Multicomponent Separation Using a Column-Switching Chromatographic Method

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A cyclic chromatographic process based on the method of column switching was used to separate a three-component carbohydrate mixture. It permits continuous introduction of the feed and is designed to produce higher product concentration compared to a normal elution cyclic process. A fixed-bed model incorporating axial dispersion and a linear driving force for mass transfer was successfully used to estimate optimum operating conditions (switch times and fluid-flow rates). Its experimental setup can be easily constructed by modifying the apparatus of a simulated countercurrent process since both systems comprise segmented columns equipped with on-off valves for fluid-flow control. This allows one to conduct either multicomponent separation based on elution operation or binary separation based on countercurrent operation using essentially the same set of experimental apparatus with minor modification.

Introduction

Many industrial mass- and heat-transfer operations involve contacting two streams in a countercurrent mode. This is because countercurrent contact maximizes the driving force and therefore the efficiency of the process. However, countercurrent motion is not normally implemented in chromatographic and adsorption separation processes, because it is generally difficult to obtain steady movement of settled solids. However, it has been shown that most of the benefit of countercurrent operation can be achieved without the problems associated with moving the solid phase by using multiple fixed beds, with an appropriate sequence of column switching designed to simulate a counter flow system (Ruthven and Ching, 1989). One such example is the "Sorbex" process developed by UOP (Johnson, 1989) for industrial applications in which effective countercurrent flow of the solid adsorbents is achieved by moving the fluid introduction and draw-off points at regular intervals through a fixed-bed divided into many subsections.

The Sorbex type of simulated countercurrent process can resolve a binary feed into two pure products or a multicomponent feed into two product streams with one component appearing as pure product in one of the two streams. To resolve a multicomponent feed into its individual components, a cascade of simulated countercurrent separators may be employed (a feed of n components requires $n-1$ units of simulated countercurrent separators). However, such a process scheme is obviously impractical and expensive. Multicomponent separation using a single unit of the simulated countercurrent apparatus was apparently first proposed by Szepesy et al. (1975). The idea, however, was not pursued until Hashimoto et al. (1993) reported a simulated countercurrent process which can resolve a three-component mixture into its individual components. The process employed a series of individual columns which were packed alternately with two types of adsorbents. To separate a feed containing components A, B and C, a pair of adsorbents was selected so that component A is the most strongly adsorbed solute on one type of adsorbent; component B is the most strongly adsorbed solute on the other type of adsorbent; and component C is the least strongly adsorbed solute on both types of adsorbents. Under properly selected operating conditions, it was demonstrated that component C was recovered as pure product in the raffinate stream while components A and B were collected alternately as pure product in the extract stream. Although the process is attractive for multicomponent separation as it possesses the efficiency of a countercurrent process, it may not find wide applications because a suitable combination of different adsorbents must be found for each multicomponent feed.

