Intensification of Pressure Swing Adsorption Processes

Scaling rules have been developed which are able to change the dimension of a pressure swing adsorption plant keeping its main performance constant. Such scaling rules result from a system of algebraic equations which arises by constraining the solution of a fairly general dimensionless mathematical model to be the same in the old and new plant configuration. Different heat and mass transfer mechanisms, purification, and multicomponent bulk separation processes, both isothermal and nonisothermal, have been considered. Furthermore, the influence of different equilibrium isotherms and the main practical limitations have been discussed. The application of these rules shows that column size can be reduced significantly by using smaller particles in shorter beds with rapid cycles.

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Introduction

The use of adsorption as a tool to separate different kinds of mixtures is now quite common. One of the most powerful processes is pressure swing adsorption (PSA), which was originally developed by Skarstrom (1959). Various modifications of the original process, reviewed by many authors (Ruthven, 1984; Wankat, 1986; Yang, 1987), are presented. The aim of such modifications varies, but they basically try to improve the performance of the apparatus by changing the plant configuration. Different numbers of columns, as well as different pressurization and blowdown methods, have been proposed.

One way of improving the utilization of the system (known as intensification) is to modify some parameters of the process, such as the pressure ratio, the purge-to-feed ratio, the cycle time, the particle and column diameters, and so on. Unfortunately, the reasons for high productivity in a complex system like PSA often are not easy to understand, since process parameters are strongly related to one another. The intensifications of PSA processes (Jones and Keller, 1981; Keller and Kuo, 1982) achieve good performance, but are difficult to understand and generalize.

On the other hand, for simpler processes, such as simple adsorption or liquid chromatography, theoretical analysis can be performed to find simple scaling rules that improve the performance of the plant (Knox and Pyper, 1986; Wankat, 1987; Wankat and Koo, 1988). The results of such analyses lead to shorter (pancake) columns, filled with smaller pellets. Despite the reduction of the particle diameter, the pressure drop across the column can be kept constant because of the reduced column length. The duration of different operations, such as feed or elution, has to be reduced too.

The aim of this paper, following a previous study on isothermal PSA processes dealing with binary mixtures (Suh and Wankat, 1990), is to find a general procedure to intensify an existing PSA design. To achieve this goal, a fairly general dimensionless mathematical model has been developed by introducing suitable reference variables. The influence of different dimensionless groups on some objective functions, namely the product recovery and purity, and the adsorbent productivity, has been investigated. If one constrains the solutions of the dimensionless model to be the same for the old and the new PSA configuration, the process can be intensified by reducing the cycle time. With this constraint, a set of algebraic equations arises relating the cycle time to the other process parameters, such as the particle diameter, the column length, the feed velocity, and so forth. In many limiting cases, these equations can be solved analytically to arrive at some simple scaling rules. Multicomponent (chromatographic) nonisothermal processes, different equilibrium isotherms, and mass/heat transfer controlling mechanisms, as well as the influence of the extracolumn volume are also discussed.

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Mathematical Model

Balance and transfer equations

Industrial PSA processes dealing with purification of gaseous streams can be regarded as isothermal, since their typical temperature range is ±5°C at steady-state conditions, while in bulk separation processes the temperature range is wider [up to 100°C (Yang, 1987)]. Because the equilibrium and mass transfer properties are influenced strongly by the temperature, suitable scaling rules for such processes should account for thermal effects. From the structure of a general dimensionless mathematical model that simulates the behavior of nonisothermal multicomponent PSA systems, we wish to obtain information about the intensification procedure. Usual assumptions of plug flow models have been retained, particularly

- Ideal gas behavior
- Laminar flow
- Negligible axial dispersion
- Negligible radial gradients
- Negligible potential energy
- Negligible irreversible conversion of mechanical to thermal energy
- Constant cross-sectional area and porosity
- Adiabatic columns
- Spherical particles
- Negligible pressure gradient inside a particle.

The equations governing the dynamic of the process are the NC mass balance equations for the fluid phase, one for each component, the NC multicomponent equilibrium isotherms, the Blake-Kozeny equation relating the pressure drop to the other column parameters, the energy balance, and the stoichiometric equation. The unknowns related to these equations are the NC concentrations in the fluid phase, c_i; the NC amounts adsorbed, q_i; the pressure, p; the gas-phase temperature, T; and the interstitial velocity, u. Moreover, to evaluate the rate of mass and heat transfer from the fluid to the solid, we need the mass and energy balances for the particles. The form of these relations depends on which mechanism controls the mass and heat transfer. Different limiting cases are discussed below. The final equation we need is related to the heat exchange between fluid and wall, as will be discussed later. All the above equations are made dimensionless by lumping parameters and dividing every variable involved by an arbitrary reference variable. The choice of reference variables, as well as the definition of the dimensionless groups, is arbitrary and does not influence the results.

The dimensionless equation variables and reference parameters constituting the mathematical model are summarized in Table 1. The mass balance equations are the same as in Suh and Wankat (1990). The term f_i is the disappearance rate of solute i into the particle, while F_i is the dimensionless form of f_i. The disappearance rate of energy from the fluid is g, which includes heat transfer to the particles and the walls, $g = g_p + g_w$. The dimensionless disappearance of energy from the fluid is G.

Table 1. Dimensionless Equations for Model

Mass balance:	$\frac{\partial \bar{c}_i}{\partial \tau} + \frac{\partial (\bar{c}_i U)}{\partial Z} + F_i = 0$	(1)
Langmuir isotherm:	$Q_i = \frac{\bar{b}_i P_{i\bullet} Q_i^{\mathrm{sat}}}{1 + \sum_{j=1}^{NC} \bar{b}_j P_{j\bullet}}$	(2)
Arrhenius dependence:	$\bar{b}_i = P_0 b_i = P_0 b_i(T_0) \exp\left(-\frac{\Delta H_i^{\mathrm{ads}}}{R_g T_0}\left(\frac{T_0}{\overline{T}} - 1\right)\right)$	(3)
Pressure drop (laminar flow):	$\frac{\partial P}{\partial Z} = -U$	(4)
Energy balance:	$\frac{\partial \overline{T}}{\partial \tau} + U\frac{\partial \overline{T}}{\partial Z} + (K_\gamma - 1)\overline{T}\frac{\partial U}{\partial Z} + \frac{\overline{T}}{P} G = 0$	(5)
Stoichiometry:	$\sum_{j=1}^{NC} \bar{c}_i = \frac{P}{\overline{T}}$	(6)
Dimensionless variables:	$Z = z/z_o, \tau = t/t_o, \bar{c}_i = c_i/c_o, P = p/p_o, U = u/u_o, Q = q/q_o, \overline{T} = T/T_o$	(7)
	$F_i = \frac{6}{d_p}\left(\frac{1-\epsilon}{\epsilon}\right)\frac{t_0}{c_0} f_i$	(8)
	$G = G_w + G_p = \frac{t_0}{p_0}(K_\gamma - 1)(g_w + g_p)$	(9)
Reference parameters:	$z_0 = L, t_0 = \frac{z_0}{u_0}, u_0 = \frac{p_0 d_p^2}{150 \mu z_0}\left(\frac{\epsilon}{1-\epsilon}\right)^2 q_0 = \frac{c_0}{\rho_p}\left(\frac{\epsilon}{1-\epsilon}\right),$	
	$c_0 = \frac{p_0}{R_g T_0}$	(10)

