



## Pressure-Swing Adsorption Using Layered Adsorbent Beds with Different Adsorption Properties: I—Results of Process Simulation

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**Abstract.** A simulation study was conducted on layered-bed pressure-swing adsorption, PSA, processes with adsorbents that differ in their adsorption properties. As an example, an oxygen,  $O_2$ , vacuum-swing adsorption, VSA, process was analyzed to investigate relationships between process performance and adsorption properties of the adsorbents used. For two adsorbents with identical nitrogen-to-oxygen,  $N_2/O_2$ , selectivity but different  $N_2$  and  $O_2$  capacities, placing the high-capacity adsorbent at the product end and the low-capacity adsorbent at the feed end of the adsorption bed gives a better performance than the case of reversing layering of these adsorbents. However, for two adsorbents with different values of  $N_2/O_2$  selectivity but identical  $N_2$  capacity, changing the bed-layer configuration does not show a significant difference in  $O_2$ -VSA performance. The advantages of layering a high-capacity adsorbent on product end of the bed are demonstrated by an examination of the  $N_2$ -loading difference in a VSA cycle. The modeling study also reveals an effect of cycle features (e.g., equalization step) on the effectiveness of using layered-bed configurations in VSA/PSA processes. It suggests that layering appropriately two adsorbents with different adsorption properties could result in better VSA/PSA-process performance than using a single-layer bed with either of the two adsorbents.

**Keywords:** VSA/PSA processes, performance simulation, layered beds, positioning of adsorbents, variation in capacity and selectivity

### 1. Introduction

Layered-bed configurations in VSA/PSA processes with adsorbents that have different adsorption properties could maximize the utilization of the adsorbents' inherent performance potential and reduce product costs. The *optimum* bed-layer configuration of

adsorbents depends on the specific adsorption properties of the latter ones (in both equilibrium and kinetic behavior), but also on feed-mixture composition, and product-purity requirements.

If more than one component needs to be removed from a feed-gas mixture, more than one adsorbent can be layered in a given adsorber bed based on their specific adsorption properties towards the feed components, cf., separation of  $H_2$ -CO-CO<sub>2</sub>-H<sub>2</sub>O mixtures

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by adsorption using activated carbons and/or zeolite materials (Park et al., 1998, 2000). Even in processes such as O<sub>2</sub>-VSA or PSA, in which only one component, viz., N<sub>2</sub>, is adsorbed selectively, layering NaX and LiX zeolite adsorbents could result in a decrease of overall product cost (Toussaint, 1993; Watson et al., 1996).

A simple model to investigate the usage of layered beds in cycling-zone adsorption processes was developed by Fray (1982–1983). Later, Pigorini and LeVan (1997) studied the effects of adsorption-isotherm shape and adsorbent capacity on the performance of an isothermal pressure-swing adsorber, in which the bed comprised two layers of different adsorbents. These authors utilized an adsorption-equilibrium approach and considered a feed that consists of a single adsorbing species in inert gas.

Despite a few papers and patents on layered-bed PSA processes, a clear understanding is still missing of how process performance is affected by particular adsorption properties of adsorbents involved, and how the performance is related to process-operation parameters such as those of equalization and purge steps. The objective of this study is to investigate the effects of adsorbent properties, bed configuration, and PSA-cycle features on the performance of layered-bed PSA processes. The PSA model used is a non-isothermal one with both adsorption equilibrium and kinetics being considered. A PSA process with different bed-layer configurations is analyzed in terms of bed utilization using loading changes and a concentration profile.

## 2. The PSA Model

A PSA process simulator, DAPS (Dynamic Adsorption Process Simulator), described by Doong and Propsner (1998), was adapted to study the layered-bed O<sub>2</sub>-PSA process. This simulation program comprises a rigorous mathematical model that embraces mass and energy balances, adsorption equilibrium, mass and heat transfer, etc., which, in particular, enables a description of the transport phenomena in adsorption columns. For the case of layered-bed configurations, the fundamental assumptions and equations made remain unchanged.

The following assumptions were made for model derivation: (i) the ideal-gas law applies to all the gases; (ii) no axial-pressure gradient exists across the bed; (iii) thermal equilibrium exists between the fluid and

solid phases; and (iv) there is no radial variation in both concentration and temperature.

The current study employs a two-bed O<sub>2</sub>-VSA cycle with equalization, purge, and backfill. The cycle steps considered are as follows: (i) adsorption step: air is introduced into the bed from the feed end of the bed, and O<sub>2</sub> product is drawn from its product end; (ii) equalization (–) step: feed supply is terminated, and the bed is depressurized by transferring the O<sub>2</sub>-rich gas through the product end to the second bed; (iii) vent step: the bed is connected to a vacuum pump from the feed end, and it is further depressurized; (iv) purge step: the bed is regenerated by receiving a portion of the O<sub>2</sub> product at the product end from the second bed, which is generated in step (i) while the feed end still being connected to the vacuum system; (v) equalization (+) step: the bed is re-pressurized from the product end using the depressurization gas from the other bed that undergoes step (ii), at this conjuncture; (vi) backfill step: the bed is pressurized with product from the product end; and (vii) feed-pressurization step: the bed is pressurized by feed gas.