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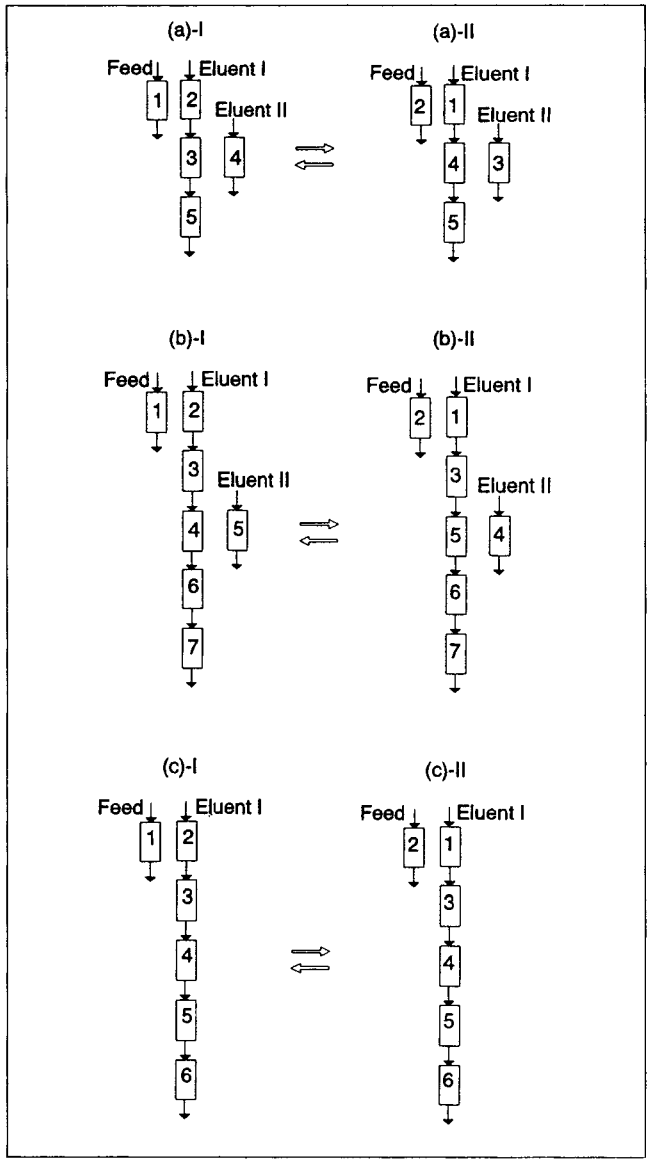

Figure 1. Column-switching procedures for three different cyclic processes.

The present study proposes a simple cyclic process which can resolve a three-component mixture into its individual components using the apparatus of a simulated countercurrent process. It should be noted that the cyclic process does not have the advantages associated with a countercurrent process. It is essentially a chromatographic elution technique based on the method of column switching.

Principle of Operation

In this work, we employ a column-switching procedure similar to that of Row and Lee (1987) which allows the introduction of feed into the cyclic process on a continuous basis. Figure 1 shows typical process schemes which can be applied to the separation of multicomponent mixtures. The optimum way to operate these cyclic processes depends on the purpose of the separation. To illustrate the operating principle, we assume that a feed containing three components (A-B-C) is to be resolved into three pure products using the process scheme depicted in Figure 1a. We further assume that component A is the slowest moving solute while component C is the fastest moving solute, that three columns are needed to provide adequate separation of components B and C (the more difficult separation), and two columns are sufficient to separate component A from component B (the less difficult separation). At zero time the feed is introduced into column 1 for a predetermined period (Figure 1a-I). At the end of this period, columns 1 and 2 and columns 3 and 4 are rotated simultaneously, as indicated by the arrows, to achieve the desired periodic movement of columns. Column 2 now receives the feed while column 1 carries out the separation of the feed mixture (Figure 1a-II). The flow rate of eluent I to column 1 is adjusted so that at the end of the switch period, column 4 contains only component A while the two faster moving and more difficult to separate components (B and C) are passed into column 5. At the next switch time, columns 2 and 1 interchange positions again so that column 1 receives the feed and column 2 performs further separation (Figure 1a-I). At the same time, column 4 and 3 are rotated so that component A which is contained in column 4 is flushed out by another stream of eluent and collected as pure product at the column outlet. Solutes B and C, which have been passed into column 5 to continue the separation, are collected alternately as pure product at the column outlet. Thus, one complete cycle consists of two switching periods. It should be noted that the cyclic process depicted in Figure 1a allows the withdrawal of component A once it has been separated from components B and C.

