Design of Chromatographic Multicomponent Separation by a Pseudo-Simulated Moving Bed

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DOI 10.1002/aic.11003
Published online September 26, 2006 in Wiley InterScience (www.interscience.wiley.com).

The continuous chromatographic separation of multicomponent mixtures using a pseudo-simulated moving bed illustrated by Japan Organo (JO) technology has been studied. The behavior and performance of a system operating with this technology have been described by an algorithm that simulates its operating cycle: chromatographic fixed-bed process in step 1 and simulated moving bed process in step 2. To design a four-section JO system some concepts were presented and two strategies were developed to set the operating conditions of the system in the case of mixtures with linear adsorption isotherms for each species. The influence of operating parameters in separating the mixtures was addressed and improvements in both productivity and eluent consumption have been achieved. The four-section JO system has been applied to a set of ternary mixtures with different degrees of separation difficulty to analyze its performance. A novel extension of the JO system with five sections has been designed for quaternary separations and high-purity species can be collected for a case of "moderately difficult" linear separation. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3794–3812, 2006
Keywords: JO technology, multicomponent separation, simulated moving bed, continuous separation process, design strategies

Introduction

Several important chromatographic separation processes have been developed using the *simulated moving bed* (SMB) technology, providing the high purification potential of these continuous countercurrent methods. Since it was introduced by Broughton in the 1960s,[1] this technology has been used in the petrochemical and sugar industries,[2-4] and later in the pharmaceutical and fine chemistry industries and bioseparations.[5-7]

Many publications on SMB technology have focused on operations with classical four-section SMB. In spite of the advantages associated with such configuration (high-purity products, low eluent consumption, continuous feed and production), it is limited to two outlet streams (extract and raffinate), allowing only the separation of binary mixtures. When the feed is a multicomponent mixture, one of the outlet streams will contain several components and the other will contain only one component (the weakest adsorbed components in raffinate or the strongest adsorbed component in extract).

In recent years various alternatives have been suggested to perform multicomponent separation using SMB technology and several ideas were considered such as SMB with five sections,[7-10] cascade of two SMBs in series, which, in this case, can be either separated[11] or combined in a single device (SMB with eight sections[12] and SMB with nine sections[13] are examples), cascade of SMB systems for ternary[14,15] and quaternary[15,16] separations, and pseudo-SMB.[17] Some of these alternative SMB configurations have been tested experimentally.[8,10,13] It was shown by application of the equilibrium theory that neither a five-section SMB nor an eight-section SMB can separate three compounds into three pure fractions.[9,18,19] The pseudo-SMB system represents the New JO Chromatographic Separation Device, which has been reported as adequate in the separation of mixtures such as fractionation of beet molasses

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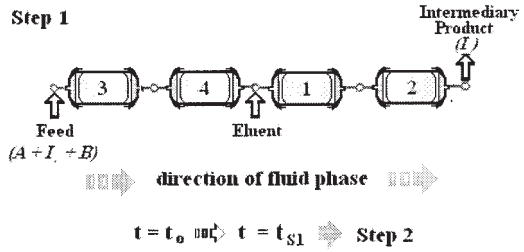

Figure 1. Scheme of the JO system operating in step 1.

into raffinose, sucrose, glucose, and betaine[20]; high level purification of diethylnaphthalene isomers; and separation of high-purity maltitol from a mixture of maltitol, monosaccharides, and polysaccharides.[21] The New JO Chromatographic Separation system uses a patented chromatographic separation technology developed by the Japan Organo Co.[21,22] Very little has been published concerning JO technology and, in this article, we will address the design of JO systems.

