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Fractionation of multicomponent sugar mixtures using a pseudo simulated moving bed

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ABSTRACT

A model for the fractionation of a ternary mixture of sugars by pseudo-simulated moving bed chromatography, according to the JO process of Japan Organo Co., is presented. The process cycle is divided in two steps. In step 1 feed and eluent streams are introduced in the system, equivalent to a series of preparative chromatographic columns, and the intermediate component is produced. In step 2, similar to a simulated moving bed (SMB), there is no feed and the less adsorbed species is collected in the raffinate while the more retained species is collected in the extract; this step is described by an equivalent TMB model. This methodology is then applied to the separation of a ternary mixture constituted by two sugars - sucrose (disaccharide) and fructose (monosaccharide) - and one non-sugar – betaine.

INTRODUCTION

Simulated moving bed (SMB) is one of the most powerful and promising techniques for preparative and industrial scale chromatography. In particular, the SMB technology allows the continuous injection and separation of binary mixtures. The simulated countercurrent contact between the solid and liquid phases maximizes the mass-transfer driving force, leading to a significant reduction in mobile and stationary phases consumption when compared with elution chromatography [1,2].

Although the SMB technology offers many advantages over preparative chromatography, leading to cleaner, smaller, safer and faster processes, the main disadvantage of this process is the limitation to the separation of binary mixtures or to the recovery of one component from a multicomponent mixture.

The process described here is based on the New JO SMB process first applied by the Japan Organo Company (http://www.organo.co.jp/technology/hisepa/en_hisepa/) [3] using patented technology [4,5]. This technique of pseudo-simulated moving bed chromatography is being applied in the separation of complex multicomponent mixtures, e.g., separation of beet molasses mixtures into raffinose, sucrose, glucose and betaine [5] and in the production of raffinose [6] from beet molasses.

In this work, the Pseudo-SMB model of the JO process for the separation of a ternary mixture is developed and applied to the separation of three important sugar components, namely: sucrose, fructose and betaine.

PSEUDO-SMB MODEL FOR THE JO PROCESS

The JO process for the separation of a ternary mixture, is divided in two main steps:

In the first step the feed and eluent streams enter the system and the component B with intermediate affinity is recovered; this step is modeled as a series of preparative chromatographic columns.

In the second step there is only one inlet flow of eluent and no feed; the more retained component C is recovered in the extract and the less adsorbed species A is recovered in the raffinate; this step is modeled as a pseudo true moving bed with no feed.

Figures 1a) and 1b) show the traditional True Moving Bed (TMB) system and the schematic diagram of both step1 and step 2 of the JO process, respectively.

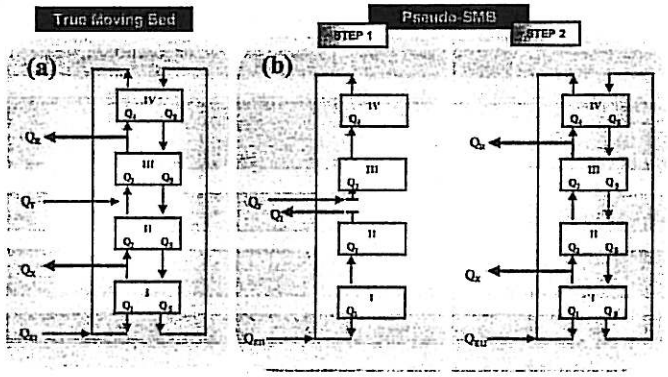

Figure 1. Schematic diagram of (a) TMB and (b) Pseudo-SMB.

In the traditional TMB system [7], shown in Figure (1a) there are four sections separated by the inlet and outlet streams; section 1 is between the eluent and extract ports, section 2 between extract and feed ports, section 3 between feed and raffinate ports and section 4 between raffinate and eluent ports and the fluid leaving section 4 is recycled to the section 1. Each section contains N_C columns with length L_C.