Mathematical Model

The operating conditions (switch times and fluid-flow rates) for the cyclic processes depicted in Figure 1 may be derived from a fixed-bed theory. In formulating the mathematical model of a fixed bed, we assume uniform packing, uniform velocity distribution, isothermal behavior, and constant physical properties. Convection and axial dispersion are considered the only mechanisms of mass transfer in the axial direction. An overall linear driving force model is assumed to represent transport of solutes in and out of the sorbent particles. Under these conditions, mass balances for a solute over a differential section of the packed column with bed voidage, ϵ, yield the following differential equations:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} - \left(\frac{1-\epsilon}{\epsilon}\right) k(q^* - q) \tag{1}$$

$$\frac{\partial q}{\partial t} = k(q^* - q) \tag{2}$$

with the corresponding initial and boundary conditions:

$$c(z,\ t=0) = q(z,\ t=0) = 0 \tag{3}$$

$$D_L \frac{\partial c}{\partial z}(z=0,\ t) = -v[c_o(z=0^-,\ t) - c(z=0^+,\ t)] \tag{4}$$

$$\frac{\partial c}{\partial z}(z=L,\ t) = 0 \tag{5}$$

$$c_o(z=0^-,\ t)=c_F \qquad 0\le t\le t_F$$
$$=0 \qquad \text{otherwise} \tag{6}$$

where $c_o(z=0^-,\ t)$ is a square function and t_F is the feed introduction time. For linear systems, the equilibrium relationship takes the following form:

$$q^*=Kc \tag{7}$$

Written in dimensionless form, Eqs. 1-6 become:

$$\frac{\partial U}{\partial T}=\frac{1}{Pe}\frac{\partial^2 U}{\partial x^2}-\frac{\partial U}{\partial x}-\beta St(KU-Q) \tag{8}$$

$$\frac{\partial Q}{\partial T}=St(KU-Q) \tag{9}$$

$$U(x,\ T=0)=Q(x,\ T=0)=0 \tag{10}$$

$$\frac{\partial U}{\partial x}(x=0,\ T)=-Pe[U_o(x=0^-,\ T)-U(x=0^+,\ T)] \tag{11}$$

$$\frac{\partial U}{\partial x}(x=1,\ T)=0 \tag{12}$$

$$U_o(x=0^-,\ T)=1 \qquad 0\le T\le T_F$$
$$=0 \qquad \text{otherwise} \tag{13}$$

For ease and speed of computation, a combination of the method of orthogonal collocation and the IMSL integration routine DGEAR was used to obtain the solution of Eqs. 8-13. All computations were carried out on an IBM 3090 mainframe. The number of internal collocation points required to give an accurate solution varied between 8 and 16, depending on the parameter values. The solution procedure for the single-column case described above can be easily adapted to the multicolumn problem of the cyclic processes depicted in Figure 1. To do so, the initial and operating conditions for each column in the cyclic processes must be adjusted at each switch time. Predictions of concentration profiles may be obtained by first solving the partial differential equations with the boundary and initial conditions given by Eqs. 8-13 for column 1 in Figure 1. The numerical solution procedure is then stopped at time $= T_F$, at which the columns are switched in position. At this time the initial and boundary conditions for each column are changed accordingly and the integration continued until time $= 2T_F$, when a new column switch occurs. This algorithm is followed repeatedly and the solute concentration profiles become periodic functions of time with period equal to the imposed switch interval, T_F.

Experimental Section

Materials

A ternary mixture of fructose-dextran T6 (M.W. $\approx$ 6,000)-dextran T2000 (M.W. $\approx$ 2,000,000) was used as feed while deionized water was used as eluent. Fructose pentahydrate and dextran T2000 were obtained from Sigma Chemical Co. (U.S.A.) while dextran T6 was supplied by Fluka Chemie AG

