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Xiaochun Lu[a]; Daniel Rothstein[a]; Richard Madey[a]; Jan-Chan Huang[b]
[a] DEPARTMENT OF PHYSICS, KENT STATE UNIVERSITY, KENT, OHIO [b] DEPARTMENT OF PLASTIC ENGINEERING, UNIVERSITY OF LOWELL, LOWELL, MASSACHUSETTS

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Pressure Swing Adsorption for a System with a Langmuir Isotherm

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XIAOCHUN LU, DANIEL ROTHSTEIN, and RICHARD MADEY

DEPARTMENT OF PHYSICS
KENT STATE UNIVERSITY
KENT, OHIO 44242

JAN-CHAN HUANG

DEPARTMENT OF PLASTIC ENGINEERING
UNIVERSITY OF LOWELL
LOWELL, MASSACHUSETTS 01854

Abstract

An analytical expression is obtained for the equilibrium relationship between the enrichment factor of the product stream and the ratio of the pressure in the feed stream to that in the product stream for a pressure-swing-adsorption system with a Langmuir isotherm. The enrichment factor is defined as the ratio of the mole fraction of adsorbate gas in the product stream to that in the feed stream. The Langmuir isotherm is characterized by two parameters k_1 and k_2, where k_1 is proportional to the monolayer adsorption capacity and k_2 characterizes the nonlinearity of the adsorption isotherm. It is found that the enrichment factor decreases with increasing values of k_2; thus, the nonlinearity of the isotherm reduces the enrichment factor. A numerical calculation shows that the reduction of the enrichment factor is significant. Also, the enrichment factor increases with increasing values of k_1; thus, the enrichment factor increases as the monolayer adsorption capacity increases.

INTRODUCTION

Since Skarstrom (*1*) introduced the heatless adsorption cycle in 1959, pressure swing adsorption (PSA) has become a well-established industrial technique for the separation of gaseous mixtures. The PSA process is used to enrich hydrogen produced from various hydrocarbon feedstocks (*2–4*), separate oxygen from air (*5*, *6*), remove water vapor from air (*1*), and enrich isotopes (*7*, *8*). PSA has advantages over other adsorption methods in that its cyclic operation can lead to process improvements because it requires no separate desorption steps that need heat input and because it runs continuously with virtually no adsorbent handling required. Despite the wide commercial application of PSA, its theoretical understanding remains in a primitive stage. Two different approaches to the theoretical studies of PSA are apparent. Simulations of nonequilibrium conditions, based on either diffusion or linear-driving-force models, have evaluated numerically the steady-state separation that can be achieved by the PSA process, both with linear (*9*, *10*) and nonlinear isotherms (*11–14*). If mass transfer is rapid, the assumption of local equilibrium is valid throughout the adsorder beds at all times. A linear isotherm is used in most of these equilibrium studies (*15–19*); however, the assumption of a linear isotherm is valid only at low concentrations of the adsorbate gas or at high temperatures. The few equilibrium studies with nonlinear isotherms include those with Langmuir (*17*, *20*), Freundlich (*21–23*), and Langmuir-Freundlich (*11*) isotherms.

The purpose of this paper is to deduce an analytical relationship between the enrichment factor and the ratio of the pressure in the feed stream to that in the product stream for a PSA system with a Langmuir isotherm. The enrichment factor is defined as the ratio of the mole fraction of adsorbate gas in the product stream to that in the feed stream. This relationship will be based on the assumption of instantaneous adsorption equilibrium.

MATHEMATICAL MODEL

The basic pressure-swing-adsorption cycle involves four distinct steps, as shown in Fig. 1 for a PSA system with two packed beds. During Step 1, a high-pressure feed gas is introduced into Bed 2, where adsorption takes place. A small fraction of the product gas is reduced in pressure and used to purge Bed 1. In Step 2, Bed 1 is pressurized with feed gas while Bed 2 is subjected to a pressure reduction (blowdown). The blowdown causes the desorption of some of the adsorbate which is removed during the purge step. The same cycle is repeated in Steps 3 and 4 with high-pressure flow and adsorption occurring in Bed 1 and desorption and purging occurring in Bed 2.