Table 2. Dimensionless Transfer Equations

	Local Equilibrium Model	
Mass balances:	$F_i = \frac{\partial Q_i}{\partial \tau}$	(11)
	$\bar{c}_{i*} = \bar{c}_i$	(12)
Energy balance:	$G_p = \chi \frac{\partial \overline{T}}{\partial \tau} + \sum_{i=1}^{NC} \zeta_i F_i$	(13)
	$\overline{T}_p = \overline{T}$	(14)
Dimensionless groups:	$\chi = \left(\frac{1-\epsilon}{\epsilon}\right) \frac{T_0}{p_0} (K_\gamma - 1) \rho_p C_{P_p}$	(15)
	$\zeta_i = \frac{\Delta H_i^{\mathrm{ads}}}{C_V T_0}$	(16)
	External Film Model	
Biot number:	$(Bi)_m = \frac{a}{2\epsilon} \frac{D_m}{D_e} Re^{1+b} Sc^{1/3}$	(17)
	$(Bi)_h = \frac{a}{2\epsilon} \frac{k_g}{k_e} Re^{1+b} Pr^{1/3}$	(18)
Mass transfer:	$F_i = \frac{\partial Q_i}{\partial \tau} = \nu_{fi} (\bar{c}_i - \bar{c}_{i*})$	(19)
Heat transfer:	$G_p = \lambda (\overline{T} - \overline{T}_p)$	(20)
	$\chi \frac{\partial \overline{T}_p}{\partial \tau} + \sum_{i=1}^{NC} \zeta_i F_i - G_p = 0$	(21)
Dimensionless groups:	$\nu_{fi} = 6 \frac{k_{fi} t_0}{d_p} \left(\frac{1-\epsilon}{\epsilon}\right), \lambda = 6 (K_\gamma - 1) \left(\frac{1-\epsilon}{\epsilon}\right) \frac{T_0}{p_0} \frac{h_p t_0}{d_p}$	(22a,b)
Film coefficients:	$J_m = J_h = \frac{a}{\epsilon} Re^b$	(23)
	$J_m = Sh\, Re^{-1} Sc^{-1/3}, J_h = Nu\, Re^{-1}\, Pr^{-1/3}$	(24a,b)
	Internal Resistances Model	
Mass transfer:	$F_i = 3\Omega_{ei} \epsilon_d \frac{\partial \bar{c}_{i*}}{\partial \eta}\bigg\rvert_{\eta=1} + 3\Omega_{si} \frac{\partial Q_i}{\partial \eta}\bigg\rvert_{\eta=1}$	(25)
	$\frac{\partial Q_i}{\partial \tau} + \epsilon_d \frac{\partial \bar{c}_{i*}}{\partial \tau} = \Omega_{ei} \epsilon_d \left(\frac{\partial^2 \bar{c}_{i*}}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial \bar{c}_{i*}}{\partial \eta}\right) + \Omega_{si} \left(\frac{\partial^2 Q_i}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial Q_i}{\partial \eta}\right)$	(26)
Boundary conditions:	$\frac{\partial \bar{c}_{i*}}{\partial \eta}\bigg\rvert_{\eta=0} = 0, \bar{c}_{i*}(\eta = 1) = \bar{c}_i$	(27a,b)
Heat transfer:	$G_p = 3\Lambda \frac{\partial \overline{T}}{\partial \eta}\bigg\rvert_{\eta=1}$	(28)
	$\chi \frac{\partial \overline{T}_p}{\partial \tau} = \sum_{i=1}^{NC} \zeta_i \frac{\partial Q_i}{\partial \tau} + \Lambda \left(\frac{\partial^2 \overline{T}_p}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial \overline{T}_p}{\partial \eta}\right)$	(29)
Boundary conditions:	$\frac{\partial \overline{T}_p}{\partial \eta}\bigg\rvert_{\eta=0} = 0, \overline{T}_p(\eta = 1) = \overline{T}$	(30a,b)
Dimensionless variables:	$\eta = r/r_{po}, \Omega_{ei} = \frac{4 D_{ei} t_0}{d_p^2}, \Omega_{si} = \frac{4 D_{si} t_0}{d_p^2}$	(31)
	$\epsilon_d = \left(\frac{1-\epsilon}{\epsilon}\right) \epsilon_p, \Lambda = 4 (K_\gamma - 1) K_p \left(\frac{1-\epsilon}{\epsilon}\right) \frac{t_0 T_0}{p_0 d_p^2}$	
Reference parameter:	$r_{po} = d_p/2$	(32)
	Series Resistances Model	
Boundary conditions:	$3\Omega_{ei} \epsilon_d \frac{\partial \bar{c}_{i*}}{\partial \eta}\bigg\rvert_{\eta=1} + 3\Omega_{si} \frac{\partial \overline{Qi}}{\partial \eta}\bigg\rvert_{\eta=1} = \nu_{fi} (\bar{c}_i - \bar{c}_{i*}\rvert_{\eta=1})$	(33)
	$3\Lambda \frac{\partial \overline{T}}{\partial \eta}\bigg\rvert_{\eta=1} = \lambda (\overline{T} - \overline{T}_p\rvert_{\eta=1})$	(34)
	Linear Driving Force Model	
Mass transfer:	$F_i = \nu_{\mathrm{tot}i} (\bar{c}_i - \bar{c}_{i*}^{av})$	(35)
Mass balance:	$\frac{\partial Q_i}{\partial \tau} + \epsilon_d \frac{\partial \bar{c}_{i*}^{av}}{\partial \tau} = \nu_{\mathrm{tot}i} (\bar{c}_i - \bar{c}_{i*}^{av})$	(36)
where	$\bar{c}_{i*}^{av} = \frac{1}{V_p} \int \bar{c}_{i*}\, dV, \nu_{\mathrm{tot}i} = 6 \frac{k_{\mathrm{tot}i} t_0}{d_p} \left(\frac{1-\epsilon}{\epsilon}\right), \frac{1}{k_{\mathrm{tot}i}} = \frac{1}{k_{fi}} + \frac{1}{k_p \epsilon_p}$	(37)

The equations for mass and heat transfer through the surface of the particle depend on the controlling resistance, which can be located either in the external film or inside the particle. Different combinations of the resistances, both in series and in parallel, are possible. The structure of such equations is similar for both mass and heat transfer if the same mechanism controls.

The simplest case, the so-called *local equilibrium model,* arises if we assume that no mass or heat transfer resistance exists. These equations are given in Table 2. These equations are very simple and have been widely used to simulate PSA processes. In particular, the assumption of thermal equilibrium between the solid and gas phase is usually retained when dealing with numerical simulation of nonisothermal adsorbers (Yang, 1987).

Unfortunately, at least for the mass transfer phenomena, the resistances are not always negligible and must be considered to achieve quantitative agreement between model predictions and experiments. A measure of the relative importance of the internal and external resistances is given by the value of the Biot number, which represents the ratio between internal and external gradients. Thus, high values of this number mean that the main resistance is located within the particle, and the opposite is true for small Biot number values. Many relationships have been proposed to evaluate both the mass and heat Biot number in fixed packed beds. Typical equations are shown in Table 2 (Butt, 1980).

Using the results of Petrovich and Thodos (1968), for the Reynolds number in the range 3–2,000, the above coefficients assume the values $a = 0.357$ and $b = -0.359$. When $Bi \ll 1$ (*external film model*), the resistances are concentrated in the external film. The equations governing mass and heat transfer are given in Table 2.

When the Biot number is large ($Bi \gg 1$), we can use the *internal resistances model.* The equations for this model are also given in Table 2. This model refers to a system where both pore and surface diffusion in parallel (*parallel resistance model*) play a role, as in adsorptive gas separation processes. If only pore diffusion is important, the last term on the righthand side of Eqs. 25 and 26 has to be neglected (*pore diffusion model*). If the surface diffusion is the only resistance, however, the first term on the righthand side of Eqs. 25 and 26 must be neglected (*surface diffusion model*). In any event, the structure of the model, which is most important for the scaling rule procedure outlined below, does not change for the three cases (parallel, pore, or surface diffusion). Thus, the resulting scaling rules, when any one of these situations is controlling, will be the same.

If $Bi \approx 1$, both of the internal and external resistances play a role (*series resistances model*). A complete model for this case should involve all the equations discussed above for internal and external resistances, coupled by suitable boundary conditions, which are in Table 2 (Eqs. 33 and 34).

When dealing with numerical simulation of adsorbers, a very useful simplification of the particle mass balance is the *linear driving force model.* This approximation, originally due to Glueckauf and Coates (1947), can be introduced when resistances are in series to obtain the lumped equations given in Table 2 (Santacesaria et al., 1982). The lumped parameter k_p can be evaluated by the relationship proposed by Glueckhauf and Coates (1947)

$$k_p = K\frac{D_e}{r_p} \tag{38}$$

The applicability of this approximation to cyclic processes has been discussed by Nakao and Suzuki (1983), and by Raghavan et al. (1986). The main result is that such an approximation can be used safely for cyclic processes if the value of the parameter K in Eq. 38, depending on the dimensionless cycle time $\theta_c = D_e t_C / r_p^2$, is properly chosen.

Wall heating

If the thickness of the wall is not negligible, the accumulation of heat in the wall of the column can influence the behavior of the apparatus. This is also true if the apparatus is regarded as adiabatic. Such an effect is accounted for by the term G_w in Eq. 9 which, if included, seriously complicates the mathematical model. A simple way to model the wall heating is to utilize a local average wall temperature defined as $T_w^{av} = (T + T_a)/2$, leading to the following energy balance for the column walls:

$$G_w = \chi_w \frac{\partial \overline{T}}{\partial \tau} \tag{39}$$

where

$$\chi_w = \left(\frac{\delta_w^2 + 2\delta_w}{2\epsilon}\right)\frac{T_0}{p_0}(K_\gamma - 1)\,\rho_w C_{Pw} \tag{40}$$

In the last equation, δ_w is the ratio between the wall thickness and the column radius. By substituting the equilibrium model relation for G_p (Eq. 13), and the wall heating equation above for G_w into Eq. 5, we obtain the following form of the fluid-phase energy balance:

$$\left(1 + \frac{\overline{T}}{P}(\chi + \chi_w)\right)\frac{\partial \overline{T}}{\partial \tau} + U\frac{\partial \overline{T}}{\partial Z} + (K_\gamma - 1)\,\overline{T}\frac{\partial U}{\partial Z} + \sum_{i=1}^{NC} \zeta_i F_i = 0 \tag{41}$$

It is clear that the influence of the wall heating may be neglected only if $\chi \gg \chi_w$, which means

$$(1 - \epsilon)\,\rho_p C_{Pp} \gg (\delta_w + \delta_w^2/2)\,\rho_w C_{Pw} \tag{42}$$

For industrial adsorbers, the constraint above is usually fulfilled because $\delta_w \ll 1$; in the following, the term G_w will be neglected in the energy balance equation.