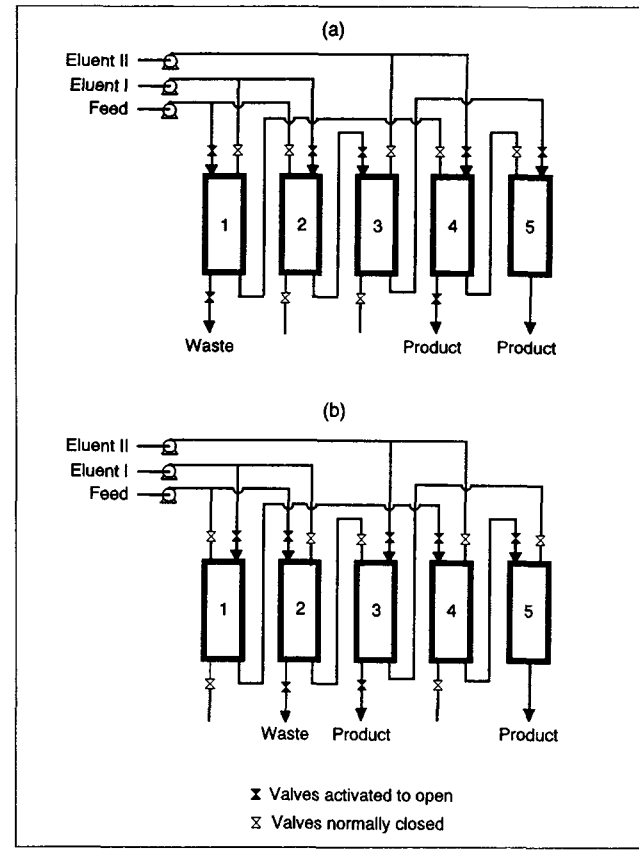

Figure 2. Physical arrangement of columns and valves for the cyclic process depicted in Figure 1a.

(a) Corresponds to Figure 1a-I while (b) refers to Figure 1a-II.

(Switzerland). The feed was prepared by dissolving the three carbohydrates in deionized water to the desired concentration. Dilute feed solutions (5% w/v of each solute) was used so that they may be considered as an example of a system in which the equilibrium isotherms for all components are linear and uncoupled. The columns were packed with silica gel (pore size = 66 Å, particle size = 22 μm) obtained from Fuji-Davison Chemical Ltd (Japan).

Apparatus and procedures

In this study the three cyclic process schemes shown in Figure 1 were used to separate the ternary carbohydrate mixture. These process configurations may be constructed by modifying the simulated countercurrent setup described previously (Ching et al., 1992). The experimental setup consists of a series of individual columns equipped with on-off valves for fluid-flow control. For the sake of simplicity, only the cyclic process depicted in Figure 1a will be discussed in detail here. Figure 2 shows the diagram of the corresponding physical arrangement of the cyclic process. The experimental unit comprises five identical stainless steel columns, each 0.014 m ID $\times$ 0.475 m. Each column is surrounded by a water jacket for temperature control. Instead of rotating the columns, a total of 14 solenoid valves (Asco Valves, U.S.A.) are employed to cause the distribution of the various fluid streams to reproduce the column-switching action described in Figure 1a. Except for column 5, all columns are equipped with two inlet lines and

Table 1. Operating Conditions for the Cyclic Processes

Run	1	2	3	4
Process Scheme	Figure 1a	Figure 1a	Figure 1b	Figure 1c
Feed (m^3/s)	8.33×10^{-9}	8.33×10^{-9}	8.33×10^{-9}	8.33×10^{-9}
Eluent I (m^3/s)	7.0×10^{-8}	2.67×10^{-8}	4.67×10^{-8}	7.17×10^{-8}
Eluent II (m^3/s)	5.0×10^{-8}	2.5×10^{-8}	2.5×10^{-8}	—
Switch time (s)	1,200	3,000	3,000	3,000

two outline lines. The opening and closing of these lines are controlled by the solenoid valves which are activated automatically by a programmable logic controller (Model Sysmac-S6, Omron Tateisi Electronics Co., Japan). All the valves are normally closed unless energized to open. To simulate the condition depicted in Figure 1a-I, Figure 2a shows that at zero time the feed valve for column 1 is activated to allow the feed solution to enter column 1 while the eluent I valve for column 2 and the eluent II valve for column 4 are simultaneously energized to allow the eluents to flow into columns 2 and 4. The transfer valves between columns 2 and 3 and between columns 3 and 5 are also activated so that fluid can flow from column 2 to column 5. The outlet lines which open are the waste line for column 1 and the product line for column 4. It should be noted that the product line for column 5 is not equipped with a valve, and it is therefore always open. At switch time, Figure 2b shows that the set of valves mentioned above is deactivated and the remaining valves in the system are now activated to simulate the condition depicted in Figure 1a-II. Thus, one complete cycle consists of two switching periods. Solvent metering pumps (Model 2510, Varian, U.S.A.) were used to deliver the feed, eluent I, and eluent II to the setup. Samples collected from the sampling port located at the outlet of columns 3, 4, and 5 were analyzed by liquid chromatography. The operating conditions for the cyclic processes depicted in Figure 1 are summarized in Table 1. Operation was continued for a few cycles in each experimental run.

