

Adsorption Dynamics of Binary System (Purge Step)

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ABSTRACT

The separation of a binary system by Molecular Sieve as conceived consists of the following steps.

1. Separation of the mixture by adsorption at high pressure.
2. Desorption of adsorbed gas mixture rich in component a by lowering the system pressure (blowdown).
3. Further desorption by purging the residual adsorbed gas mixture with product mixture which is lean in component a.
4. Repressurization of the bed either with the product mixture or the air after which the cycle repeats.

This work discusses a method of predicting the performance of the third step when pure component isotherms and the knowledge of relative adsorptivity are available. A numerical example is given to illustrate the method and compared with the experimental findings.

INTRODUCTION

The use of adsorption technique for industrial separations has primarily been concerned with fixed bed operation although moving bed systems too have been studied. Some examples of these processes are simultaneous removal of CO_2 and moisture from air, solvent recovery, and separation of hydrocarbons. One of the steps often encountered in the above processes is purging of the bed which is predominantly loaded with strongly adsorbed components. Either a gas mixture or a pure component which is weaker in adsorptivity is introduced into the bed to accomplish the object. For example, the bed at the end of blowdown (depressurization) will be loaded with a mixture which is rich in component a. The product gas (say 65% b, 35% a), then, is introduced to partially strip the bed to prepare for the subsequent pressurization and

adsorption steps. This memorandum discusses a method of analyzing the purge step mentioned above.

The assumptions which must be made to enable the analysis are shown below.

1. Equilibrium conditions between the gas and the adsorbed phase prevail at all points in the column. No rate factor, therefore, is involved.
2. The bed remains isothermal.
3. Longitudinal molecular diffusion is negligible.

The advantages of making these assumptions are as follows:

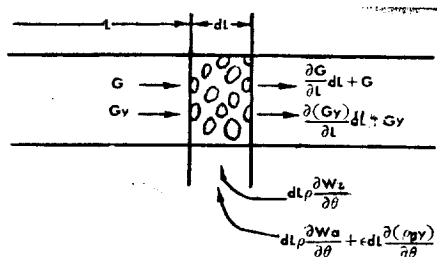
1. An analytical solution can be obtained from which one can study the influence of independent variables involved.
2. Any boundary condition can be included, i. e., the rigid restriction of having a uniformly loaded bed need not be made.
3. Only, pure component isotherms and the knowledge of relative adsorptivity are necessary to analyze the system.

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Many experiments have been performed to test the analytical solution and good agreement was found. A numerical example of obtaining the elution curve is included and the result is compared with the experiment.

THE MATERIAL BALANCE

Consider the volume element in the packed bed as shown below.



By equating (Input-Output) equal to (Accumulation) or (Output-Input) equal to (Depletion), one obtains the following material balances; one for overall, the other for component a.

$$-\left(G \frac{\partial y}{\partial L} + y \frac{\partial G}{\partial L}\right) = \epsilon \rho_s \frac{\partial y}{\partial \theta} + \rho \frac{\partial W_a}{\partial \theta} \quad (1)$$

$$-\frac{\partial G}{\partial L} = \rho \frac{\partial W_t}{\partial \theta} \quad (2)$$

Where

G = Total flow rate of gas which is a function of L and θ (or z and t) ($\text{ft}^3 \text{ NTP}/\text{ft}^2 \text{ hr.}$)

L = Length measured from the entrance of the bed (ft.)

y = Mol fraction of a in gas phase

ϵ = Void fraction (0.52 for CaA Molecular Sieves)

ρ_s = Density of a gas mixture ($\text{ft}^3 \text{ NTP}/\text{ft}^3$ of bed)

ρ = Bulk density of the bed (lb. of adsorbent/ ft^3 of bed)

θ = Elapsed time (hr.)

W_a = Coadsorption loading of a ($\text{ft}^3 \text{ NTP}/\text{lb.}$ of adsorbent)

W_t = Total loading of the mixture ($\text{ft}^3 \text{ NTP}/\text{lb.}$ of adsorbent)

Now, it is often advantageous to express the independent variables, L and θ , in terms of dimensionless quantities. We will therefore define,

$$z = \frac{L}{L_0} \quad (3)$$

$$t = \frac{\theta}{\theta_0} \quad (4)$$

where L_0 = Total length of the bed (ft.)

θ_0 = Total purge time (hr.)

