Parametric study of CO₂ separation using carbon molecular sieve, zeolite and silica gel

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Abstract. Performances of Pressure swing adsorption (PSA) dependent on the type of adsorbent and efficiency of the regeneration cycle. In this work, a model describing CO₂ mixture flow, mass and heat transfer with multi-component adsorption model are developed in Aspen Adsorption environment to compare the performance of PSA cycles with three different adsorbents (CMS 3K, zeolite 13x and silica gel). Adsorption capacity of CO₂ for three adsorbents was found to be in the order of CMS>zeolite>silica gel. Hence, CMS was chosen as the adsorbents to evaluate PSA performances on different feed flowrate and pressure based on the purity, recovery and productivity of the CO₂ separation. The result shows that, within a certain range, higher adsorption pressure will increase all purity, recovery and productivity of CO₂ while higher feeding rate leads to increase recovery but lower purity and productivity.

1. Introduction
Pressure Swing Adsorption (PSA) technology has been widely studied for CO₂ capture at both pilot-scale or laboratory levels in pursuit of more low-energy, environmentally friendly and cost-effective separation techniques [1]. The behaviour of a PSA unit is mainly determined by two important factors that are employing a high capacity adsorbent and effective engineering strategy for regeneration. The studies on PSA process performances aimed at separating CO₂ by experiment and simulation using different adsorbent and working configuration have been reviewed in literature elsewhere [1, 2].

One of the important basis subjects to study the adsorption process performances is by the breakthrough curve [3, 4]. Shafeeyan et al. has performed a parametric study of CO₂/H2/N2 gas mixture on commercial activated carbon. The CO₂ partial pressure was observed to be the most influential variable, with high values leading to an increase in both the CO₂ capture capacity and the breakthrough time [5]. However, an increase in the temperature led to a decrease in adsorption capacity and breakthrough time [5,6]. In order to determine the performance of the carbon molecular sieve for separation of binary CO₂/CH4 mixture, Rocha et al. have studied the breakthrough curve of CO₂ at 10 and 70 bars. The result shows that at higher pressure, more content of CO₂ has been detected at the outlet which reduces the selectivity and capacity of the adsorbent [7]. More breakthrough experiments were performed to study various parameters and adsorption capacity [8–17].

With the basis of breakthrough curve study, a reliable full-cycle PSA experiment and simulations can be carried out [3]. The performance indicators for PSA cycle depends on the purity, recovery and productivity of the product. Most current reports show that CO₂ PSA process to achieve CO₂ purities of over 90% with recovery ranging from 70% to 90% [18–20]. Cho et al. studied a 2-bed PSA with the 2-stage process at each stage using zeolite 13X to obtain 99.7% CO₂ purity with 78.8% recovery. Delgado
et al. conducted experimental and simulation study of CO₂ adsorption on activated carbon with 3-bed 12-step. The objective of this work is to study the feasibility of carbon dioxide concentration and recovery using a novel VSA cycle without rinse step, which has the potential of significantly reducing the power consumption of this process. According to the simulated results, it is possible to CO₂ with high purity (>93%) and recovery (>90%) [21]. Webley et al. address the concern on a typical 2-bed cycle that poor due to the lack of room to incorporate more relevant auxiliary intermediate process steps such as pressure equalization, co-current purge, etc. A breakthrough and performance study on 4-bed VPSA that has been developed shows >75% recovery with a purity of > 95% was obtained [18].

The performances of PSA unit is highly dependent on ideal adsorbent with high capacity and selectivity as well effective process configuration and engineering strategy. Therefore, it is very important to identify the best material for adsorbent and to carried out parametric study on different operating parameter in order to evaluate the PSA performances. The current work has focused on building a mathematical model of a single adsorption bed and PSA system in Aspen Adsorption environment. The breakthrough study was conducted to compare the CO₂ adsorption performances of carbon molecular sieve (CMS), zeolite and silica gel in. Based on the comparison, the best adsorbent has been selected for further study on PSA 2-bed 4-step process towards the separation of CO₂ and N₂. Subsequently, parametric study has been done to discover the effect of adsorption pressure and feed flow rate on the CO₂ purity and recovery.