Results and Discussion

The operation of the cyclic processes shown in Figure 1 is dictated by the various equilibrium distributions of the feed components. The equilibrium constants as well as the overall mass-transfer coefficients for our model system have been determined from independent pulse response experiments and are listed in Table 2. Retention time in elution chromatography is largely determined by the magnitude of a solute's equilibrium constant. The order of elution during a separation of a mixture containing the three solutes of interest is inversely proportional to the magnitude of the equilibrium constants. Hence, fructose which has the largest equilibrium constant elutes last while dextran T2000 which is totally excluded from the pores of the sorbent ($K=0$) elutes first. The equilibrium values also suggest

Table 2. Equilibrium and Kinetic Parameters for Fructose, Dextran T6, and Dextran T2000 on Silica Gel

Solute	Equilibrium Constant, K	Mass-Transfer Coefficient, k (s^{-1})
Fructose	0.69	0.092
Dextran T6	0.23	0.047
Dextran T2000	0.00	—

that dextran T6 and dextran T2000 are closest in affinity and therefore control the total column length needed to resolve this three-component mixture into individual pure components. On the other hand, it may be seen that fructose can be easily separated from the two dextran species and it can therefore be withdrawn as product as soon as it is sufficiently separated from dextran T6.

The cyclic process depicted in Figure 1a is designed according to the above strategy where columns 2 and 3 (or columns 1 and 4) are used to separate fructose from the dextran species. Fructose is subsequently withdrawn as product at the outlet of either column 3 or column 4. An additional column (column 5) is provided to give a total length of 1.425 m for the separation of dextran T6 from dextran T2000. The dextran species therefore travel the full distance of three columns and are collected alternately as pure product at the outlet of column 5.

Since the feed flow rate and column length are arbitrarily chosen for the cyclic process depicted in Figure 1a the maximum period for feed introduction then becomes the controlling parameter to be optimized so that the most difficult separation is adequate. Equations 8-13 were solved to obtain the maximum feed introduction time, T_F, which would still give a good resolution of the dextran species using the three columns. This feed introduction time would in fact be the switch time for the cyclic process depicted in Figure 1a. At zero time column 1 receives the feed solution and by the end of this first feed introduction period the feed line is switched to column 2 while column 1 begins to receive eluent I (see Figure 1a-II). The flow rate of eluent I is the next parameter to be determined. The conditions to be satisfied are that fructose should reach the outlet of column 4 and be sufficiently separated from the dextran species, having traveled the full length of two columns by the end of the second switch interval. The mathematical model was again used to determine this optimum flow rate of eluent I. The parameters used in the simulation are as follows:

- Equilibrium constant and effective mass-transfer coefficient for fructose listed in Table 2.
- Dispersion coefficient, $D_L=0.16v$, and average bed voidage, $\epsilon=0.45$ [both determined from pulse response experiments (Chu, 1992)].
- Number of columns = 2.
- Initial conditions for column 1 (fructose concentration profile in column 1 at the end of the first switch interval) and for column 4 (a clean bed).
- Simulation interval is from zero to T_F where T_F is the dimensionless feed time which is equivalent to the switch time.

Using the above parameter values, the model was solved to determine the value of v, the interstitial velocity of eluent I, which must satisfy the conditions mentioned previously.

