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# Correlations between adsorbent characteristics and the performance of pressure swing adsorption separation process

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ABSTRACT

In the pressure swing adsorption (PSA) technique for gas separation, the working performance of the adsorbent determines the efficiency of the separation unit. Excellent kinetic performance, high adsorption capacity, and selectivity are all critical for the utilization of adsorbents. This work presents a 4-bed PSA model for $H_2/CO_2$ separation to evaluate the real-time $H_2$ purification capability of adsorbents with different kinetic performance, adsorption capacity, and selectivity. The experimental data on a test-scale PSA apparatus were used for model validation. The purity of $H_2$ at the outlet was exactly 99% and the $H_2$ recovery rate ranged from 70% to over 95%; hence, the extent of gas recovery was representative of the working performance. Theoretical analysis of the PSA process indicates that $H_2$ is discharged at the blow-down and purge steps, and that the amount of $H_2$ wasted in these steps is inversely proportional to the adsorption capacity and selectivity. This inverse relation was demonstrated by simulation, in which the correlation coefficient reached 0.99. When the kinetic performance was poor, the kinetic parameter $k_{a-CO_2}$ was less than 0.1, and separation was highly dependent on the adsorption and desorption rate. When $k_{a-CO_2} > 0.3$, the dependency was not evident. The simulation results were used to analyze the limitations of the kinds of $CO_2$ adsorbents, identify areas of improvement, and thus achieve better working performance.

## 1. Introduction

Pressure swing adsorption (PSA) is considered a promising technique for gas separation because of its flexibility; its scale varies from a 2-bed system to a 16-bed system that has a capacity in excess of 100,000 $Nm^3/h$ [1]. Different adsorbents, such as activated carbon (AC), carbon molecular sieves, hydrotalcite, and metal oxide adsorbents, have been used in PSA for air separation, pure hydrogen production, and carbon capture. With the development of new adsorbents over time, PSA has found wider applications. Ji et al. [2,3] reported a PSA system packed with metal–organic frameworks to separate the polymerization products into a gas stream and polymer stream. Kuznicki [4] and coworkers prepared modified ETS-10 zeolites for olefin separation, wherein the adsorbent had a good balance of adsorption capacity and selectivity.

PSA for $H_2/CO_2$ separation from syngas is competitive with absorption and membrane separation. A combination of reforming or gasification, water-gas shift, and the PSA separation system proved to be an efficient method for pure hydrogen production and pre-combustion $CO_2$ capture [5–11]. Elevated-temperature PSA (ET-PSA) separation can save sensitive heat from syngas. Nevertheless, the hydrogen purity is higher than 99%, while simultaneously, recovery can reach 90% [12,13]. Wang et al. reported an effective method for $CO_2$ capture from flue gas by connecting two PSA units; over 90% $CO_2$ could be recovered with a purity of 95.6% [14].

PSA has also become a vital technique for air separation. Zeolite is typically used as an adsorbent for commercial oxygen production. Compared to cryogenic equipment, it is more economical to acquire PSA equipment; moreover, production is continuous, albeit with lower purity. Perovskite oxide has been explored as an oxygen adsorbent for high-purity oxygen production [15–18]. Jin et al. [19] studied the selectivity performance of four adsorbents for the production of argon by PSA, and found that carbon molecular sieves showed the highest selectivity. Hermes presented an approach for removing nitrogen from contaminated natural gas, in which the gas stream was treated by a PSA unit capable of $CH_4/N_2$ separation [20]. The final nitrogen purity was found to be greater than 96%, while the recovery was beyond 50%.

