Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gong, Sung Yong and Lee, Won Kook(1993) 'The Effect of the Time Length of Pressure Changing Steps on Concentration in the Gas Phase in the Pressure Swing Adsorption Process', Separation Science and Technology, 28: 11, 1995 — 2005

To link to this Article: DOI: 10.1080/01496399308016729

URL: http://dx.doi.org/10.1080/01496399308016729

SEPARATION SCIENCE AND TECHNOLOGY, **28**(11&12), pp. 1995–2005, 1993

The Effect of the Time Length of Pressure Changing Steps on Concentration in the Gas Phase in the Pressure Swing Adsorption Process

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ABSTRACT

To investigate the effect of the time length of pressure changing steps theoretically, mathematical expressions for the gas-phase concentration of pressure changing steps in the pressure swing adsorption process were derived under the simple initial conditions and compared with numerical solutions using the orthogonal collocation method. At this time, the linear driving force model was used. We examined whether the time length of the pressure changing steps influenced the concentration in the gas phase for various mass transfer coefficients. The time length did not affect the concentration in the gas phase for the two extreme cases, i.e., a very large mass transfer coefficient or a very small mass transfer coefficient, but the effect of time length was large for a small mass transfer coefficient. A detailed discussion of the pressure-changing steps is included.

INTRODUCTION

Pressure swing adsorption (PSA) is a gas separation process in which the adsorbent is regenerated by reducing the partial pressure of the adsorbed component, either by lowering the total pressure or by using a purge gas. Since Skarstrom (1) invented the PSA cycle, many PSA processes have been developed and commercialized because of its low energy requirements and low capital investment costs (2).

Despite the industrial use of PSA, relatively limited analysis and simulation exists in the literature (3–7). Brief reviews of the theoretical develop-

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ments have been made by Wankat (8) and Yang (9). Most of the published models are equilibrium models. Another approach involves numerical solution of mass and energy balance equations plus the mass transfer rate equations (10–12). However, most of these models make two extreme assumptions for the pressure-changing steps (i.e., equilibrium or frozen solid model). To understand PSA performance more accurately, it will be helpful to investigate the pressure-changing steps. This problem has rarely been investigated either theoretically or experimentally except in works by Sundaram and Wankat (13) and Doong and Yang (14). Sundaram and Wankat (13) first investigated the pressure drop effects in the pressurization and blowdown steps of the PSA cycle with an equilibrium model. Doong and Yang (14) examined the pressure drop effects on gas adsorption processes by numerical simulation. According [illegible] ir work, pressure drop effects can be negligible for a system with [illegible] articles and a relatively long step time.

In this paper, mathematical expressions for the gas-phase concentration of the pressure-changing steps are derived under simple initial conditions where the finite mass transfer rate and the negligible pressure drop effects through the bed are assumed.

These expressions will be useful for understanding the effect of the time length of pressure-changing steps on cyclic PSA performance.

MATHEMATICAL MODEL

Assuming no radial variations in concentration and no axial dispersion, the dynamic behavior of the system may be described by the following set of equations.

Mass Balance

External fluid:

$$\frac{\partial py}{\partial t} + \frac{\partial upy}{\partial z} + \frac{1 - \epsilon}{\epsilon} RT \frac{\partial q}{\partial t} = 0 \tag{1}$$

Overall continuity (neglecting tracer):

$$\frac{\partial p}{\partial t} + \frac{\partial up}{\partial z} = 0 \tag{2}$$

Mass transfer rate expression:

$$\partial q/\partial t = k(q^* - q) \tag{3}$$

Adsorption equilibrium:

$$q^* = K\frac{py}{RT} \tag{4}$$

Pressure change:

$$p = at + p_l \quad \text{(for pressurization step)} \tag{5-1}$$

$$p = -at + p_h \quad \text{(for blowdown step)} \tag{5-2}$$

Initial and Boundary Conditions

Pressurization step:

$$y(z, 0) = 0; \quad q(z, 0) = 0 \tag{6-1}$$

$$u(L, t) = 0; \quad y(0, t) = y_{\text{in}} \tag{6-2}$$

Blowdown step:

$$y(z, 0) = y_{\text{in}}; \quad q(z, 0) = q^* \tag{7-1}$$

$$u(L, t) = 0; \quad \partial y/\partial z|_{z=0} = 0 \tag{7-2}$$

In principle, the above set of equations cannot be solved analytically. But if it is assumed that the pressure is a staircase function as shown in Fig. 1, we can derive mathematical expressions for the gas-phase concen-

