Vacuum swing CO₂ adsorption cycles in Waste-to-Energy plants

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Abstract

The performance of vacuum swing adsorption-based processes applied to CO₂ capture in Waste-to-Energy plants is explored for the first time. CO₂ capture and storage (CCS) are gaining increasing attention in this sector. The analysis of simple cycle configurations for this particular application provides a reference scenario to explore the potentiality of the adsorption technology. Under these premises, the objective of this study is to maximize the CO₂ separation from the flue gas of a solid waste incineration facility.

Three vacuum swing adsorption (VSA) and one vacuum and temperature swing adsorption (VTSA) configurations were assessed in a fixed-bed laboratory unit and the influence of the cycle design, the number of columns and the operational conditions were analyzed. The adsorbent employed is an activated carbon produced from pine sawdust, a forestry by-product with great availability in our region. Mathematical modeling developed in Aspen Adsorption complemented the experimental study which in turn validated the created model. Additional simulations were performed to further evaluate the effect that the different vacuum swing adsorption configurations have on product purity and recovery. With relatively simple configurations consisting of a maximum of 4-beds, CO₂ recoveries above 95% were achieved and CO₂ purity was increased from 8% to approximately 35-40%.

Keywords: CO₂ adsorption; Waste-to-Energy; Vacuum swing adsorption; Pine sawdust

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1. Introduction

Under the Paris Climate Agreement, 195 countries committed to keep global temperatures from rising “well below 2°C and to pursue efforts to limit the increase to 1.5 °C above pre-industrial levels” [1]. To meet this goal a substantial reduction in global CO₂ emissions is needed.

In this context, bioenergy with carbon capture and storage (Bio-CCS or BECCS) is regarded as a major mitigation strategy [2]. It involves applying carbon capture technologies to biomass conversion processes. Therefore, it has the additional advantage of not only reducing CO₂ emissions but leading to carbon negative values.

Bio-CCS could potentially be applied to a wide range of plants, including Waste-to-Energy (WtE) facilities [3]. Around 522 WtE plants in Europe are transforming residual waste into a usable form of energy such as heat or electricity. Bio-CCS demonstration projects are presently underway at Saga City (Japan), Twence B.V. (Hengelo, Netherlands) [4] and Klemetsrud (Norway) Waste-to-Energy plants [5].

Currently, the most widely employed carbon capture technology is absorption gas separation using chemical solvents. However, since WtE plants are subjected to strict environmental regulations, they would require the use of other gas separation processes with lower energy penalties and more environmentally benign.

Adsorption-based processes are considered of minimal environmental impact opposite to amine-based solvents, which tend to decompose and form toxic and/or corrosive compounds [6,7]. One of the main challenges of adsorption-based post-combustion CO₂ capture processes is the associated carbon footprint. Two-stage pressure/vacuum swing adsorption processes are generally needed to achieve the required targets in CO₂ purity and recovery [8–10] and this results in increased cost. However, industrial processes, due to the higher CO₂ partial pressure or the lower volumetric flow rates appear to be more suitable applications.

The utilization of biomass-based carbon materials as adsorbents has also shown advantages in terms of stability and ease of regeneration. The activated carbon selected as the adsorbent in this work was prepared from pine sawdust and was fully characterized in our previous works [11,12]. It presents competitive adsorption capacities at equilibrium, favorable adsorption kinetics and has already been tested under dynamic conditions in a purpose-built fixed-bed reactor [12]. Breakthrough curves tests showed the suitability to employ the pine sawdust-based activated carbon to capture CO₂ from incineration flue gas, both in dry and wet conditions.

2. Vacuum swing adsorption processes

2.1. Design rationale

Any commercial adsorption process operates by consecutive cycles whose basic steps are adsorption and regeneration. The separation of one of the components in a gaseous mixture is usually based on the preferential adsorption of one or more components of the mixture (equilibrium separation) although in other cases is determined by kinetics.

The first patents related to pressure swing adsorption (PSA) processes date from the '30s [13]. Regeneration with vacuum was originally proposed by Guerin and Domine [14] some years later. The main commercial applications of PSA processes are: air separation to obtain oxygen and nitrogen, air dehumidification and hydrogen purification. PSA processes are considered an attractive technology due to its operation simplicity, high performance at ambient temperature and fast regeneration of the adsorbent bed. The basic cycle configuration was described for the first time by Skarstrom in 1960 [15] and it is generally used as the benchmark scenario to establish the performance of a PSA system. It consists of two beds that, in sequence, go over the following steps: pressurization, adsorption, blowdown, and purge. The operation in both columns should be synchronized to guarantee the continuous operation of the process without feed interruption.

The performance of the adsorption process can be defined by product purity and recovery, operational pressure range, energy requirements, and scale-up. Operating pressure and temperature affect both CO₂ purity and recovery of the product, due to variation in the working capacity of the adsorbent. On the other hand, the pressure drop in the column, given by the superficial gas velocity and the bed porosity, is another important parameter in the cyclic configuration, as it can affect both CO₂ adsorption and desorption.

A key aspect of the adsorption process design is setting the steps' sequencing. The number of beds and the configuration of steps should be such that a regenerated column is available and ready to start the adsorption step, just before the adsorbent bed in adsorption mode is exhausted. Thus, the number of beds required is determined by the feed conditions, the adsorbent, the composition of the feed gas mixture, and the purity grade needed.

In our case study, a waste-to-energy facility, great volumes of gas at atmospheric pressure would be treated; thus, a vacuum swing adsorption (VSA) process would be the preferred option to avoid the compression of the feed gas in a PSA operation. The CO₂ purity and recovery will depend greatly on the configuration of the VSA cyclic operation. For instance, CO₂ purity could be improved by conducting the adsorption step at a pressure slightly higher than atmospheric and including a depressurization step co-currently to the feed up to atmospheric pressure to release part of the N₂ present in the bed. Another option frequently employed when the product of interest is the strong adsorbate, as it is in our case, and it is to be recovered at high purity, consists of adding a purge step by recirculating part of the product fraction co-current to the feed before the blowdown step. During this stage, the CO₂ fed to the column displaces the N₂ present in the adsorbent porosity and the composition of the adsorbed phase is enriched in CO₂.

To avoid reaching high vacuum levels or reducing the cycle time, it is possible to introduce a purge step with a fraction of the raffinate (N₂) at reduced pressure after the evacuation step.

This favors the regeneration of the bed and the CO₂ desorbed is easily removed due to the sweeping effect of the purge stream.