For purposes of comparison, an O<sub>2</sub>-VSA cycle without equalization and backfill steps was simulated as well.

The mass balances for the gas species in a packed bed read as follows:

$$\varepsilon \frac{\partial C_i}{\partial t} + \frac{\partial u C_i}{\partial z} - D_L \frac{\partial^2 C_i}{\partial z^2} - S_i = 0 \quad i = 1, \dots, n \quad (1)$$

where  $\varepsilon$  is the interparticle void-volume fraction;  $C_i$  is the concentration of component  $i$  in the gas phase;  $u$  is the superficial gas velocity;  $z$  is the bed distance;  $D_L$  is the axial-dispersion coefficient; and  $S_i$  is the sorption rate of component  $i$  per unit volume of the bed.

The energy balance in the bed is given as follows:

$$\begin{aligned} \frac{\partial}{\partial t} \left\{ \left( \varepsilon C_{pg} C + \rho_B C_{ps} + \rho_B C_{pg} \sum_{j=1}^n q_j \right) T \right\} \\ + \frac{\partial (u C_{pg} C T)}{\partial z} - K_L \frac{\partial^2 T}{\partial z^2} - \sum_{j=1}^n \Delta H_j \frac{\partial q_j}{\partial t} \rho_B \\ + \frac{4h_w}{d_i} (T - T_w) = 0 \end{aligned} \quad (2)$$

where  $C_{pg}$  is the heat capacity of the gas;  $C$  is the overall gas concentration in the gas phase;  $\rho_B$  is the bulk

density of the adsorbent;  $C_{ps}$  is the heat capacity of the adsorbent;  $q_j$  is the adsorbed amount of component  $j$  in the solid phase;  $\Delta H_j$  is the adsorption heat of component  $j$ ;  $h_w$  is the heat-transfer coefficient between the packed bed and the wall;  $K_L$  is the axial thermal conductivity;  $d_i$  is the inside diameter of the bed; and  $T_w$  is the average wall temperature.

Another energy-balance equation can be written for the wall of the bed:

$$A_w \rho_w C_{pw} \frac{\partial T_w}{\partial t} = \pi d_i h_w (T - T_w) - \pi d_o h_o (T_w - T_a) + K_w A_w \frac{\partial^2 T_w}{\partial z^2}, \quad (3)$$

where  $A_w$  is the cross-section area of the wall;  $\rho_w$  is the density of the wall;  $C_{pw}$  is the heat capacity of the wall;  $d_o$  is the outside diameter of the bed;  $K_w$  is the thermal conductivity of the wall;  $T_a$  is ambient temperature; and  $h_o$  is the heat-transfer coefficient between wall and surroundings.

In this paper, a *Glueckauf* model of linear-driving force, LDF, is used to describe the mass-transfer resistance of adsorbent particles. The sorption rate is expressed as follows:

$$S_i = -\rho_B \frac{q_{io} R T_o}{P_o} \frac{\partial Q_i}{\partial \tau} = -\rho_B k \frac{L}{u_o} \frac{q_{io} R T_o}{P_o} (Q_i^s - Q_i), \quad (4)$$

where  $k$  represents the LDF-rate coefficient; and  $Q_i^s$  is the equilibrium value of adsorbed amount at gas-phase composition  $Y_i$ .

In the above equations, particular values of voidages, packing densities, and adsorption isotherms for different layers can be either identical with or different from each other.

A finite-difference method is employed to convert the model equations into ordinary differential equations. Backward difference for the first-order derivative with respect to the bed distance was used to ensure numerical stability. For  $O_2$ -VSA systems, where gas velocities tend to be very high, the dispersion term is much smaller than the convection term. Therefore, central difference was used for the second-order derivative with respect to the bed distance without any numerical difficulty. A standard-time integrator, the Runge-Kutta method, is then used to solve those equations. Boundary and initial conditions can be written based

on PSA-process steps. Although the gas-flow direction can alter in a PSA bed depending on step sequence, the condition at one end of the bed is always known.

### 3. Simulation Results and Discussion

A layered-bed  $O_2$ -VSA process was studied by simulating the VSA process with two adsorbent layers that exhibit either different adsorption capacity or different selectivity. The volume ratio of the two adsorbents was kept at 1:1. Adsorbent-vessel geometry and operating conditions used in the simulation are listed in Table 1. The adsorbent beds are of cylindrical shape with 12-cm layers of alumina packed at the feed end.