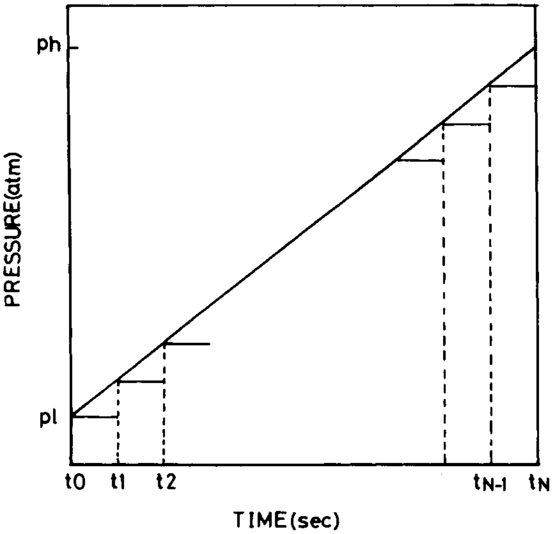

FIG. 1 Staircase function of pressure.

trations by using the Laplace transform. In this case, Eqs. (5-1) and (5-2) can be expressed as follows.

Pressurization step:

$$p' = ant^* + p_l \qquad [\text{for } nt^* \leq t \leq (n+1)t^*, n = 0, 1, \ldots, N] \tag{8-1}$$

Blowdown step:

$$p' = -ant^* + p_h \qquad [\text{for } nt^* \leq t \leq (n+1)t^*, n = 0, 1, \ldots, N] \tag{8-2}$$

where N is the number of pressure-changing steps and

$$Nt^* = (p_h - p_l)/a \tag{8-3}$$

SOLUTION OF PARTIAL DIFFERENTIAL EQUATIONS

(1) Pressurization Step

Denoting the Laplace transform with respect to time by a bar over a function, we have the following equations from Eqs. (1)–(4) and Eq. (8-1).

For $t_0 \leq t \leq t_1$:

$$\frac{\partial \bar{y}}{\partial z} + \frac{A1(s)}{a(L-z)}\bar{y} = \frac{A2(s)}{a(L-z)} \tag{9}$$

where

$$A1(s) = p_1 s + \lambda_1 p_1 ks/(s+k)$$

$$A2(s) = p_1 y(z, 0) + \frac{1-\epsilon}{\epsilon} RTq(z, 0)\frac{k}{(s+k)}$$

$$\lambda_1 = \frac{1-\epsilon}{\epsilon} K$$

Since $y(z, 0) = q(z, 0) = 0$, the solution of Eq. (9) is

$$\bar{y} = \frac{y_{\text{in}}}{s} F_1(z, s) \tag{10}$$

where

$$F_1(z, s) = \exp\left(-\frac{p_1\lambda_2}{a} s\right)\exp\left(-\frac{p_1\lambda_2}{a}\frac{1-\epsilon}{\epsilon} K\frac{ks}{s+k}\right) \tag{11}$$

$$\lambda_2 = \ln\frac{L}{L-z}$$

The inverse Laplace transform of Eq. (11) is

$$\begin{aligned} F_1(z,t) &= k\exp(-\lambda_1\lambda_{31})\exp(\lambda_{31} - kt)\sqrt{\frac{\lambda_1\lambda_{31}}{kt-\lambda_{31}}}I_1(2\sqrt{\lambda_1\lambda_{31}(kt-\lambda_{31})}) \\ &\quad + k\exp(-\lambda_1\lambda_{31})\exp(\lambda_{31}-kt)\delta(kt-\lambda_{31}), \qquad \text{for } kt \geq \lambda_{31} \\ &= 0, \qquad \text{for } kt \leq \lambda_{31} \end{aligned} \tag{12}$$

where

$$\lambda_{31} = p_1 k\lambda_2/a$$

If we put $p_i = p'$ for $t_{i-1} \leq t \leq t_i$, then

$$\begin{aligned} F_i(z,t) &= k\exp(-\lambda_1\lambda_{3i})\exp(\lambda_{3i} - kt)\sqrt{\frac{\lambda_1\lambda_{3i}}{kt-\lambda_{3i}}}I_1(2\sqrt{\lambda_1\lambda_{3i}(kt-\lambda_{3i})}) \\ &\quad + k\exp(-\lambda_1\lambda_{3i})\exp(\lambda_{3i}-kt)\delta(kt-\lambda_{3i}), \qquad \text{for } kt \geq \lambda_{3i} \\ &= 0, \qquad \text{for } kt \leq \lambda_{3i} \end{aligned} \tag{13}$$

e

$$\lambda_{3i} = p_i k\lambda_2/a$$

From Eq. (13) we can obtain the inverse Laplace transform equation of Eq. (10). For $t = t_N$

$$\frac{y}{y_{\text{in}}} = \sum_{i=1}^{N} \int_{\max(t_{i-1},\lambda_{3i}/k)}^{t_i} F_i(z,\,t)\,dt \tag{14}$$