Another modification of the cycle sequencing for the Skarstrom configuration is the introduction of pressure equalization steps (developed at ESSO Research group [16,17]). In this step, two columns at different pressure levels are put in contact to reduce the energy required for the pressure change. In addition to energy savings, it improves product recovery.

Taking all the above into account, the step configuration of a VSA process for CO₂ separation does not seem a straightforward task. A design study and experimental data, combined with mathematical modeling of the dynamics of the adsorption unit, are required to optimize the configuration for the proposed targets, usually regarding CO₂ recovery and purity for a particular application.

Ben-Mansour et al. [18] published a detailed review including mathematical models reported in the literature for adsorption-based CO₂ separation processes. Computer simulations provide a useful tool to handle process model equations. Several commercial software packages have been recently applied with satisfactory results to modeling studies of adsorption processes such as Matlab [19,20], Aspen Adsorption [21–23], gProms [24,25] or Comsol Multiphysics [26–29].

Simulation and optimization of VSA processes for post-combustion CO₂ capture from dry flue gas (85% N₂, 15% CO₂) have been published for different types of adsorbents. Shen et al. [30] investigated the effect of different operating parameters in a two-stage VSA process employing activated carbon beads. The performance of three different adsorbents available for CO₂ capture was compared by Nikolaidis et al. [31] simulating a two-bed six-step VSA configuration. Modeling of VSA processes for post-combustion CO₂ capture with zeolites 13X [32,33] and 5A [34] have also been reported, whereas Pai et al. [35] evaluated the potential of MOFs. These studies highlighted the importance of the VSA cycle configuration on the process

performance and showed the difficulties of achieving high purity and recovery of CO₂ from low concentration flue gases.

To simulate conditions resembling a real process at industrial scale, short VSA cyclic experiments were performed in the present work. The feed stream consisted of a gas mixture of N₂/CO₂ (92/8 vol.%), representative of a Waste-to-Energy plant flue gas. The duration of the adsorption step was set to a value close to the breakthrough time; the bed did not reach saturation in CO₂ during the adsorption step nor achieve complete regeneration during the desorption step. Different configurations for the VSA cycles were evaluated. Dynamic simulation of the adsorption process was carried out using Aspen Adsorption V9.0.

2.2. Experimental work

In this section, the focus is on gathering experimental data and analyzing several VSA configurations to determine the effect that the characteristic parameters have on the cyclic adsorption-desorption process applied to a WtE plant flue gas.

Dynamic CO₂ adsorption cycles were carried out experimentally in the fixed-bed lab set-up shown in Figure 1, which was described in detail elsewhere [12]. The characteristics of the solids bed, later used also as inputs in the simulation, are listed in Table 1. The activated carbon (IH3) employed as adsorbent was produced from pine sawdust pellets and physically activated with CO₂ in a single-step. Preparation procedure and characterization data are described elsewhere [11].

Table 1. Characteristics of the adsorbent bed used in the cyclic experiments.

Parameter	Value
Height of adsorbent layer x10 ² (m)	12.5
Internal bed diameter x10 ² (m)	1.30
Mass of adsorbent (g)	4.48
Inter-particle voidage (—)	0.56
Intra-particle voidage (—)	0.68

Micropore volume (cm ³ /g)	0.30
Average micropore width (nm)	0.75

Figure 1. Fixed-bed set-up used for the experimental study.

In the single fixed-bed unit, conditions representative of an industrial process with three and four columns were recreated. Unlike the dynamic experiments called breakthrough curves, these cycles are configured for short times and therefore neither full saturation nor complete regeneration of the bed is achieved. For this reason, the duration of the adsorption step was set to a value close to the breakthrough time: 3.5 minutes for pressurization and adsorption.

The total feed flow rate used was 140 mL/min with a composition of 8 vol.% CO₂ (N₂ balance).

The bed was directly pressurized with the feed. At the beginning of each run, the bed was completely regenerated by flowing nitrogen at 150 °C for 1 h. At least 25 cycles of each configuration were carried out and a stationary cyclic state was achieved. The adsorption temperature was set at 50 °C.

The R/F CO₂ ratio (amount of gas used in the purge with product step/amount of feed introduced in the adsorption and feed pressurization steps) was set at 0.65. The minimum vacuum pressure in the line during the regeneration stage was 5 mbar (500 Pa).

Table 2 presents a summary of all different configurations studied experimentally in this work:

A, B, and C correspond to VSA cycles and D is a VTSA configuration.

Table 2. Description of conditions used for each step in all cyclic configurations studied.

	Pressure (bar)	Temperature (°C)	N ₂ flow (mL/min)	CO ₂ flow (mL/min)	Duration time (min)
<i>Configuration A</i>					
Pressurization	1	50	128.8	11.2	1
Adsorption	1	50	128.8	11.2	2.5
Rinse with CO ₂	1	50	0	7.3	3.5
Vacuum	0.005	50	0	0	3.5
<i>Configuration B</i>					
Pressurization	1	50	128.8	11.2	1
Adsorption	1	50	128.8	11.2	2.5
Rinse with CO ₂	1	50	0	7.3	1.75
Vacuum	0.005	50	0	0	3.5
Purge with N ₂	0.005	50	10	0	1.75
<i>Configuration C</i>					
Pressurization	1	50	128.8	11.2	1
Adsorption	1	50	128.8	11.2	2.5
Rinse with CO ₂	1	50	0	7.3	3.5
Vacuum	0.005	50	0	0	3.5
Purge with N ₂	0.005	50	10	0	3.5
<i>Configuration D</i>					
Pressurization	1	50	128.8	11.2	1
Adsorption	1	50	128.8	11.2	2.5
Rinse with CO ₂	1	50	0	7.3	1.75
Vacuum	0.005	70	0	0	3.5
Purge with N ₂	0.005	50	10	0	1.75

It is necessary to define characteristic parameters of the adsorption-desorption process to compare the results of the different configurations tested. These parameters were: raffinate (N₂) purity, product (CO₂) purity and CO₂ recovery and were estimated with the following formulae:

$$\text{Raffinate purity} = \frac{\int_0^{t_R} F_{N_2 \text{out}} dt}{\int_0^{t_R} F_{N_2 \text{out}} dt + \int_0^{t_R} F_{CO_2 \text{out}} dt} \quad (1)$$

$$\text{Product purity} = \frac{\int_{t_R}^{t_B} F_{CO_2 \text{out}} dt}{\int_{t_R}^{t_B} F_{N_2 \text{out}} dt + \int_{t_R}^{t_B} F_{CO_2 \text{out}} dt} \quad (2)$$

$$\text{CO}_2 \text{ recovery} = \frac{\int_{t_R}^{t_B} F_{CO_2 \text{out}} dt}{\int_0^{t_R} F_{CO_2 \text{in}} dt} \quad (3)$$