In the pseudo-SMB model of the JO process, shown in Figure (1b) we still consider four sections for convenience: a) in step 1 the feed flows through sections 3 and 4 and the sum of feed plus eluent flowrates flows through sections 1 and 2 ; b) in step 2, equivalent to a TMB model, the flow-rate in sections 2 and 3 is the same since there is no feed.

The detailed mathematical model for the JO process is described below.

Step 1

This step is modeled as a series of chromatographic columns arranged in four sections. The circuit is cut between section 2 and 3 by a shut-off valve, allowing an intermediate stream, rich in the intermediate component, to be collected. During step 1, there are two input flows: eluent, Q_{E1}, and feed, Q_F, and one output flow of the intermediate species B, Q_I (see Figure 1b).

The model equations are:

Mass balances for species i in the bulk fluid phase

The mass balance in a volume element of section j is:

$$\frac{\partial c_{ij}}{\partial t} = D_{Lj}\frac{\partial^2 c_{ij}}{\partial z^2} - v_j\frac{\partial c_{ij}}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}k_P\left(q_{ij}^{*} - q_{ij}\right) \qquad [1]$$

where the subscripts i $(i = A,B,C)$ refers to the species in the mixture, and j $(j = 1,2,...,N_S = 4)$ is the section number, c_{ij} and q_{ij} are the fluid phase and average adsorbed phase concentrations of species i in section j of the preparative column series, respectively, z is the axial co-ordinate, t is the time variable, ε is the bed porosity, v_j is the interstitial

fluid velocity in the j^{th} section, D_{Lj} is the axial dispersion coefficient, and k_P is the intraparticle mass transfer coefficient.

Mass balances for species i in the particle

The mass balance in the particle is:

$$\frac{\partial q_{ij}}{\partial t} = k_P\left(q_{ij}^{\bullet} - q_{ij}\right) \qquad [2]$$

where $q_{ij}^{\bullet}$ is the adsorbed phase concentration in equilibrium with c_{ij}.

Initial and boundary conditions

The initial condition for step 1 is:

$$t = 0 \quad (cycle1): \qquad c_{ij} = q_{ij} = 0 \qquad [3a]$$

$$t = t_{S2}(cycle\ k): c_{ij} = c_{ij}(cycle\ k-1, step2); q_{ij} = q_{ij}(cycle\ k-1, step2) \qquad [3b]$$

and the two boundary conditions for section j are given by:

$$z = 0: c_{ij,0} = c_{ij} - \frac{D_{Lj}}{v_j}\frac{dc_{ij}}{dz} \qquad [4a]$$

where $c_{ij,0}$ is the inlet concentration of species i in section j.

$z = L_j$:

Feed node: $c_{i3,0} = c_i^F$ [4b]

Eluent node: $c_{i1,0} = \frac{Q_4}{Q_1} c_{i4,1}$ [4c]

Raffinate (j=3) and extract (j=1) nodes: $c_{ij,1} = c_{ij+1,0}$ [4d]

The initial condition and the boundary conditions for x=1 are the same as defined above in Equations 4b-d. The boundary condition for x=0, in the dimensionless form becomes:

$$c_{ij,0} = c_{ij} - \frac{1}{Pe_j}\frac{dc_{ij}}{dx} \qquad [5]$$

Step 2

This step is modeled as an equivalent TMB with four sections and with recycling. During step 2, there is one input flow of eluent, Q_{EI2} and two output flows of extract, Q_X, rich in the more retained component C, and raffinate, Q_R, rich in the less retained component A. Since there is no feed the flow-rates in sections 2 and 3 are equal.