If a packed bed in a PSA system operates under isothermal conditions,

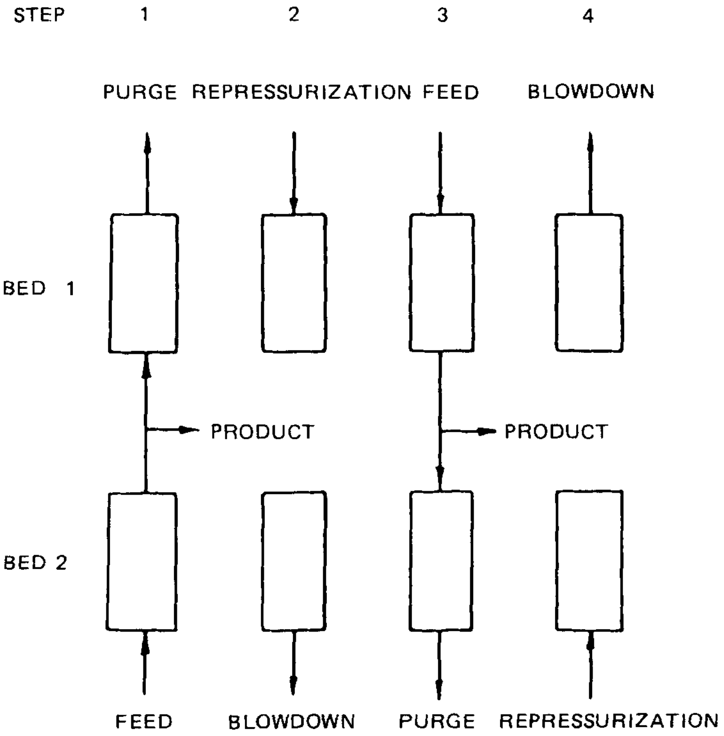

FIG. 1. The four steps involved in a two-bed pressure-swing-adsorption process.

and if longitudinal and radial dispersion in the gas-phase and solid-phase diffusion are negligible, then the PSA process can be described by the following mass-balance equation (*16*) for an adsorbate flowing through a packed bed:

$$\varepsilon[\partial C/\partial t + \partial(uC)/\partial z] + (1 - \varepsilon)\partial q/\partial t = 0 \qquad (1)$$

Here C is the concentration of the adsorbate in the gas phase, q is the concentration of the adsorbate in the solid phase, z is the position along the bed, u is the interstitial velocity, ε is the external void fraction of the packed bed, and t is the time. For an ideal gas undergoing an isothermal process, the overall equation of continuity for the carrier gas can be written (*16*)

$$\partial P/\partial t + \partial(uP)/\partial z = 0 \qquad (2)$$

where P is the total gas pressure in the bed. Equation (2) assumes that the concentration of the adsorbable component is small compared with that of the carrier component. The Langmuir isotherm for the adsorbate gas is

$$q = k_1C/(1 + k_2C) \tag{3}$$

where k_1 and k_2 are the two parameters that characterize the particular gas–adsorbent system. Both parameters decrease monotonically with increasing temperature (*24*). The coefficient k_2 is a measure of the nonlinearity of the isotherm. In the Langmuir theory the surface saturates at the monolayer coverage at high pressures, which requires the coefficient k_1 ($= k_2q_0$) to be equal to k_2 times the monolayer adsorption capacity q_0. The nonlinearity decreases with decreasing values of k_2, and as k_2 becomes zero, the Langmuir isotherm becomes a linear one ($q = k_1C$).

By utilizing the continuity equation and Eq. (3), rewriting the mass balance in Eq. (1) in terms of the mole fraction in the gas phase y ($= p/P$) and the parameters of the Langmuir isotherm, we obtain

$$\begin{aligned}&\varepsilon[P\partial y/\partial t + Pu\partial y/\partial z]\\&\quad + [y\partial P/\partial t + P\partial y/\partial t](1 - \varepsilon)k_1/(1 + k_2yP/RT)^2 = 0\end{aligned} \tag{4}$$

where the ideal gas law $p = CRT$ has been used. Equation (4) can be rearranged to read as follows:

$$\begin{aligned}&[\varepsilon + (1 - \varepsilon)k_1/(1 + k_2yP/RT)^2]\partial y/\partial t + \varepsilon u(\partial y/\partial z)\\&\quad + [(1 - \varepsilon)k_1y/(1 + k_2yP/RT)^2]\partial \ln P/\partial t = 0\end{aligned} \tag{5}$$