The equations used in each case depend on the precise configuration. When introducing the purge step with N₂, the CO₂ purity and recovery could be also determined for both the blowdown step and the purge step, hence the time limits of the integral would change as follows:

$$\text{Product purity} = \frac{\int_{t_R}^{t_{Pu}} F_{CO_2 \text{out}} dt}{\int_{t_R}^{t_{Pu}} F_{N_2 \text{out}} dt + \int_{t_R}^{t_{Pu}} F_{CO_2 \text{out}} dt} \quad (4)$$

$$\text{CO}_2 \text{ recovery} = \frac{\int_{t_R}^{t_{Pu}} F_{CO_2 \text{out}} dt}{\int_0^{t_R} F_{CO_2 \text{in}} dt} \quad (5)$$

In Equations (1) to (5), t_R refers to the time of the cycle at which the rinse step ends, t_B refers to the time at which the blowdown step is finalized, and t_{Pu} to the end time of the purge with raffinate step. $F_{N_2 \text{out}}$ and $F_{CO_2 \text{out}}$ are the molar flow rate of N₂ and CO₂, respectively, leaving the adsorber.

2.3. Modeling in Aspen Adsorption

Simulations were performed using the commercial software Aspen Adsorption to develop an adsorption model validated by the experimental data. This model is a combination of the mass,

momentum, and energy conservation equations applied to the single fixed-bed adsorption unit. The following assumptions were used for a 1-D vertically oriented column:

- The gas phase is described by the ideal gas law.
- The mass, energy, and momentum gradients are considered only in the axial direction.
- The mass transfer resistances into the particle are expressed according to the linear driving force (LDF) approach.
- Constant void and bed density along the column.

The set of model equations here described was numerically solved and the first-order upwind differencing scheme (UDS1) with 50 nodes was selected as the method for spatial discretization.

The importance of accurate characterization of the extra-column void volumes in the experimental unit has been confirmed by Joss et al. [36]. Dead volumes of the experimental system were accurately measured. In the simulation flowsheet, tanks representing voids at the top and bottom of the adsorption bed were included. The dead volume before the adsorber which accounts for the volume of tubing between the feed section and the adsorber and the void space inside the reactor above the solids bed was 3.55 cm³. After the column, the mass flow meter and the vacuum pump are installed before the gas analyzer. Therefore, the dead volume at the exit is 10.4 cm³ and when the vacuum line is connected, another 44.8 cm³ are added.

Isotherm parameters for N₂ and CO₂ were estimated from the pure adsorption isotherms experimental data at three different temperatures [12] using Aspen Adsorption's estimation interface. The pure adsorption equilibrium data were fitted to the Langmuir-Freundlich isotherm model. The form of the isotherm equation used in Aspen Adsorption is:

$$w_i = \frac{IP_1IP_2P_i^{IP_3}e^{IP_4/T_s}}{1 + IP_5P_i^{IP_3}e^{IP_6/T_s}} \quad (6)$$

where w_i is the equilibrium loading of component i (kmol/kg adsorbent), P_i is the equilibrium partial pressure of component i (bar) and T_s is the temperature (K). Table 3 shows the parameters used for each gas. The Ideal Adsorbed Solution Theory (IAST) was applied to account for multicomponent adsorption.

Table 3. Langmuir-Freundlich adsorption equilibrium parameters of CO₂ and N₂ used in Aspen Adsorption simulations.

Gas	IP ₁ (kmol/kg)	IP ₂ (1/bar)	IP ₃ (—)	IP ₄ (K)	IP ₅ (1/bar)	IP ₆ (K)
CO ₂	5.54 x10 ⁻³	4.87 x10 ⁻⁴	0.811	2297	1.80 x10 ⁻³	1918
N ₂	3.75 x10 ⁻³	5.43 x10 ⁻⁴	0.937	1610	1.04 x10 ⁻¹	0

The momentum balance was described using the Ergun Equation [37]:

$$\frac{\partial P}{\partial z} = 150 \frac{\mu(1 - \varepsilon_i)^2}{\varepsilon_i^3 (2r_p \psi)^2} v_g + 1.75 \frac{(1 - \varepsilon_i) \rho_g}{\varepsilon_i^3 2r_p \psi} v_g^2 \quad (7)$$

where ψ is the particle sphericity or shape factor, r_p is the particle radius and ε_i is the interparticle voidage. The Ergun equation is useful as it is a general pressure drop correlation and can be used in laminar and turbulent flow regimes. The cylindrical pellets used in this work were treated as spherical particles using a shape factor approximation of 0.91 [38] with a particle radius of 1.48 mm.

A linear valve model was assumed to represent the pressure drop across the valve [39] and the valve constant was fitted to reproduce the experimental rate of pressure drop during the evacuation step.

The axial dispersion term is included in the material balance to lump all mechanical dispersion effects together with molecular diffusion. The Peclet number could reach a small value for some steps of the cycle and therefore, the effect of the axial dispersion on the bed performance would be significant. Axial dispersion in the fixed bed was estimated using the following correlation [40]:

$$E_{z,k} = 0.73D_{mk} + \frac{v_g r_p}{\varepsilon_i \left(1 + 9.49 \frac{\varepsilon_i D_{mk}}{2v_g r_p} \right)} \quad (8)$$

where D_{mk} is the molecular diffusivity of species k in the gas mixture, v_g is the superficial velocity, r_p is the particle radius and ε_i is the interparticle porosity. The molecular diffusivities for each component in the binary mixture were calculated using the Chapman–Enskog theory [41].

The rate of mass transfer for each component from the gas to the adsorbed phase was described by a lumped resistance model based on a Linear Driving Force (LDF) approximation [13] in the solid phase:

$$\frac{dq_k}{dt} = MTC_k (q_{eq,k} - q_k) \quad (9)$$

where q_k and $q_{eq,k}$ are the amount of the component k adsorbed at a given time and at equilibrium, respectively and MTC_k refers to the mass transfer coefficient.

The LDF equation has been adopted as the mass transfer rate model in most adsorber simulation studies for CO₂ capture [42]. The mass transfer coefficient of CO₂ in our activated carbon was previously estimated using data from gravimetric tests [11] and that of N₂ was fitted to the experimental breakthrough curves.