Equations (1) and (2) then can be rewritten as

$$-\left(G \frac{\partial y}{\partial z} + y \frac{\partial G}{\partial z}\right) = \frac{\epsilon \rho_s L_0}{\theta_0} \frac{\partial y}{\partial t} + \rho \frac{L_0}{\theta_0} \frac{\partial W_a}{\partial t} \quad (5)$$

$$-\frac{\partial G}{\partial z} = \rho \frac{L_0}{\theta_0} \frac{\partial W_t}{\partial t} \quad (6)$$

Thus, the solution which satisfied (5) and (6) and the given boundary condition will enable one to predict the concentration profile of the effluent as well as the effluent flow rate. Now, in equations (5) and (6), there are four dependent variables and only two partial differential equations. The first objective therefore is to represent W_t and W_a in terms of y thereby reducing the dependent variables to two. This can be done by studying the coadsorption isotherms.

THE COADSORPTION ISOTHERMS

For a binary sorption system, the relative adsorptivity (or separation factor) can be defined as

$$\alpha = \frac{y_b}{y_a} \cdot \frac{x_a}{x_b} = \frac{y_b}{y_a} \cdot \frac{W_a}{W_b} = \left(\frac{1-y}{y}\right) \left(\frac{x}{1-x}\right) \quad (7)$$

where x, y = Solid and gas phase mol fractions.

W_b = Coadsorption loading of b ($\text{ft}^3 \text{ NTP}/\text{lb.}$ of adsorbent)

As it can be seen in the last term of eq. (7), when mol fractions are used without subscripts, they will all refer to component a.

Now, an empirical equation relating coadsorbed adsorbates as proposed by Lewis and Gilliland (Ref. 1) can be written as

$$\frac{\bar{W}_a}{W_a} + \frac{\bar{W}_b}{W_b} = 1 \quad (8)$$

Where the bar, —, denotes pure component loadings for a given system pressure and temperature.

When equation (7) is rearranged one gets the following relationships between mol fractions.

$$y = \frac{x}{1 + (\alpha - 1)(1 - x)} \quad (9)$$

$$x = \frac{\alpha y}{1 + (\alpha - 1)y} \quad (10)$$

And when equations (7) and (8) are solved simultaneously and simplified by (9) and (10), one obtains the desired relationships as shown below.

$$W_a = \left[\frac{\bar{W}_a}{1 + \left(\frac{1-y}{\alpha y} \right) \frac{\bar{W}_a}{\bar{W}_b}} \right] = f_1(Y) \quad (11)$$

$$W_t = \left[\frac{\bar{W}_b \left(1 + \frac{1-y}{\alpha y} \right)}{1 + \left(\frac{1-y}{\alpha y} \right) \frac{\bar{W}_a}{\bar{W}_b}} \right] = f_2(Y) \quad (12)$$

Now that we have expressed W_N and W_T as a function of N_2 mol fraction y , we can say

$$\frac{\partial W_a}{\partial t} = \frac{\partial f_1}{\partial y} \frac{\partial y}{\partial t} = f'_1 \frac{\partial y}{\partial t} \quad (13)$$

$$\frac{\partial W_t}{\partial t} = \frac{\partial f_2}{\partial y} \frac{\partial y}{\partial t} = f'_2 \frac{\partial y}{\partial t} \quad (14)$$

also, substitution of (6) into (5) gives

$$-G \frac{\partial y}{\partial z} + y \rho \frac{L_0}{\theta_0} \frac{\partial W_t}{\partial t} = \frac{L_0}{\theta_0} \left(\epsilon \rho_g \frac{\partial y}{\partial t} + \rho \frac{\partial W_a}{\partial t} \right) \quad (15)$$

Thus, substituting (13) and (14) into (15) and (6), we get

$$G \frac{\partial y}{\partial z} + \frac{L_0}{\theta_0} (\epsilon \rho_g + \rho f'_1 - y \rho f'_2) \frac{\partial y}{\partial t} = 0 \quad (16)$$

$$\frac{\partial G}{\partial z} + \frac{L_0}{\theta_0} \rho f'_2 \frac{\partial y}{\partial t} = 0 \quad (17)$$

We will now solve (16) and (17) simultaneously. First of all it can be seen that equation (16) is a quasi-linear equation of first order. By comparing with the definition of total differential for y , (16) can be rewritten as

$$\frac{dt}{dz} = \frac{\frac{L_0}{\theta_0} (\epsilon \rho_g + \rho f'_1 - y \rho f'_2)}{G}; \quad y = \text{const.} \quad (18)$$

Equation (18) describes characteristic lines on which y is constant in a three dimensional space of y , z and t coordinates. In other words, equation (18) describes a trajectory of a volume element of constant concentration y as it travels down the t - z plane (Fig. 1).