Equation (5) is a quasi-linear first-order partial-differential equation which can be solved by the method of characteristics (*25*). This method yields the following pairs of ordinary differential equations:

$$\begin{aligned}dz/\varepsilon u &= dt/[\varepsilon + (1 - \varepsilon)k_1/(1 + k_2yP/RT)^2]\\&= -dy/[(d \ln P/dt)(1 - \varepsilon)k_1/(1 + k_2yP/RT)^2]\end{aligned} \tag{6}$$

Here the partial derivative of ln P is replaced by the total derivative because the pressure P changes only with time if the frictional pressure drop in a single bed can be neglected (*1*, *13*). Rearrangement of the second equality of Eq. (6) yields:

$$-d\ln P/d\ln y = \varepsilon[(1 + k_2yP/RT)^2/(1 - \varepsilon)k_1] + 1 \tag{7}$$

Introduce the dimensionless variables:

$$S = P/P_H \tag{8}$$

$$Y = y/y_H \tag{9}$$

Here the subscript H refers to quantities at high pressure in the feed stream. Let the subscript L denote quantities at low pressure in the product stream; then, when $P = P_L$ and $y = y_L$, $S_L = P_L/P_H$ and $Y_L = y_L/y_H$. The quantity $1/S_L$ is the pressure ratio P_H/P_L, and Y_L is the enrichment factor of the product stream. Equation (9) can be rewritten in terms of these dimensionless variables:

$$-d\ln S/d\ln Y = 1 + \alpha[1 + k_2(y_HP_H)SY/RT]^2/k_1 \tag{10}$$

where

$$\alpha \equiv \varepsilon/(1 - \varepsilon) \tag{11}$$

Define the following two dimensionless parameters:

$$\gamma \equiv k_2(y_HP_H)/RT = k_2C_H \tag{12}$$

$$\beta \equiv \alpha/k_1 = \alpha C_H/[q_H(1 + \gamma)] \tag{13}$$

The quantity γ is the product of the nonlinearity factor k_2 and C_H, the adsorbate gas concentration at high pressure. The right-hand member of Eq. (13) follows from the Langmuir isotherm Eq. (3) and the fact that the coefficient k_1 is independent of concentration. If $\gamma \ll 1$, the system behaves as a linear system. If $\gamma > 1$, the solid phase will be saturated by the adsorbate. When $\gamma = 1$, the order of magnitude of parameter β is given by the volume of the bed divided by the volume of the gas processed. Equation (10) can now be written in dimensionless form:

$$-d\ln S/d\ln Y = 1 + \beta(1 + \gamma SY)^2 \tag{14}$$

In order to solve Eq. (14) for S as a function of Y, let

$$V = SY \tag{15}$$

Then Eq. (14) can be rewritten:

$$-d \ln V/(1 + \gamma V)^2 = \beta d \ln Y \tag{16}$$

Integration of Eq. (16) from P_H to P results in

$$-\ln SY + \ln [(1 + \gamma SY)/(1 + \gamma)] - 1/(1 + \gamma SY) = \beta \ln Y - 1/(1 + \gamma) \tag{17}$$

Since $Y = Y_L$ when $S = S_L$, Eq. (17) becomes

$$-\ln (S_L Y_L) + \ln [(1 + \gamma S_L Y_L)/(1 + \gamma)] - 1/(1 + \gamma S_L Y_L)$$
$$= \beta \ln Y_L - 1/(1 + \gamma) \tag{18}$$

or

$$[(1 + \gamma S_L Y_L)/(1 - S_L Y_L)] \ln [(1 + \gamma S_L Y_L)/(1 + \gamma) Y_L^{\beta+1} S_L] = \gamma/(1 + \gamma) \tag{19}$$

Equations (18) and (19) are the required relationships between enrichment factor Y_L and the pressure ratio $1/S_L$ for a PSA system with a Langmuir isotherm. For a linear isotherm, k_2 (or γ) equals zero, and Eq. (18) reduces to

$$Y_L = S_L^{-1/(1+\alpha/k_1)} \tag{20}$$

which is the result of Shendalman and Mitchell (*16*).