Regarding the energy balance, the VSA experiments conducted are isothermal, where the temperature of the column is kept constant throughout the cycle. The gas temperature, T_g , the wall temperature, T_w , and the solids temperature, T_s , are equal. However, in the VTSA case, the temperature of the bed is risen during the blowdown step and cooled down in the low-pressure purge step. Therefore, the system is considered non-isothermal with gas and solid heat conduction, i.e., the thermal conduction term is considered in the energy balance for both the gas and solid phases.

Isosteric heats of adsorption for the pure components were estimated by means of the Clausius–Clapeyron equation and assumed constant, with a value of 18.0 kJ/mol for N₂ and 24.9 kJ/mol for CO₂.

The determination of the specific heat capacity of the adsorbent was carried out following the same procedure as in our previous work [43]. For the activated carbon used in this study the value at the adsorption temperature (50 °C) was 1.03 J/g K.

A constant value was used for the heat transfer coefficient between gas and wall ($hw=28.7$ W/m²K), estimated for the feed conditions using the correlation proposed by Yagi and Kunii for cylindrical packed beds [44–46].

An effective thermal conductivity for the adsorbent bed was calculated using the empirical correlation developed by Prakash et al. [47] ($k_s \approx 0.11$ W/m K), while the effective thermal conductivity of the gas was estimated by Aspen Adsorption based on the axial dispersion as a function of the gas heat capacity (10):

$$k_{gz} = C_{pg} \sum_k (E_{zk} y_k) \rho_g \quad (10)$$

C_{pg} and ρ_g are the specific heat capacity and density of the gas phase, respectively. E_{zk} is the axial dispersion coefficient of component k estimated previously by the correlation (8) and y_k refers to the molar fraction of component k in the gas phase.

3. Results and discussion

In this section, experimental concentration and molar flow rate profiles along the cycle time at cyclic steady state are presented and compared to the modeling results for the four configurations evaluated in the single fixed-bed unit. Other configurations were additionally simulated and the characteristic performance parameters of all the configurations (experimental and simulation data) were discussed and compared.

3.1. Simulation of the experimental cycles

The simulation results of the four cyclic configurations evaluated experimentally in a single fixed-bed reactor are discussed below and the effect of the operating conditions (number of columns and steps and regeneration temperature) is analyzed.

3.1.1. Configuration A: VSA with 4 steps, 3 columns

The simplest VSA configuration studied comprises 4 steps: pressurization (P), adsorption (A), purge with CO₂ (R) and blowdown (B). The schematic diagram of the 4-step VSA process is illustrated in Figure 2.

During the adsorption step, the strong adsorbate in the incineration flue gas (CO₂) is preferentially adsorbed in the adsorbent bed in such a way that the gas phase (raffinate) becomes enriched in the weak adsorbate (N₂). This stage takes place at the highest pressure in the cycle to favor the potential of adsorption (in our case of study the pressure is slightly above atmospheric).

Afterward, a purge with the product (rinse) stage is carried out. A fraction of the product is recycled and fed co-currently with two main purposes: displacing the raffinate volume retained in the bed after the adsorption step and enriching the adsorbed phase. Experimentally it was simulated with a small flow of CO₂ co-current to the feed (7.3 mL/min) which represents 65% of the CO₂ in the feed during the pressurization and adsorption steps.

The product is recovered by reducing the pressure in the so-called blowdown step. In this configuration, the time of the regeneration step under vacuum was equal to the sum of the duration of pressurization with the feed and adsorption steps. Then, it requires a minimum of three columns working simultaneously to process the feed continuously.

To return to the adsorption pressure, the pressurization of the bed is carried out with the feed gas.

Figure 2. Schematic diagram of a 4-step VSA cycle.

Figure 3 compares the experimental and simulation results for the 4-step VSA experiment. Consecutive cycles, once the cyclic stationary stage is reached, are represented by overlapped symbols. Concentration profiles measured at the exit of the column are plotted for the duration of the cycle. CO_2 concentration varies from less than 5% to above 90% during the evacuation step.

Looking at the total pressure profile in Figure 3, it can be noted that the cycle starts with the pressurization of the bed, which takes less than 1 min. The drop in the total pressure of the bed during the rinse with CO_2 is caused by the reduction of the feed flow rate (from 140 mL/min during adsorption to 7.3 mL/min during rinse). At the beginning of the evacuation step, the bed pressure rapidly falls from 1.2 bar to 0.2 bar (1.2×10^5 Pa to 2×10^4 Pa). From this point, the pressure keeps decreasing but at a slower pace until it reaches the final pressure of around 40 mbar (4000 Pa). This low pressure is maintained during the purge with N_2 .

During the pressurization step, there is no gas flow at the exit of the column and so the CO_2 and N_2 concentrations detected can only be residuals in the outlet line. During both the adsorption and rinse stages, the CO_2 flow rate at the exit of the bed is negligible because CO_2 is preferentially adsorbed over N_2 and the adsorption step is ended before saturation of the activated carbon bed.

When the vacuum pump is connected to the system for the blowdown step, a peak in the flow rate is observed. The sharp N_2 peak is due to the nitrogen retained in the void spaces of the

unit and the interparticle volume of the bed. The CO₂ profile shows two consecutive peaks: the first one is probably due to the gas retained in the void volume and the second one can be attributed to the CO₂ desorbed from the activated carbon as a result of the pressure reduction.

Figure 3. Comparison of experimental (symbols) and simulated (lines) profiles at the bed exit for a 4-step VSA (configuration A): (a) N₂ (blue) and CO₂ (red) concentration and bed total pressure (green), (b) N₂ and CO₂ molar flow rates.

Simulation results show good agreement to the experimental total bed pressure (Figure 3a) and molar flow rate (Figure 3b) profiles. The simulated concentration profiles show, however, some deviation from the experimental data at the end of the evacuation step.

3.1.2. Configuration B: VSA with 5 steps, 3 columns

An additional step of purge with N₂ (Pu) can be included to concentrate the CO₂ that has not been already desorbed, preventing it from leaving the column with the raffinate during the adsorption step. This purge step is carried out at low pressure with a fraction of the raffinate after the blowdown.

Experimentally, 10 mL/min of N₂ were fed at low pressure, i.e., keeping the same vacuum level of the blowdown step. The total cycle time in this configuration was 10.8 min. To maintain a configuration with three columns, the feed and blowdown steps are scheduled to the same duration whereas the duration of both purge steps (rinse with CO₂ and purge with N₂) is reduced to half of that.