Model equations are the species mass balances in the section j of the equivalent true moving bed. In dimensionless form we have:

Bulk fluid phase:

$$\frac{\partial c_{ij}}{\partial t} = D_{Lj}\frac{\partial^2 c_{ij}}{\partial z^2} - v_j\frac{\partial c_{ij}}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}k_P\left(q_{ij}^{\bullet} - q_{ij}\right) \qquad [6]$$

Particle:

$$\frac{\partial q_{ij}}{\partial t} = u_S \frac{dq_{ij}}{dz} + k_P\left(q_{ij}^{\bullet} - q_{ij}\right) \qquad [7]$$

Initial and boundary conditions

The initial condition for this step is:

$$t = 0(cycle1): c_{ij} = c_{ij}(cycle1, step1); q_{ij} = q_{ij}(cycle1, step1) \qquad [8a]$$

$$t = t_{S1}(cycle\ k): c_{ij} = c_{ij}(cycle\ k, step1); q_{ij} = q_{ij}(cycle\ k, step1) \qquad [8b]$$

and the two boundary conditions for section j are given by Equations (4b-d) and (5).

NUMERICAL SOLUTION

The transient Pseudo-SMB model equations are numerically solved, starting from an initial condition where the columns are filled only with the eluent until the cyclic steady-state, CSS, is reached.

Model equations were numerically solved by using the software package PDECOL [8] based on the method of lines and uses orthogonal collocation in finite elements (OCFE) for the discretization of the space variable. For a ternary system there are six PDEs per section; they are discretized in the axial direction using 20 finite elements and two interior collocation points in each element; the resulting system of ODE's in the time variable is integrated with the solver GEARIB [9].

PROCESS OPTIMIZATION

Once the model for the pseudo-SMB JO system has been set one has to determine the operating conditions, i.e., internal flow-rates in each section and the duration of steps 1 and 2 in order to obtain the desired separation. In this work a method is suggested based on the definition of velocity of propagation of concentration of a species i and on constraints for steps 1 and 2 of the cycle [10]. For a given feed flow-rate, Q_F, and a given t_{S2} conditions have to be met in order to separate all the three different components. These conditions and the equations needed to calculate all the variables of the system are shown in table 1.

EXPERIMENTAL RESULTS

The adsorption equilibrium isotherms for sucrose, fructose and betaine were determined using a Gilson 302 HPLC unit. The column used is 2.6 cm in diameter and 11.8 cm in length. The packing consists in a 300-320 μm strongly acidic cation exchange resin Amberlite CR1310 Na^+ form, from Rohm&Hass, France. The elution was performed at 25°C and at a fluid velocity of 3 ml/min.

The concentrations of the aqueous solutions for sucrose (SU), fructose (FR) and betaine (BE) were, respectively: $c_{SU} = 15$ g/l, $c_{FR} = 15$ g/l and $c_{BE} = 80$ g/l, respectively.

The experiments were carried out injecting 200 μl pulses of mono-component aqueous solutions of each key component at the inlet of the column. The samples were analyzed using a Gilson 131 IR detector, connected to the HPLC unit. Figure 2 shows the response curves obtained for all the components.

Considering that all the components have a linear adsorption response behavior, the mean

Table 1. Conditions for the optimization of Step 1 and step 2.