A dual-site *Langmuir*-isotherm model (DSLM) was used to express the adsorption isotherm:

$$n_i = \frac{n_{i,I} b_{i,I} p_i}{1 + b_{i,I} p_i} + \frac{n_{i,II} b_{i,II} p_i}{1 + b_{i,II} p_i}. \quad (5)$$

where  $n_i$  is the amount adsorbed for single component  $i$  at its partial equilibrium pressure,  $p_i$ ;  $n_{i,I}$  and  $n_{i,II}$  are the “monolayer”-adsorption capacities of sites I and II; and  $b_{i,I}$  and  $b_{i,II}$  are the *Langmuir*-equilibrium constants for adsorption on sites I and II, respectively, the dependences on temperature of which can be expressed as follows:

$$b_{i,I} = b_{i,I}^o \exp\left(\frac{q_{i,I}}{RT}\right), \quad (6)$$

and

$$b_{i,II} = b_{i,II}^o \exp\left(\frac{q_{i,II}}{RT}\right), \quad (7)$$

Table 1. Vessel geometry and operation conditions for the simulation study.

Ambient temperature	25°C
Feed temperature	25°C
High pressure	19.55 psia
Vacuum level	6.29 psia
Cycle time	29 sec
Bed ID	59.69 cm
Bed height	90 cm

Table 2. DSLM parameters (values are normalized against those of Adsorbent-1).

Parameters	Adsorbent 1		Adsorbent 2		Adsorbent 3		Adsorbent 4	
	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
$n_{i,I}$	1	1	1.5	1.5	1	1	1.25	1.25
$n_{i,II}$	1	1	1.5	1.5	1	1	1.25	1.25
$b_{i,I}^o$	1	1	1	1	1	0.75	1	1
$b_{i,II}^o$	1	1	1	1	1	0.75	1	1
$q_{i,I}$	1	1	1	1	1	1	1	1
$q_{i,II}$	1	1	1	1	1	1	1	1

with  $q_{i,I}$  and  $q_{i,II}$  representing adsorption heats of component  $i$  on sites I and II, respectively.

The values of model parameters for three different adsorbents, normalized against those of Adsorbent-1, are given in Table 2. The adsorption-monolayer capacities of Adsorbent-2 and Adsorbent-4 are assumed to be higher than those for Adsorbent-1, by 50% and 25%,

respectively. For Adsorbent-3, the *Langmuir*-equilibrium constants for O<sub>2</sub> adsorption on sites I and II are by 25% smaller than those for Adsorbent-1. All parameters for argon, Ar, are considered to be the same as those for O<sub>2</sub>.

Adsorption capacity and selectivity are the two critical adsorbent properties that determine PSA-process

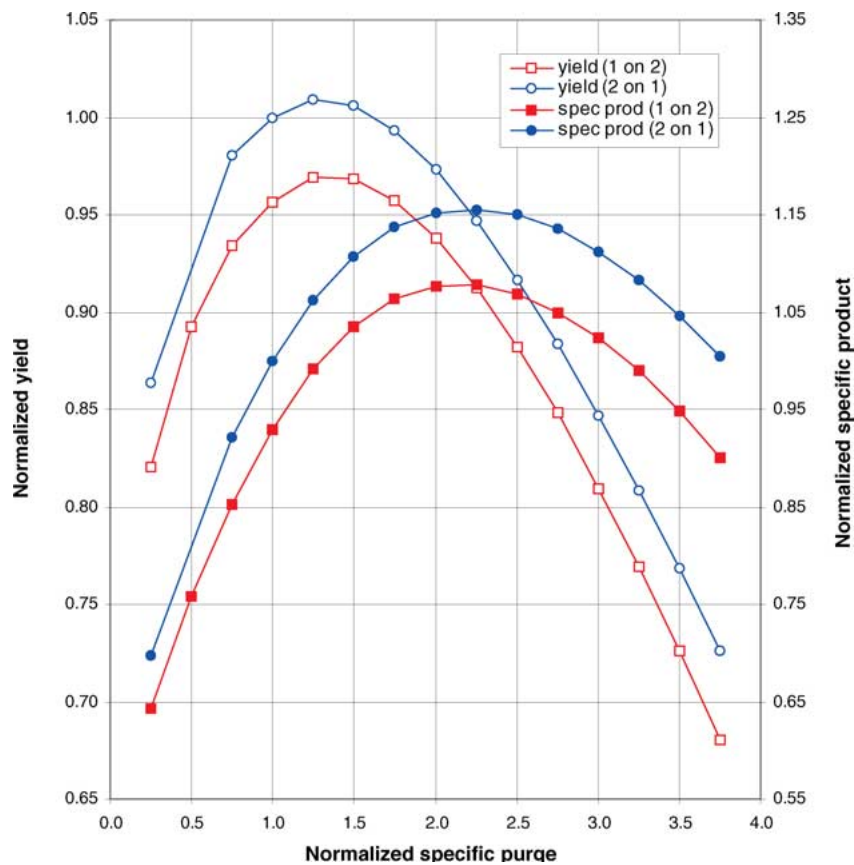


Figure 1. Performance of layered-bed oxygen VSA using two adsorbents that have different capacities, as functions of specific purge.

performance based on adsorption-equilibrium separation. To distinguish their impacts on a layered-bed PSA process, the simulation study conducted was based on two pairs of model adsorbents that are different in either adsorption capacity or selectivity. The selectivity is defined as the ratio of the adsorption capacity for  $N_2$  to that for  $O_2$ .