Boundary and initial conditions for cyclic operation

For the sake of simplicity, in the first part of this study the simple two-column four-step Skarstrom cycle, shown in Figure 1, has been considered. The effect of different plant configurations, which influence the boundary conditions of the model, will be discussed later. In what follows, the boundary conditions for column 1 are discussed. Of course, the same boundary conditions, at different times, hold for column 2. Because the following boundary conditions are the same for every cycle, an integer variable $n = 1, 2, \ldots,$ (*number of cycle* $- 1$) will be used.

Step 1: repressurization from p_L to p_H.

$$n \cdot \tau_C \le \tau < n \cdot \tau_C + \tau_I \begin{cases} P(\tau, Z = 0) = P^{(1)} = P_H \\ \overline{c}_i(\tau, Z = 0) = \overline{c}_i^{(1)} \\ \overline{T}(\tau, Z = 0) = \overline{T}^{(1)} \\ U(\tau, Z = 1) = 0 \end{cases} \tag{43}$$

Step 2: feed at p_H.

$$n \cdot \tau_C + \tau_I \le \tau < n \cdot \tau_C + \tau_{II}$$

$$\cdot \begin{cases} P(\tau, Z = 0) = P^{(2)} = P_H \\ \overline{c}_i(\tau, Z = 0) = \overline{c}_i^{(2)} \\ \overline{T}(\tau, Z = 0) = \overline{T}^{(2)} \\ U(\tau, Z = 0) = U^{(2)} \end{cases} \tag{44}$$

Step 3: blowdown from p_H to p_L.

$$n \cdot \tau_C + \tau_{II} \le \tau < n \cdot \tau_C + \tau_{III}$$

$$\cdot \begin{cases} P(\tau, Z = 0) = P^{(3)} = P_L \\ \dfrac{\partial \overline{c}_i(\tau, Z = 1)}{\partial Z} = 0 \\ \dfrac{\partial \overline{T}(\tau, Z = 1)}{\partial Z} = 0 \\ \dfrac{\partial U(\tau, Z = 1)}{\partial Z} = 0 \end{cases} \tag{45}$$

Step 4: purge at p_L.

$$n \cdot \tau_C + \tau_{III} \le \tau < (n + 1) \cdot \tau_C$$

$$\cdot \begin{cases} P(\tau, Z = 0) = P^{(4)} = P_L \\ \overline{c}_i(\tau, Z = 1) = \overline{c}_i^{(4)} \\ \overline{T}(\tau, Z = 1) = \overline{T}^{(4)} \\ U(\tau, Z = 1) = U^{(4)} \end{cases} \tag{46}$$

The cycle time has been defined as $\tau_C = \Sigma_{i=1}^{4} \tau^{(i)}$, while $\tau_{III} = \Sigma_{i=1}^{3} \tau^{(i)}$ is the end time of the third step (blowdown). Of course, $\tau_{II} = \Sigma_{i=1}^{2} \tau^{(i)}$ and $\tau_I = \tau^{(1)}$ are the end times for the second and the first step, respectively.

Either the feed or the product can be used to repressurize the column. If the former is employed, $\overline{c}_i^{(1)} = \overline{c}_{i_p}$; if the latter, $\overline{c}_i^{(1)} = \overline{c}_{i_{PROD}}$. For every step, the initial conditions are the conditions at the end of the previous step. At $\tau = 0$, arbitrary initial conditions may be chosen.

The above mathematical model, which is constituted by coupled algebraic and partial differential equations and controls the mass and heat transfer depending on the mechanism, can be solved numerically by suitable techniques. These methods would be useful in obtaining the initial design. Our purpose is different in that we obtain information from the structure of the equations without solving the model.

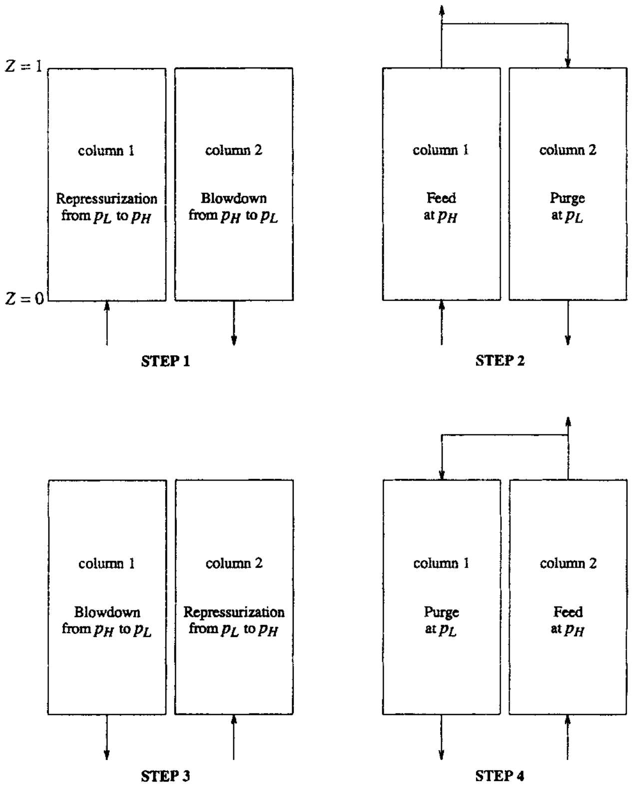

Figure 1. Two-column four-step Skarstrom PSA cycle.

Dimensional Analysis

Objective functions

The performance of a PSA apparatus is usually expressed in terms of product purity, product recovery, and sorbent productivity. These interrelated parameters are defined for the *k*th component for a single cycle at steady-state conditions. In the following, the relationships are written for repressurization with feed. No differences arise in the final scaling rules if the product is used to repressurize the column: obviously, in this case, all the following equations change.

1. The product recovery (REC) is the ratio between the quantity of the *k*th compound collected in the product stream and the quantity of *k*th compound fed:

$$\text{REC} = \frac{\int_{\tau_I}^{\tau_{II}} (\overline{c}_k U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\overline{c}_k U)_{Z=1}\, d\tau}{\int_0^{\tau_{II}} (\overline{c}_k U)_{Z=0}\, d\tau} \tag{47}$$

2. The product purity (PUR) is a volume-averaged concentration of the *k*th compound taken over the step time in which this component is recovered.

$$\text{PUR} = \frac{\int_{\tau_I}^{\tau_{II}} (\overline{c}_k U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\overline{c}_k U)_{Z=1}\, d\tau}{\sum_{j=1}^{NC} \left(\int_{\tau_I}^{\tau_{II}} (\overline{c}_j U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\overline{c}_j U)_{Z=1}\, d\tau \right)} \tag{48}$$

3. The adsorbent productivity (AP) is the amount of the kth compound product per adsorbent weight and time.

$$\mathrm{AP} = \frac{c_0 u_0 \left(\int_{\tau_I}^{\tau_{II}} (\bar{c}_k U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\bar{c}_k U)_{Z=1}\, d\tau \right)}{\tau_C (1-\epsilon)\rho_p L} \tag{49}$$

The goal of the intensification procedure is to improve the sorbent productivity without changing the product recovery and purity. We assume there exists an old design, from a mathematical model or an existing plant, which accomplishes the separation we need with satisfactory product recovery and purity. To compare this old configuration with a new one, it is useful to introduce the operator ratio, R, defined as (Wankat and Koo, 1988)

$$R(\alpha) = \frac{\alpha_{\mathrm{NEW}}}{\alpha_{\mathrm{OLD}}} \tag{50}$$

where α is any parameter related to the process (e.g., the feed velocity, an independent variable, as well as the adsorbent productivity, a dependent variable), and the new subscripts NEW and OLD mean the new and old configuration, respectively. Properties of such an operator are easily developed. We wish to find suitable scaling rules to keep $R(\mathrm{REC}) = R(\mathrm{PUR}) = 1$ and able to improve $R(\mathrm{AP})$.

To evaluate the values of the three ratios above from Eqs. 47 to 49, the $\bar{c}_i$ and U profiles for the old and new configuration must be known. If such dimensionless profiles do not change from the old to the new configuration, we can simplify the ratio expressions because the integrals involving only dimensionless variables do not change. If we keep the same profiles of all the dimensionless variables in the old and in the new configuration of the apparatus, the ratio of the recovery becomes

$$R(\mathrm{REC}) = \frac{\left(\dfrac{\int_{\tau_I}^{\tau_{II}} (\bar{c}_k U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\bar{c}_k U)_{Z=1}\, d\tau}{\int_0^{\tau_{II}} (\bar{c}_k U)_{Z=0}\, d\tau} \right)_{\mathrm{NEW}}}{\left(\dfrac{\int_{\tau_I}^{\tau_{II}} (\bar{c}_k U)_{Z=1}\, d\tau - \int_{\tau_{III}}^{\tau_C} (\bar{c}_k U)_{Z=1}\, d\tau}{\int_0^{\tau_{II}} (\bar{c}_k U)_{Z=0}\, d\tau} \right)_{\mathrm{OLD}}} = 1 \tag{51}$$

because the values of the integrals at the numerator (the NEW configuration) and at the denominator (the OLD one) are the same. Analogously, for the ratio of the purity one can show that

$$R(\mathrm{PUR}) = 1 \tag{52}$$

while the ratio of the sorbent productivity, which include other terms, becomes

$$R(\mathrm{AP}) = \frac{\left(\dfrac{c_0 u_0}{\tau_C (1-\epsilon)\rho_p L} \right)_{\mathrm{NEW}}}{\left(\dfrac{c_0 u_0}{\tau_C (1-\epsilon)\rho_p L} \right)_{\mathrm{OLD}}} = \frac{R(c_0) R(u_0)}{R(\tau_C) R(1-\epsilon) R(\rho_p) R(L)} \tag{53}$$

If we scale the PSA plant keeping constant the dimensionless profiles, the new apparatus will show the same product recovery and purity as the old one, but a different sorbent productivity.