DISCUSSION

To examine how the nonlinearity of the Langmuir isotherm affects the enrichment factor, the enrichment factor is plotted in Fig. 2 versus the pressure ratio with three values of γ for two different values of β. A value of $\gamma = 0$ yields a linear isotherm at all pressures; for $1 = \gamma \equiv k_2 C_H$, one can see from the isotherm Eq. (3) that one-half of the available surface is occupied at the high pressure p_H; for $\gamma = 10$, the adsorbent is virtually saturated at the high pressure. The values of γ are typical of Langmuir

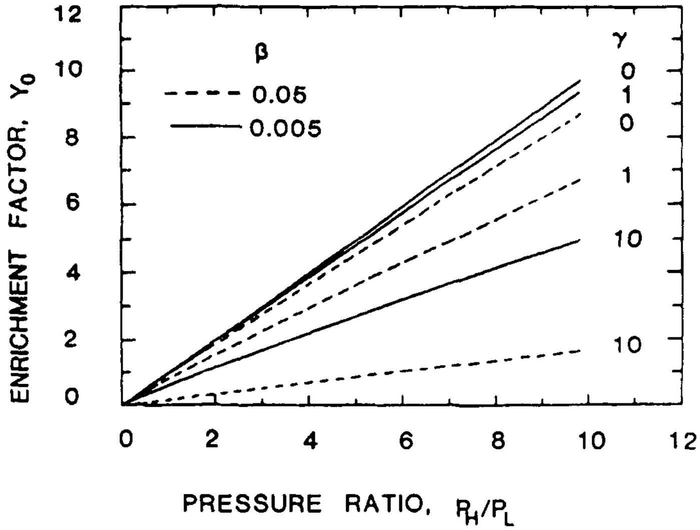

FIG. 2. The enrichment factor versus the pressure ratio in a PSA system for three different values of γ at $\beta = 0.05$ and $\beta = 0.005$.

isotherms (*26–28*) which show considerable departure from linearity. The values of β were chosen at the upper end of the literature range to exaggerate the effects of γ. An increase of γ above unity quickly reduces the efficiency of the bed. The linear case gives the maximum enrichment factor for the given values of β and the pressure ratio. As can be seen in Fig. 2, the effect on the enrichment factor of increasing the nonlinearity parameter γ is much larger for the larger value of β. For $\gamma = 1$, at a pressure ratio of 10, the enrichment factor is reduced by 20% from the linear case for $\beta = 0.05$; however, at $\beta = 0.005$, the reduction is only 4%.

In Fig. 3 the enrichment factor for two values of γ is plotted as a function of the pressure ratio with three values of the parameter β (viz., different values of k_1). The adsorption of 105 ppm methane on activated carbon at 298 K has a linear isotherm (*29*) with a dimensionless adsorption capacity of 40; thus, since $\alpha = 1.3$ for this adsorbent, the value of β is 0.032. The adsorption capacity increases with the molecular weight of the adsorbate; therefore, the value of β for heavier gases will be smaller. Considering the use of different adsorbents, an upper limit of 0.05 for the value of β was chosen. For a given pressure ratio, the enrichment factor decreases with increasing β; that is, the enrichment factor decreases as the monolayer adsorption capacity decreases, which means that a smaller adsorption capacity implies a smaller enrichment factor. Also, as shown