### 3.1. Effect of Adsorption Capacity

A layered-bed  $O_2$ -VSA process was simulated with Adsorbent-1 and Adsorbent-2 that have identical values of  $N_2/O_2$  selectivity but different values of adsorption capacity. The performances of layered-bed  $O_2$ -VSA at 90%  $O_2$ -product purity with Adsorbent-1

and Adsorbent-2 are given in Fig. 1 for two bed-layering configurations: Adsorbent-1 packed near the product end (i.e., Adsorbent-1 on top of Adsorbent-2) and Adsorbent-2 packed near the product end (i.e., Adsorbent-2 on top of Adsorbent-1). The performances were evaluated at different specific purge-flow rates, while the results were expressed by plotting yields against specific product. Both yield and specific product were normalized by dividing their actual values by the corresponding yield and specific-product values obtained at specific purge with 20 L/L/hr.

As Fig. 1 shows, placing the high-capacity adsorbent, Adsorbent-2, near the product end gives better a performance than layering the adsorbents in the opposite manner. If one compares performances of the

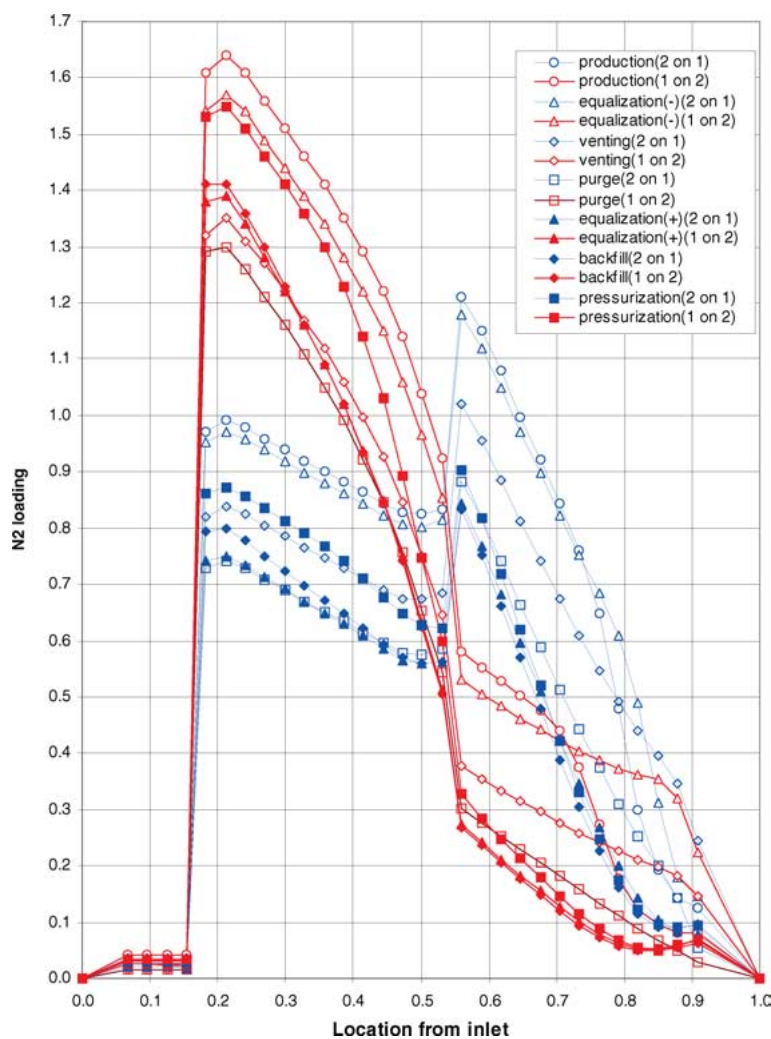


Figure 2. Concentration profiles at the end of steps for layered-bed oxygen VSA with adsorbents that have different capacities.

two bed-layer configurations at maximum-yield values, layering the high-capacity adsorbent at the product end would give 4% higher yield and 7% higher specific product.