	STEP 1	**STEP 2**
Variables:	t_{S1}, $Q_{I,S1}$, $Q_{2,S1}$, $Q_{3,S1}$, $Q_{4,S1}$, Q_F, Q_{EI1}, Q_B	t_{S2}, Q_S, $Q_{I,S2}$, $Q_{2,S2}$, $Q_{3,S2}$, $Q_{4,S2}$, Q_X, Q_R, Q_{EI2}
Assumptions:	Q_{FE} is known Component B is injected only in one column N_{CS}=3 (number of columns per section)	t_{S2} is known Component B moves $(x_{B,S1}+L)$ with the solid Component C moves $(x_{C,S1}+3L)$ with the liquid N_{CS}=3 (number of columns per section)
Equations:	$t_{S1}=\bar{t}_B-\sqrt{\frac{8}{k_P}}\sqrt{(\bar{t}-\tau)}$ $Q_{EI1}=\frac{\varepsilon A(2L_C)}{t_{S1}}\left(1+\frac{1-\varepsilon}{\varepsilon}K_B\right)-Q_F$ $Q_{3I,S1}=Q_{4,S1}=Q_F$ $Q_{1,S1}=Q_{2,S1}=Q_B$ $Q_B=Q_F+Q_{EI1}$	$Q_{III}=\frac{\varepsilon A}{t_{s2}}\left\{\frac{K_B}{K_B-K_C}\left[x_{C,S2}\left(1+\frac{1-\varepsilon}{\varepsilon}K_C\right)-x_{B,S2}\left(1+\frac{1-\varepsilon}{\varepsilon}K_B\right)\right]+x_{B,S2}\left(1+\frac{1-\varepsilon}{\varepsilon}K_B\right)\right\}$ $Q_S=\frac{\varepsilon A}{t_{s2}}\left\{\frac{1}{K_B-K_C}\left[x_{C,S2}\left(1+\frac{1-\varepsilon}{\varepsilon}K_C\right)-x_{B,S2}\left(1+\frac{1-\varepsilon}{\varepsilon}K_B\right)\right]\right\}$ $Q_{1,S2}=Q_S K_C\beta-(Q_F+Q_{EI1})\frac{t_{s1}}{t_{s2}}$ $Q_{2,S2}=Q_{3,S2}$ $Q_{4,S2}=\frac{Q_S K_A}{\beta}-Q_F\frac{t_{s1}}{t_{s2}}$; $Q_R=Q_{3,S2}-Q_{4,S2}$ $Q_X=Q_{1,S2}-Q_{2,S2}$ $Q_{EI2}=Q_{1,S2}-Q_{4,S2}$

retention time, $\bar{t}_i$, is related to the adsorption equilibrium constant by:

$$\bar{t}_i=\tau\left(1+\frac{1-\varepsilon_T}{\varepsilon_T}K_i\right),\quad \tau=\frac{L}{v}=\frac{\varepsilon_T V}{Q} \qquad [9]$$

where L is the column length, ε_T is the total bed porosity, v is the fluid velocity, K_i is the slope of the linear adsorption equilibrium isotherm parameter for component i, V is the column volume and Q is the fluid flow-rate.

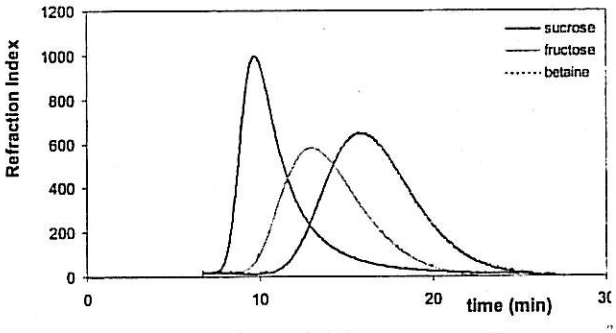

Figure 2. Experimental pulse responses for sucrose, fructose and betaine

The value of $\bar{t}_i$ for each component is calculated from the experimental pulse responses using the following expression: $\bar{t}_i=\int_0^\infty c_i t\,dt \Big/ \int_0^\infty c_i\,dt$, where c_i is the concentration of component i.

The values of $\bar{t}_i$ obtained from experimental HPLC data and the values of K_i derived from equation 9 are given in table 2.

The mass transfer coefficient, considering the linear driving force model (LDF) for homogeneous particles can be estimated from the mass transfer coefficient obtained using the LDF model for porous particles [11], i.e.,

$$k_P = \frac{k_{pe}}{\varepsilon_P + K_P} = \frac{k_{pe}}{K} \qquad [10]$$

where k_P is the mass transfer coefficient used in the LDF model for homogeneous particles, k_{pe} is the mass transfer coefficient used in the LDF model for porous particles, ε_P is the particle porosity, K_P is the initial slope of the isotherm considering the adsorbent as homogeneous particles (the one used in this work).