At the beginning of the third switch interval, we return to the situation in Figure 1a-I. Here, the unknown operating parameter is the flow rate of eluent II. This flow rate must clear out the fructose product in column 4 by the end of this interval. The parameter values required for this simulation are the same as those used in the previous simulation except for the number of columns and the initial condition. This time only one column is employed whose initial condition is the fructose profile in column 4 at the end of the second switch interval.

The general strategy for determining the operating condi-

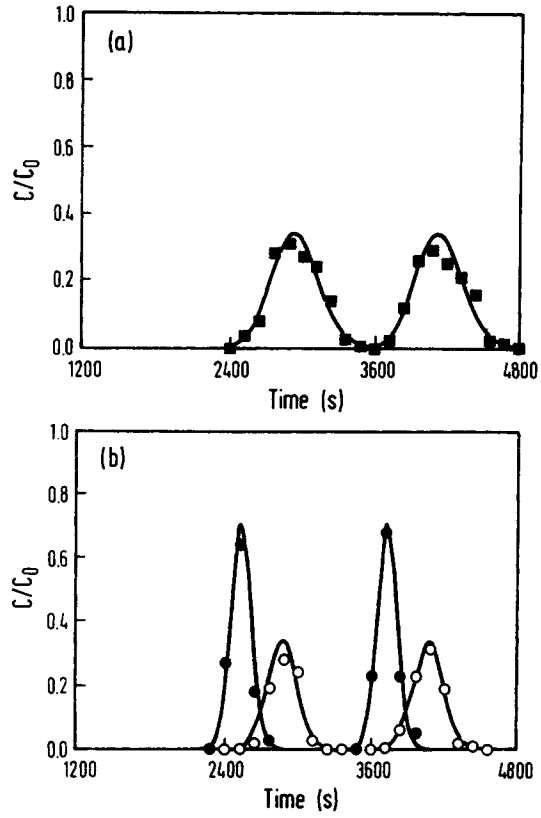

Figure 3. Experimental (points) and theoretical (curves) product concentration profiles for run 1.

(a) Fructose (■) collected from the outlet of either column 3 or column 4; (b) dextran T6 (○) and dextran T2000 (●) collected from the outlet of column 5.

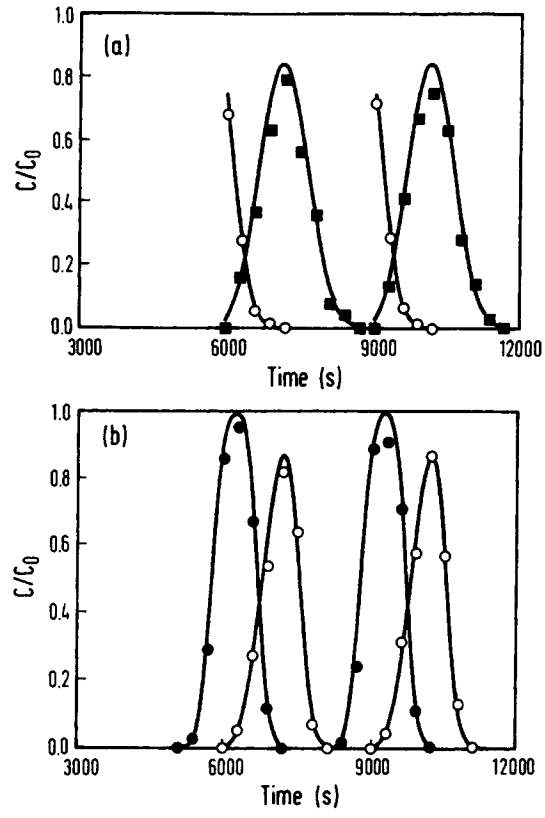

Figure 4. Experimental (points) and theoretical (curves) product concentration profiles for run 2.