(2) Blowdown Step

From Eqs. (1)–(4) and Eq. (8-2), we have the following transformed equation.

$$\frac{\partial\bar{y}}{\partial z} - \frac{A1(s)}{a(L-z)}\bar{y} = -\frac{A2(s)}{a(L-z)} \tag{15}$$

Using initial and boundary conditions, the solution of Eq. (15) is as follows. For $t_{i-1} \leq t \leq t_i$:

$$\begin{aligned} y_i(t',z) &= \frac{y_{i-1}(t^*,z) + \dfrac{1-\epsilon}{\epsilon}\dfrac{RT}{p_i}q_{i-1}(t^*,z)}{1+\lambda_1} \\ &\quad + y_{i-1}(t^*,z) - \frac{y_{i-1}(t^*,z) + \dfrac{1-\epsilon}{\epsilon}\dfrac{RT}{p_i}q_{i-1}(t^*,z)}{1+\lambda_1}\exp(-(1+\lambda_1)kt') \end{aligned} \tag{16}$$

where

$$q_i(t^*, z) = Kp_iy_i(1 - \exp(-kt^*))/RT + q_{i-1}(t^*, z)\exp(-kt^*) \quad (17)$$

$$q_0(t^*, z) = Kp_hy_{\text{in}}/RT$$

$$y_0(t^*, z) = y_{\text{in}}$$

$$t' = t - t_{i-1}$$

DISCUSSION

Under simple initial conditions, mathematical expressions for the gas-phase concentrations for the pressurization step and the blowdown step have been derived (such as Eq. 14 and Eq. 16, respectively).

The original mass balance (Eqs. 1–5) was solved numerically by the method of orthogonal collocation for $a = 1$ and 0.1, and compared with Eqs. (14) and (16), respectively. As shown in Figs. 2 and 3, agreement of the two solutions improved as the dividing number increased. The parameters are given in Table 1, where the mass transfer coefficient and the adsorption equilibrium constant are from Mitchell and Shendalman's data (15). Figures 4 and 5 show the effect of the time length of the pressurization step and the blowdown step on the gas-phase concentration, respectively.

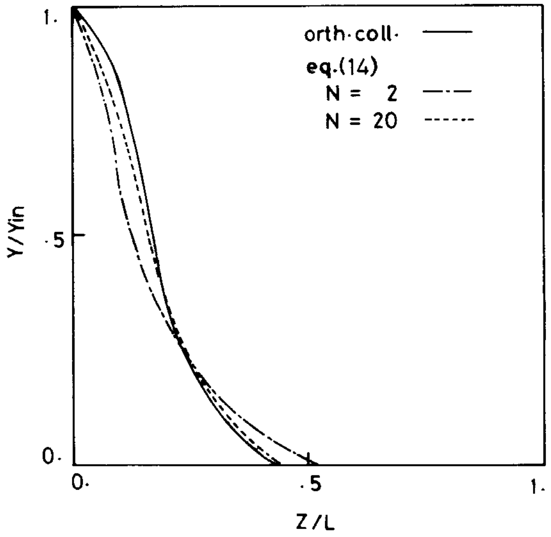

FIG. 2 Comparison of our work with numerical solution for pressurization step. $a = 1$.

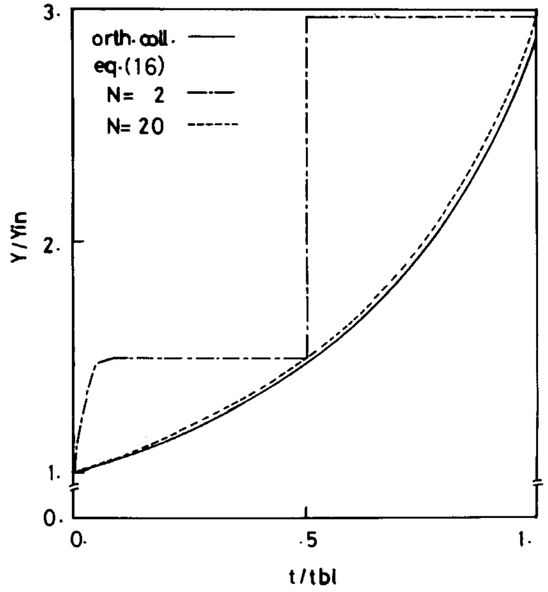

FIG. 3 Comparison of our work with numerical solution for blowdown step. $a = 0.1$.

