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A SIMPLE PARAMETER FOR SELECTING AN ADSORBENT FOR GAS SEPARATION BY PRESSURE SWING ADSORPTION

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ABSTRACT

A simple parameter is proposed for comparing the performance of two or more adsorbents for a particular binary gas separation by pressure swing adsorption. The parameter is most suitable for separations based on differences in equilibrium adsorption capacity rather than on differences in adsorption kinetics. The two main components of the parameter are the ratio of the delta loadings (differences in adsorbed amounts at high and low pressures) of the 2 gases ($\Delta q_1/\Delta q_2$) and the equilibrium selectivity ($\alpha_{1,2}$) of the sorbent for the strongly adsorbed species. A dimensionless sorbent selection parameter (S) is defined. For a given separation, the sorbent that yields the highest S value is the best sorbent. In the cases of sorbate-sorbent systems showing Langmuir-type isotherms,

$$S = \frac{\Delta q_1}{\Delta q_2}\left(\frac{q_{S1}b_1}{q_{S2}b_2}\right)$$

This parameter is simple to calculate and is sensitive to subtle differences in adsorption isotherms. The effectiveness of the

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proposed parameter was demonstrated through two examples of air separation using molecular-sieve zeolites.

INTRODUCTION

In the recent past, pressure swing adsorption (PSA) has emerged as an economical and popular process because it suits a wide variety of gas separation applications. It is particularly adaptable for low volume production (1,2). The commercial success of the PSA process has resulted in extensive research that has led to the discovery of a broad range of adsorbent materials for each application. These adsorbents are typically microporous materials, such as zeolite molecular sieves, activated carbon, and polymeric resins, either in their original form or as modified by techniques such as ion exchange. The separation of the gas mixture into its components occurs either by virtue of a preferential affinity of the adsorbent surface for one of the components (equilibrium separation) or due to a difference in uptake rates due to differing diffusivities (kinetic separation).

During the process development stage, several adsorbents may be identified as suitable materials to effect a viable separation for a particular application. The preliminary viability can be judged by a visual comparison of the isotherms and/or the uptake rates of the pure components of the gas mixture. However, a cursory visual inspection can be misleading and does not quantify the merit or the efficiency of the sorbent for the separation under consideration. For a detailed comparison of adsorbent performances, completion of lab-scale PSA experiments that use a suitable cycle or computer simulations with a proven mathematical model is necessary. These techniques are time consuming, and a quick and easily calculable parameter is highly desirable for selecting the optimum sorbent for a particular gas-separation application.

A simple method for determining sorbent selectivity, which involved taking the ratio of Henry's law constants, was proposed by Knaebel (3). This rough estimate for selectivity can serve as a crude sorbent-selection parameter. A more precise estimate can be obtained through a comparison of the isothermal, binary, working selectivity of the sorbents as defined by Gaffney et al. (4). An adiabatic separation factor, computed by taking the ratio of working capacities determined under nonisothermal, multicomponent conditions, was proposed by Ackley (5). By taking the product of working capacity and adiabatic separation factor, Ackley et al. (6) compared the relative merits of different sorbents for a particular gas-separation application. An example of a sorbent parameter appears in a patent, assigned to Notaro et al. (7), that addresses the separation of N_2 from air. This parameter, termed the "adsorption figure of merit" (AFM), was defined as follows:

$$\mathrm{AFM} = \Delta N_2 \cdot \frac{\alpha_{\mathrm{ads}}^2}{\alpha_{\mathrm{des}}} \tag{1}$$

where ΔN_2 was the difference between N_2 adsorption amounts at high and low pressures, and α_{ads} and α_{des} were the adsorption selectivities under adsorption and desorption conditions. The AFM was used to assign the zones in which different adsorbents would be used in a layered bed configuration. However, the reasoning behind the AFM was not explained by Notaro et al. (7) and so this parameter is used as an empirical rule of thumb. Also, this parameter is not dimensionless and so its general use is restricted.