The JO separation system works using the concept of the SMB technology. Its configuration allows not only the recovery of the less retained component and more adsorbable species, but also the recovery of an intermediate component of intermediate affinity with adsorbent phase, which is of interest for multicomponent separations. The JO system is a cyclic process consisting of two steps: (1) in *step 1*, which corresponds to the operation of a sequence of chromatographic columns (fixed beds), the intermediate species is collected; and (2) in *step 2*, the concept of SMB is used but with no feed. The shifting of the steps changes the operation method of the JO system during a cycle. After some operation cycles, the system reaches a cyclic steady state in which the unit behavior is the same in periodic intervals. To better understand how the JO technology works let us consider a set of preparative chromatography columns connected in series as the SMB in open loop. The times t_{S1} and t_{S2} are the operation times of step 1 and step 2 in a JO system, respectively. In each step, the configuration is as follows:

- *Step 1*. The feed is introduced in the unit. In the system shown in Figure 1, the liquid phase flows through a number of fixed-bed columns packed with the solid adsorbent. Species *A* is the less retained component and species *B* is the more retained component. Species *I* has intermediate adsorptive affinity. The difference of adsorptive affinity allows the chromatographic separation as in a simple chromatographic column. At a particular point of the system, a stream of eluent is also introduced to elute the intermediate species *I* in the only outlet stream in step 1.
- *Step 2*. Now, the system operates in closed-loop circuit and the solid movement is simulated by the change in the positions of ports in the inlet (eluent stream) and outlet streams (extract and raffinate). There is no feed stream in step 2. In this way, the JO process could seem as an operation in partial feed where the feed stream (and other external streams) is added and withdrawn at a constant rate.[23,24] In the system shown in Figure 2, the countercurrent operation, leading to the high mass-transfer driving forces, is accomplished by the simultaneous shift of the inlet and outlet streams, at fixed time intervals, called switching time (t^*), in the liquid-phase flow direction. The system operates in step 2 exactly as an SMB without feed.

In this work, the design of JO process units is addressed. A decision-helping tool has been developed to aid in the analysis of equipment sizing and finding adequate operating conditions of units based on the JO technology. The choice of working flow rates for step 2 of the JO process for ternary separation was based on two different strategies depending on the adsorptive properties of the various species in the mixture. The performance parameters of the system (purity, productivity, eluent consumption) for the separation of ternary mixtures with different degrees of separation difficulty are discussed. A novel configuration—a JO system with five sections—is presented and is applied to the separation of a quaternary mixture.

Mathematical Modeling

Description of the four-section JO system

The JO system is illustrated in Figure 3. Because of the fact that all inlet and outlet flows, whatever the current operation step is, divide the system into four sections, we will consider this JO system as a "four-section JO"; in fact, during step 1 there are only two sections with two different flow rates and during step 2 there are three sections with three different flow rates. Each section can have one or more fixed-bed columns. In this configuration, during step 1, section 3 is fed with a ternary mixture (species *A*, *I*, and *B*). The flow-rate condition should be such that no species *I* is transported into section 4. Sections 3, 4, 1, and 2 are connected in series in this sequence as a chromatographic column, with the outlet port located at the end of section 2. This corresponds to the intermediate outlet stream where the species with intermediate adsorptive affinity (*I*) is collected. The eluent port is located between section 4 and section 1; the eluent stream will elute species *B* and *I* from sections 1 and 2.

When the time of step 1 (t_{S1}) is reached, the unit is already loaded with the feed mixture and intermediate species is already collected; thus, step 2 starts. In step 2, the solid phase moves countercurrent with the liquid phase using SMB technology where the solid movement is simulated by change of the inlet/outlet ports at fixed time intervals, in the direction of the liquid phase. The fixed time interval to shift the inlet and outlet positions is the switching time (t^*) and it is linked to the solid

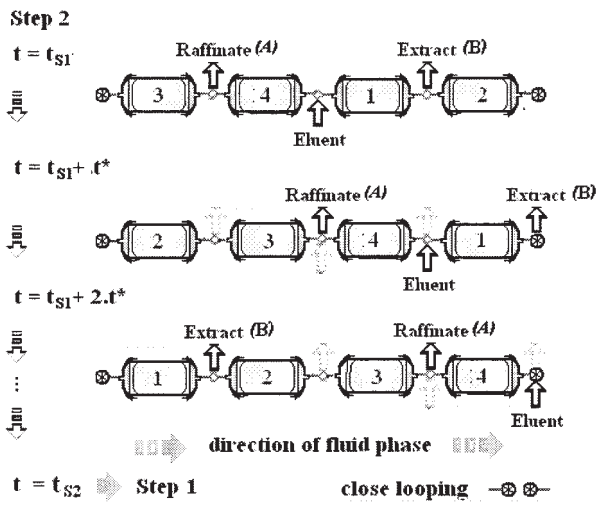

Figure 2. Scheme of the JO system operating in step 2.