Fundamental relationships

Before analyzing the mathematical model in detail, it is worthwhile to establish a few relationships which arise from the definitions of the reference variables. Such definitions are arbitrary, and the scaling rules are not influenced by the particular reference parameters which are used. Using the operator ratio, Eqs. 10 lead to the following relations:

$$R(q_0) = R(c_0) = \frac{R(p_0)}{R(T_0)} \tag{54}$$

$$R(L) = R(u_0) R(t_0) \tag{55}$$

$$R(d_p) = \left(\frac{R(u_0) R(L) R(\mu)}{R(p_0)} \right)^{0.5} = R(u_0) \left(\frac{R(t_0) R(\mu)}{R(p_0)} \right)^{0.5} \tag{56}$$

Moreover, the total feed rate, N, is defined as

$$N = \epsilon \frac{\pi D^2}{4} \frac{p^{(2)} u^{(2)}}{T^{(2)} R_g} = \epsilon \frac{\pi D^2}{4} \frac{P^{(2)} U^{(2)}}{\overline{T}^{(2)} R_g} \frac{p_0 u_0}{T_0} \tag{57}$$

while the pressure drop across the packed bed is

$$\Delta p^{(i)} = p_H^{(i)} - p_L^{(i)} = p_0 (P_H^{(i)} - P_L^{(i)}) \quad i = 1 \text{ to } 4 \tag{58}$$

From the latter two equations, in terms of the operator ratio,

$$R(D) = \left(\frac{R(N) R(T_0)}{R(p_0) R(u_0)} \right)^{0.5} \tag{59}$$

$$R(\Delta p) = R(p_0) \tag{60}$$

To obtain the relations above, we have assumed that the same sorbent in both of the configurations is used, so that $R(\rho_p) = R(\epsilon) = 1$. Note that the porosity can be regarded as constant only for spherical particles when $D/d_p > 30$ (Cohen and Metzner, 1981).

Keeping the profiles of all the dimensionless variables constant implies that the solutions of the mathematical model must be the same for both the old and new configurations. This will occur if the values of all the dimensionless groups involved in the model (Eqs. 1, 2, 4, 5 and 6), and the boundary conditions (Eqs 43 to 46), are the same for both configurations, and the initial values of all the dimensionless variables are the same. However, keeping the dimensionless variables constant does not mean that the dimensional variables are the same in the two configurations because the reference variables may be different.

The constraints concerning the boundary conditions can be expressed in terms of the operator ratio as follows:

$$R(\tau^{(i)}) = R(P^{(i)}) = 1 \quad i = 1 \text{ to } 4 \tag{61}$$

$$R(\bar{c}_j^{(i)}) = R(\overline{T}^{(i)}) = 1 \quad i = 1, 2, 4; j = 1 \text{ to } NC \tag{62}$$

$$R(U^{(i)}) = 1 \quad i = 2, 4 \tag{63}$$

In particular, the above relations constrain all the dimensionless variable values related to the feed in the new configuration to be the same as in the old one

$$R(P_F) = R(\overline{c}_{iF}) = R(\overline{T}_F) = R(U_F) = 1 \qquad (64)$$

Consequently, the ratios of the feed dimensional variable must be equal to the ratios of the reference variables:

$$R(p_F) = R(p_0), \quad R(c_{iF}) = R(c_0), \quad R(T_F) = R(T_0), \quad R(u_F) = R(u_0) \qquad (65)$$

The same is true for the cycle time, as well as for all the switching times:

$$R(t_C) = R(t_{\mathrm{III}}) = R(t_{\mathrm{II}}) = R(t_{\mathrm{I}}) = R(t_0) \qquad (66)$$

The dimensionless groups present in the mathematical model are $G, F_i, \overline{b}_i, Q_i^{\mathrm{sat}}$, and $(K_\gamma - 1)$; because their values must be the same in the old and new configuration, their ratio values have to be equal to unity. In particular, the constraint

$$R(\overline{b}_i) = R(P_0)R(b_i(T_0))\, R \cdot \left\{ \exp\left[-\frac{\Delta H_i^{\mathrm{ads}}}{R_g T_0}\left(\frac{T_0}{\overline{T}} - 1\right)\right]\right\} = 1 \qquad (67)$$

can be fulfilled by setting $R(T_0) = R(p_0) = 1$. These constraints are very important because they not only state, from Eqs. 54 and 65, that the pressure, temperature and composition of the feed must be equal in the old and new configuration (from Eqs. 61 and 62 the same is true for all the other inlet streams), but also that, from Eq. 60, the pressure drop across the bed must be the same. Moreover, the constraint $R(Q_i^{\mathrm{sat}}) = R(q_i^{\mathrm{sat}}) = 1$ is also satisfied because setting $R(T_0) = 1$ implies that in the space $Z - \tau$ not only the dimensionless profile of the temperature, but also the dimensional temperature profile is equal in the two configurations. Furthermore, the dimensional pressure and concentration profiles do not change; consequently, all the physical variables depending on temperature, composition, and pressure, such as viscosity, thermal conductivity and so forth, do not change from the old to the new configuration, and the operator ratio values for these variables are equal to unity. It turns out that the constraint $R(K_\gamma - 1) = 1$ is also fulfilled.

Summarizing, from the relations discussed above, the constraints arising from the structure of the model and from the variable definitions can be written as follows:

$$R(q_0) = R(c_0) = R(\mathrm{T}_0) = R(p_0) = R(\Delta p) = R(p^{(j)}) = R(T^{(k)}) = R(c_i^{(k)}) = 1 \qquad (68)$$

where $i = 1$ to NC, $j = 1$ to 4, $k = 1, 2, 4$.

$$R(L) = R(u_F)R(t_C) \qquad (69)$$

$$R(d_p) = R(u_F)R(t_C)^{0.5} \qquad (70)$$

$$R(D) = R(N)^{0.5}\, R(u_F)^{-0.5} \qquad (71)$$

$$R(AP) = R(t_C)^{-1} \qquad (72)$$

It is worth noting that the adsorption productivity depends only on the cycle time change: the shorter the cycle time, the greater the sorbent productivity. Furthermore, in the relations above we have chosen N, t_C, and u_F as independent variables.

There are two more constraints we have not considered in the discussion above: $R(G) = R(F_i) = 1$. Because the equations representing these terms depend on which mechanism controls mass and heat transfer, the relation between feed velocity and cycle time arising from these equations also depends on the controlling step for mass and heat transfer. Note that we have only one degree of freedom, the ratio of the feed velocity in the two designs. It turns out that we are allowed to introduce only one more constraint. Different limiting situations, which originate different scaling rules, are discussed next.

Scaling Rules

Isothermal PSA processes

For isothermal PSA processes, the energy balance, Eq. 5, is not necessary because the temperature is not a variable and it is equal in two different plant configurations. This situation was analyzed by Suh and Wankat (1990) for different limiting situations. They found that if no resistances to mass transfer exist, the feed velocity can be arbitrarily chosen. Moreover, if internal resistances control, the feed velocity must be the same in both the configurations

$$R(u_F) = 1 \qquad (73)$$

while if external film diffusion controls, the feed velocity is related to the cycle time by

$$R(u_F) = R(t_C)^{(b+1)/4b} \qquad (74)$$

These results follow straightforwardly from the models above.

One implicit assumption is that the controlling step for mass (and, in the next sections, heat) transfer is the same for all the components and both of the configurations. This can be checked by looking to the values of the Biot number for each compound in both configurations. From Eqs. 17 and 18, by introducing Eq. 70, we can find for both the mass and heat Biot number

$$R(Bi) = R(u_F)^{2(1+b)}\, R(t_C)^{(1+b)/2} \qquad (75)$$

When external diffusion controls in the old configuration, the ratio of the Biot number becomes $R(Bi) = R(t_C)^{(b+1)/2b}$. Because $-1 < b < 0$, reducing the cycle time to improve sorbent productivity implies reducing the Biot number; in the new configuration the Biot number will be less than in the old one. This guarantees that film diffusion will also control in the new configuration. If the internal resistances control, $R(Bi) = R(t_C)^{(1+b)/2}$, and reductions in cycle time result in lower Biot numbers. Depending on both the original Biot number value and the cycle time reduction magnitude, external film resistance can become important. This is a dangerous situation because, as can be easily proved for simpler adsorption separation processes (Wankat and Koo, 1988), the most conservative scaling rules arise as one decreases cycle time if a film-controlled situation is assumed.