Building on the various methods described above, we propose a simple parameter for comparing two adsorbents for a particular binary gas separation on the basis of their equilibrium adsorption capacities. The parameter is composed of two factors, including one related to the equilibrium selectivity of the sorbent, which is an inherent property of the sorbent. The other factor is related to the working capacity of the sorbent, which is defined as the difference in the adsorbed amount at the adsorption and the desorption pressures. Thus, the latter factor is related to the particular PSA cycle employed for the separation. The applicability of the parameter is demonstrated with two examples from an air separation process.

Theoretical Basis for the PSA Parameter

A parameter for the selection of an adsorbent should have the following attributes: It should be readily estimable without complicated calculations, and it should incorporate the essential nature of the isotherms under the PSA operating conditions. The conditions will dictate the selectivities and hence the performances of the adsorbents. The PSA parameter discussed in this work applies only to sorbents with negligible mass-transfer limitations or, at most, those that have close diffusivity values for both components. We also assumed that the adsorption isotherms follow Langmuir behavior; that is, the sorbents exhibit monolayer coverage as the saturation pressure is approached and have an energetically homogeneous surface. However, this parameter can be easily extended to other isotherm models as well. The Langmuir equation for a pure component can be written in the following form:

$$q_i = \frac{q_{\mathrm{m}_i} b_i P_i}{1 + b_i P_i} \tag{2}$$

where q_i is the molar adsorbed amount.

For a binary mixture, the above equation can be extended to predict mixed adsorption amounts as follows (1):

$$q_i = \frac{q_{\mathrm{m}_i} b_i P_i}{1 + b_1 P_1 + b_2 P_2} \tag{3}$$

The first factor in the PSA parameter is the equilibrium selectivity ($\alpha_{1,2}$) and is defined as follows:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \tag{4}$$

where x_1, x_2 are the mol fractions of the two components on the adsorbent surface, and y_1, y_2 are the corresponding mol fractions in the gas phase. We assumed that the components on the adsorbed surface are the more strongly adsorbed species throughout this work. Using the extended-Langmuir equation (Eq. 3) in conjunction with the definition given in (Eq. 4), the adsorbent selectivity for the surface adsorbents is shown to be a constant for the entire range of partial pressures as follows:

$$\alpha_{1,2} = \frac{q_{\mathrm{m}_1} b_1}{q_{\mathrm{m}_2} b_2} \tag{5}$$

The product ($q_{\mathrm{m}i} b_i$) corresponds to the initial slope of the isotherm, or Henry's constant, for component i. Hence, the adsorbent selectivity is equivalent to the ratio of the initial isotherm slopes of the two components. The selectivity has resulted in a constant value simply because of the nature of the Langmuir isotherm. However, if a different model, such as the loading ratio correlation (LRC, also known as the Langmuir-Freundlich model), is used, the selectivity is likely to be dependent on the operating pressures of the PSA cycle.

Another important factor for PSA separations is the change in the adsorbed amounts of the two components upon pressure cycling. The working capacity of a sorbent typically refers to the strongly adsorbed species and is defined as the difference between the adsorbed amounts at the adsorption (high) pressure and the desorption (low) pressure. Strictly speaking, the working capacity should be defined with respect to the adsorbed amounts under the mixture conditions (that is, through the use of a binary component isotherm). However, a pure component isotherm can be sufficient to make a facile calculation of the parameter. A ratio of the working capacities of the 2 components would provide information about the adsorption performance for a particular PSA cycle. Hence, the second factor of the parameter is the working capacity selectivity ratio and is defined as:

$$W = \frac{\Delta q_1}{\Delta q_2} \tag{6}$$

With the 2 contributing factors to the parameter, the PSA sorbent selection parameter (S) can be written as follows:

$$S = W \cdot \alpha_{1,2} \tag{7}$$

or in its expanded form (using the Langmuir isotherm):

$$S = \frac{\Delta q_1}{\Delta q_2} \cdot \frac{q_{m_1} b_1}{q_{m_2} b_2} \tag{8}$$

The above parameter can be used to compare the performances of two sorbents. The better sorbent will have a higher *S* value.