(a) Fructose (■) and dextran T6 (○) collected from the outlet of either column 3 or column 4; (b) dextran T6 (○) and dextran T2000 (●) collected from the outlet of column 5.

tions for the cyclic processes depicted in Figures 1a and 1b by using mathematical simulation may therefore appear like this:

- Determine the maximum feed introduction time (switch time) which permits a good resolution of the feed components closest in affinity.
- Determine the flow rate of eluent I which retains the slowest moving component within a specified column length while passes on the faster moving components to additional column length for further separation.
- Determine the flow rate of eluent II which clears out the slowest moving component within the switch interval.

The operating conditions for runs 1 and 3 in Table 1 have been determined using the above simulation procedures.

Figure 3 shows the experimental results for run 1. The first cycle for this run was from 0 to 2,400 s since the switch time was set at 1,200 s. A small amount of dextran T2000 was collected from the outlet of column 5 near the end of this cycle. From the second cycle onward, the separated products were collected continuously at the outlet of column 5 (dextran T2000 and dextran T6) and column 3 or 4 (fructose). It is evident that in this case two columns are sufficient to separate fructose from the dextran species. However, a complete base line resolution of the two dextran species is not achieved even though they travel the full distance of three columns. To investigate the effect of feed introduction time on process performance, run 2 was carried out on the same apparatus with a larger feed introduction period (3,000 s). Figure 4 shows the experimental results for this run. It is apparent that under volume overloading condition the performance of the process has deteriorated. The overlapping of the dextran peaks is considerably larger than that in run 1. Furthermore, the fructose product is contaminated with dextran T6. This occurs because two columns are no longer sufficient to separate fructose from dextran T6 when a larger feed time is applied to the system.

One way to avoid the presence of dextran T6 in the fructose product is to increase the flow rate of eluent I so that the unresolved mixture containing fructose and dextran T6 is passed on to column 5 for further separation. However, this would split the fructose product. To avoid this as well as to reduce the overlapping of the dextran peaks, run 3 was carried out on the apparatus shown in Figure 1b. In this configuration, three columns are used to separate fructose from dextran T6 and five columns to separate the two dextran species for a feed time of 3,000 s. Figure 5 shows the product concentration profiles for this run. There is very little dextran T6 in the fructose product collected from the outlet of either column 4 or column 5. Comparison with the results of run 2 shows that the overlapping of the dextran peaks has been substantially reduced. However, this improved performance is achieved by employing a greater number of columns and consuming more eluent. The flow rate of eluent I in run 3 is 4.67×10^{-9} m^3/s, a 75% increase over run 2.

The simple cyclic process shown in Figure 1c represents the

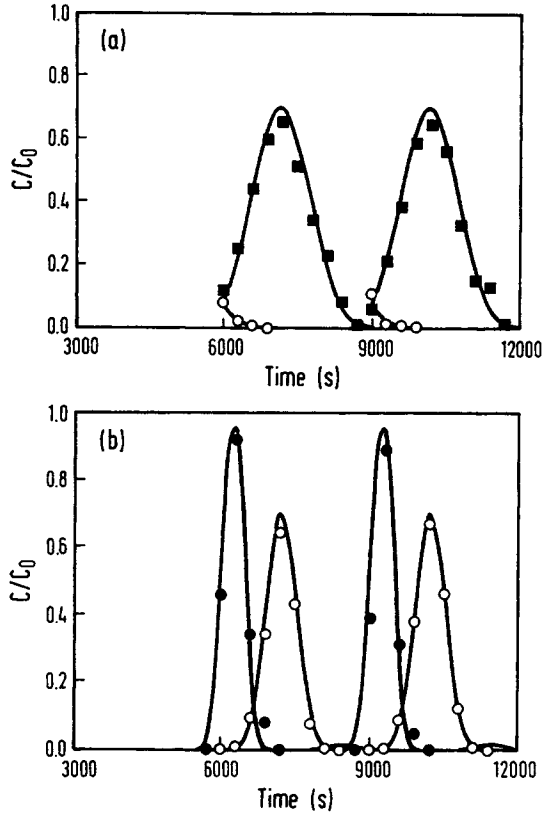

Figure 5. Experimental (points) and theoretical (curves) product concentration profiles for run 3.