Concentration, molar flow rate and bed pressure profiles for the adsorption, rinse and blowdown steps are similar to the ones observed for the previous configuration (see Figure 4).

Figure 4. Comparison of experimental (symbols) and simulated (line) profiles at the bed exit for a 5-step VSA (configuration B): (a) N₂ (blue) and CO₂ (red) concentration and bed total pressure (green), (b) N₂ and CO₂ molar flow rates.

In this configuration, some CO₂ also exits the column during the purge step and the CO₂ concentration shows a simultaneous decay. At the beginning of the purge step (approximately $t = 550$ s), an instantaneous increase in the CO₂ molar flow rate in the effluent is observed (Figure 4b), due to sweeping effect of the N₂ purge that pushes the remaining CO₂ in the effluent line out of the bed. There is good agreement between the experimental and simulated flow rate profiles except the higher experimental CO₂ flow rate observed at the beginning of the purge step.

The simulated concentrations of both gases during the purge step seem to get ahead to the experimental profiles. This could be attributed to a delay in the experimental measurement due to the low gas flow rate at the outlet of the column.

3.1.3. Configuration C: VSA with 5 steps, 4 columns

Previous results showed the feasibility of a 5-step configuration in a VSA system. In this section, the effect of the number of columns is assessed. For that purpose, an experiment was carried out in the single fixed-bed unit simulating a 5-step VSA operation with 4 columns.

When increasing the number of columns from 3 to 4, the cycle duration needs to be extended to keep a continuous feed to the process. The total cycle time was established in 14.4 min, setting a R/F ratio of 0.65 and a set point for the evacuation pressure of 5 mbar (500 Pa).

A similar pressure profile to configuration B previously analyzed is observed (see Figure 5a). The total pressure of the bed is around atmospheric values for the adsorption and rinse steps, while sub-atmospheric pressure is reached when the vacuum pump is connected to the system. The extension of the rinse and purge steps slightly changes the CO₂ and N₂ concentration profiles at the column outlet.

Comparing this configuration with the 4-step VSA cycle with the same duration for the rinse step (configuration A), the CO₂ concentration at the exit during adsorption and rinse is somehow lower, less than 1.5% vs around 5% in the previous case. Hence, it will result in a higher purity of N₂ and a lower loss of CO₂ during these two stages. Experimental results show that the final concentration of CO₂ reached at the end of the blowdown step is similar to case A (Figure 3a) but slightly higher than in case B (Figure 4a). Besides, desorption seems to be somehow faster.

Figure 5. Comparison of experimental (symbols) and simulated (lines) profiles at the bed exit for a 5-step VSA (configuration C): (a) N₂ (blue) and CO₂ (red) concentration and bed total pressure (green), (b) N₂ and CO₂ molar flow rates.

The N₂ purge step time is twice that in configuration B. This results in a better correspondence between the associated experimental and simulated concentration profiles. Regarding the molar flow rate profiles of both gases, the simulated and experimental results overlapped. However, as previously observed for configuration B, the CO₂ peak at the beginning of the purge stage does not reach the high values measured in the experimental cycles.

3.1.4. Configuration D: VTSA with 5 steps, 3 columns

An alternative to enable a deeper regeneration of the adsorbent and, therefore, a higher recovery would be a combination of thermal regeneration and vacuum, i.e., VTSA (Vacuum Temperature Swing Adsorption) process. Energy requirements of a VTSA could be even lower than those of a VSA process if a residual heat source was available; when applying moderate heating to the bed, the vacuum required to achieve the regeneration could be reduced.

Hence, a final experiment with the 5-step/3-bed configuration was studied combining VSA and TSA. During the regeneration stage, the pressure is lowered to vacuum levels and at the same time, the temperature of the bed is raised to 70 °C. The simulation of this case was carried out considering a non-isothermal energy balance.

Similar conditions of step times, R/F ratio and vacuum level as in case B were applied in this configuration. The corresponding profiles are illustrated in Figure 6. Some differences can be noticed during the evacuation step due to the rise in temperature. For instance, the maximum concentration of CO₂ achieved is higher than in configuration B. Also, the desorption seems to be faster as observed from the steeper concentration profile compared with configuration B where the blowdown temperature was kept at 50 °C.

Figure 6. Comparison of experimental (symbols) and simulated (lines) profiles at the bed exit for a VTSA (configuration D): (a) N₂ (blue) and CO₂ (red) concentration and bed total pressure (green), (b) N₂ and CO₂ molar flow rates.

3.2. Other configurations

In VSA processes, the blowdown stage is generally carried out counter-current to the feed to maximize the product purity and prevent contamination with the raffinate accumulated at the exit of the bed. This also applies to the purge with raffinate (N_2).

Due to limitations of our laboratory set-up, counter-current configurations could not be tested experimentally. However, taking advantage of the mathematical model developed and validated experimentally for the co-current configurations they could be simulated.

A schematic diagram of a counter-current configuration is indicated in Figure 7. The 5-step VSA cycle considered in this simulation consists of the following steps: pressurization with feed (P), adsorption (A), co-current rinse with CO_2 (R), counter-current evacuation (B) and counter-current purge (Pu).

Figure 7. Example of the scheme followed for a 5-step counter-current VSA process.

The blowdown step takes place counter-current to the feed. Hence, CO_2 desorbed exits the column from the top. As can be seen in Figure 8, the CO_2 peak appears at the same time as the N_2 , while in the co-current evacuation (Figure 5b) it was delayed. In the case of the counter-current evacuation, CO_2 departs the adsorber immediately as the more concentrated stream is now near the exit.

Figure 8. N_2 (blue) and CO_2 (red) throughout the cycle for the counter-current simulation of configuration C: (a) molar flow rate and (b) concentration profile at the exit and bed pressure (green).

Besides, the flow rate profiles of N_2 and CO_2 in Figure 8 show a faster regeneration than when carried out in co-current; this would allow shortening the evacuation time without causing a significant reduction in CO_2 recovery.

To enhance the CO_2 purity, the N_2 flow rate during the purge step should be optimized to the minimum. Therefore, configuration C was simulated both co-and counter-current introducing just 2.5 mL/min of N_2 during the purge stage (see Figure 9).

As it could be expected, a reduction of the N_2 flow changes the gas concentration profiles in this stage (see Figure 9a): the CO_2 concentration at the end of the purge step almost doubles (42.7% vs 24.8%) compared to the higher purge flow rate (see Figure 5a).