As shown in Figs. 4 and 5, the time lengths of the pressure-changing steps have a large effect on concentration. For the blowdown step, the time length is included in the second term on the right-hand side of Eq. (16), which is an exponential function of the time length. Therefore, y is strongly affected by a short time length. Moreover, Eq. (16) implies that this effect increases as the mass transfer coefficient decreases. When k approaches zero, y/y_{in} approaches 1, regardless of the time length.

TABLE 1
Parameters Used in Calculation of Theoretical Values

Feed composition	1.0%
High pressure, p_h	3.0 atm
Low pressure, p_l	1.0 atm
Temperature	25°C
Column length	60 cm
Bed porosity	0.42
Adsorption equilibrium constant, K	52.7
Mass transfer coefficient, k	0.0467 (second^{-1})

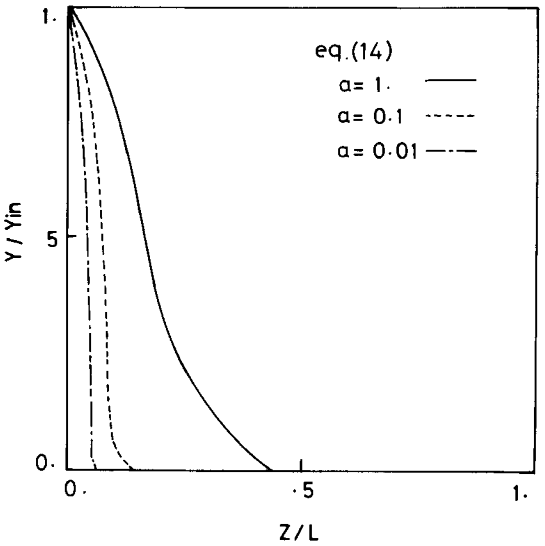

FIG. 4 Effect of the time length on the gas-phase concentration for pressurization step. $N = 20$.

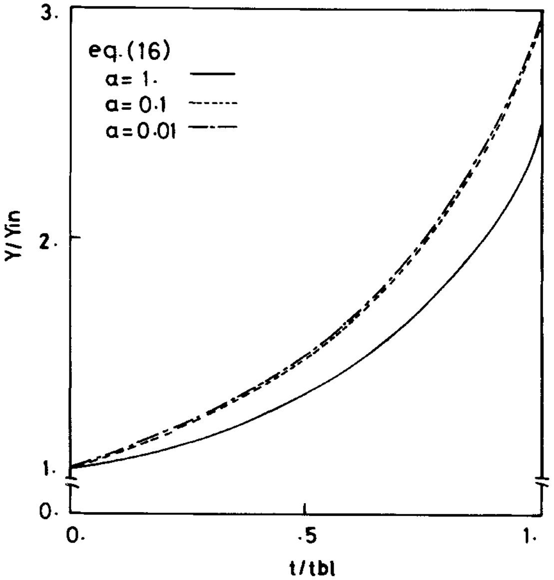

FIG. 5 Effect of the time length on the gas-phase concentration for blowdown step. $N = 20$.

Figure 5 shows that the gas-phase concentration is greatly affected by the time length of the pressurization step. However, Eq. (14) is so complicated that the asymptotic behavior of y cannot be easily understood. We now introduce an asymptotic approximation of the integral that has been proposed by Klinkenberg (16).

$$\alpha = \exp(-M)\int_0^N \exp(-L)I_0(2\sqrt{ML})dL + \exp(-M - N)I_0(2\sqrt{MN})$$

$$\cong \frac{1}{2}(1 + \operatorname{erf}(\sqrt{N + \tfrac{1}{4}} - \sqrt{M + \tfrac{1}{4}})) \tag{18}$$

Although the application of Eq. (18) is restricted to $M \geq 2$ and $N \geq 1$, the asymptotic prediction of the effect of the time length on y is still useful. Consider Eq. (14) for the case of $t_{i-1} \leq \lambda_{3i} \leq t \leq t_i$.