To understand these results, one needs to examine the variations in concentration of the gas and adsorption phases throughout the entire cycle. Figure 2 shows the  $N_2$ -concentration profile inside the adsorbent bed in all of the seven steps of the  $O_2$ -VSA cycle. The  $N_2$  concentration (expressed as mmol  $N_2$ /g adsorbent) is plotted against the dimensionless position from the bed inlet (position = 0) to its outlet (position = 1). Figure 3 gives the temperature profile inside the adsorbent bed. Generally speaking, bed temperature increases from the feed end to the discharge end. Composite-adsorbent

beds that contain different adsorbent materials positioned in separate zones were reported by Notaro et al. (1998) such that the temperature conditions favor adsorption performance of the particular adsorbent material in each zone.

Although heat transfer and bed-temperature distributions are not the focus of this study, it ought still to be noticed that, as obvious from Fig. 3, the two layering configurations exhibit different bed-temperature profiles. Temperature profile is a combined result of adsorption/desorption heats and upward/downward flows of gas streams inside the adsorption bed. In the adsorption step, for example, the upward gas flow carries the heat generated by adsorption of  $N_2$  on the adsorbent, which causes a temperature increase in the upper

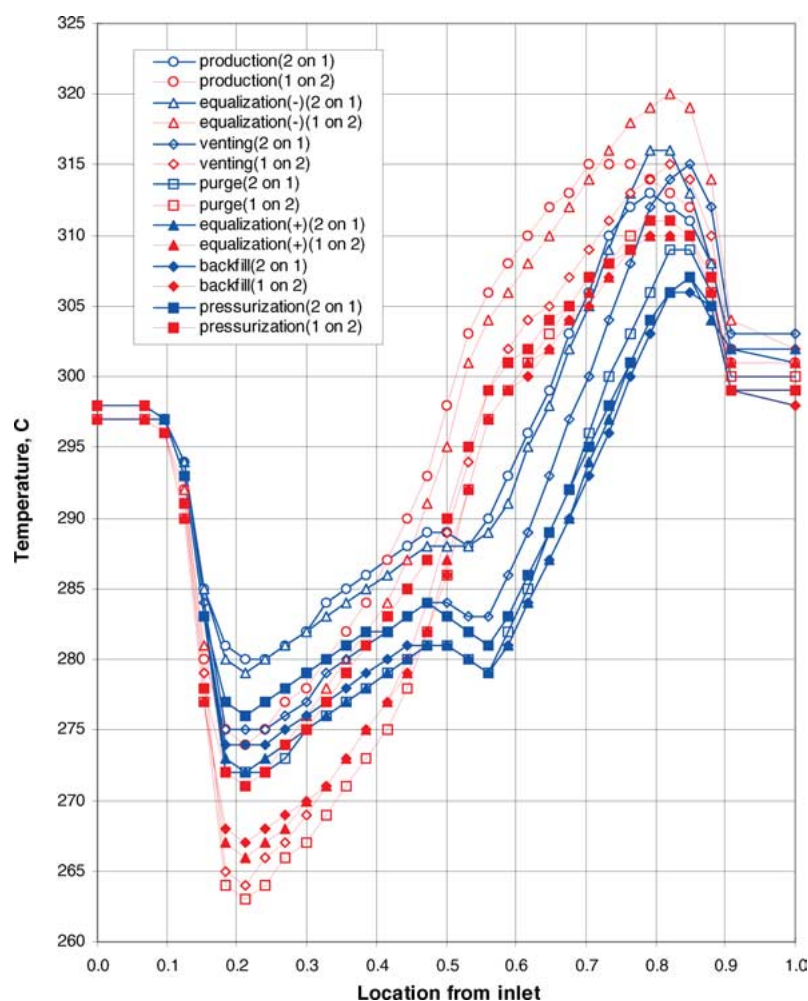


Figure 3. Bed-temperature profiles at the end of steps for layered-bed oxygen VSA with adsorbents that have different capacities.

portion of the adsorption bed. In the venting step, however, the heat consumed by desorption of  $N_2$  reduces the local bed temperature as the desorption stream moves toward the feed end of the adsorbent bed, which causes a temperature drop in the lower portion of the adsorption bed. Thus, as shown in Fig. 3, the temperature increases from the feed end (bottom) to the product end (top) of the adsorbent bed. When the low-capacity adsorbent (Adsorbent 1) is packed on the high-capacity adsorbent (Adsorbent 2), more heat is generated in the lower portion of the bed near the feed end during adsorption step, and the upward gas-stream flow gives rise to a larger temperature increase in the upper bed. During the desorption step, the heat taken by (endothermic)

desorption in the upper bed (packed with low-capacity adsorbent) is not sufficient to offset the heat generated and carried up into the region and, thus, the temperature of the upper portion of the bed remains higher than ambient temperature. At the lower portion of the bed, where high-capacity adsorbent is packed, a larger temperature drop is observed due to the (endothermic) desorption. When the high-capacity adsorbent is packed on the top, more heat generated during the adsorption step will be carried out of the bed from the product end, as compared to packing the high-capacity adsorbent at the bottom, and less temperature drop is observed in the lower portion of the bed, where the low-capacity adsorbent is placed.