Figure 9. N₂ and CO₂ concentration and bed pressure profiles for the simulated configuration C: (a) co-current and (b) counter-current with 2.5 mL/min of N₂ flow rate throughout the purge step, and (c) including two equalization steps (7-step configuration).

When more than two adsorption columns are contemplated, pressure equalization steps can also be employed to enhance CO₂ purity [48–50]. In the present simulation, two equalization steps were incorporated to the configuration C (4 columns), in co-current conditions, from bottom-to-top of the bed. After the rinse with CO₂ step at atmospheric pressure, the gas at the bottom of the column, mainly composed of N₂, is transferred to another bed at a lower pressure until their pressures are equal. Hence, the cycle step sequence, shown in Figure 10, is as follows: (I) pressurization, (II) adsorption, (III) rinse, (IV) pressure equalization down, (V) blowdown, (VI) purge and (VII) pressure equalization up. In the pressure profile displayed in Figure 9c, the equalization steps can be perceived as the pressure remains constant for a few seconds during the pressurization and depressurization sections.

Figure 10. Description of the consecutive steps of the VSA cycle with pressure equalization stages.

3.3. Comparison of experimental and simulated results

Table 4 summarizes the CO₂ purity and recovery achieved for the experimental and simulated configurations, both co- and counter-current. The parameters were determined using equations (2) and (3), in the case of configuration A, and equations (4) and (5), for the configurations B, C and D. Raffinate purity, estimated using equation (1), is also presented. The deviation between experimental and simulation results for the co-current configurations are shown in parentheses.

Table 4. Summary of the characteristic parameters estimated for the cyclic configurations studied.

Configuration			Raffinate purity (vol.% N ₂)	Product purity (vol.% CO ₂)	Product recovery (vol.% CO ₂)
A	Experimental	Co-current	96.4	39.1	61.3
	Simulation		92.9	40.7	66.5
		Co-current	(-3.6 %)	(+4.0 %)	(+8.5 %)
		Counter-current	96.9	44.3	82.2
B	Experimental	Co-current	98.7	33.8	89.9
	Simulation		97.1	33.1	84.1
		Co-current	(-1.6 %)	(-2.0 %)	(-6.5 %)
		Counter-current	98.6	32.8	89.0
C	Experimental	Co-current	99.4	39.4	96.0
	Simulation		97.8	36.6	95.4
		Co-current	(-1.6 %)	(-7.1 %)	(-0.6 %)
		Counter-current	98.9	35.4	98.5
D	Experimental	Co-current	99.3	38.8	91.5
	Simulation		97.9	35.2	90.4
		Co-current	(-1.4 %)	(-9.3 %)	(-1.2 %)
		Counter-current	98.8	35.0	93.4

The minimum N₂ purity achieved experimentally was 96.4% (4-step VSA configuration) and a maximum concentration of 99.4% was reached for the 5-step VSA configuration. When comparing the simulation results, slightly higher values of N₂ purity are obtained in counter-current than in co-current for a defined configuration.

The purge with N₂ favors CO₂ desorption, therefore a significant increase in CO₂ recovery can be perceived in configurations B, C, and D compared to configuration A. However, this results in a small loss of purity in CO₂ when a higher flow rate of N₂ (10 mL/min) is applied.

Increasing the number of columns has a favorable effect in terms of both CO₂ purity and recovery. Likewise, these parameters are slightly benefited from the increase of the bed temperature during the blowdown step in the VTSA configuration.

Comparing the values estimated from experimental runs with the results obtained after the simulation with Aspen Adsorption, it is observed that product purity and recovery in the simulation are slightly overpredicted when the evacuation step is contemplated solely, while the opposite occurs when a purge stage is incorporated to the cycle. Nevertheless, the same trend is observed both experimentally and in the simulation of the different configurations.

The greatest CO₂ purity was accomplished in configuration A and the lowest in case B, whereas the minimum and maximum product recovery were obtained in configurations A and C, respectively. As stated before, this is related to the introduction of the purge step in the cyclic configuration. Consequently, the purity and recovery of CO₂ attained during the blowdown stage exclusively, for the configurations B, C, and D, are plotted in Figure 11.

Figure 11. Comparison of CO₂ purity (a) and recovery (b) estimated for the blowdown step: co-current (green solid fill) and counter-current (diagonal yellow stripes) simulation results for the 5-step configurations B, C and D.

The product purity notably increases in all counter-current configurations (see Figure 11a) compared to the average values presented in Table 4. On the other hand, CO₂ recovery in counter-current operation is also favored (see Figure 11b) but the values obtained are significantly lower to those reported in Table 4 where the purge step is also considered.

As previously mentioned further simulations were performed with the 5-step, 4-column VSA (configuration C) reducing the N₂ purge flow rate and including pressure equalization. The values estimated for the characteristic parameters (equations (1), (4) and (5)) are collected in Table 5.

Table 5. Comparison of the results obtained for the additional simulations of configuration C.

Configuration		Raffinate purity (vol.% N ₂)	Product purity (vol.% CO ₂)	Product recovery (vol.% CO ₂)
Lower N ₂ purge flow rate	Co-current	96.7	38.7	87.6
	Counter-current	98.4	39.2	93.7
With two equalization steps	Co-current	98.0	45.2	90.7

Comparing with the simulation results of configuration C (see Table 4), a decrease in the N₂ flow rate during the purge step diminishes CO₂ recovery. This effect is particularly relevant in the co-current configuration. Conversely, CO₂ purity increases: values of 38.7% and 39.2%

were reached for the co- and counter-current simulations, respectively. Similar behavior also occurs when adding the two pressure equalization steps. It is for the 7-step configuration carried out co-currently where the highest CO₂ purity is reached (45.2%). The raffinate purity is less affected by both changes introduced in the cycles.

4. Conclusions

One-stage vacuum swing adsorption configurations intended for the separation of CO₂ from a Waste-to-Energy plant were experimentally tested in a lab-scale fixed-bed unit. For this purpose, pine sawdust activated carbon was selected as adsorbent.

Introducing a purge step with N₂ increased greatly the total product recovery at the expense of a reduction in the CO₂ purity whereas additional columns improved both the purity and recovery of CO₂. The maximum CO₂ purity, 39.4%, was reached experimentally in the 5-step VSA configuration simulating an operation with 4 adsorption beds.

With the aid of commercial software, the mathematical model of the adsorption process was developed and the experimental configurations were simulated. Despite some differences observed in the concentration curves during the evacuation stage between the experiments and the simulation, the prediction of the characteristic parameters of the cyclic configurations analyzed was accurate.

