and heat, besides that of a permanent (storage) or temporary (utilization) CO₂ sink. The design of the direct air capture plant and of its cycle and operation will have to account for this. Therefore, the availability of a sound model and process simulator as presented here will be indispensable to quantify the trade-offs and realize an optimal design and operation, in terms of productivity and energy intensity.

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