The value for k_{pe} can be estimated using the following relation:

$$k_{pe} = \frac{15 D_{pe}}{r_P^2} \qquad [11]$$

where D_{pe} is the effective diffusivity and r_P is the particle porosity. The value of D_{pe} is evaluated through:

$$D_{pe} = \frac{\varepsilon_P D_m}{\tau_{ort}} \qquad [12]$$

being D_m the molecular diffusivity (cm^2s^{-1}) and τ_{ort} the tortuosity factor. An approximate value of D_m for each component can be calculated using the Wilke-Chang estimation method [12]. The resulting estimated values of k_P are shown in table 2.

Table 2. Values of mean retention time, adsorption parameters and mass transfer coefficients for the ternary mixture.

Component i	$\bar{t}_i$ (min)	K_i	k_P (s-1)
A - Sucrose	10.76	0.19	0.20
B - Fructose	13.91	0.44	0.13
C - Betaine	16.51	0.65	0.11

SIMULATION RESULTS

The pseudo- SMB model for the JO process was tested using the ternary system shown in Table 2. The characteristics of the physical system (Japan Organo Catalog, 1998) are shown in Table 3.

Table 3. Characteristics of the SMB columns

Column Number (total)	12
Column length (cm)	120
Column diameter (cm)	10.84
Column volume (l)	11.1
Number of columns per section	3
Bed Porosity, ε	0.4

The assumed feed flow-rate and duration of step 2 are: $Q_F = 350$ ml/min and $t_{S2} = 66$ min [3]. The duration of step 1 is $t_{S1} = 17.8$ min. The parameters of the model and all variables used are shown in Figure 3.

Figure 4 shows the concentration profiles in the liquid phase at the end of (a) step 1 and (b) step 2, obtained after cyclic steady state, CSS, was achieved. The feed containing the three solutes at species concentration, $C_0 = 100$ g/l is injected in step 1 of the cycle during

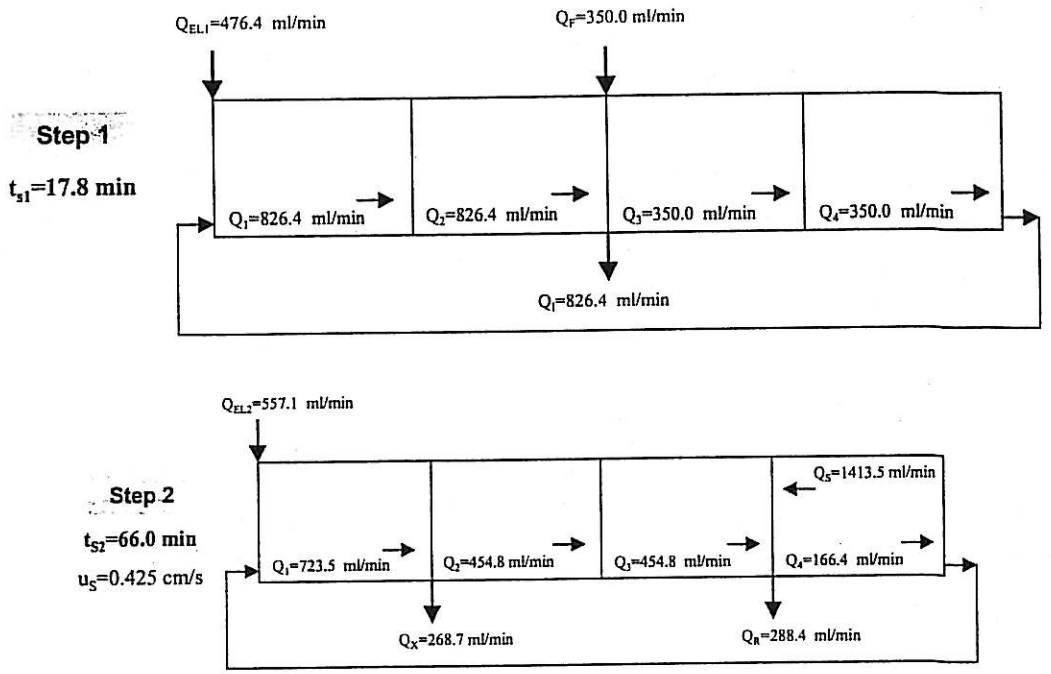

Figure 3. Flowrates and step duration used for the simulation of the pseudo-SMB: (a) step 1 and (b) step 2.