In this event, as well as when the old configuration has a

$(Bi)_m \approx 1$, both internal and external resistances must be considered in scaling the apparatus. From the *linear driving force model* (Eqs. 35 and 36) the new constraint is represented by

$$R(v_{\text{tot}\,i}) = \frac{R(t_C)\,R(K_{\text{tot}\,i})}{R(d_p)} = 1 \qquad (76)$$

This equation leads to Eq. 74 if $k_p \gg k_{fi}$, and to Eq. 73 if $k_p \ll k_{fi}$. While obtaining the former is straightforward, the latter can be obtained by noting that, if internal resistances control, $R(K) = 1$ because $R(\theta_C) = R(t_C)/R(d_p)^2 = 1$. This last equality can be proved by means of Eqs. 70 and 73. In any event, by introducing Eqs. 37c, 38 and 70 into Eq. 76 and rearranging the resulting equation, we obtain

$$R(t_C)^{(b+1)/2}\,R(u_F)^{2b} - \frac{\dfrac{a}{\epsilon}\,\mathrm{Re}^{b+1}\,Sc^{1/3}\,R(u_F)^{2(b+1)}R(t_C)^{(b+1)/2}\,R(K)^{-1} + \dfrac{2\epsilon_p K}{\tau^*}}{\dfrac{a}{\epsilon}\,\mathrm{Re}^{b+1}\,Sc^{1/3} + \dfrac{2\epsilon_p K}{\tau^*}} = 0 \qquad (77)$$

where *Re*, *Sc*, and *K* refer to the old configuration. This equation cannot be solved analytically, but suitable numerical methods can be used. For a given value of $R(t_C)$ and a known old configuration, Eq. 77 gives the corresponding value of $R(u_F)$. The tortuosity $\tau^* = D_e/D_m$ has also been introduced. Note that the *series resistances model* is not useful in this particular approach because it leads to two incompatible constraints, overconstraining the problem.

The values of the main scale-up parameters vs. the cycle time ratio are shown, for different mass transfer controlling steps, in Figures 2 to 5. The scaling rules discussed above are also summarized in Table 3. This analysis, in agreement with the results reported by Suh and Wankat (1990), leads to shorter columns filled with smaller particles and operating with faster cycle times. Because of the simultaneous reduction of the bed length and particle size, the pressure drop across the bed can be kept constant. These results are consistent with the trend in column chromatography towards "pancake" columns.

Adiabatic PSA processes

The isothermal assumption is reasonable only when dealing with purification processes, such as drying air, while industrial bulk separation devices can usually be regarded as adiabatic. In this event, the fluid phase and particle energy balances must also be considered, and the constraint $R(G) = 1$ has to be satisfied. It should be stressed that the constraints resulting from such a relation must be compatible with the others discussed above because we have no more degrees of freedom.

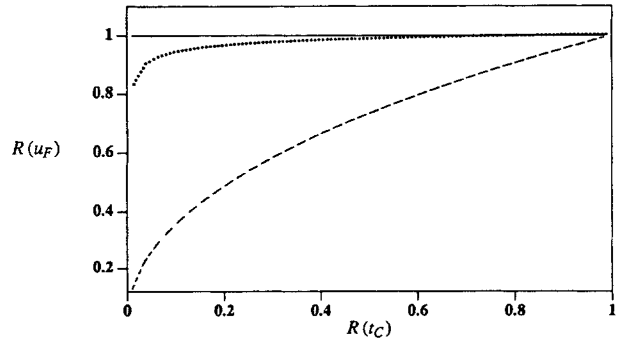

Figure 2. Ratio of feed velocity vs. ratio of cycle time for different mass and heat controlling steps, and $R(N) = 1$.

---, models as in part 2 of Table 3 (external resistance).
—, models as in part 3 of Table 3 (internal resistance).
. . . , models as in part 4 of Table 3 (series).
Old configuration: $Re = 10$; $Sc = 0.7$; $K = 5$; $R(K) = 1$; $\epsilon = 0.4$; $\epsilon_p = 0.2$; $\tau^* = 5$

The simplest energy particle model regards the particle temperature as equal to the local gas temperature (Eqs. 13 and 14). To keep the dimensionless rate of disappearance of the energy from the gas phase, *G*, constant, the dimensionless parameters present in this model, χ and ζ_i, must be constant; this means $R(\chi) = R(\zeta_i) = 1$. From Eqs. 15 and 16, we can see that because $R(T_0) = R(p_0) = 1$ (Eq. 68), these requirements are fulfilled. It turns out that no more constraints arise from this model, and it may be coupled with every mass transfer model discussed in the previous section. The scaling rules developed for isothermal processes and summarized in Table 3 are also fully valid for adiabatic processes, as long as the fluid and the solid phase are in local thermal equilibrium.

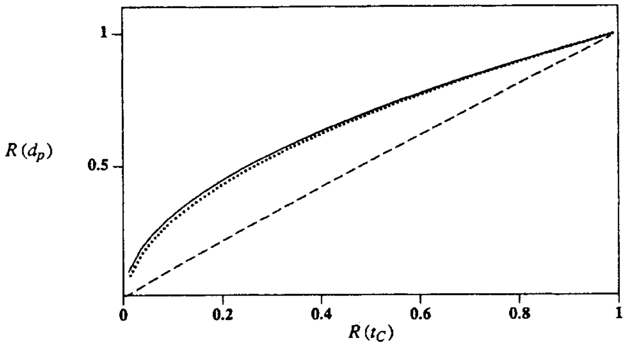

Figure 3. Ratio of particle diameter vs. ratio of cycle time for different mass and heat controlling steps.

Legend as in Figure 2.

If $(Bi)_h \ll 1$, the parameter *G* can be evaluated by means of Eqs. 20 and 21. Besides χ and ζ_i, which do not involve any new constraints as discussed above, we have to set $R(\lambda) = 1$. Exactly as reported in the previous section for mass transfer, by use of Eqs. 22b, 24b and 70, this constraint leads to the same relation (Eq. 74). As shown in the second part of Table 3, this heat transfer mechanism may be coupled with both the film-controlled mass transfer model and the equilibrium assumption. The same scaling rules discussed in the previous section for an isothermal apparatus arise. The considerations about the Biot

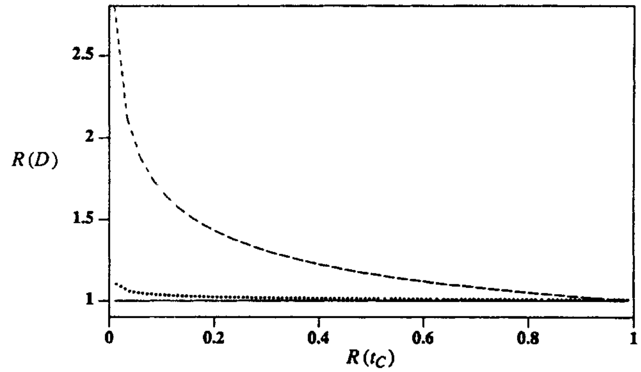

Figure 4. Ratio of column diameter vs ratio of cycle time for different mass and heat controlling steps.
Legend as in Figure 2.

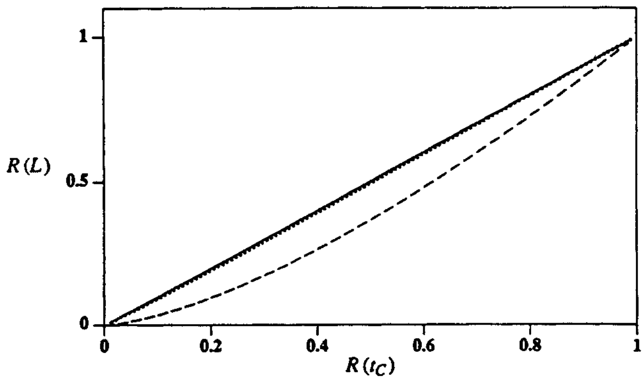

Figure 5. Ratio of column length vs ratio of cycle time for different mass and heat controlling steps.
Legend as in Figure 2.

number in the new and old configuration stated in the previous section are also valid for an adiabatic apparatus.

If internal resistances control the heat transfer, we have to deal with Eqs. 28 to 30. Analogously to the film-controlled situation, no more constraints arise from the dimensionless parameters χ and ζ_i, while from the relation $R(\Lambda) = 1$, by means of Eqs. 31e and 70, Eq. 73 results. It turns out that the same scaling rules discussed in the previous section result if both heat and mass transfer are controlled by internal resistances or if equilibrium is assumed for mass transfer. These scaling rules are summarized in the third part of Table 3. Again, the previous discussion about the mass Biot number variation between the old and new configuration also holds for the heat Biot number.