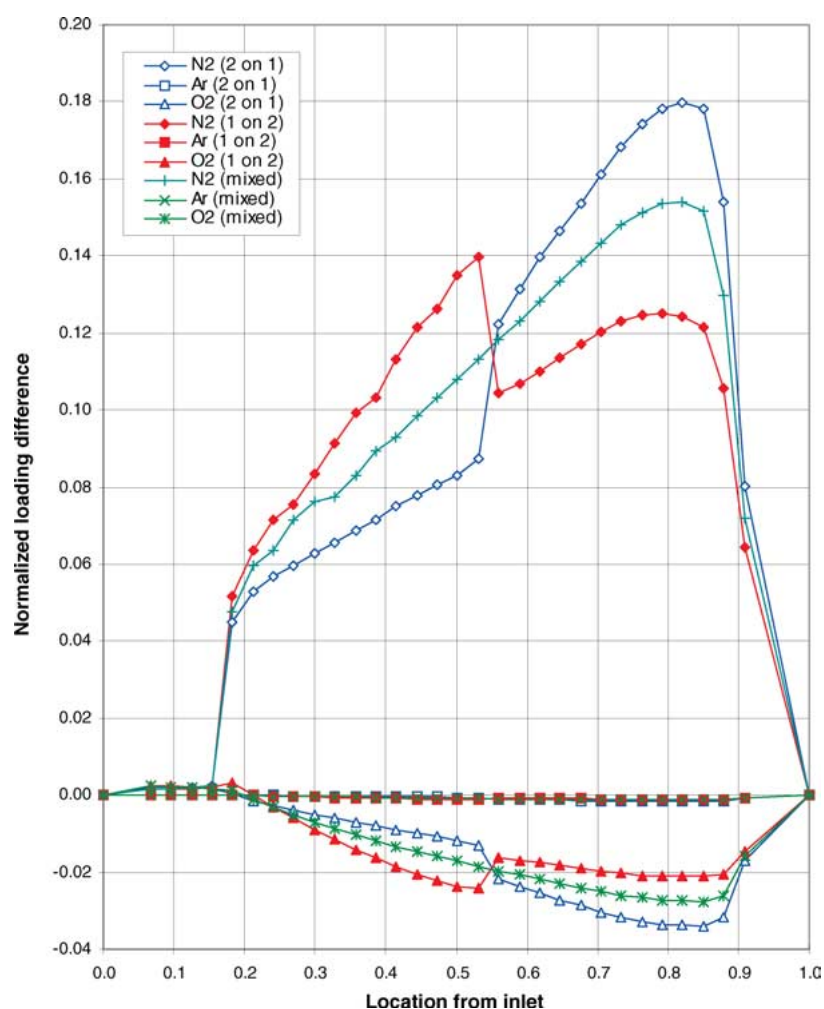


Figure 4. Loading difference between the end of feeding step and the end of regeneration step in layered-bed oxygen VSA with adsorbents that have different capacities.



Although the temperature profile within the bed is more stretched if the high-capacity adsorbent is packed near the feed end as shown in Fig. 3, as discussed below, the improvement in performance stems from a better adsorbent utilization. In the first three steps, i.e., pressurization, production, and equalization (–), the flow direction inside the beds is upward and, as shown in Fig. 2, the  $N_2$ -loading profile moves toward the product end. On the other hand, the gas stream inside the bed flows downward in the other four steps, i.e., venting, purge, equalization (+), and backfill. Therefore, the  $N_2$ -loading difference between the end of equalization (–) step, which is the end of upward flow, and the end of backfill step, which is the end of downward flow, is used as measure of bed usage in one VSA cycle.

The loading differences between the ends of equalization (–) and backfill steps for  $N_2$ , Ar and  $O_2$  with a single-layer bed packed with Adsorbent-4 are plotted in Fig. 4 as functions of the dimensionless axial position inside the adsorption bed.

Adsorbent-4 with an adsorption capacity that equals to an average of the capacities of Adsorbent-1 and Adsorbent-2, was chosen to represent a single-layer bed with an 1:1 mixture of Adsorbent-1 and Adsorbent-2. The  $N_2$ -loading difference increases from the feed end to the product end of the bed. The profile of the  $N_2$ -loading change reveals that the region near the outlet at the product end of the bed has the highest loading difference, which suggests that, as to separation efficiency, the product-end region is more important than the feed-end region of the bed. Placing the high-capacity adsorbent at the product end makes best possible use of adsorbents chosen for layering, and it is, therefore, beneficial to pack the high-capacity adsorbent in the region near the product end.