$$\int_{\lambda_{3i}/k}^{t_i} F_i(z, t)\, dt = \exp(-\lambda_1\lambda_{3i})\exp(\lambda_{3i} - kt)I_0(2\sqrt{\lambda_1\lambda_{3i}(kt - \lambda_{3i})})$$

$$+ \exp(-\lambda_1\lambda_{3i})\int_0^{kt-\lambda_{3i}} k\exp(-(kt - \lambda_{3i}))I_0(2\sqrt{\lambda_1\lambda_{3i}(kt - \lambda_{3i})})\, dt$$

$$\cong \frac{1}{2}(1 + \operatorname{erf}(\sqrt{kt - \lambda_{3i} + \tfrac{1}{4}} - \sqrt{\lambda_1\lambda_{3i} + \tfrac{1}{4}})) \tag{19}$$

Equation (19) shows that y decreases as the time length increases. We can also expect the effect of the time length to increase as the mass transfer coefficient decreases because of the error function property. We now introduce another integral defined by Brinkley and Brinkley (17) and its property (18):

$$\beta(M, N) = \exp(M)\int_0^N \exp(-L)I_0(2\sqrt{ML})\, dL \tag{20-1}$$

$$\lim_{M\to\infty} \exp(-M - N)\beta(M, N) = 1 \tag{20-2}$$

$$\beta(M, N) + \beta(N, M) + I_0(2\sqrt{ML}) = \exp(M + N) \tag{20-3}$$

When $k \to \infty$, it is obvious from Eqs. (20-1)–(20-3) that

$$\int_{\max(\lambda_{3i}/k, t_{i-1})}^{t^i} F_i(z, t)\, dt \to 0$$

regardless of the time length. When $k \to 0$, the following result is obtained from Eq. (13):

$$y/y_{\text{in}} = 1, \qquad \text{for } t_i \geq p_i\lambda_2/a$$

$$= 0, \qquad \text{for } t_i \leq p_i\lambda_2/a$$

From these results, we expect there is a mass transfer coefficient region in which an effect of the time length of pressure-changing steps exists.

In this paper we have derived mathematical expressions for the pressure-changing steps and have theoretically examined the effect of the time length of the pressure-changing steps. Although this discussion was for pressure-changing steps only, these phenomena will probably occur in the same way in continuous PSA cycles. We will examine the effect of time on cyclic PSA performance in another paper.

CONCLUSION

To investigate the theoretical effects of the time length of pressure-changing steps, we have derived mathematical expressions for the gas-phase concentration of pressure-changing steps. To confirm the usefulness of the resulting equations, the original mass balance equations were solved numerically under the same conditions by using the orthogonal collocation method. As the dividing number was increased, agreement between the two solutions increased. There is a certain region of the mass transfer coefficient value where the effect of the time length on the gas-phase concentration can be ignored. The effect of the time length was large when the mass transfer coefficient was small. These phenomena can be explained by the derived equations.

SYMBOLS

a	pressure changing rate defined by Eqs. (5-1) and (5-2)
$A1$, $A2$	function in Laplace domain defined by Eq. (9)
F	function defined by Eq. (12)
I_0, I_1	modified Bessel function of orders 0 and 1, respectively
k	external film mass transfer coefficient (second^{-1})
K	adsorption equilibrium constant
L	column length (cm)
N	dividing number of the time length of pressure-changing step
p	pressure (atm)
p'	pressure defined by Eqs. (8-1) and (8-2) (atm)
p_h, p_l	high and low pressure, respectively (atm)
q	adsorbate concentration in solid phase (mol/cm^3)
q^*	q at equilibrium with y
R	gas constant
s	Laplace domain variable
t	time (second)
t^*	time segment defined by Eq. (8-3) (second)

t_{bl}	the time length of blowdown step (second)
T	bed temperature (°K)
u	interstitial velocity (cm/s)
y	gas phase mole fraction of adsorbate
y_{in}	gas phase mole fraction of adsorbate in feed
z	position in the bed (cm)

Greek Symbols

α, β	function defined by Eqs. (18) and (20), respectively
δ	delta function
ϵ	bed porosity
λ_1	$\frac{1-\epsilon}{\epsilon}K$
λ_2	$\ln\frac{L}{L-z}$
λ_{3i}	$p_i k\lambda_2/a$

Subscript

i	ith time segment

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Received by editor November 2, 1992