Unfortunately, this method of analysis is not useful when different mechanisms control heat and mass transfer because two incompatible constraints result. These constraints are represented by Eqs. 73 and 74, which cannot be simultaneously satisfied. In these cases, as well as if $(Bi)_h \approx 1$, the problem is overconstrained and the method discussed up to now is not able to find simple scaling rules. The numerical solution of the suitable mathematical model seems to be mandatory. In this event, the simple relation results arising from the limiting cases discussed above can be regarded as good starting points for a detailed simulation.

PSA processes with negligible pressure drop

The scaling rules discussed up to now result from a mathematical model which include the pressure variation along the column through Eq. 4. To keep the pressure drop across the column constant, reductions in particle diameter must be coupled with suitable reductions in bed length or fluid velocity. If the axial gradient of pressure is small enough to be practically unimportant, it can be neglected and the mathematical model simplified by removing Eq. 4. This is a very common approximation when dealing with numerical simulation of a PSA apparatus. It turns out that the definition of the reference velocity (Eq. 10c) disappears; and consequently, the relation between particle diameter, feed velocity, and cycle time (Eq. 70) is not valid any more. Moreover, the boundary conditions concerning the pressure disappear from Eqs. 43 to 46, and P is now regarded as a dimensionless group in Eqs. 2, 5 and 6, which must be kept constant.

Except for $R(\Delta p) = 1$ in Eq. 68, which does not hold any more, the fundamental relationships resulting in this case are Eqs. 68, 69, 71 and 72. Note that the constraints $R(p^{(j)}) = 1$, with $j = 1$ to 4 do not disappear because of the new relation $R(P) = 1$.

Because one constraint, represented by Eq. 70, has been removed, we have one more degree of freedom which can be used

Table 3. Scaling Rules for Different Heat and Mass Transfer Controlling Steps

	Transfer Models					
Part	Mass	Heat	$R(u_F)$	$R(d_p)$	$R(D)$	$R(L)$
1	Equilib. Equilib.	Isotherm Equilib.	any	$R(u_F)R(t_c)^{0.5}$	$R(N)^{0.5}R(u_F)^{-0.5}$	$R(u_F)R(t_C)$
2	Film (*) Film (*) Film (*) Equilib.	Isotherm Equilib. Film (*) Film (*)	$R(t_C)^{-(b+1)/4b}$	$R(t_C)^{(b-1)/4b}$	$R(N)^{0.5}R(t_C)^{(b+1)/8b}$	$R(t_C)^{(3b-1)/4b}$
3	Internal Internal Internal Equilib.	Isotherm Equilib. Internal Internal	1	$R(t_C)^{0.5}$	$R(N)^{0.5}$	$R(t_C)$
4	Series Series	Isotherm Equilib.	Eq. 77	$R(u_F)R(t_C)^{0.5}$	$R(N)^{0.5}R(u_F)^{-0.5}$	$R(u_F)R(t_C)$

(*)$b = -0.359$ (Petrovich and Thodos, 1968)

Table 4. Scaling Rules for PSA Systems with Negligible Pressure Drop Across the Bed

Transfer Models						
Mass	Heat	$R(u_F)$	$R(d_p)$	$R(D)$	$R(L)$	$R(\Delta p)$
Series	Series	$R(t_c)^{-0.5}$	$R(t_c)^{0.5}$	$R(N)^{0.5}R(t_C)^{0.25}$	$R(t_C)^{0.5}$	$R(t_C)^{-1}$

to deal with different controlling steps for heat and mass transfer. Without considering any limiting case, it is possible to directly utilize the most general model for heat and mass transfer (Eqs. 25 to 27a, 28 to 30a, 33 and 34), which is adequate to represent every kind of heat and mass transfer, and can be used at every value of the Biot number. The constraints resulting from this model are:

$$R(\nu_{fi}) = R(\Omega_{ei}) = R(\Omega_{si}) = R(\lambda) = R(\Lambda) = R(\chi) = R(\zeta_i) = 1 \quad (78)$$

Besides the latter two relations, which are fulfilled because $R(T_0) = R(p_0) = 1$, the former five constraints, coupled with Eqs. 22, 31, 69 and 71, lead to the scaling rules summarized in Table 4.

To improve the adsorbent productivity, we have to reduce the cycle time (Eq. 72). Such a reduction results in shorter columns, with smaller diameter and filled with particles of smaller size. The feed velocity increases. Of course, such scaling rules are not able to keep the pressure drop across the column constant, but this is not a problem if such a pressure drop is negligible. For laminar flow, the Blake-Kozeny equation (Bird et al., 1960)

$$\frac{\Delta p}{L} = \frac{150\,\mu\,u_F}{d_p^2}\left(\frac{1-\epsilon}{\epsilon}\right)^2 \quad (79)$$

may be used to check the pressure drop in the new configuration to be sure it is still negligible. From this equation, coupled with the scaling rules reported in Table 4, it can be shown that $R(\Delta p) = R(t_C)^{-1}$. Reducing the cycle time results in increasing the pressure drop across the bed.

Purification PSA processes

The scaling rules developed above involve the equilibrium multicomponent Langmuir isotherm, Eq. 2. From this equation, the constraint $R(p_0) = 1$ arises (Eq. 67), which implies that the pressure drop across the column must be the same in the old and new configuration (Eq. 60). Such an isotherm is usually employed when the nonlinearity of the isotherms is not negligible, such as for bulk separation processes. With purification processes, the concentration of the adsorbable component is low, and the equilibrium relationships can often be regarded as linear. Moreover, such processes do not involve a large variation of temperature. In these cases, isothermal conditions can be assumed, and the Henry equilibrium *isotherm*

$$Q_i = \overline{K}_i P_i \quad (80)$$

instead of the Langmuir one can be utilized, where

$$\overline{K}_i = b_i(T)\,\rho_g R_g T_0\left(\frac{1-\epsilon}{\epsilon}\right) \quad (81)$$

Consequently, Eq. 67 is substituted by

$$R(\overline{K}_i) = R[b(T)]\,R(T_0) = 1 \quad (82)$$

The constraint above does not involve the reference pressure, but only $R(T_0) = 1$. Because the constraint $R(p_0) = 1$ does not arise from any other relationship involved in the isothermal models, in dealing with a linear system we are allowed to change the pressure drop from the old to the new configuration (Eq. 60). Of course, from Eq. 61, the pressure of all the steps must also be scaled as the pressure drop:

$$R(p^{(i)}) = R(\Delta p) = R(p_0) \quad i = 1 \text{ to } 4 \quad (83)$$

and one has to assume that all the physical properties are not influenced by the pressure.

Table 5. Scaling Rules for Isothermal PSA Systems with Linear Isotherms

Mass Transfer	$R(u_F)$	$R(d_p)$	$R(D)$	$R(L)$
Equilib.	any	$R(u_F)\,\dfrac{R(t_c)^{0.5}}{R(\Delta p)^{0.5}}$	$\dfrac{R(N)^{0.5}}{R(u_F)^{0.5}R(\Delta p)^{0.5}}$	$R(u_F)R(t_C)$
Film (*)	$\dfrac{R(t_C)^{-(b+1)/4b}}{R(\Delta p)^{(3b+7)/12b}}$	$\dfrac{R(t_C)^{(b-1)/4b}}{R(\Delta p)^{(9b+7)/12b}}$	$\dfrac{R(N)^{0.5}R(t_C)^{(b+1)/8b}}{R(\Delta p)^{(9b-7)/24b}}$	$\dfrac{R(t_C)^{(3b-1)/4b}}{R(\Delta p)^{(3b+7)/12b}}$
Internal	$R(\Delta p)^{0.5}$	$R(t_C)^{0.5}$	$R(N)^{0.5}R(\Delta p)^{-1}$	$R(t_C)R(\Delta p)^{0.5}$
Series	numeric	$R(u_F)\,\dfrac{R(t_C)^{0.5}}{R(\Delta p)^{0.5}}$	$\dfrac{R(N)^{0.5}}{R(\Delta u_F)^{0.5}R(\Delta p)^{0.5}}$	$R(u_F)R(t_C)$

(*)$b = -0.359$ (Petrovich and Thodos, 1968)

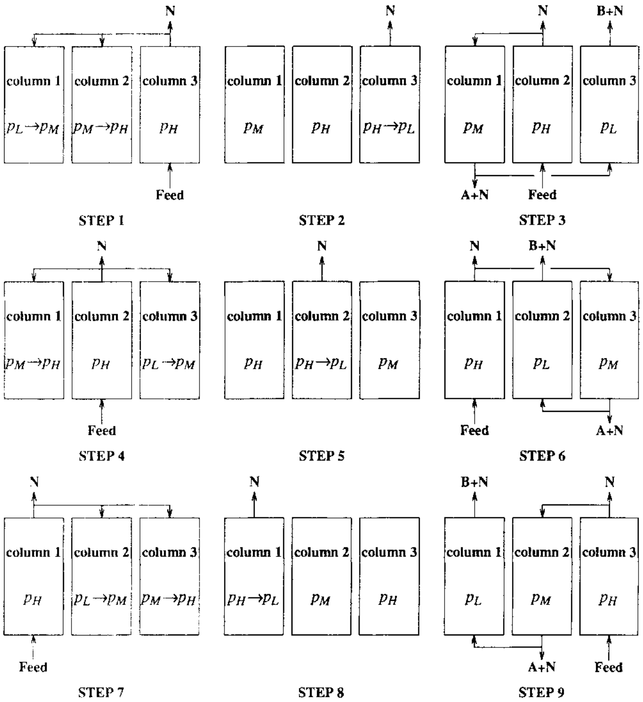

Figure 6. Three-column nine-step chromatographic PSA process

From Suh et al (1987)

From Eqs. 10e, 53 and 69, which do not change if $R(p_0) \neq 1$, and Eq. 83, the sorbent productivity results

$$R(AP) = R(\Delta p)R(t_C)^{-1} \tag{84}$$

while the ratio of the product recovery and purity does not change. Increasing the pressure drop by operating at higher pressure results in a higher sorbent productivity. The scaling rules for this case can be obtained by following the same procedure outlined in the previous sections, and they are summarized in Table 5. The results summarized in Table 5 reduce to the isothermal case in Table 3 when one sets $R(\Delta p) = 1$.