2. Methodology

The PSA system for gas mixture CO₂ and N₂ were generated using a built-in property database module from Aspen Adsorption V9 software as shown in Figure 1. The breakthrough study was carried out by a single adsorption unit and 2-bed PSA model simulated to study the performances of PSA. The PSA cycle consists of the 4 steps Skarstorm cycle which are pressurization (PR), adsorption (AD), blowdown (BD) and purge (PG). Table 1 shows the list of properties of column and adsorbents for simulation. The properties of CMS3K, zeolite and silica gel were obtained from the previous study which has been carried out experimentally and validated by simulation.

![Figure 1. (a) Single adsorption bed for breakthrough study (b) 2-bed 4-steps PSA.](image-url)
Table 1. Column and adsorbents properties.

| Properties                  | Value |
|-----------------------------|-------|
| **Column parameter**        |       |
| Bed length (in)             | 24    |
| Bed diameter                | 16    |
| Gas composition             | CO\textsubscript{2}/N\textsubscript{2} (0.4/0.6) |
| **Adsorbent parameter**     | ZEOLITE | AC | CMS |
| Inter-particle voidage      | 0.33  | 0.35 | 0.33 |
| Intra-particle voidage      | 0.54  | 0.33 | 0.46 |
| Bulk solid density of adsorbent | 756 | 522 | 715 |
| Adsorbent particle radius   | 8.00E-04 | 0.0012 | 0.009 |
| CO\textsubscript{2} Constant mass transfer coefficients | 0.00726 | 9.199 | 0.018 |
| N\textsubscript{2} Constant mass transfer coefficients | 0.00474 | 1.786 | 0.112 |
| **Isotherm parameter**      |       |
| IP(1,"CO\textsubscript{2}") | 4.98E-04 | 0.00554 | 0.00033 |
| IP(1,"N\textsubscript{2}") | 3.37E-06 | 0.00375 | 0.0022 |
| IP(2,"CO\textsubscript{2}") | 0.0105 | 0.00049 | 0.0021 |
| IP(2,"N\textsubscript{2}") | 0.871 | 0.00054 | 0.00042 |
| IP(3,"CO\textsubscript{2}") | 0.492 | 0.811 | 0.43 |
| IP(3,"N\textsubscript{2}") | 0.796 | 0.937 | 0.885 |
| IP(4,"CO\textsubscript{2}") | 2160 | 2300 | 2850 |
| IP(4,"N\textsubscript{2}") | 1460 | 1610 | 1740 |
| IP(5,"CO\textsubscript{2}") | 0.00147 | 0.0018 | 0.0031 |
| IP(5,"N\textsubscript{2}") | 0.00106 | 0.00104 | 0.0001 |
| IP(6,"CO\textsubscript{2}") | 2040 | 1720 | 2450 |
| IP(6,"N\textsubscript{2}") | 1360 | 0 | 1970 |

2.1. Mathematical modeling

A summary of theoretical assumptions employed for the dynamic simulation of CO\textsubscript{2} adsorption on packed bed column is presented below:

- Discretization: Upwind Differencing Scheme 1,
- Mass balance: Convection only
- Momentum balance: Ergun equation
- Kinetic assumption: Linear Lumped resistance
- Isotherm: Extended Langmuir-Freundlich
- Energy balance: Non-isothermal with no conduction
- Reaction: None
- No radial concentration profiles
- No velocity gradients

**Mass conservation equation**

The overall mass conservation equation can be written as follows:

\[-D_i \frac{\partial^2 y_i}{\partial z^2} + \frac{\partial u_i}{\partial t} + u_x \frac{\partial y_i}{\partial z} + \frac{RT}{p} \frac{1}{\varepsilon_b} \rho_p \left( \sum_{j=1}^{N} \frac{\partial q_j}{\partial t} \right) = 0 \]  \hspace{1cm} (1)
where $D_L$ is the axial dispersion coefficient, $u_z$ is the axial physical velocity, $y_i$ and $q_i$ are the molar fraction and the adsorbed phase concentration of species $i$, respectively, $e_b$ is the bed void fraction, $r_p$ is the pellet density of the adsorbent, $R$ is the universal gas constant and $p$ is pressure in the adsorption bed, $t$ and $z$ are the time and axial position in the bed, respectively.