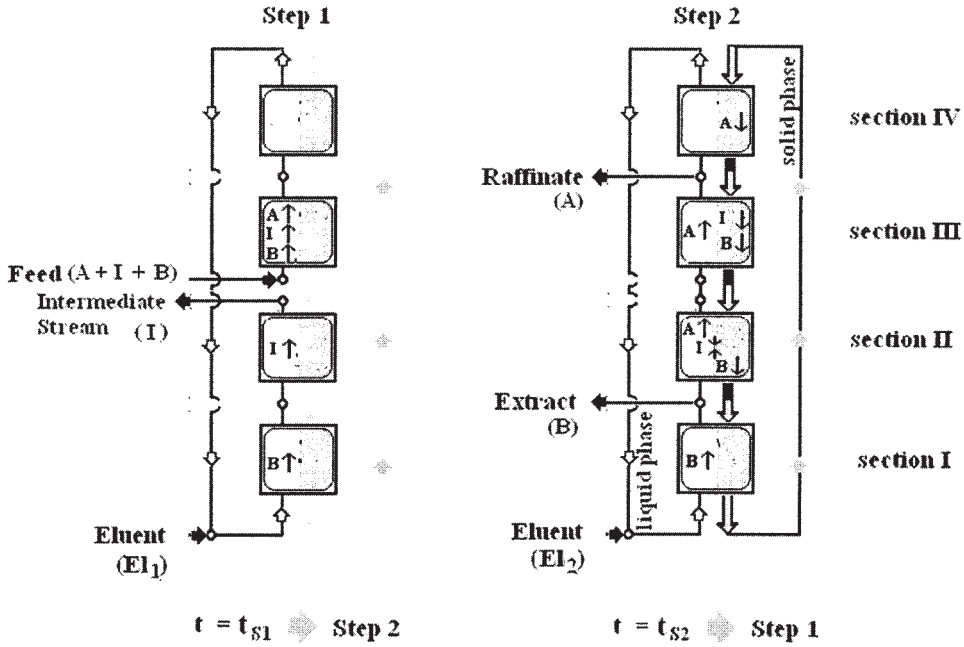

Figure 3. Scheme of operating step for the "four-section JO" in which the SMB operating in step 2 is replaced by an equivalent TMB operation.

flow rate of an equivalent true moving bed [$Q_S = (1 - \varepsilon)V_C/t^*$]. Figure 3 shows such an operation in a *true moving bed* (TMB) equivalent to the real SMB unit. There is no feed stream in step 2. Between sections 3 and 4 and sections 1 and 2 is the raffinate stream and the extract stream, respectively. To obtain adequate separation of the species, there is a need to properly choose the flow rates of the solid (or switching time) and of the liquid in the unit sections. Species *A* must be transported toward the raffinate, whereas species *B* must be adsorbed in sections 2 and 3 and transported by the solid phase until it is withdrawn from the extract. At the end of step 2, the intermediate component must be positioned mainly in section 2 to be recovered during the next step 1. Removal of the more retained species *B* from the solid phase must occur in section 1 to enable the regeneration of the adsorbent. In addition, the less retained species *A* should not break through to section 1 to ensure the recycling of pure eluent. Regarding the start-up of system, the JO system is fed during step 1 in cycle 1 (and, of course, there is no intermediate species in intermediate outlet in this first cycle). In step 2 of cycle 1 the JO system works as the SMB technology. At the end of the cycle 1, the system starts step 1 of cycle 2 where the intermediate species is collected.