$0 < t \leq t_{S1}$ with flow-rate Q_F, at the inlet of section 3. At the same time, there is an intermediate stream, Q_I, rich in fructose, coming out from the end of section 2. During the second step of the cycle for $t_{S1} < t \leq t_{S2}$, the feed flow and the flow of intermediate species are stopped: there are two outlet streams: one at the end of section 1 - Extract, Q_X, and the other at the end of section 2 - Raffinate, Q_R. At the same time, it is assumed that the solid starts moving in the opposite direction of the fluid, i.e., from right to left. The less retained component, sucrose, moves in the direction of the fluid but both fructose and betaine move in the opposite direction, i.e., in the direction of the solid phase.

Figure 5 shows the movement of each component in the liquid phase during its recovery, namely, it shows:

(a) the evolution of the internal liquid sucrose profile during step 2 (from the end of step 1 to the end of step 2); during this time, t_{S2}, sucrose is recovered at the bottom of section 3, in the intermediate stream.

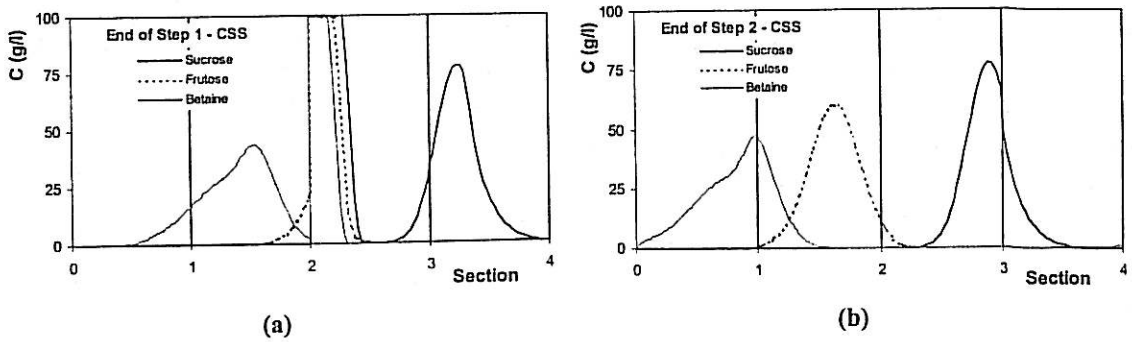

Figure 4 Profiles of Sucrose, Fructose and Betaine, at the end of: (a) Step 1 and (b) Step 2.

(b) the evolution of the internal liquid fructose profile during step 1 (from the end of step 2 to the end of step 1); during this time, t_{S1}, fructose is recovered at the bottom of section 2, in the intermediate stream.

(c) the evolution of the internal liquid betaine profile during step 2 (from the end of step 1 to the end of step 2); during this time, t_{S2}, betaine is recovered at the bottom of section 1, in the extract stream.