**Energy conservation equation**

The energy conservation for the gas and solid phase of an adsorption bed is given by

$$-\varepsilon_b K_L \frac{\partial^2 T}{\partial z^2} + (\varepsilon_t \rho_g C_{pg} + \rho_b C_{ps}) \frac{\partial T}{\partial t} + \rho_b C_{ps} \varepsilon_b u_z \frac{\partial T}{\partial z} - \rho_b \sum_i Q_i \frac{\partial q_i}{\partial t} + \frac{2h}{k} (T - T_w) = 0$$

(2)

where $K_L$ is the thermal axial dispersion coefficient, $C_{pg}$ is the heat capacity of the gas phase, $C_{ps}$ is the specific heat capacity of the adsorbent, $\varepsilon_t$ is the total void fraction of the bed, $Q_i$ is the heat of adsorption of species $i$, $T_w$ is the wall temperature.

**Adsorption isotherms and kinetics**

The extended Langmuir-Freundlich model was used to express the adsorption isotherms of a multicomponent gas:

$$q_i^* = \frac{q_{mi} B_i p_i}{1 + \sum_{j=1}^{N} B_j p_j}$$

(3)

Where $q_i^*$ is the equilibrium adsorbed phase concentration, $q_{mi}$ and $B_i$ are the extended Langmuir-Freundlich isotherm parameters, and $p_i$ is the partial pressure of species $i$.

**Momentum conservation equation**

The momentum balance in a bed is given by Ergun’s equation:

$$-\frac{dp}{dz} = a \mu v_z + b \rho v_z |\vec{v}|$$

(4)

with the coefficients:

$$a = \frac{150}{4R_p^2} \frac{(1-e_b)^2}{\varepsilon_b^3}, \quad b = 1.75 \frac{1-e_b}{2R_p \varepsilon_b^3}$$

(5)

where $m$ is the dynamic viscosity, $v_z$ is Darcy's velocity, and $R_p$ is the particle radius.

**Equation of state**

From the ideal gas equation of state, $pV = nRT$, the molar concentration of the mixture can be written as $c = pV = nRT$. The molar concentration of component $i$ can be written as

$$y_i = \frac{n_i}{n} = \frac{n_i/V}{c} = \frac{c_i}{c} \frac{c_{RT}}{p}, \quad i = 1, \ldots, N.$$  

(6)

The specific heat capacity of the mixture is calculated from the molar fraction weighted average as

$$C_{pg} = \sum_{i=1}^{N} y_i C_{pi}$$

(7)

The density of the mixture can be calculated by

$$\rho = cM = c \sum_{i=1}^{N} y_i M_i$$

(8)
PSA performance indicator
The performance with measuring some important performance indicators such as product purity, product recovery, product productivity:

\[
\text{CO}_2 \text{ purity (\%)} = \frac{\int_{t=0}^{t=\text{tBD}} n_{\text{CO}_2} |_{\text{Extract}} \, dt + \int_{t=0}^{t=\text{tPG}} n_{\text{CO}_2} |_{\text{Extract}} \, dt}{\sum_{i=0}^{n} \int_{t=0}^{t=\text{tBD}} n_{i} |_{\text{Extract}} \, dt + \sum_{i=0}^{n} \int_{t=0}^{t=\text{tPG}} n_{i} |_{\text{Extract}} \, dt}
\] (9)

\[
\text{CO}_2 \text{ recovery (\%)} = \frac{\int_{t=0}^{t=\text{tBD}} n_{\text{CO}_2} |_{\text{Extract}} \, dt + \int_{t=0}^{t=\text{tPG}} n_{\text{CO}_2} |_{\text{Extract}} \, dt}{\int_{t=0}^{t=\text{tPR}} n_{\text{CO}_2} |_{\text{Feed}} \, dt + \int_{t=0}^{t=\text{tAD}} n_{\text{CO}_2} |_{\text{Feed}} \, dt}
\] (10)

\[
\text{Productivity (mol/kg.s)} = \frac{\int_{t=0}^{t=\text{tBD}} n_{\text{CO}_2} |_{\text{Extract}} \, dt + \int_{t=0}^{t=\text{tPG}} n_{\text{CO}_2} |_{\text{Extract}} \, dt}{t_{\text{cycle}} \times m_{\text{adsorbent}}}
\] (11)

3. Result and discussion
The column dynamic breakthrough study was built by using a single column adsorption bed. The gas mixture of CO\textsubscript{2}/N\textsubscript{2} has been introduced to the bed with fixed operating condition for all the adsorbents to solely study their adsorption capacity. The operating pressure and temperature were fixed at 5 bar and 298.15K respectively.