### 3.2. Effect of Selectivity

To investigate the selectivity effect on layered-bed  $O_2$ -VSA performance, Adsorbent-1 and Adsorbent-3

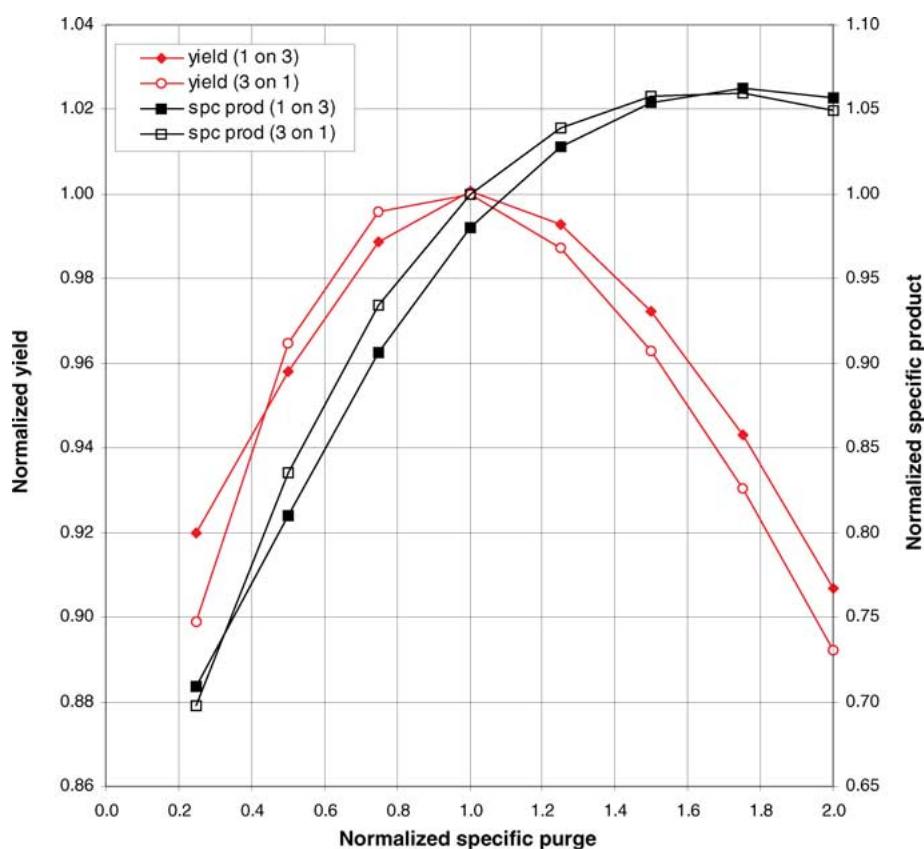


Figure 5. Performances of layered-bed oxygen VSA using two adsorbents that have different  $N_2/O_2$  selectivities as functions of specific purge.



were used for an assessment of two bed-layer configurations: Adsorbent-1 packed near the product end (i.e., Adsorbent-1 on top of Adsorbent-3) and Adsorbent-3 packed near the product end (i.e., Adsorbent-3 on top of Adsorbent-1). Again, process performance was evaluated at 90% O<sub>2</sub>-product purity for different specific purge-flow rates, while the simulation results were expressed by plotting the values for yield and specific product against those of specific purge.

As shown in Fig. 5, unlike the layered-bed configuration with two adsorbents of differing adsorption-capacity values, placing the low-selectivity adsorbent, Adsorbent-1, at the product end results into an only slightly improved performance compared with that of placing the high-selectivity adsorbent, Adsorbent-3, at the product end of the adsorption beds. Thus, layering configuration is not critical for adsorbents with different adsorption selectivities.

### 3.3. Effect of Cycle Features

It is obvious that any change in cycle features should affect the profile of N<sub>2</sub>-loading difference. For example, during the equalization step, the N<sub>2</sub>-adsorption front moves further toward the bed outlet, which results into better a utilization of the adsorbent packed near the bed outlet. If no equalization step is used in the cycle, the loading-difference profile for N<sub>2</sub> should be more flat compared to that for a cycle with equalization. Figure 6 shows the loading-difference profile for N<sub>2</sub> without equalization and backfill steps for a single-layer bed that comprises Adsorbent-4, and also for two layered-bed configurations, Adsorbent-1 on Adsorbent-2, and vice versa.