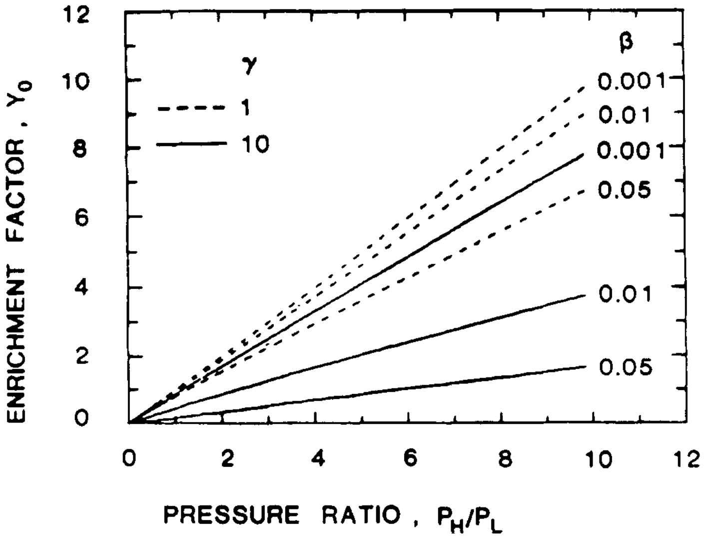

FIG. 3. The enrichment factor versus the pressure ratio in a PSA system for three different values of β at $\gamma = 1.0$ and $\gamma = 10$.

in Fig. 2, the enrichment factor decreases with increasing values of the nonlinearity parameter γ. For values of $\gamma \gg 1$, the surface saturates and the enrichment factor becomes quite small; physically, very little gas can be desorbed since the isotherm is nearly flat near saturation. For this reason, the PSA system should be operated away from the saturated condition and close to the linear region. The enrichment factor versus pressure ratio curves for $\beta \leqslant 0.001$ are virtually indistinguishable. For sufficiently low values of β, the enrichment factor is equal to the pressure ratio.

The separating ability of the PSA system with a Langmuir isotherm can be compared to that for a PSA system with a Freundlich isotherm (*23*). For both isotherm types the relation between the pressure ratio and the enrichment factor can be described in terms of a nonlinearity parameter and the adsorption capacity at the feed pressure. For the Langmuir isotherm, the dimensionless nonlinearity parameter is the quantity $(1 + \gamma)$; for the Freundlich system, it is the exponent of the Freundlich isotherm. These two nonlinearity parameters are not comparable quantitatively because the Freundlich coefficient cannot exceed unity, and the parameter γ has an explicit pressure dependence which the Freundlich exponent does not. In each case, a second dimensionless parameter β is inversely proportional to the product of the adsorption capacity and the nonlinearity parameter. The enrichment factor depends strongly on the pressure range. A PSA system with a Langmuir isotherm does not show a significant improvement in separating ability over the Freundlich system. At high pressures the saturation of the adsorbate reduces the enrichment factor. Even at low pressures where the Langmuir is essentially linear, the difference in separating ability between the two types is not large (*23*).

Both k_1 and k_2 decrease monotonically with increasing temperature (*24*), and an increase in k_1 increases the total gas processed in unit time, while an increase in k_2 decreases the enrichment factor; therefore, there is an optimum operating temperature for enriching a gas in an inert carrier. When two adsorbate gases are present, the situation will be more complicated depending on whether the two gases interfere with each other (*30*).

CONCLUSION

We examined the pressure-swing-adsorption process for a system with a Langmuir isotherm and instantaneous adsorption equilibrium, and obtained an analytical relation between the enrichment factor of the product stream and the ratio of the pressures in the feed and purge streams. The enrichment factor for a Langmuir system is reduced significantly compared with a linear system.

Acknowledgment

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SYMBOLS

C	gas-phase concentration of adsorbate (mol/cm^3)
k_1	Langmuir isotherm constant
k_2	Langmuir isotherm constant (cm^3/mol)
p	partial pressure in adsorbate gas (mmHg)
P	total pressure in the bed (mmHg)
P_H	high pressure in feed gas stream (mmHg)
P_L	low pressure in product stream (mmHg)

q	solid-phase concentration of adsorbate (mol/cm^3)
q_0	monolayer adsorption capacity (mol/cm^3)
S_L	inverse of pressure ratio
t	time (s)
u	interstitial velocity (cm/s)
V	constant defined in Eq. (15) (= SY)
y	gas-phase mole fraction of adsorbate
y_H	gas-phase mole fraction of adsorbate in the high-pressure feed stream
y_L	gas-phase mole fraction of adsorbate in the low-pressure product stream
Y_L	enrichment factor of product stream
z	longitudinal position in bed (cm)
α	constant defined in Eq. (11)
ε	void fraction of adsorber bed
β	constant defined in Eq. (13)
γ	constant defined in Eq. (12)

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