Breakthrough occurs when adsorbate reaches the end of the column and leaves with the column effluent. Breakthrough curves are plots of the adsorbate concentration in the column effluent as a function of time. Comparison of CO\textsubscript{2} adsorption on CMS 3K, zeolite 13x and silica gel have been studied by the breakthrough graph. The longest breakthrough time favour adsorption the most because it provides enough residence time for the adsorption process to reach equilibrium. The steepness of the graph also plays important roles as it represents the adsorption capacity. The result of the breakthrough graph in Figure 2. shows that CMS 3K proved to be the best material for separation of CO\textsubscript{2} and N\textsubscript{2}, with the longest breakthrough time at 322s and the steepest graph compares to the other two adsorbents which represent high CO\textsubscript{2} adsorption capacity. Zeolite 13x showed the second-largest breakthrough time at 295s and lastly silica gel with the shortest breakthrough time at 124s. Hence, CMS was chosen as the adsorbents for further study of PSA separation of CO\textsubscript{2} and N\textsubscript{2} due to its highest CO\textsubscript{2} adsorption capacity.

![Figure 2. Breakthrough graph for zeolite 13x, silica gel and CMS 3K.](image)

The effect of adsorption pressure and feeding flowrate on the PSA cycle performance are studied while other parameters are being constant. The influence of adsorption pressure was studied by varies the pressure from 1 to 7 bar. Figure 3. shows that as the pressure increases, the purity, recovery and productivity of CO\textsubscript{2} also increase up to 79.3%, 95% and 0.89 mol/s/kg respectively. However, it is noticeable that the purity of CO\textsubscript{2} is low and being stagnant from 4 bars onwards. This is reasonable...
because of the positive correlation between adsorption pressure and adsorption capacity. When the pressure is high, both adsorbates (CO$_2$/N$_2$) tend to adsorb more deeply into the adsorbent. The purity also was influenced by the raffinate gas that been supply from another column at the blowdown stage.

![Figure 3. Effect of different pressure on CO2 purity, recovery and productivity.](image)

**Figure 3.** Effect of different pressure on CO2 purity, recovery and productivity.

![Figure 4. Effect of different feed flow rates of CO2 purity, recovery and productivity.](image)

**Figure 4.** Effect of different feed flow rates of CO2 purity, recovery and productivity.

The feed flow rate of the gas mixture into the column during feed and adsorption stages also an important factor affecting the process performances. An excessive flow rate could deteriorate process performances. With other parameters fixed, the flow rates have been varied by 0.03 to 0.07 kmol/s. Figure 4. shows as the flow rate increases, the recovery increases by up to 97%, inversely the purity and productivity decrease to 63% and 0.88 kmol/s/kg respectively. The faster flow rate indicates more amount of gas is being introduced into the column and more CO$_2$ can be adsorbed. However, it also means that the adsorbent could saturate faster, results in more CO$_2$ escaped from the column, decreasing recovery of CO$_2$.

4. Conclusion
A model describing CO$_2$/N$_2$ mixture flow, mass and heat transfer with multi-component adsorption has been developed for studying breakthrough curves and 2-bed 4-step PSA cycle using Aspen Adsorption. The adsorption capacity of CO$_2$ on CMS 3K, zeolite 13x and silica gel have been studied using a single bed adsorption unit. The comparison of the three adsorbents result shows that CMS 3K had the highest adsorption capacity based on the longest breakthrough time and steepest graph. A parametric study on the PSA cycle is then being conducted using CMS 3K to investigate the effect of adsorption pressure and feed flowrate on purity, recovery and productivity of CO$_2$. The result shows that, within a certain range, higher adsorption pressure will increase all purity, recovery and productivity of CO$_2$ while higher feeding rate leads to increase recovery but lower purity and productivity.
References

[1] L. Riboldi and O. Bolland 2017 Overview on Pressure Swing Adsorption (PSA) as CO2Capture Technology: State-of-the-Art, Limits and Potentials Energy Procedia 114 2390–2400.

[2] A. D. Wiheeb, Z. Helwani, J. Kim, and M. R. Othman 2016 Pressure Swing Adsorption Technologies for Carbon Dioxide Capture Sep. Purif. Rev. 45 108–121.

[3] J. Xiao, L. Fang, P. Bénard, and R. Chahine 2018 Parametric study of pressure swing adsorption cycle for hydrogen purification using Cu-BTC Int. J. Hydrogen Energy 43 13962–13974.