The profile for the single-layer bed is an almost flat line except in the outlet region, where a dip in the loading difference occurs. As one would expect, the two

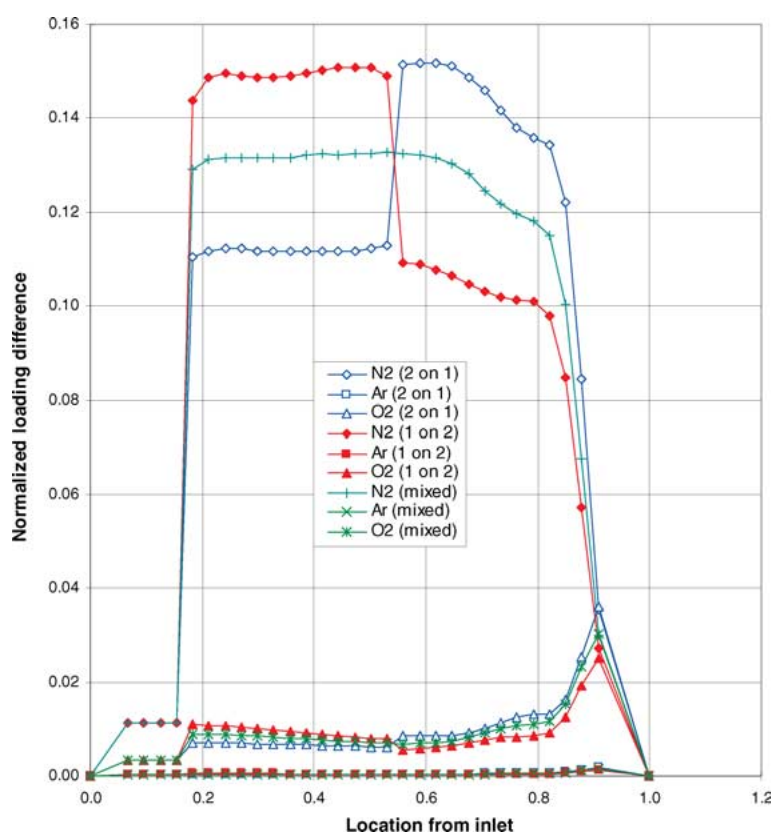


Figure 6. Loading difference between the end of feeding step and the end of regeneration step in layered-bed oxygen VSA with adsorbents that have different capacities (no purge and backfill cycles).

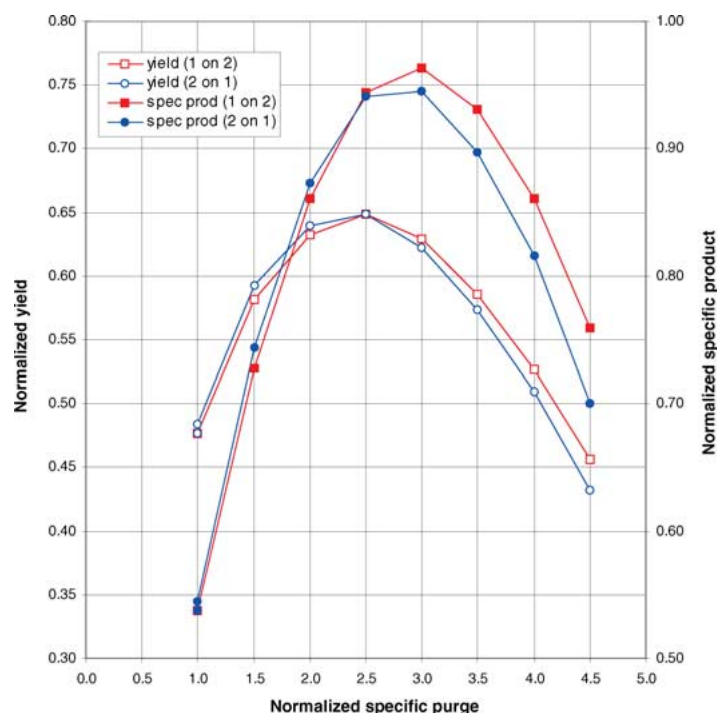


Figure 7. Performances of layered-bed oxygen VSA using two adsorbents that have different capacities as functions of specific purge (no purge and backfill cycles).

packing configurations exhibit essentially the same performance, cf., Fig. 7.

#### 4. Conclusions

In the adsorbent columns of a PSA unit, the concentration of components to be separated changes dramatically from the feed end to the discharge end. Therefore, adsorbents with different adsorption characteristics should be arranged appropriately to optimize the overall bed performance. To utilize effectively adsorbents with different adsorption properties, one should layer the high-capacity adsorbent at the discharge end and the high-selectivity adsorbent at the feed end of the adsorption beds. If one adsorbent has lower values for both capacity and selectivity compared to these parameters of the other adsorbent, layering these adsorbents might be economically feasible if only there is a sufficiently high cost difference between the two adsorbents. As far as performance is concerned, one should always and only use the adsorbent with both higher capacity and selectivity. However, it could be the case that one of the adsorbents has higher capacity, and the other has higher selectivity. Then, layering the

high-capacity adsorbent at the product end and the high-selectivity adsorbent at the feed end of the bed could result in better performance compared to that achieved by using single-layer beds with either of the two adsorbents. It is important to select and arrange adsorbents in PSA processes based on adsorbent-material characteristics and process conditions so that the adsorbents are utilized optimally, and/or the overall-process cost is minimized.

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