It was also possible to evaluate the effect of the N₂ flow rate used during the purge step, as well as the introduction of two pressure equalization steps. Both alternatives increase the CO₂ purity and the highest value, 45.2%, was reached when pressure equalization was introduced in the cycle configuration.

As far as the regeneration method is concerned, the increase of the bed temperature during the evacuation stage showed benefits on the product purity and recovery. Therefore, this option is of particular interest in Waste-to-Energy plants where residual heat sources are readily available.

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References

- [1] UNFCCC. Conference of the Parties (COP), Adoption of the Paris Agreement-Conference of the Parties COP 21, (2015). doi:FCCC/CP/2015/L.9/Rev.1.
- [2] International Energy Agency, 20 Years of Carbon Capture and Storage: Accelerating Future Deployment, 2016. doi:10.1787/9789264267800-en.
- [3] N. Pour, P.A. Webley, P.J. Cook, Potential for using municipal solid waste as a resource for bioenergy with carbon capture and storage (BECCS), *Int. J. Greenh. Gas Control*. 68 (2018) 1–15. doi:10.1016/J.IJGGC.2017.11.007.
- [4] P. Huttenhuis, A. Roeloffzen, G. Versteeg, CO₂ capture and re-use at a waste incinerator, *Energy Procedia*. 86 (2016) 47–55. doi:10.1016/j.egypro.2016.01.006.
- [5] Global CSS Institute, Bioenergy and carbon capture and storage, 2019.
- [6] C. Gouedard, D. Picq, F. Launay, P.L. Carrette, Amine degradation in CO₂ capture. I. A review, *Int. J. Greenh. Gas Control*. 10 (2012) 244–270. doi:10.1016/j.ijggc.2012.06.015.
- [7] X. Chen, G. Huang, C. An, Y. Yao, S. Zhao, Emerging N-nitrosamines and N-nitramines from amine-based post-combustion CO₂ capture – A review, *Chem. Eng. J.* 335 (2018) 921–935. doi:10.1016/j.cej.2017.11.032.
- [8] K.T. Leperi, R.Q. Snurr, F. You, Optimization of Two-Stage Pressure/Vacuum Swing Adsorption with Variable Dehydration Level for Postcombustion Carbon Capture, *Ind. Eng. Chem. Res.* 55 (2016) 3338–3350. doi:10.1021/acs.iecr.5b03122.
- [9] G.N. Nikolaidis, E.S. Kikkinides, M.C. Georgiadis, An Integrated Two-Stage P/VSA Process for Postcombustion CO₂ Capture Using Combinations of Adsorbents Zeolite 13X and Mg-MOF-74, *Ind. Eng. Chem. Res.* 56 (2017) 974–988. doi:10.1021/acs.iecr.6b04270.

- [10] J.-H. Park, H.-T. Beum, J.-N. Kim, S.-H. Cho, Numerical Analysis on the Power Consumption of the PSA Process for Recovering CO₂ from Flue Gas, *Ind. Eng. Chem. Res.* 41 (2002) 4122–4131. doi:10.1021/ie010716i.
- [11] M.G. Plaza, I. Durán, F. Rubiera, C. Pevida, CO₂ adsorbent pellets produced from pine sawdust: Effect of coal tar pitch addition, *Appl. Energy*. 144 (2015) 182–192. doi:10.1016/j.apenergy.2014.12.090.
- [12] I. Durán, F. Rubiera, C. Pevida, Separation of CO₂ in a solid waste management incineration facility using activated carbon derived from pine sawdust, *Energies*. 10 (2017) 827–846. doi:10.3390/en10060827.
- [13] D. Ruthven, S. Farooq, K. Knaebel, *Pressure Swing Adsorption*, VCH Publishers, 1994.
- [14] P. Guerin de Montgareuil, D. Domine, Process for separating a binary gaseous mixture by adsorption, U.S. patent no 3155468, 1964.
- [15] C.W. Skarstrom, Method and apparatus for fractionating gaseous mixtures by adsorption, U.S. patent no. 2944627, 1960.
- [16] W.D. Marsh, F.S. Pramuk, R.C. Hoke, C.W. Skarstrom, Pressure equalization depressuring in heatless adsorption, U.S. patent no. 3142547, 1964.
- [17] N.H. Berlin, Method for providing an oxygen-enriched environment, U.S. patent no. 3280536, 1966.
- [18] R. Ben-Mansour, M.A. Habib, O.E. Bamidele, M. Basha, N.A.A. Qasem, A. Peedikakkal, T. Laoui, M. Ali, Carbon capture by physical adsorption: Materials, experimental investigations and numerical modeling and simulations – A review, *Appl. Energy*. 161 (2016) 225–255. doi:10.1016/j.apenergy.2015.10.011.
- [19] Y.J. Kim, Y.S. Nam, Y.T. Kang, Study on a numerical model and PSA (pressure swing adsorption) process experiment for CH₄/CO₂ separation from biogas, *Energy*. 91 (2015) 732–741. doi:10.1016/j.energy.2015.08.086.
- [20] M. Xu, H.-C. Wu, Y.S. Lin, S. Deng, Simulation and optimization of pressure swing