Note that by introducing Eqs. 37c and 38, and the expression of $R(d_p)$ reported in the first part of Table 5 into Eq. 76, a relation similar to Eq. 77 can be obtained. Such an equation, which also involves the ratio of the pressure drop, can be solved numerically to give the ratio of the feed velocity when $(Bi)_m \approx 1$.

If the energy exchanges are accounted for, the constraint $R(p_0) = 1$ results from the dimensionless parameter χ, which is always involved; in this event, the scaling rules summarized in Tables 3 and 4 must be employed.

Analogously, if the equilibrium relations are not linear, any multicomponent equilibrium isotherm can be used instead of the Langmuir one without invalidating the scaling rules reported both in Tables 3 and 4 because the constraint $R(p_0) = 1$ always results.

Chromatographic PSA processes

The scaling rules developed above for a simple two-column four-step Skarstrom cycle are fully valid for other plant configurations. For example, we will consider the three-column nine-step PSA cycle shown in Figure 6 working at three different levels of pressure (Suh et al., 1987). This plant configuration deals with a three-component mixture, A, B and N, where A is more strongly adsorbed than B and N is the carrier gas. Such an apparatus can produce pure component N and two streams containing $N + A$ and $N + B$. This process can be easily extended to systems with n solutes (plus the carrier gas) by using $n + 1$ columns.

Beside the boundary conditions, the mathematical model for this cycle is the same as discussed in the previous sections. However, the expressions of the product recovery and purity, and sorbent productivity are different. We wish to show that such differences do not invalidate the scaling rules previously discussed. By use of a nomenclature analogous to that previously employed and referring to Figure 6, the boundary conditions for steps 1 and 4 of the first column of this chromatographic plant are:

Steps 1 and 4: repressurization from p_L to p_M and from p_L to p_H; $k = 1$ or 4.

$$n \cdot \tau_C \leq \tau < n \cdot \tau_C + \tau_I$$

or

$$n \cdot \tau_C + \tau_{III} \leq \tau < n \cdot \tau_C + \tau_{IV}$$

$$\cdot \begin{cases} P(\tau, Z = 1) = P^{(k)} = P_M \quad (\text{or } P_H) \\ \bar{c}_i(\tau, Z = 1) = \bar{c}_i^{(k)} \\ \bar{T}(\tau, Z = 1) = \bar{T}^{(k)} \\ U(\tau, Z = 0) = 0 \end{cases} \tag{85}$$

The boundary conditions for every other step can be easily written. Note that the structure of these conditions is the same as that of the Skarstrom cycle. Thus, constraints similar to that reported in Eqs. 61 to 66 arise. Despite the complexity of the plant configuration, such relations basically state that the pressure, temperature and concentration of the feed stream, as well as that of every other inlet stream, must be the same in both of the configurations. Moreover, the dimensionless switching times have to be the same too. These requirements are the same as those resulting from the previous analysis; no differences are induced by the different boundary conditions.

Because more than one product is recovered, expressions for the product purity and recovery, and the sorbent productivity are required for each component. The sorbent productivity, with respect to the carrier gas, is:

$$AP_N = \frac{c_0 u_0 \left(\int_{\tau_V}^{\tau_{VIII}} (\bar{c}_N U)_{Z=1}\, d\tau - \int_0^{\tau_I} (\bar{c}_N U)_{Z=1}\, d\tau - \int_{\tau_{II}}^{\tau_{IV}} (\bar{c}_N U)_{Z=1}\, d\tau \right)}{\tau_C (1 - \epsilon) \rho_p L} \tag{86}$$

Similar expressions can be written for the other compounds. It is worth nothing that the quantities outside the integrals are the same as that in Eq. 49. Consequently, by introducing Eqs. 68 and 69, if the dimensionless profiles are kept constant the relation above leads to $R(AP_N) = R(AP_A) = R(AP_B) = R(t_C)^{-1}$, that is, the same as the expression arising from the Skarstrom cycle. In the same way, it is also easy to show that $R(PUR_N) = R(PUR_A) = R(PUR_B) = 1$, and $R(REC_N) = R(REC_A) = R(REC_B) = 1$. Thus, the scaling rules arising from such a complex plant configuration are the same as developed in the previous sections for the simple Skarstrom cycle.

Extra-Column Effects

All the previous analyses concern the adsorbent bed. The intensification procedure, which leads to shorter beds with faster cycles, also requires a more careful design of the entire apparatus because the "dead" volume outside the bed, the timing of the valves, or the gas distribution, for example, can play important roles. In particular, the effect of the dead volume (valves, pipes, distribution, headspace, etc.) on the separation performance of an apparatus is well known to be important in chromatographic processes, where it is called "extra-column effects."

In a PSA apparatus, the extra-column volume, at the beginning of each step, is filled by the gaseous mixture at the end of the previous step, which can be totally different from the stream which is entering. To keep the boundary conditions from the old to the new configuration constant, the stream leaving such a volume, which is the inlet stream of the adsorbent bed, must have the same characteristics in both configurations. In chromatography, the extra-column variance evaluation is usually performed by approximating the system behavior with two limiting models: the open tube and the mixing chamber model (Snyder and Kirkland, 1979). Since the latter is more conservative, it will be used in the following. The goal of this section is to find some indication of how the extra-column volume has to be scaled.

Let us consider a perfectly well-mixed volume before the inlet of the sorbent bed (the same conclusion can be reached by considering a volume after the column). For such a volume, the outlet conditions are the same as the internal ones. A simple mathematical model, which is able to represent the dynamic behavior of such a volume, is summarized as follows:

Mass balance for the ith component

$$V\frac{dC_i}{dt} = W_{\mathrm{IN}}\, C_{i\mathrm{IN}} - W_{\mathrm{OUT}}\, C_i \qquad (87)$$

where W is the volumetric flow rate and the subscripts IN and OUT mean at the inlet and outlet of such a volume, respectively.

Energy balance

$$V\rho C_V\frac{dT}{dt} = W_{\mathrm{IN}}\rho_{\mathrm{IN}}C_{P\mathrm{IN}}(T_{\mathrm{IN}} - T_0) - W_{\mathrm{OUT}}\rho C_P(T_{\mathrm{OUT}} - T_0) - \frac{1}{2}V_w\rho_w C_{PW}\frac{dT}{dt} \qquad (88)$$

where the potential and kinetic energy have been neglected and an average wall temperature $T_w = (T + T_a)/2$ has been assumed.

Continuity equation

$$V\frac{d\rho}{dt} = W_{\mathrm{IN}}\rho_{\mathrm{IN}} - W_{\mathrm{OUT}}\,\rho \qquad (89)$$

The equations above, coupled with the ideal gas equation of state, can be made dimensionless by lumping parameters, and they lead to the following relations:

$$\frac{d\overline{C}_i}{d\tau} = \Phi\left(\overline{C}_{i\mathrm{IN}} - \frac{\overline{T}_{\mathrm{IN}}}{\overline{T}}\,\overline{C}_i\right) + \frac{\overline{C}_i}{\overline{T}}\frac{d\overline{T}}{d\tau} \qquad (90)$$

$$\left(1 - K_\gamma\frac{\overline{T} - 1}{T} + \phi\right)\frac{d\overline{T}}{d\tau} = \Phi K_\gamma\left(\frac{(\overline{T} - \overline{T}_{\mathrm{IN}})(\overline{T} + \overline{T}_{\mathrm{IN}} + \overline{T}\,\overline{T}_{\mathrm{IN}})}{\overline{T}\,\overline{T}_{\mathrm{IN}}}\right) \qquad (91)$$

where

$$\Phi = \frac{W_{\mathrm{IN}}t_0}{V}, \quad \phi = \frac{\rho_w C_{Pw}V_w}{2\overline{\rho}C_V V}T_0 \qquad (92a, b)$$

To obtain the relations above, $\overline{W}_{\mathrm{OUT}} \approx \overline{W}_{\mathrm{IN}}$ and $C_p \approx C_{P\mathrm{IN}}$ have been assumed. Moreover, V_w represents the volume of the wall surrounding the extra-column volume.