The AFM similarity to the parameter *S* (Eq. 8) now becomes obvious. If the equilibrium adsorption data seems to give a good fit to the Langmuir equation (as is usually the case for the common gas-separation applications), then the selectivity $\alpha_{1,2}$ would not be significantly different under adsorption and desorption conditions. As a result, $\alpha^2_{\text{ads}}/\alpha_{\text{des}}$ would reduce to $\alpha_{1,2}$, as is the case with the parameter *S* proposed in this work. Also the ΔN_2 (or Δq_1) factor is common to both parameters; the only difference is the addition of the parameter Δq_2 in the denominator. The latter parameter serves to increase the sensitivity of the *S* parameter, and more important, makes it a nondimensional value.

PSA Cycle Description

To demonstrate the usefulness of the PSA selectivity in comparing adsorbent performances, examples from previously published PSA simulation results were used. Both of these examples deal with the production of O_2 through its separation from N_2 present in atmospheric air. The 2 pairs of sorbents to be compared were 1) LiX (Al/Si = 1.0, 100% Li^+ exchange) and NaX, and 2) LiX (Al/Si = 1.0, 100% Li^+ exchange) and LiAgX (Al/Si = 1.0, 1.1 Ag^+ per unit cell). These 2 pairs have been previously analyzed for their performances on air separation by PSA though computer simulations that used a proven model by Rege and Yang (8) and Hutson, Rege, and Yang (9).

A 5-step PSA cycle was used for both sorbent groups in this study. The steps involved in each cycle were as follows: 1) pressurization with the feed gas of 22% O_2 (mixture of O_2 with Ar impurity included) and 78% N_2; 2) high pressure adsorption with the feed gas (feed step); 3) co-current depressurization; 4) countercurrent blowdown; and 5) countercurrent low-pressure purge with the product of the feed step (oxygen).

All the above steps were of equal duration (30 seconds). Thus the time required for the completion of each PSA cycle was 2.5 minutes. The model assumed only 2 adsorbable components: O_2 and N_2. The less strongly adsorbed species, such as Ar, were grouped with O_2, and all contaminants in air, such as CO_2 and water vapor, were assumed to be removed completely through pretreatment beds prior to feeding. Each cycle product was comprised of a volumetric mixture of the feed-step output stream and the co-current depressurization step. This product stream was partly used to purge the bed countercurrently in step no. 5. The gas was fed to the PSA beds at 298 K.

For the model used, we assumed an adiabatic bed, a negligible pressure drop in the bed, and axial dispersion. Further details about the simulation model used as well as the numerical method are discussed in detail in (8,9). The merit of the sorbent pairs was judged by subjecting them to similar PSA cycles and studying the performance parameters, such as product purity, recovery, and throughput. The cycle parameters were adjusted so that two of these performance parameters were nearly constant and the third was compared to determine the better sorbent. The product recovery and product throughput were defined as follows:

$$\text{product recovery} = \frac{(\text{O}_2 \text{ from steps 2 and 3}) - (\text{O}_2 \text{ used in steps 5})}{(\text{O}_2 \text{ fed in steps 1 and 2})} \tag{9}$$

$$\text{product throughput} = \frac{\text{amount of O}_2 \text{ produced per hour (kg/h)}}{\text{amount of adsorbent used in the bed (kg)}} \tag{10}$$

$$\text{Purge-to-feed ratio} = \frac{\text{Amount of O}_2 \text{ used in step 5}}{\text{Amount of O}_2 \text{ fed in steps 1 and 2}} \tag{11}$$

RESULTS AND DISCUSSION

The first group of sorbents considered included LiX (Al/Si = 1.0, 100% Li^+ exchange) and NaX (13X) zeolites. The Langmuir equation parameters for the N_2 and O_2 isotherms at 298 K for this group as well as LiAgX are summarized in Table 1. The results of the PSA simulation runs with corresponding process parameters previously given by Rege and Yang (8) are shown in Table 2. The performances of the adsorbents for air separation to give about 95% pure O_2 product (with Ar impurity included in the O_2 product) were determined by keeping the product throughput fixed at approximately 0.03 kg O_2/h·kg sorbent at constant product purity. Pressure ratios (P_H/P_L) from 2–10 were considered. LiX had been shown to be a superior sorbent to NaX in the entire range of pressure ratios (8). The sorbent parameter S was computed for each of these cases and was plotted against the O_2 product recovery as shown in Fig. 1. The figure clearly shows an increasing product recovery with an increased value of the sorbent parameter. More important, the value of S for the LiX sorbent is much greater than that for NaX, which shows that it is a valid parameter for comparing sorbents.