- adsorption process for high-temperature air separation by perovskite sorbents, *Chem. Eng. J.* 354 (2018) 62–74. doi:10.1016/J.CEJ.2018.07.080.
- [21] T.S. Bhatt, G. Storti, R. Rota, Detailed simulation of dual-reflux pressure swing adsorption process, *Chem. Eng. Sci.* 122 (2015) 34–52. doi:10.1016/j.ces.2014.09.013.
- [22] D. Ferreira, P. Bárcia, R.D. Whitley, A. Mendes, Single-Stage Vacuum Pressure Swing Adsorption for Producing High-Purity Oxygen from Air, *Ind. Eng. Chem. Res.* 54 (2015) 9591–9604. doi:10.1021/acs.iecr.5b02151.
- [23] M. Rokanuzzaman, A. Veawab, A. Aroonwilas, Design Method for Layered-bed Adsorption Column for Separation of CO₂ and N₂ from Natural Gas, *Energy Procedia.* 114 (2017) 2441–2449. doi:10.1016/j.egypro.2017.03.1391.
- [24] D. Nikolic, A. Giovanoglou, M.C. Georgiadis, E.S. Kikkinides, Generic Modeling Framework for Gas Separations Using Multibed Pressure Swing Adsorption Processes, *Ind. Eng. Chem. Res.* 47 (2008) 3156–3169. doi:10.1021/ie0712582.
- [25] S. Cavenati, C.A. Grande, A.E. Rodrigues, Removal of Carbon Dioxide from Natural Gas by Vacuum Pressure Swing Adsorption, *Energy & Fuels.* 20 (2006) 2648–2659. doi:10.1021/ef060119e.
- [26] P.G. Aguilera, F.J. Gutiérrez Ortiz, Prediction of fixed-bed breakthrough curves for H₂S adsorption from biogas: Importance of axial dispersion for design, *Chem. Eng. J.* 289 (2016) 93–98. doi:10.1016/j.cej.2015.12.075.
- [27] M.S. Shafeeyan, W.M.A.W. Daud, A. Shamiri, N. Aghamohammadi, Modeling of Carbon Dioxide Adsorption onto Ammonia-Modified Activated Carbon: Kinetic Analysis and Breakthrough Behavior, *Energy & Fuels.* 29 (2015) 6565–6577. doi:10.1021/acs.energyfuels.5b00653.
- [28] J. Xiao, Y. Peng, P. Bénard, R. Chahine, Thermal effects on breakthrough curves of pressure swing adsorption for hydrogen purification, *Int. J. Hydrogen Energy.* 41 (2016) 8236–8245. doi:10.1016/j.ijhydene.2015.11.126.

- [29] R.R. Vemula, M. V. Kothare, S. Sircar, Lumped heat and mass transfer coefficient for simulation of a pressure swing adsorption process, *Sep. Sci. Technol.* 52 (2017) 35–41. doi:10.1080/01496395.2016.1242629.
- [30] C. Shen, Z. Liu, P. Li, J. Yu, Two-Stage VPSA Process for CO₂ Capture from Flue Gas Using Activated Carbon Beads, *Ind. Eng. Chem. Res.* 51 (2012) 5011–5021. doi:10.1021/ie202097y.
- [31] G.N. Nikolaidis, E.S. Kikkinides, M.C. Georgiadis, Model-Based Approach for the Evaluation of Materials and Processes for Post-Combustion Carbon Dioxide Capture from Flue Gas by PSA/VSA Processes, *Ind. Eng. Chem. Res.* 55 (2016) 635–646. doi:10.1021/acs.iecr.5b02845.
- [32] P. Xiao, J. Zhang, P. Webley, G. Li, R. Singh, R. Todd, Capture of CO₂ from flue gas streams with zeolite 13X by vacuum-pressure swing adsorption, *Adsorption*. 14 (2008) 575–582. doi:10.1007/s10450-008-9128-7.
- [33] R. Haghpanah, R. Nilam, A. Rajendran, S. Farooq, I.A. Karimi, Cycle synthesis and optimization of a VSA process for postcombustion CO₂ capture, *AIChE J.* 59 (2013) 4735–4748. doi:10.1002/aic.14192.
- [34] Z. Liu, C. a. Grande, P. Li, J. Yu, A.E. Rodrigues, Multi-bed vacuum pressure swing adsorption for carbon dioxide capture from flue gas, *Sep. Purif. Technol.* 81 (2011) 307–317. doi:10.1016/j.seppur.2011.07.037.
- [35] K.N. Pai, J.D. Baboolal, D.A. Sharp, A. Rajendran, Evaluation of diamine-appended metal-organic frameworks for post-combustion CO₂ capture by vacuum swing adsorption, *Sep. Purif. Technol.* 211 (2019) 540–550. doi:10.1016/j.seppur.2018.10.015.
- [36] L. Joss, M. Mazzotti, Modeling the extra-column volume in a small column setup for bulk gas adsorption, *Adsorption*. 18 (2012) 381–393. doi:10.1007/s10450-012-9417-z.
- [37] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, 1st Ed., John Wiley & Sons, Hoboken, 1960.

- [38] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, John Wiley & Sons, 1984.
- [39] K.R. Wood, Y.A. Liu, Y. Yu, Simulation of Adsorption Processes, in: Des. Simulation, Optim. Adsorpt. Chromatogr. Sep. A Hands-On Approach., 2018.
- [40] W. Kast, Adsorption aus der Gasphase: ingenieurwissenschaftliche Grundlagen und technische Verfahren, Wiley-VCH, 1988. In German.
- [41] R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, 7th Ed., McGraw-Hill, 1997.
- [42] M.S. Shafeeyan, W.M.A.W. Daud, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, J. Anal. Appl. Pyrolysis. 89 (2010) 143–151. doi:10.1016/j.jaap.2010.07.006.
- [43] M.G. Plaza, I. Durán, N. Querejeta, F. Rubiera, C. Pevida, Experimental and Simulation Study of Adsorption in Postcombustion Conditions Using a Microporous Biochar. 1. CO₂ and N₂ Adsorption, Ind. Eng. Chem. Res. 55 (2016) 3097–3112. doi:10.1021/acs.iecr.5b04856.
- [44] S. Yagi, D. Kunii, Studies on heat transfer near wall surface in packed beds, AIChE J. 6 (1960) 97–104. doi:10.1002/aic.690060119.
- [45] D. Kunii, J.M. Smith, Heat transfer characteristics of porous rocks, AIChE J. 6 (1960) 71–78. doi:10.1002/aic.690060115.
- [46] J. Park, J.W. Lee, Dynamic modeling of fixed-bed adsorption of flue gas using a variable mass transfer model, Korean J. Chem. Eng. 33 (2016) 438–447. doi:10.1007/s11814-015-0180-1.
- [47] M.J. Prakash, M. Prasad, K. Srinivasan, Modeling of thermal conductivity of charcoal–nitrogen adsorption beds, Carbon N. Y. 38 (2000) 907–913. doi:10.1016/S0008-6223(99)00202-X.
- [48] R.T. Yang, Gas Separation by Adsorption Processes, Butterworth, 1987.

- [49] P.A. Webley, A. Qader, A. Ntiamoah, J. Ling, P. Xiao, Y. Zhai, A New Multi-bed Vacuum Swing Adsorption Cycle for CO₂ Capture from Flue Gas Streams, *Energy Procedia*. 114 (2017) 2467–2480. doi:10.1016/j.egypro.2017.03.1398.
- [50] A. Ntiamoah, J. Ling, P. Xiao, P.A. Webley, Y. Zhai, CO₂ capture by vacuum swing adsorption: role of multiple pressure equalization steps, *Adsorption*. 21 (2015) 509–522. doi:10.1007/s10450-015-9690-8.