The new constraints resulting from these equations, which should be added to the previously discussed scaling rules, are $R(\Phi) = R(\phi) = 1$, which lead to $R(V_w) = R(V) = R(t_C)\,R(N)$. Both the extra-column and the wall volume should be scaled to take full advantage of the reduction of the cycle time. This can be a formidable task if the required reduction is very large. However, if the extra-column volume is quite small compared to the total volume of the column, its contribution should be irrelevant.

Discussion and Conclusions

Intensification means building more compact apparatus which can achieve the same goals as the bigger ones. Light and compact apparatus are of crucial importance in offshore oil plants, and a plant involving smaller apparatus needs less initial capital cost because less civil engineering and structural steelwork are needed. Also, for a PSA plant the amount of sorbent is reduced. This could become important if new sorbents with higher selectivity and price are developed. Furthermore, smaller devices involve a smaller inventory of chemicals and thereby they are intrinsically safer. A major disaster such as Flixborough should be impossible if the plant inventories are drastically reduced.

In this study, scaling rules have been developed which can improve the sorbent productivity (and consequently reduce the dimension of the apparatus) keeping the main performance of a PSA process constant. Such scaling rules depend on the mechanism which controls heat and mass transfer, but they do not depend on the particular plant configuration. Different heat and mass transfer mechanisms, purification, as well as multicomponent bulk separation processes, both isothermal and not, have been discussed. The same results should be valid for vacuum PSA processes. Furthermore, the influence of different equilibrium isotherms has been investigated and the method can be applied for any isotherm. The only difference arises between linear and nonlinear isotherms. The former allow scaling without constraining the pressure drop in the old and new design to be the same.

This scaling procedure requires a detailed "old" design obtained either from experimental data or from simulation. If the old design is based on experimental data, one may not know the controlling resistances. The conservative approach, as one decreases particle diameter, is to assume film resistances control. If film resistances do not control this will result in a column which provides more separation than is necessary.

In the most general case, all of the diffusivities and transfer coefficients can be functions of temperature, concentration and pressure. This is included formally in the model if we assume that all such parameters are functions of temperature, concentration and pressure. The scaling method remains valid if the dimensionless temperature, concentration and pressure profiles throughout the column are kept exactly the same. Keeping the profiles the same keeps the dimensionless groups the same at identical (Z, τ) values. Thus, the dimensionless solutions must remain identical. This is quite intriguing and useful. The scaling procedure can be used to give a "family" of solutions from a single experiment or detailed simulation. Of course, if one wants to change feed concentration, pressure or temperature, a new experiment must be run for a new family of solutions.

The concentration, pressure and temperature of the feed gas often vary. If the variation is controlled by the operator, then the scaling procedures can be used. The operator makes $\bar{c}_F(\tau)$, $P_F(\tau)$, and $\bar{T}_F(\tau)$ identical in the two designs. If the fluctuations are uncontrolled either in random or systematic fashion, then the old and new designs will not be identical if the cycle time differs in the two designs. This occurs since uncontrolled fluctuations will be different in terms of dimensionless time τ for the two designs; hence, the boundary conditions for the two designs are different. For totally random fluctuations, however, the average performances of the old and new designs will be very similar.

If some of the assumptions made to develop these scaling rules are not valid for a real apparatus, these rules should be regarded as a good starting point for a more detailed computer simulation. However, it should be noted that such assumptions are usually retained by most of the mathematical models previously presented.

All these scaling rules lead to smaller columns filled with particles of smaller size. The cycle time is also reduced. There are a few limitations, both practical and theoretical, to these results. When the particles become smaller and smaller, the mass transfer rate increases and the adsorption kinetics can play a role. The scaling rules developed are not valid in this event. Moreover, it requires a more careful design of the apparatus (including valve speed, timing, gas distributor, holddown devices, and so forth) and particular care in packing the bed. The sorbent is assumed to have a long life; faster cycles could reduce this life. An analysis performed to find the influence of the extra-column volume shows that such a volume should be reduced to take full advantage of the intensification procedure. This could not always be possible.

In this study, laminar flow has been assumed. If scaling rules for turbulent flow are required, a different equation [for example the Burke-Plummer equation (Bird et al., 1960)] must replace Eq. 4. Thus, a different definition of the reference velocity (Eq. 10c) and a different fundamental relationship for the particle diameter (Eq. 70) will result. The entire analysis can be easily redone on these bases and has been carried out for simple adsorption (Wankat, 1987).

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Notation

a = constant in film transfer correlations
b = constant in film transfer correlations
b = constant in Langmuir and Henry isotherms, m^3/mol
$\bar{b}$ = dimensionless coefficient, Eq. 3
$(Bi)_h$ = heat Biot number, $h_p r_p / k_e$
$(Bi)_m$ = mass Biot number, $k_f r_p / D_e$
c = concentration, mol/m^3
C = concentration, kg/m^3
$\bar{c}$ = dimensionless concentration, c/c_0
C_P = Specific heat at constant pressure, j/kg · K
C_V = Specific heat at constant volume, j/kg · K
D = column diameter, m
d_p = particle diameter, m
D_e = effective diffusivity in particle, m^2/s
D_m = molecular diffusivity, m^2/s
D_s = surface diffusivity in particle, m^2/s
f = disappearance rate of mass, mol/s · m^3
F = dimensionless disappearance rate of mass, Eq. 8
g = disappearance rate of energy, j/s · m^3
G = dimensionless disappearance rate of energy, Eq. 9
h_p = film heat transfer coefficient, W/m^2 · K
J = J factor for heat and mass transfer
K = constant in Eq. 38
K_P = effective thermal diffusivity in particle, m^2/s
$\bar{K}$ = dimensionless coefficient, Eq. 81
K_γ = specific heat ratio, C_P/C_V
k_e = thermal conductivity of particle, W/m · K
k_f = film mass transfer coefficient, m/s
k_g = thermal conductivity of gas, W/m · K
k_{tot} = global film mass transfer coefficient, m/s
k_p = lumped mass transfer coefficient, Eq. 38, W/m · K
L = bed length, m
n = total feed rate, mol/s
n = integer variable
NC = number of components
Nu = Nusselt number, $h_p d_p / k_g$
p = pressure, kPa
p_i = partial pressure of ith compound, $p c_i / \Sigma_{j=1}^{NC} c_j$, kPa
P = dimensionless pressure, p/p_0
P_i = dimensionless partial pressure of ith compound, $P \cdot \bar{C}_i / \Sigma_{j=1}^{NC} \bar{c}_j$, kPa
Pr = Prandtl number, $C_p \mu / k_g$
q = amount adsorbed, mol/kg
Q = dimensionless amount adsorbed, q/q_0
r = radius, m
R = operator ratio, Eq. 50
Re = Reynolds number, $\rho u \epsilon d_p / \mu$
R_g = ideal gas constant, Pa · m^3/mol · K
Sc = Schmidt number, $\mu / \rho \cdot D_m$
Sh = Sherwood number, $k_f d_p / D_m$

t = time, s
T = temperature, K
$\overline{T}$ = dimensionless temperature, T/T_0
u = interstitial velocity, m/s
U = dimensionless interstitial velocity, u/u_0
V = volume, m^3
W = volumetric flow rate, m^3/s
z = bed coordinate, m
Z = dimensionless bed coordinate, z/z_0

Greek letters

α = generic variable
δ_w = ratio between wall thickness and column radius
ΔH^{ads} = heat of adsorption, j/kg
Δp = pressure drop across the bed, kPa
ϵ = porosity
ϵ_d = parameter defined by Eq. 31d
ϵ_p = particle porosity
ζ = dimensionless coefficient, Eq. 16
η = dimensionless particle radius, r_p/r_{p0}
θ_C = dimensionless parameter, $D_e t_C/r_p^2$
λ = dimensionless coefficient, Eq. 22b
Λ = dimensionless coefficient, Eq. 31e
μ = viscosity, kg/m · s
ν_f = dimensionless coefficient, Eq. 22a
ν_{tot} = dimensionless coefficient, Eq. 37b
ρ = density, kg/m^3
ρ_p = particle density, kg/m^3
τ = dimensionless time, t/t_0
τ^* = tortuosity, D_e/D_m
ϕ = dimensionless coefficient, Eq. 92b
Φ = dimensionless coefficient, Eq. 92a
χ = dimensionless coefficient, Eq. 15
χ_w = dimensionless coefficient, Eq. 40
Ω = dimensionless coefficient, Eq. 31a, b

Subscripts

a = ambient
C = cycle
e = effective
F = feed
h = heat
H = high
i, j, k, A, B, N = components
IN = inlet
L = low
m = mass
M = medium
NEW = new configuration
OLD = old configuration
OUT = outlet
p = particle
PROD = product
s = surface
w = wall
$*$ = equilibrium
0 = reference
I, II, . . . = end of the first, second, . . . step

Superscripts

av = average
sat = saturation
(1),(2), . . . , (k) = step of the cycle

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