Table 1. Langmuir Parameters for N_2 and O_2 Isotherms at 298 K on Adsorbents

	N_2		O_2	
Adsorbent	q_s (mmol/g)	b (atm^{-1})	q_s (mmol/g)	b (atm^{-1})
LiX (Si/Al = 1)	2.653	0.946	2.544	0.086
NaX	0.982	0.901	0.276	0.624
LiAgX	2.635	1.170	1.863	0.131

Table 2. PSA Simulation Operating Conditions, Performance Results (8), and PSA Parameter S for the Comparison of LiX and NaX Adsorbents for Air Separation

LiX adsorbent

Pressure Ratio P_H/P_L	Purge-to-Feed Ratio	P_{CD} (atm)	O_2 Product Recovery (%)	PSA Parameter S
2	0.44	0.80	53.5	201.7
3	0.23	0.70	61.9	220.9
4	0.13	0.70	63.3	232.0
5	0.09	0.70	64.1	239.3
6	0.06	0.65	65.3	244.4
7	0.04	0.65	65.3	248.1
8	0.03	0.65	64.5	251.0
10	0.02	0.65	64.7	255.2

NaX (13X) Adsorbent

Pressure Ratio P_H/P_L	Purge-to-Feed Ratio	P_{CD} (atm)	O_2 Product Recovery (%)	PSA Parameter S
2	0.80	0.85	20.0	110.40
3	0.49	0.80	42.3	118.29
4	0.46	0.70	53.3	122.82
5	0.35	0.70	53.4	125.77
6	0.27	0.70	53.2	127.83
7	0.21	0.70	52.8	129.36
8	0.18	0.67	52.8	130.54
10	0.14	0.67	53.1	132.24

LiX (Al/Si = 1, 100% Li^+ exchange)
$P_H = 1.0$ atm; Average product purity = 95.5%; average product throughput = 2.7×10^{-2} kg O_2/h·kg sorbent.

The second group studied consisted of LiX and LiAgX sorbents. The N_2 and O_2 isotherms for these sorbents, as well as a comparison of their performances as sorbents for air separation, appear in Hutson, Rege, and Yang (9). The parameters of the PSA cycle as well as the corresponding PSA sorbent selection parameters are shown in Table 2. Two different cycles were used with different adsorption and desorption pressures. The product purity and recovery in each run were kept roughly the same for both the sorbents by manipulating the PSA parameters, and the product throughputs were compared. As was shown by Hutson, Rege, and Yang (9), the LiAgX sorbent (with 1 Ag^+ per unit cell) showed a 12% higher product throughput than did the LiX sorbent. This is a result of slightly higher N_2 loading on LiAgX compared to that on LiX. The product throughput values for the

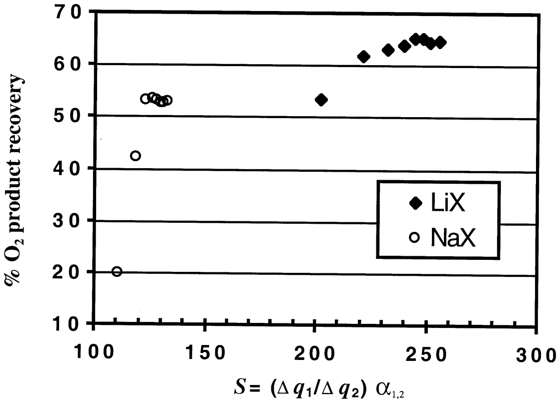

Figure 1. O_2 product recovery (%) versus PSA parameter *S* for the comparison of LiX and NaX adsorbents for air separation at different pressure ratios. Refer to Table 2 for additional details.