(a) Fructose (■) and dextran T6 (○) collected from the outlet of either column 4 or column 5; (b) dextran T6 (○) and dextran T2000 (●) collected from the outlet of column 7.

normal elution chromatography arrangement. Run 4 carried out using this process scheme acts as the basis for comparison with run 3 since both runs were conducted at the same total bed length and eluent flow rate. The results for run 4 are shown in Figure 6. In this arrangement all the feed components travel the full distance of five columns. Comparison between runs 3 and 4 shows that there is very little difference between the

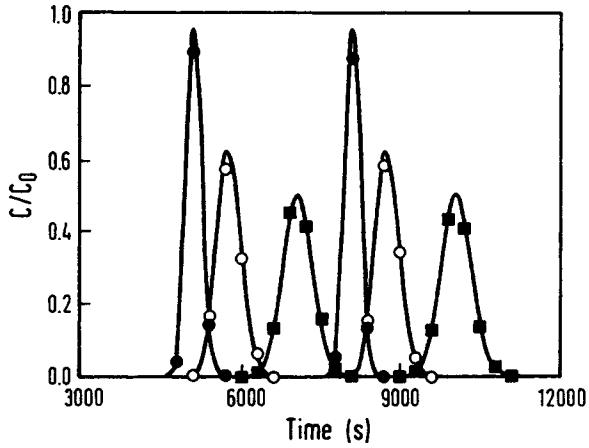

Figure 6. Experimental (points) and theoretical (curves) product concentration profiles for run 4.

Fructose (■), dextran T6 (○), and dextran T2000 (●) collected from the outlet of column 6.

results for the two dextran species since they travel the full distance of five columns in both runs. However, the late removal of fructose in run 4 yields a peak maximum which is about 40% lower than that in run 3. Hence, the cyclic process depicted in Figure 1b has been shown to allow the slowest moving component to be collected at a higher concentration.

It should be noted that the experimental setup constructed for the study of the simulated countercurrent system (Ching et al., 1992) can be easily modified for use in the study of multicomponent separations using the cyclic processes proposed here since both systems comprise segmented columns which are controlled by on-off valves.

Conclusions

This study has shown that a column-switching method applied to the separation of a three-component mixture permits continuous introduction of the feed to the cyclic process and can increase the product concentration of the slowest moving component. It is shown that the operating conditions for the cyclic process may be determined from a fixed-bed model using equilibrium constants and effective mass-transfer and dispersion coefficients found from independent experiments as input parameters. The cyclic process proposed in this study is attractive for large-scale applications since it comprises packed columns which can be easily scaled up. Furthermore, the process can be designed and optimized using well established fixed-bed theories. On the other hand, the other semicontinuous and continuous chromatographic techniques suitable for multicomponent separations such as annular chromatography and magnetically stabilized fluidized bed are generally difficult to scale up for commercial applications.

Notation

c = fluid phase concentration, % w/v
c_o = fluid phase concentration at bed inlet, % w/v
c_F = feed concentration, % w/v
D_L = axial dispersion coefficient, m^2/s
k = overall mass-transfer coefficient, s^{-1}
K = equilibrium constant
L = length of a packed column, m
Pe = vL/D_L, Peclet number
q = solid phase concentration, % w/v
q^* = solid phase concentration in equilibrium with c, % w/v
Q = q/c_F, dimensionless solid phase concentration
Q^* = q^*/c_F, dimensionless solid phase concentration in equilibrium with U
St = kL/v, Stanton number
t = time, s
t_F = feed introduction time, s
T = v/L, dimensionless time
T_F = vt_F/L, dimensionless feed introduction time
U = c/c_F, dimensionless fluid phase concentration
U_o = c_o/c_F, dimensionless fluid phase concentration at bed inlet
v = interstitial velocity, cm/min
x = dimensionless axial coordinate
z = axial coordinate, m

Greek letters

β = $(1-\epsilon)/\epsilon$, dimensionless parameter
ϵ = column voidage

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