Now, if the term $\partial y / \partial t$ is eliminated from (16) and (17), we get

$$\frac{\partial G}{\partial z} - G \left[\frac{\rho f'_2}{\epsilon \rho_g + \rho (f'_1 - y f'_2)} \right] \frac{\partial y}{\partial z} = 0; \quad t = \text{const.} \quad (19)$$

Equation (19) applies on characteristic lines on which y is constant. And since t is no longer a variable along these lines, the partial sign ∂z in (19) can be replaced by ordinary differential sign " dz ". Then

one can eliminate ∂z from (19) and get

$$\frac{dG}{dy} = \frac{G \rho f'_2}{\epsilon \rho_g + \rho (f'_1 - y f'_2)}; \quad t = \text{const.} \quad (20)$$

Thus, we have reduced two partial differential equations to a pair of ordinary differential equations in specified directions. At this point, the usual procedure is to rewrite the equations into finite difference equations and solve them numerically. Equation (20) in this case, however, does not contain the independent variable t , and presents a unique situation in which equation (20) can be solved analytically for G in terms of y .

$$\int_{G_D}^G \frac{dG}{G} = \ln \frac{G}{G_D} = \int_{y_D}^y \frac{\rho f'_2}{\epsilon \rho_g + \rho (f'_1 - y f'_2)} dy \quad (21)$$

$$\text{or } G = G_D \exp \int_{y_D}^y \frac{\rho f'_2}{\epsilon \rho_g + \rho (f'_1 - y f'_2)} dy = \Gamma G_D \quad (22)$$

$$\text{where } \Gamma = \exp \int_{y_D}^y \frac{\rho f'_2}{\epsilon \rho_g + \rho (f'_1 - y f'_2)} dy \quad (23)$$

$$\mu = \epsilon \rho_g + \rho (f'_1 - y f'_2) \cong \rho (f'_1 - y f'_2) \quad (24)$$

G_D = Purge flow at the entrance of the bed

y_D = Gas phase mol fraction of a in the purge gas

The "multiplication factor Γ ", then, enables one to calculate the flow rates as a function of the gas phase concentration at any point in the bed. And since G is now a function of y alone, one can substitute (22) in (18) to get

$$\frac{dt}{dz} = \frac{L_0}{\theta_0 \Gamma} \frac{\mu}{G_D}; \quad y = \text{const.} \quad (25)$$

Note that the term on the right hand side of (25) is still a function of y only and since we are considering paths where y is constant, we can integrate (25) without any problem, i. e.

$$t = \frac{L_0}{\theta_0} \frac{\mu}{\Gamma G_D} z + \psi(y) \quad (26)$$

where $\psi(y)$ is an integration constant expressed as a function of y . Equation (26) therefore is the general solution of (1) and (2). In order to get a particular solution for a specific problem, one must evaluate y from the boundary conditions.

NUMERICAL EXAMPLES

Purging of N_2 loaded bed with 33.5% N_2 -66.5% O_2 mixture has been performed and the concentration changes at two locations within the bed had been obtained by Beckman F-3M3 O_2 analyzer. We will try to predict this concentration changes and the maximum

flow rate of the effluent from the following information.

The bed: 6" diameter, 29" tall

$$A=0.1964 \text{ ft}^2, V=0.4746 \text{ ft}^3$$

Contains approximately 16 lb. of LiX type
Molecular Sieves

$$\text{Bulk density}=33.71 \text{ lb./ft}^3$$

Initial Condition; The bed is initially loaded with pure N_2 at 1 atm. and 24°C .

Purging: The gas mixture of 33.5% N_2 -66.5% O_2 was introduced at the rate of 25.51 ft^3/hr ft^2

Equilibrium data at 1 atm and 24°C .

$$\bar{W}_N=0.179 \text{ ft}^3 \text{ NTP/lb. of LiX}$$

$$\bar{W}_O=0.065 \text{ ft}^3 \text{ NTP/lb. of LiX}$$

$$\alpha=5.4 \text{ when } y=0.8$$

$$\alpha=6.6 \text{ when } y=0.2$$

It can be seen that the relative adsorptivity, α , is a function of the mixture composition as well as temperature and pressure. And in order to calculate the values of f_1' and f_2' at different values of y , we have to estimate the change of α when y varies from 0.335 to 1.0. This can be done by plotting $\log \alpha$ vs. $\log y$ as suggested by the Design Manual of Octane Improvement. (Ref. 2). Next step is to calculate $(\mu/\Gamma G_D)$ of equation (25) at several values of y depending upon the accuracy desired.