[4] J. C. Knox, A. D. Ebner, M. D. Levan, R. F. Coker, and J. A. Ritter 2018 On the Limitations of Breakthrough Curve Analysis in Fixed-Bed Adsorption

[5] M. S. Shafeeyan, W. M. A. W. Daud, A. Shamiri, and N. Aghamohammadi 2015 Modeling of Carbon Dioxide Adsorption onto Ammonia-Modified Activated Carbon: Kinetic Analysis and Breakthrough Behavior Energy and Fuels 29 6565–6577.

[6] P. Lestinsky, M. Vecer, P. Navratil, and P. Stehlik 2015 The removal of CO2 from biogas using a laboratory PSA unit: Design using breakthrough curves Clean Technol. Environ. Policy 17 1281–1289

[7] L. A. M. Rocha, K. A. Andreassen, and C. A. Grande 2017 Separation of CO2/CH4 using carbon molecular sieve (CMS) at low and high pressure Chem. Eng. Sci. 164 148–157.

[8] H. Ahn, C. Chun, M. Park, I. S. Ahn, and C. H. Lee 2001 Thermal effects on the breakthrough curve of a hydrogen ternary system at a fixed bed Sep. Sci. Technol. 36 2121–2145.

[9] J. H. Park, J. N. Kim, S. H. Cho, J. D. Kim, and R. T. Yang 1998 Adsorber dynamics and optimal design of layered beds for multicomponent gas adsorption Chem. Eng. Sci. 53 3951–3963.

[10] S. Garcia, M. . Gil, C. . Martin, J. . Pis, F. Rubiera, and C. Pevida, “Breakthrough adsorption study of a commercial activated carbon for pre-combustion CO2 capture S. García, M.V. Gil, C.F. Martín, J.J. Pis, F. Rubiera, C. Pevida 1 Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain,” pp. 1–25.

[11] L. F. Gomez, R. Zacharia, P. Bénard, and R. Chahine 2015 Simulation of Binary CO2/CH4 Mixture Breakthrough Profiles in MIL-53 (Al) J. Nanomater. 2015 1–15.

[12] A. Aquino et al. 2016 Carbon Dioxide Removal with Tuff: Experimental Measurement of Adsorption Properties and Breakthrough Modeling Using CFD Approach Energy Procedia 101 392–399.

[13] R. Ben-Mansour, M. Basha, and N. A. A. Qasem 2017 Multicomponent and multi-dimensional modeling and simulation of adsorption-based carbon dioxide separation Comput. Chem. Eng. 99 255–270.

[14] P. Brea, J. A. Delgado, V. I. Águeda, and M. A. 2017 Uguna Modeling of breakthrough curves of N2, CH4, CO, CO2 and a SMR type off-gas mixture on a fixed bed of BPL activated carbon Sep. Purif. Technol. 179 61–71.

[15] T. L. P. Dantas et al. 2011 Carbon dioxide-nitrogen separation through adsorption on activated carbon in a fixed bed Chem. Eng. J. 169 11–19.

[16] M. Xu, H. C. Wu, Y. S. Lin, and S. Deng 2018 Simulation and optimization of pressure swing adsorption process for high-temperature air separation by pervoskite sorbents Chem. Eng. J. 354 62–74.

[17] M. H. Chahbani and D. Tondeur 2001 Pressure drop in fixed-bed adsorbers Chem. Eng. J. 81 1–3 23–34.

[18] P. A. Webley, A. Qader, A. Ntiamoah, J. Ling, P. Xiao, and Y. Zhai 2017 A New Multi-bed Vacuum Swing Adsorption Cycle for CO2 Capture from Flue Gas Streams Energy Procedia 114 2467–2480.

[19] Q. Fu, H. Yan, Y. Shen, Y. Qin, D. Zhang, and Y. Zhou 2018 Optimal design and control of pressure swing adsorption process for N2/CH4 separation J. Clean. Prod. 170 704–714.

[20] R. Zhao et al. 2017 A comparative study on CO2 capture performance of vacuum-pressure swing adsorption and pressure-temperature swing adsorption based on carbon pump cycle Energy 137 495–509.
[21] J. A. Delgado, M. A. Uguina, J. L. Sotelo, V. I. Águeda, A. Sanz, and P. Gómez 2011 Numerical analysis of CO$_2$ concentration and recovery from flue gas by a novel vacuum swing adsorption cycle *Comput. Chem. Eng.* **35** 1010–1019