Adsorbents are the essential components of a PSA system. Some chemical adsorbents such as CaO have a large adsorption capacity, but the adsorption process is usually irreversible. Therefore, they are unsuitable for use in PSA. The most important industrialized PSA adsorbents include AC, zeolite, and carbon molecular sieves, which are all

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**Nomenclature**

| | |
|---|---|
| $t$ | time, s |
| $M_i$ | molecular mass of i, i = $H_2$,$CO_2$, g·mol$^{-1}$ |
| $R$ | ideal constant, J·mol$^{-1}$·K$^{-1}$ |
| $T$ | temperature in adsorption bed, K |
| $P_i$ | partial pressure of i, i = $H_2$,$CO_2$, Pa |
| $C_i$ | molar concentration of i, i = $H_2$,$CO_2$, mol·m$^{-3}$ |
| $X_i$ | mole fraction of i, i = $H_2$,$CO_2$, – |
| $\rho_i$ | density of i, i = $H_2$,$CO_2$, kg·m$^{-3}$ |
| $\rho_p$ | adsorbent density, kg·m$^{-3}$ |
| $k$ | parameter related to $H_2$ adsorption capacity, mmol·g$^{-1}$·Mpa$^{-1}$ |
| $e_b$ | void fraction of adsorption bed, MPa$^{-1}$ |
| $d_p$ | adsorbent diameter in adsorption bed, m |
| $q_i$ | adsorption quantity of i, i = $H_2$,$CO_2$, mmol·g$^{-1}$ |
| $z$ | height in bed, m |
| $v$ | flow speed in bed, m·s$^{-1}$ |
| $\mu$ | gas dynamic viscosity, Pa·s |
| $D$ | diffusion coefficient, m$^2$·s$^{-1}$ |
| $V_{D-i}$ | liquid state molar volume of i, i = $H_2$,$CO_2$, cm$^3$/gmol |
| $R_{bed}$ | adsorption bed radius, m |
| $q_{e-i}$ | adsorption capacity of i at given pressure, i = $H_2$,$CO_2$, mmol·g$^{-1}$ |
| $q_{s-i}$ | saturated adsorption capacity of i, i = $H_2$,$CO_2$, mmol·g$^{-1}$ |
| $b_i$ | Langmuir model adsorption parameter, i = $H_2$,$CO_2$, MPa$^{-1}$ |
| $F_{in}$ | inlet flow rate, Nm$^3$·h$^{-1}$ |
| $F_{out}$ | outlet flow rate, Nm$^3$·h$^{-1}$ |
| $F_{feed}$ | feed gas flow rate, Nm$^3$·h$^{-1}$ |
| $P_{feed}$ | feed pressure, Pa |
| $P_{blowdown}$ | blowdown pressure, Pa |
| $v_{in}$ | inlet flow velocity, m·s$^{-1}$ |
| $v_{out}$ | outlet flow velocity, m·s$^{-1}$ |
| $L$ | bed height, m |
| $k_{a-i}$ | LDF parameter of adsorption, i = $H_2$,$CO_2$, s$^{-1}$ |
| $k_{d-i}$ | LDF parameter of adsorption, i = $H_2$,$CO_2$, s$^{-1}$ |
| $F_{ads}$ | outlet flow rate of the bed which is at adsorption step, Nm$^3$·h$^{-1}$ |
| $F_{LP}$ | outlet flow rate of the bed which is at final pressurization step, Nm$^3$·h$^{-1}$ |
| $F_{Pu}$ | outlet flow rate of the bed which is at purge step, Nm$^3$·h$^{-1}$ |
| $F_{ED1}$, $F_{ED2}$ | outlet flow rate of the bed which is at pressure equalization drop step, Nm$^3$·h$^{-1}$ |
| $F_{ER1}$, $F_{ER2}$ | inlet flow rate of the bed which is at pressure equalization rise step, Nm$^3$·h$^{-1}$ |
| $C_{V1}$, $C_{V2}$ | valve parameter in pressure equalization step, Nm$^3$·Pa$^{-1}$·h$^{-1}$ |
| $x_{feed-i}$ | molar fraction of i in feed gas, i = $H_2$,$CO_2$, – |
| $x_{ads-i}$ | molar fraction of i in production, i = $H_2$,$CO_2$, – |