For example,

$$\text{at } y=0.5, \alpha=5.75$$

Therefore,

from (11) and (12), we get

$$f_1'=0.157$$

$$f_2'=0.0998$$

Substituting these values into (24), we obtain,

$$\mu=3.610$$

Similarly, we can find other values of f_1' , f_2' and at other concentration levels as shown in Table 1.

Then the value of Γ to be used in (27) for $y=0.5$ is evaluated from

$$(\Gamma)_{0.5} = \int_{0.335}^{0.5} \frac{\rho f_2'}{\mu} dy \approx \int_{0.335}^{0.5} \frac{f_2'}{(f_1' - y f_2')} dy \quad (27)$$

The last expression of (27) is obtained by neglecting the $\epsilon \rho_g$ which is small. The numerical value of

(27) can be readily found by graphical integration.

The value of Γ at $y=0.5$ therefore is 1.155. In other words, when the gas phase mol fraction of N_2 is 0.5, the flow rate at any point in the bed including the exit is 1.155 times of the purge flow. Other values of $\rho f_1'/\mu$ and the multiplication factor are also tabulated in Table 1.

Table 1

y	f_1'	f_2'	μ	$\rho f_2'/\mu$	$\Gamma^* \text{calc.}$
0.335	0.200	0.128	5.292	0.915	1.0
0.4	0.180	0.115	4.517	0.858	1.057
0.6	0.139	0.088	2.906	1.021	1.274
0.8	0.112	0.071	1.861	1.286	1.721
1.0	0.095	0.060	1.180	1.714	2.320

* Maximum value of Γ observed in the experiment was 2.03

Similarly one can compute the time required for a given concentration to reach a distance of 10 inches from the entrance from (26). The results are shown in Table 2 and Figure 2.

Table 2

y	μ/Γ	$t_{10}(\text{calc.})$	$t_{10}(\text{Exp.})$
0.335	5.292	0.346	0.397
0.4	4.273	0.279	0.240
0.5	3.126	0.204	0.173
0.6	2.281	0.149	0.132
0.8	1.081	0.071	0.075
1.0	0.509	0.033	0.038

As it can be seen the agreement between the experiment and calculation is good.

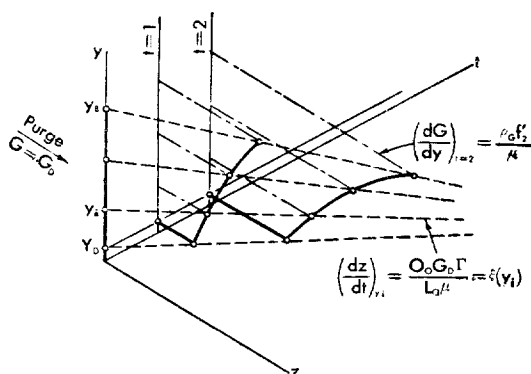
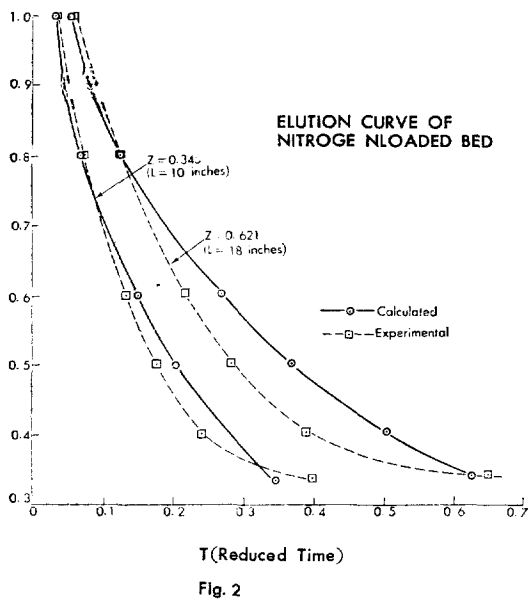


Fig. 1



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- (2) *Design Manual for Octane Improvement*, Book I, Linde Company, Tonawanda, New York (1959).