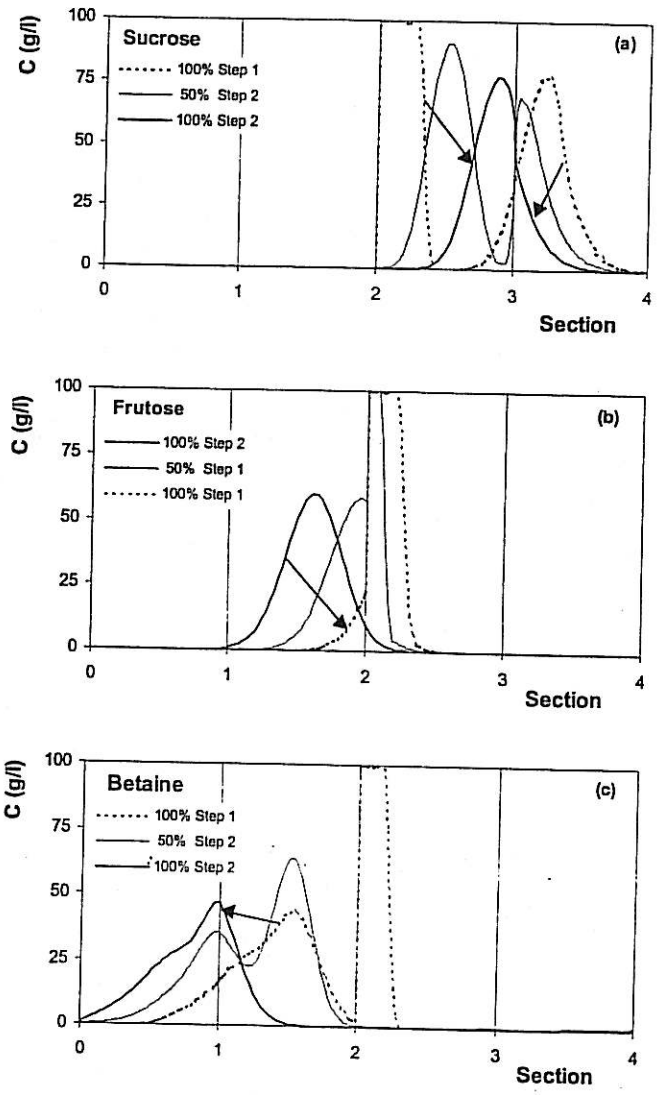

Figure 5. Evolution of profiles during the recovery of (a) Sucrose, in step 2, (b) Fructose in Step 1 and (c) Betaine in step 2.

CONCLUSIONS

A model of the JO process for the separation of a ternary mixture by Pseudo-SMB chromatography is described. It considers: (a) step 1 of the cycle as a series of preparative chromatographic columns, where an intermediate component is recovered and (b) step 2 as a true moving bed without feed, where both more and less retained components are obtained. Operating conditions for both steps of the cycle were suggested for the determination of all internal flow-rates. Simulation results showed that it is possible to obtain the three separated pure components in the output streams.

BIBLIOGRAPHY

[1] Nicoud, R.-M., LC-GC Intl. 5, 43-47 (1992).
[2] Pais, L., PhD Thesis, LSRE-FEUP, Porto, Portugal (1998).
[3] http://www.organo.co.jp/technology/hisepa/en_hisepa/
[4] Ando, M.; Tanimura, M.; Tamura, M.; U.S. Patent No. 4,970,002 (1990).
[5] Masuda, T.; Sonobe, T.; Matsuda, F.; Horie, M., U.S. Patent No. 5,198,120 (1993).
[6] Sayama, K.; Kamada, T.; Oikawa, S.; Masuda, T.; *Zucherind.* **117**, 893-898 (1992).
[7] Pais, L.S.; Loureiro, J.M.; Rodrigues, A.E., *AIChE J.*, **44**, 561-569 (1998).
[8] Madsen, N. K., Sincovec, R. F., *ACM Trans. Math.*, **5**, 328-351 (1979).
[9] Hindmarsh, A.C., Rep. UCID-30130, Lawrence Livermore Lab., Livermore, Calif. (1976).
[10] Mata, V. G., Rodrigues, A. E., submitted to J. Chromatography (2001).
[11] Glueckauf, E., Trans. Faraday Soc., 51, 1540 (1955).
[12] Reid, R.C., Prausnitz, J. M., Poling, B. E., "The properties of gases and liquids", McGraw-Hill1, N.Y. (1987).