physical adsorbents; their adsorption heats are relatively low [21–24], implying that they typically show remarkable kinetics. In addition to kinetics, adsorption capacity and selectivity are also vital measuring standards for an adsorbent. The preparation of adsorbents that simultaneously show high capacity and selectivity is an important focus of ongoing research. Typically, two adsorbents rarely show the same adsorption capacity and selectivity. Some adsorbents have higher adsorption capacity, while some others possess better selectivity. Arami et al. [25] used an AC monolith, which has a high adsorption capacity, to adsorb $CO_2$, $CH_4$, and $N_2$. However, the selectivity for $CO_2$ over $CH_4$ and $N_2$ was only ~1.5 and 2, respectively. Wei [26] synthesized a nitrogen-doped mesoporous carbon adsorbent. The $CO_2$ adsorption capacity for this adsorbent was 2.5 mmol/g at 298 K, 1 bar; while for $N_2$, it was ~0.3 mmol/g. With increasing pressure, the selectivity continued to drop. Hydrotalcite only adsorbs $CO_2$; its selectivity for $CO_2$ over $H_2$ is higher, but its working capacity is lower than AC.

Therefore, a thorough analysis of adsorbents is needed in order to design a more efficient PSA system and improve adsorbent performance. Moreover, it is important to clarify the relationship between adsorption capacity, selectivity, kinetic performance, and separation performance systematically.

Adsorption and PSA unit simulation play a critical role in system optimization and economic analysis. A number of models have been developed to measure adsorbent performance and PSA efficiency [27–34]. Riboldi [27] analyzed the PSA unit energy efficiency and separation performance in an advanced supercritical pulverized coal plant and integrated gasification combined cycle plant using the STEAM PRO, GT PRO, and THERMOFLEX software developed by Thermoflow Inc. The application of a PSA process to a pre-combustion scenario has shown promising results. Álvarez-Gutiérrez et al. [28] used Avrami's model to analyze the kinetics of $CO_2$ adsorption on biomass-based AC. George et al. [31] compared two zeolites on a two-bed PSA model. As a second step, they optimized the process and demonstrated that the modified zeolite was more efficient than the original zeolite in terms of working performance.

However, few studies have attempted to analyze the relation between adsorbent characteristics and separation performance systematically and quantitatively. In this study, a 4-bed PSA model, which uses the 4-2-1 technique (4 beds in PSA unit, 2 pressure equalization steps per cycle, any 1 bed operational at the adsorption step), was developed to simulate the working performance of an adsorbent under various operating conditions [34]. The feed gas which was a mixture of $CO_2$ and $H_2$, was used for this analysis. When the purity of $H_2$ at the outlet is kept constant, $H_2$ recovery is indicative of the separation performance. An inverse relation between recovery, adsorption capacity and selectivity was proposed. The sensitivity of $H_2$ recovery to adsorption/desorption rate is also analyzed. Simulation results are used to assess the merits and weaknesses of actual $CO_2$/$H_2$ separation adsorbents.

## 2. Model

A model for the gas separation system for the multi-bed PSA process was developed using gPROMS [35], a commercial simulation platform. In order to exclude inconsequential factors and simplify the analysis, the following assumptions were introduced:

1. The temperature is uniform and fixed at the operating temperature.
2. Adsorption beds are one-dimensional. Variations along the radial direction can be neglected in comparison to those along the axial direction.
3. The gas is a mixture of $H_2$ and $CO_2$. It is ideal and obeys the ideal gas equation:

$$1000RT\rho_i = P_iM_i \tag{1}$$

$$C_iRT = P_i \tag{2}$$

4. The isotherms for $H_2$ as well as $CO_2$ fit the Langmuir model

$$q_{e-CO_2} = q_{s-CO_2}b_{CO_2}P_{CO_2}/(1 + bP_{CO_2}) \tag{3}$$

$$q_{e-H_2} = q_{s-H_2}b_{H_2}P_{H_2}/(1 + bP_{H_2}) \tag{4}$$

Mass balance and momentum balance were considered in this model. The related equations are listed below.

Mass balance for both $CO_2$ and $H_2$ is described by the following equation: