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# The Simulation of Binary Adsorption in Continuous Countercurrent Operation and a Comparison with Other Operating Modes

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Simulation studies are presented of three different modes of operating a two-component adsorption system. The efficiency with which an activated carbon adsorbent is utilized is compared for a single fixed bed, a periodic countercurrent system in which the adsorbent is equally distributed over two, four, and six beds and a continuous countercurrent system. The carbon utilization in the single fixed bed was shown to be one third to one half of that in a continuous countercurrent adsorber of the same length, whereas the periodic countercurrent system achieved a utilization of 79 to 98% of that in the continuous system.

The mathematical models used to describe the three different modes of column operation include the effects of axial diffusion in the columns, mass transfer resistance in the boundary layer surrounding each particle, and fluid diffusion within the porous particles.

## SCOPE

Although multicomponent adsorption is often encountered in industrial application, most of the studies concerning sorption processes have dealt primarily with systems containing one adsorbable species. Svedberg (1976) reports results on single component adsorption performance from the simulation of fixed bed, periodic, and continuous countercurrent operation with film plus pore diffusion and a linear isotherm.

When more than one component is adsorbed, the shape of the concentration profiles in the adsorber will change radically, giving peaks and plateaus which result from interactions between the adsorbed solutes (Hsieh et al., 1977; Klaus et al., 1977; Liapis and Rippin, 1978) and cannot be modeled by the assumption of linear isotherms.

Klaus et al. (1977) report simulated results for two-component adsorption in periodic countercurrent operation for a two-bed system with film mass transfer resistance but in which diffusional effects are neglected. Their results show that with periodic countercurrent operation, carbon utilization is much higher than with a fixed-bed arrangement.

The purpose of the work described here was to simulate multicomponent adsorption on activated carbon in fixed bed periodic and continuous countercurrent operation in order to compare carbon utilization under the three different contacting modes. The models used include film mass transfer and diffusional resistances. The continuous countercurrent operation is theoretically the most efficient procedure but is difficult to realize in practice (Hiester et al., 1954; Westermarck, 1975). It was therefore of interest to determine how closely the performance of the periodic countercurrent adsorber would approach that of the continuous system.

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## CONCLUSIONS AND SIGNIFICANCE

It is demonstrated from simulation studies that carbon utilization in continuous countercurrent adsorption can be two to three times higher than for single columns of the same length. The periodic countercurrent system achieved 79 to 98% of the performance of the continuous countercurrent adsorption column.

It is found that in periodic multicolumn operation, the greatest improvement in carbon utilization takes place when the single column is divided into two beds. For more subdivisions, the additional improvement is smaller. For short columns, even a small number of subdivisions

gives almost the same efficiency as the continuous countercurrent operation. However, many more subdivisions would be required to achieve a performance approaching that of a very long column.

The results indicate that although continuous countercurrent operation utilizes the carbon most efficiently, the performance of the periodic countercurrent mode of operation is such that since the latter mode is easier to implement in practice (Hiester et al., 1954; Westermarck, 1975), it may represent the most attractive adsorption operation for industrial purposes.

The separation of components from a fluid stream by adsorption onto activated carbon is a well-established industrial practice. Renewed interest in this process has been aroused recently as a method for the advanced treatment of wastewater.

During the adsorption process, the column can be in either a steady or a dynamic state. During fixed-bed contacting, the column is in a dynamic state; during continuous countercurrent contacting, steady state concentration profiles are developed in the free fluid phase, while from the point of view of each particle, the process is dynamic. Periodic countercurrent operation differs from continuous operation in that the concentration profile in the free fluid phase changes periodically between two limiting profiles.

Svedberg (1976) studied the effect on carbon utilization of the above three different contacting systems for the case of single-component adsorption with a linear isotherm. His models include film plus pore diffusion and axial dispersion, but results are presented only for cases for which the latter is negligible. He found that the periodic and continuous countercurrent modes of operation are superior in carbon utilization to fixed-bed operation when the total column lengths and the fluid flow rates are the same. His results also showed that the performance of the continuous countercurrent operation was quite closely approached by the periodic mode of operation when the adsorbent is distributed over only two to four beds. Neretnieks (1974) also compares the performance of the continuous countercurrent operation for linear and irreversible isotherms with film plus pore resistance. Fornwalt and Hutchins (1966) and Erskine and Schuliger (1971) suggest a simplified graphical procedure to assess the effectiveness of multiple beds; Chen et al. (1972) used a tanks-in-series model with linear mass transfer driving force in order to study the performance of periodic, countercurrent, single-component adsorption.

The work of Klaus et al. (1977) represents the first study undertaken to examine the effectiveness of multiple beds in the case of multicomponent adsorption. They considered the adsorption of the binary system dodecylbenzene sulfonate (DBS) and phenol under periodic countercurrent operation with only two beds. Their results show that with this mode of operation, carbon utilization is much higher than with a fixed-bed arrangement. The models considered in their study include film mass transfer but neglect axial diffusion and intraparticle diffusional resistances.

In this work, the adsorption performance with respect to carbon utilization is studied for the binary system butanol-2 and *t*-amylalcohol under three different modes

of operation: fixed bed, periodic countercurrent with two, four and six beds, together with continuous countercurrent operation.

It is worth noting that the case of continuous countercurrent operation provides a convenient theoretical upper limit to the separation attainable using periodic countercurrent operation, since the continuous countercurrent mode may be regarded as an infinite number of infinitesimal beds in periodic countercurrent operation. Also, the models used in this study include film mass transfer, axial diffusion, and intraparticle diffusional resistances. This was not the case in the previous investigations found in the literature, except for the fixed-bed mode of operation (Liapis and Rippin, 1978).

## MATHEMATICAL FORMULATION

In this section, the mathematical modeling of the three alternative types of contacting for adsorption processes is presented. In these models, component 1 corresponds to butanol-2, and component 2 is taken to be *t*-amylalcohol. Liapis (1977a) gives the mathematical formulation in the case when more than two components are involved.

### FIXED-BED MODEL

This model describes the adsorption of solutes from a flowing liquid stream onto a fixed bed of particles. The mass transfer effects included in the model are intraparticle diffusion, film mass transfer, and axial diffusion. The essential assumptions are constant coefficients of dispersion and diffusion, constant porosities, no radial gradients in the bed, dilute solutions, and that the spherical adsorbent particles have uniform size and homogeneous structure. The intraparticle diffusion is assumed to take place in the liquid within the pores of the particles. The pore diffusional resistance for concentrated solutions as well as the solid diffusional resistance for both types of solutions is discussed in the work of Liapis and Rippin (1977b). Local equilibrium is assumed between solid and fluid phases at each point in the pore, since it is well established that adsorption onto the surface is virtually never rate limiting. The equations in dimensionless form are

$$\begin{aligned} \frac{\partial C'_{d1}}{\partial \tau} + \left( \frac{1 - \epsilon}{\epsilon} \right) \left( \frac{A_o}{D_{p1}} \right) \left( \frac{3}{r_o} \right) (C'_{d1} - C'_{p1}|_{r=r_o}) K_{f1} \\ = \frac{A_o V_f(\tau)}{L \epsilon D_{p1} Pe_1} \left( \frac{\partial^2 C'_{d1}}{\partial \xi^2} \right) - \frac{A_o V_f(\tau)}{L \epsilon D_{p1}} \left( \frac{\partial C'_{d1}}{\partial \xi} \right) \quad (1) \end{aligned}$$

$$\frac{\partial C'_{d2}}{\partial \tau} + \left( \frac{1-\epsilon}{\epsilon} \right) \left( \frac{A_o}{D_{p1}} \right) \left( \frac{3}{r_o} \right) (C'_{d2} - C'_{p2}|_{r=r_o}) K_{f2} \\ = \frac{A_o V_f(\tau)}{L \epsilon D_{p1} P e_2} \left( \frac{\partial^2 C'_{d2}}{\partial \xi^2} \right) - \frac{A_o V_f(\tau)}{L \epsilon D_{p1}} \left( \frac{\partial C'_{d2}}{\partial \xi} \right) \quad (2)$$

$$\psi_1 \frac{\partial C'_{p1}}{\partial \tau} + \psi_2 \frac{\partial C'_{p2}}{\partial \tau} = \frac{\epsilon_p A_o}{r_o^2} \left\{ 4\rho \frac{\partial^2 C'_{p1}}{\partial \rho^2} + 6 \frac{\partial C'_{p1}}{\partial \rho} \right\} \quad (3)$$

$$\psi_3 \frac{\partial C'_{p1}}{\partial \tau} + \psi_4 \frac{\partial C'_{p2}}{\partial \tau} = \frac{2}{Sh_{p2}} \left\{ 4\rho \frac{\partial^2 C'_{p2}}{\partial \rho^2} + 6 \frac{\partial C'_{p2}}{\partial \rho} \right\} \quad (4)$$

where

$$\psi_1 = \frac{1}{C_{o1}} \left\{ \epsilon_p C_{o1} + C^*_{so1} \frac{\partial C'_{s1}}{\partial C'_{p1}} \right\} \quad (5)$$

$$\psi_2 = \frac{C^*_{so1}}{C_{o2}} \left( \frac{\partial C'_{s1}}{\partial C'_{p2}} \right) \quad (6)$$

$$\psi_3 = \frac{\partial C'_{s2}}{\partial C'_{p1}} \left( \frac{2C^*_{so2} r_o^2 K_{f1}}{A_o \epsilon_p Sh_{p1} C_{o2} K_{f2}} \right) \quad (7)$$

$$\psi_4 = \frac{2r_o^2 K_{f1}}{A_o Sh_{p1} \epsilon_p K_{f2} C_{o2}} \left( \epsilon_p C_{o2} + C^*_{so2} \frac{\partial C'_{s2}}{\partial C'_{p2}} \right) \quad (8)$$

The initial and boundary conditions of Equations (1) to (4) are given for  $i = 1, 2$  by

$$C'_{di} = 0 \quad \text{at} \quad \tau = 0, \quad 0 \leq \xi \leq 1 \quad (9)$$

$$C'_{di}(0, \tau) = \frac{C_{i,in}}{C_{oi}} + \frac{1}{Pe_i} \frac{\partial C'_{di}}{\partial \xi} \bigg|_{\xi=0} \quad \tau > 0 \quad (10)$$

$$\frac{\partial C'_{di}}{\partial \xi} \bigg|_{\xi=1} = 0, \quad \tau > 0 \quad (11)$$

$$C'_{pi} = 0 \quad \text{at} \quad \tau = 0, \quad 0 \leq \rho \leq 1 \quad (12)$$

$$\frac{4}{Sh_{pi}} \frac{\partial C'_{pi}}{\partial \rho} \bigg|_{\rho=1} = C'_{di}(\tau, \xi) - C'_{pi}(1, \tau, \xi), \quad \tau > 0 \quad (13)$$

$$\frac{\partial C'_{pi}}{\partial \rho} \bigg|_{\rho=0} = 0, \quad \tau > 0 \quad (14)$$

The initial condition, Equation (12), implies that clean adsorbent particles are used, which is usually the case in practice. The equilibrium adsorption isotherms of the binary system butanol-2 and *t*-amylalcohol (Balzli, 1977; Liapis and Rippin, 1977b) are given by

$$C'_{s1} = \frac{1.06 (C'_{p1} C_{o1})^{1.217}}{C^*_{so1} \{ (C'_{p1} C_{o1})^{0.812} + 0.626 (C'_{p2} C_{o2})^{0.760} \}} \quad (15)$$

$$C'_{s2} = \frac{1.07 (C'_{p2} C_{o2})^{1.254}}{C^*_{so2} \{ (C'_{p2} C_{o2})^{0.906} + 0.045 (C'_{p1} C_{o1})^{0.634} \}} \quad (16)$$

These isotherms are of the so-called Fritz and Schlunder types. Liapis and Rippin (1977b) and Fritz and Schlunder (1974) discuss the functional properties of the isotherms of this kind.

The fixed-bed pore diffusion model described by Equations (1) to (16) permits column performance to be predicted very well (Liapis and Rippin, 1978; Balzli et al., 1978) over a wide range of operating and design conditions. The effective pore diffusivities  $D_{pi}$  can be obtained from simple, fast, and inexpensive multicomponent

batch experiments (Liapis and Rippin, 1977b), while the axial diffusivities  $D_{Li}$  and the film mass transfer coefficients  $K_{fi}$  can be obtained from the literature data of Liles and Geankoplis (1960), Wilson and Geankoplis (1966), and Mandelbaum and Böhm (1973).

## PERIODIC COUNTERCURRENT MODEL

The mathematical model that describes periodic countercurrent adsorption is the same as that of a fixed bed. The solution procedure for the single-column case can easily be adapted to the multicolumn problem. After a saturated column has been removed from the end of the sequence of columns corresponding to the fluid input and replaced by a fresh column at the other end, the initial conditions must be adjusted for the start of the new operating period. That part of the profile is deleted which corresponds to the saturated column that has been removed. The profile of the remaining columns is shifted, and the profile of the newly regenerated column is added at the other end.

The criterion for when to remove the spent bed at the upstream fluid end and to introduce a fresh bed at the other end can be based on instantaneous outlet concentrations when simulations are carried out. There may be many possible effluent specifications for a multicomponent system that would determine the time of bed switching in practice.

## CONTINUOUS COUNTERCURRENT MODEL

Here, adsorption is considered in a moving bed of adsorbent. It is assumed that a stream of solid adsorbent at constant velocity enters one end of the column, Figure 1, and moves in rodlike flow countercurrent to the fluid flow, simultaneously adsorbing solutes from the free fluid. The rodlike flow implies that the particles are so small that the adsorbent stream behaves essentially as an ideal fluid in its flow properties. It is understood that the introduction and removal of adsorbent are continuous.

Equations (1), (2), and (9) to (11) still describe the concentration profiles of the solutes in the free fluid phase. The adsorbent particles, because of the assumption of rodlike particle flow, will have the constant dimensionless velocity given by

$$\frac{V_s A_o}{D_{p1} L} = - \frac{\partial \xi}{\partial \tau} \quad (17)$$

Then, the partial derivatives of the dependent variables  $C'_{si}$  and  $C'_{pi}$  with respect to dimensionless time  $\tau$ , in Equations (3) and (4), are replaced by the partial derivatives of the same dependent variables with respect to dimensionless space  $\xi$ , using the following relationship:

$$\partial \tau = - \left( \frac{D_{p1} L}{V_s A_o} \right) \partial \xi \quad (18)$$

The resulting particle equations have the following boundary condition at the inlet of the adsorbent stream, for  $i = 1, 2$ :

$$C'_{pi} = 0 \quad \text{at} \quad \xi = 1 \quad \text{for} \quad 0 \leq \rho \leq 1 \quad (19)$$

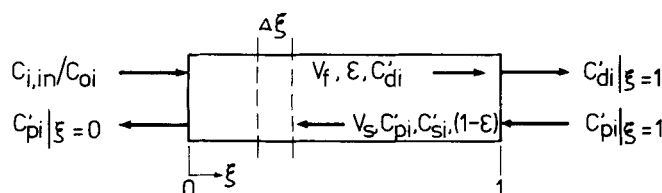


Fig. 1. Schematic diagram of a continuous countercurrent column.

Equation (19) replaces Equation (12) in the solution procedure and implies that it is assumed that clean adsorbent particles are entering the column. The boundary conditions, Equations (13) and (14), remain unchanged as well as Equations (15) and (16) which describe the equilibrium isotherms of our adsorption system.

The same equations are applicable to parallel flow of adsorbent and fluid if proper adjustment is made to the algebraic signs of the flow rates.

## NUMERICAL SOLUTION

The above models were solved numerically by the method of orthogonal collocation (Villadsen and Stewart, 1967; Villadsen, 1970; Michelsen and Villadsen, 1972; Finlayson, 1972) combined with numerical methods which integrate the ordinary nonlinear differential equations obtained after the application of orthogonal collocation on the space variables  $\xi$  and  $\rho$ .

The Legendre orthogonal polynomials  $P_N(\xi)$  for the equations of the moving fluid are of the order  $N = 8$ , since this proved to be sufficient to obtain differences in only the fourth digit as compared to the higher approximation. The boundary points  $\xi = 0$  and  $\xi = 1$  were taken as external collocation points. The approximation order  $N$  of the orthogonal polynomials  $P_N(\rho)$  for the diffusion equations in the particles were tested with  $N = 4, 6, 8, 10$ .  $N = 8$  proved to be sufficient to obtain differences in only the fourth digit in the predictions of concentrations, as compared to the higher approximation. The boundary point  $\rho = 1$  was taken as an external collocation point.

In the case of the fixed-bed model, the nonlinear ordinary differential equations resulting from the application of orthogonal collocation were integrated using a fifth-order Runge-Kutta method developed by Butcher (1964). Typical computing times on a CDC 6500 for a FORTRAN program were in the range of 4 to 15 min/case, depending on the column length.

The solution method for the equations of periodic countercurrent operation is the same as that of the fixed bed. The only addition to the solution procedure for a single column is that after a column switch, the initial conditions for the start of the new operating period are adjusted using Lagrangian interpolation.

The particle equations of the continuous countercurrent model for small values of the particle velocity result, after the application of orthogonal collocation, in a set of moderately stiff nonlinear ordinary differential equations. Their integration is performed using a third-order semiimplicit Runge-Kutta method developed by Michelsen (1976). Countercurrent operation results in a steady state profile for the moving fluid when there are no inlet disturbances in fluid flow and concentration. The time taken to compute the steady state profile is strongly dependent on the relative values of the particle and fluid velocities. Typical computing times on a PDP 11/45 computer for a FORTRAN program to attain the steady state profile were in the range of 4 to 25 min. The same computer program runs approximately twenty times faster on a CDC-6500 computer.

## RESULTS AND DISCUSSION

The model equations of the three different modes of adsorption operation have been solved for six different column lengths ( $L = 0.30, 0.41, 0.82, 1.23, 1.50, 2.00$  m) for the binary system butanol-2 and *t*-amylalcohol. The parameters used in these column calculations have the following values:

$$\begin{aligned} C_{o1} &= C_{o2} = 1.0 \text{ kg/m}^3, & D_{L1} &= D_{L2} = 0.04 \times 10^{-4} \text{ m}^2/\text{s} \\ V_f &= 0.14 \times 10^{-2} \text{ m/s}, & r_o &= 5.0 \times 10^{-4} \text{ m} \\ K_{f1} &= 2.12 \times 10^{-5} \text{ m/s}, & K_{f2} &= 1.95 \times 10^{-5} \text{ m/s} \\ D_{p1} &= 7.40 \times 10^{-10} \text{ m}^2/\text{s}, & D_{p2} &= 13.03 \times 10^{-10} \text{ m}^2/\text{s} \\ \epsilon &= 0.45, \epsilon_p = 0.94, & C_{1,\text{in}} &= C_{2,\text{in}} = C_{o1} = C_{o2} \end{aligned}$$

The axial diffusivities  $D_{L1}$  and  $D_{L2}$  and the film mass transfer coefficients  $K_{f1}$  and  $K_{f2}$  were obtained from the correlations given by Liles and Geankoplis (1960) and Wilson and Geankoplis (1966). The effective pore diffusivities  $D_{p1}$  and  $D_{p2}$  were estimated from binary batch experiments using data of Balzli (1977) and the approach of Liapis and Rippin (1977b).

The effluent specification was, in all cases, arbitrarily taken to be that for neither of the components should the instantaneous outlet concentration be allowed to exceed 1% of the corresponding inlet value. The effluent specification in the case of periodic countercurrent operation provides the criterion for bed switching, and in the case of continuous countercurrent adsorption, it determines the velocity of the adsorbent particles. For a given column length  $L$ , a particle velocity  $V_s$  is found such that the effluent specification is satisfied. Figure 2 shows the relationship between particle velocity and column length that satisfies the above effluent specification for the case considered. It is observed that, as the column length increases, the particle velocity decreases and, in the limit for a semiinfinite column length, the particle velocity will approach zero asymptotically. It can also be seen that as the column length decreases, the particle velocity increases. The production of the curve in Figure 2 is a

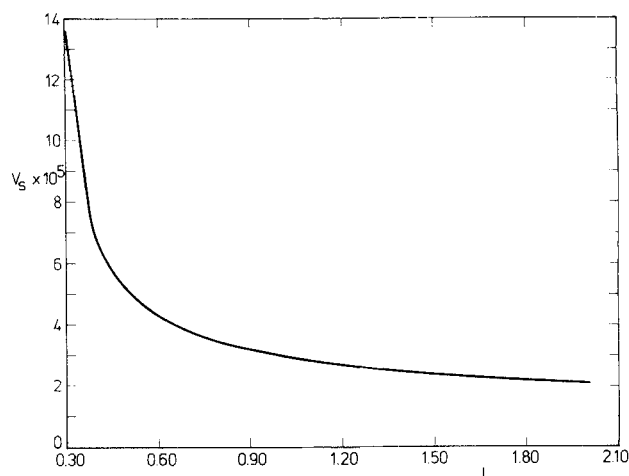


Fig. 2. Countercurrent bed velocity vs. column length for a given effluent specification.

TABLE 1. COMPARISON OF CARBON UTILIZATION FOR DIFFERENT MODES OF OPERATION

Column length (mm)	Fixed-bed operation	Continuous countercurrent operation	Carbon utilization ratio
0.30	8.18%	18.49%	2.26
0.41	13.70%	40.57%	2.96
0.82	26.17%	77.72%	2.97
1.23	30.32%	95.20%	3.14
1.50	31.40%	96.34%	3.07
2.00	33.18%	99.54%	3.00

tedious process because for each column length, the required particle velocity has to be found by successive approximation. Each step in the successive approximation is a complete simulation to steady state.

In Table 1, a comparison is made between the efficiencies with which the adsorptive capacity of a given amount of carbon is used in a fixed bed and a continuous countercurrent column.

For the fixed bed, the carbon utilization is defined as the total mass of material adsorbed at breakthrough on the carbon column to be removed, divided by the total mass of material that would be adsorbed if the whole of that column were in equilibrium with the entering fluid. For the continuous countercurrent operation, the carbon utilization is defined as the total amount of material adsorbed per unit mass of carbon leaving the column divided by the total mass which would be adsorbed if that carbon leaving were in equilibrium with the entering fluid. The carbon utilization ratio defined as the ratio of the utilization in the continuous column to that in the fixed bed is seen to pass through a maximum. This is expected, since for a semiinfinite column, the utilization of the adsorptive capacity of the carbon should approach the same value for both fixed bed and continuous countercurrent operations, while for small columns, the particle velocity required to satisfy the effluent specification is so high that the capacity of the carbon is very much underused.

Figure 3 shows the relationship between carbon utilization and column length for different numbers of subdivisions of a given total length. Carbon utilization of 100% means again adsorption of the amount of material corresponding to the equilibrium isotherms. The value of  $NP = \infty$  corresponds to the continuous countercurrent operation. It is seen that the highest improvement in carbon utilization takes place when the single column is divided into two sections, while for more subdivisions, the extra improvement is smaller. For small columns, even a small number of subdivisions gives almost the same efficiency as the continuous countercurrent operation. For longer columns, many more subdivisions would be required. It is also seen that the carbon utilization in periodic countercurrent operation is 79 to 98% of that in continuous countercurrent operation.

The criterion for bed switching is sometimes that the instantaneous effluent concentration should not exceed a certain value as in the above calculations, and sometimes (for example, Svedberg, 1976) that a given mean value of the exit fluid concentration should not be exceeded.

If the same numerical value is used for both criteria, the average value criterion permits the column to operate longer before switching, resulting in a higher carbon utilization. Calculations based on the graphs in Svedberg (1976) suggest that for the single-component case, the additional utilization arising from use of the average value criterion is unlikely to exceed 5 to 12% of the potential but unrealized utilization. Figures of the same order of magnitude may be expected for the multicomponent case because the initial part of the breakthrough curves has much the same shape as for a single component. In fact, calculations carried out for the binary system using the same numerical value for the average value criterion as for the instantaneous effluent concentration show that 3 to 8% higher carbon utilization can be obtained when the former criterion is used. This extra utilization is greatest for single-column operation, approaching zero as  $NP$  becomes large. This is clear because in the limit when  $NP = \infty$  (continuous countercurrent operation), the instantaneous and mean values are equal.

In periodic countercurrent operation, the periodic pattern of the concentration profile of the free fluid becomes constant after two to four column switches, depending on the number of subdivisions of the bed. For a small number of subdivisions, fewer column switches were required for stabilization of the concentration profile of the free fluid, while more column switches were required for a larger number of subdivisions.

The multicolumn switching procedure, in comparison with the single-column operation, decreases the area under the butanol-2 profile of the fluid phase, since it increases the concentration difference between the fluid and solid phases. It also pushes the profiles of both components back into the column that is removed. The average concentration of butanol-2 adsorbed onto the particles of the column removed is greater than the concentration which would be in equilibrium with the feed. In the initial part of the remaining ( $NP - 1$ ) columns, the ratio of the concentration of butanol-2 to that of *t*-amylalcohol was found to be greater in the feed.

The above results lead to the conclusion that subdividing a column into two or more columns and operating them periodically in a countercurrent mode gives a much better utilization of the adsorbent. Furthermore, although continuous countercurrent operation utilizes the carbon most efficiently, the practical problems associated with this form of operation may make it less attractive in practice than periodic countercurrent operation. The primary problems to be overcome in the continuous coun-

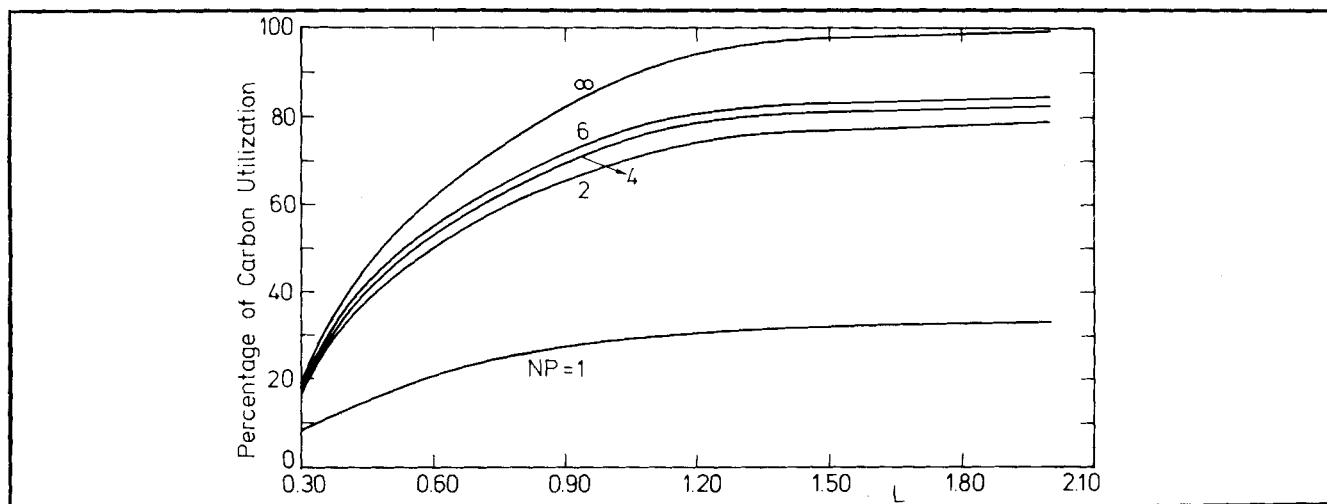


Fig. 3. Percentage of carbon utilization vs. column length with number of columns as parameter.

tercurrent operation are: mechanical complexity of equipment, gradual attrition of the solid adsorbent, limitations in particle size range to avoid excessive pressure drop, channeling (nonuniform flow) of either fluid or solid, and contamination between functional sections of the equipment due to the granular and porous structure of the solid.

Hiester et al. (1954) and Westermarck (1975) have shown that an analysis of some of the technical and economic factors involved, in the case of single-component adsorption, suggests that there is generally no overwhelming basis for preferring a continuous countercurrent system over fixed-bed units.

Although the continuous countercurrent column provides an upper limit for the performance of the periodic process, it is probable that for the multicomponent case, as for the single-component case, the increase in carbon utilization attainable in comparison with the periodic process will not be sufficient to compensate for the design and operating difficulties of the continuous countercurrent system referred to above. Thus, the periodic countercurrent operation will be preferred for practical application.

#### NOTATION

- $A_o$  = external surface area of the spherical particles,  $m^2$   
 $C_{di}$  = concentration of solute in free fluid phase,  $kg/m^3$   
 $C'_{di}$  = dimensionless concentration of solute in free fluid phase,  $C_{di}/C_{oi}$   
 $C_{i,in}$  = concentration of solute at  $x < 0$ ,  $kg/m^3$   
 $C_{oi}$  = reference concentration,  $kg/m^3$   
 $C_{pi}$  = concentration of solute in pore fluid phase,  $kg/m^3$   
 $C'_{pi}$  = dimensionless concentration of solute in pore fluid phase,  $C_{pi}/C_{oi}$   
 $C_{si}$  = concentration of solute in solid phase (per unit volume of particles),  $kg/m^3$   
 $C'_{si}$  = dimensionless concentration of solute in solid phase,  $C_{si}/C^*_{soi}$   
 $C^*_{soi}$  = value of  $C_{si}$  in equilibrium with  $C_{oi}$ ,  $kg/m^3$   
 $D_{Li}$  = axial diffusivity of solute,  $m^2/s$   
 $D_{pi}$  = effective diffusivity of solute,  $m^2/s$   
 $K_{fi}$  = film mass transfer coefficient,  $m/s$   
 $L$  = length of column,  $m$   
 $N$  = number of internal collocation points  
 $Pe_i$  = Peclet number,  $(= LV_f/\epsilon D_{Li})$   
 $P_N(\xi)$ ,  $P_N(\rho)$  = orthogonal polynomials  
 $r$  = radial distance in particle,  $m$   
 $r_o$  = radius of particle,  $m$   
 $R$  = dimensionless radius,  $r/r_o$   
 $Sh_{pi}$  =  $2r_o K_{fi}/\epsilon_p D_{pi}$   
 $t$  = time from start of sorption process,  $s$   
 $V_f$  = superficial fluid velocity,  $m/s$   
 $V_s$  = solid velocity,  $m/s$   
 $x$  = bed length coordinate,  $m$

#### Greek Letters

- $\epsilon$  = void fraction in the bed  
 $\epsilon_p$  = void fraction in particles  
 $\rho$  =  $R^2$   
 $\xi$  = dimensionless bed length coordinate,  $x/L$   
 $\tau$  = dimensionless time,  $tD_{pi}/A_o$   
 $\psi_1, \psi_2, \psi_3, \psi_4$  = functions given by Equations (5) to (8)

#### Superscripts

- \* = equilibrium value

#### Subscripts

- $f$  = fluid  
 $i$  = integer value  
 $p$  = pore  
 $s$  = solid

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