2 runs were plotted against the PSA parameter *S* and is shown in Fig. 2. Although the two sorbents showed subtle performance differences, the better performance of the LiAgX sorbent is reflected accurately by the parameter. In both cases, *S* was higher for LiAgX than it was for LiX under the noted operating pressures. Thus, the proposed parameter is shown to be sensitive to even slight differences in the adsorption isotherms.

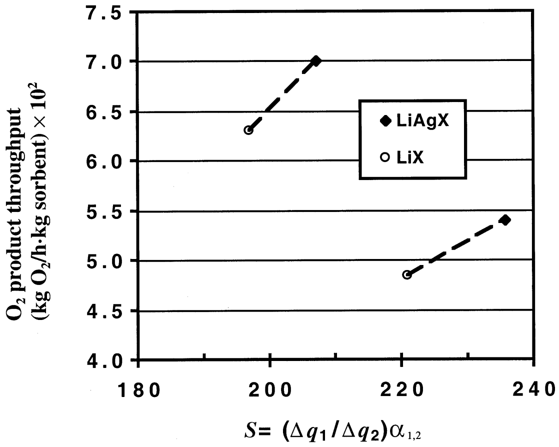

Figure 2. O_2 product throughput (kg O_2/h·kg adsorbent) versus PSA parameter *S* for the comparison of LiX and LiAgX adsorbents for air separation under different cycle conditions. Refer to Table 3 for additional details.

Table 3. PSA Simulation Operating Conditions, Performance Results (9), and PSA Parameter *S* for the Comparison of LiAgX and LiX Adsorbents for Air Separation

Run 1.

Sorbent	P_H (atm)	P_L (atm)	P_{CD} (atm)	O_2 Product Purity (%)	O_2 Product Recovery (%)	Product Throughput (kg O_2/h·kg adsorbent) × 10^2	PSA Parameter *S*
LiX	1.0	0.33	0.70	96.11	62.03	4.84	220.9
LiAgX	1.0	0.33	0.69	96.42	62.74	5.40	235.6

Run 2.

Sorbent	P_H (atm)	P_L (atm)	P_{CD} (atm)	O_2 Product Purity (%)	O_2 Product Recovery (%)	Product Throughput (kg O_2/h·kg^{-1} adsorbent) × 10^2	PSA Parameter *S*
LiX	1.2	0.4	0.70	90.68	78.02	6.31	196.9
LiAgX	1.2	0.4	0.71	90.83	78.48	7.01	207.0

LiAgX (1 Ag^+ per unit cell) and LiX (Al/Si = 1, 100% Li^+ exchange). $P_H = 1.0$ atm.

CONCLUSIONS

A new sorbent selection parameter was proposed to discriminate between two or more candidate adsorbents of a particular binary gas-separation application by PSA. The parameter applies mainly for separations affected by a difference in equilibrium isotherms rather than separations driven by a difference in adsorption kinetics. The two main components of the parameter are the ratio of the delta loadings ($\Delta q_1/\Delta q_2$) of the two components and the equilibrium selectivity ($\alpha_{1,2}$) of the sorbent for the strongly adsorbed species. For sorbents showing Langmuir-type isotherms, the parameter

$$S = \frac{\Delta q_1}{\Delta q_2}\left(\frac{q_{S1}b_1}{q_{S2}b_2}\right)$$

This parameter is simple to calculate and is sensitive to subtle differences in adsorption isotherms. The effectiveness of the proposed parameter was demonstrated by 2 examples from air separation processes.

NOMENCLATURE

b_i Langmuir parameter (atm^{-1})
P_i partial pressure (atm)

q_i	amount adsorbed (mmol/g)
q_{mi}	monolayer saturation amount (mmol/g) $= q_{si}$
S	sorbent selection parameter for PSA (–)
W	working capacity ratio
x_i	adsorbed phase mol fraction
y_i	gas phase mol fraction

Greek Symbols

$\alpha_{i,j}$	equilibrium selectivity $(x_i/x_j)(y_j/y_i)$

Subscripts

ads	adsorption step
des	desorption step
H	high pressure (adsorption)
L	low pressure (desorption)
CD	co-current depressurization pressure

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