Each section of the system has a specific task to achieve high-performance separation; a large number of operating variables should be designed and optimized. Because of its complex operation and configuration, modeling and simulation serve as tools that help in a deeper analysis of the system behavior and performance.

Mathematical model

The mathematical model used to describe the behavior of a JO process is described in Table 1. For the liquid phase, plug flow with axial dispersion is assumed, whereas for the solid phase (adsorbent considered as homogeneous particle) the linear driving force (LDF) approximation is applied. Because we are dealing with systems with linear adsorption equilibrium isotherms, this lumped mass-transfer model gives results equivalent to those of more detailed porous rate models.[25,26] In the computational algorithm, two situations corresponding to step 1 and 2—fixed-bed chromatography and SMB, respectively—were considered. When the system operates as an SMB unit during step 2, the model is based on the description of a true moving-bed unit, which must be equivalent to the actual simulated moving-bed unit. Regarding the boundary conditions, they depend on the location of column *k* in the system and the mass balances in the nodes must be considered.

Cyclic steady state

The steady state of a JO system is a cyclic steady state (CSS) because there is a time dependency of the boundary conditions for each column in the system. To know the operation of the system, its behavior should be analyzed based on concentration profiles in step 1 (when unit operates as a fixed bed) and in step 2 (when unit operates as an SMB). It should be noted that step 2 could be addressed in two ways: as a real SMB (with changes of ports at specified time intervals), that is, the SMB approach; or using an equivalent TMB model, that is, the TMB approach. In the first case, the description of system behavior description can be accomplished by the three different forms: the exact evolution of the concentration profiles, the average concentration profile, and the instantaneous concentration evaluated in some specific time of the switch time interval.

Figure 4 is a schematic representation of the concentration profile of a component in raffinate, after cyclic steady state is reached. Figure 4a shows (1) the CSS behavior, characteristic of an SMB operation, described for the three ways of concentration profiles and (2) how the TBM approach predicts the CSS for an SMB unit: a real steady state is reached (no

Table 1. Mathematical Modeling Used in This Work to Predict the Behavior of a JO Process*

Step 1	Step 2
Mass balance in the liquid phase for species i in column k	
$\frac{\partial C_{ik}}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon}\left[\frac{\partial \bar{q}_{ik}}{\partial t} - u_S \frac{\partial \bar{q}_{ik}}{\partial z}\right] + v_k \frac{\partial C_{ik}}{\partial z} - D_k \frac{\partial^2 C_{ik}}{\partial z^2} = 0 \quad (u_S = 0 \text{ for step 1})$	
Mass balance for solid phase	
$\frac{\partial \bar{q}_{ik}}{\partial t} = u_S \frac{\partial \bar{q}_{ik}}{\partial z} + k_i(q_i^* - \bar{q}_{ik}) \quad (u_S = 0 \text{ for step 1})$	
Initial conditions	
Cycle 1: $t = 0 \quad C_{ik} = \bar{q}_{ik} = 0$	Cycle 1: $t = t_{S1}$ $\begin{cases} C_{ik} = C_{ik}(\text{cycle 1, end of step 1}) \\ \bar{q}_{ik} = \bar{q}_{ik}(\text{cycle 1, end of step 1}) \end{cases}$
Cycle θ: $t = (\theta - 1)(t_{S1} + t_{S2})$	Cycle θ: $t = \theta t_{S1}$ $\begin{cases} C_{ik} = C_{ik}(\text{cycle } \theta, \text{ end of step 1}) \\ \bar{q}_{ik} = \bar{q}_{ik}(\text{cycle } \theta, \text{ end of step 1}) \end{cases}$ $(\theta = 2,3,4, \ldots)$
$\begin{cases} C_{ik} = C_{ik}(\text{cycle } \theta - 1, \text{ end of step 2}) \\ \bar{q}_{ik} = \bar{q}_{ik}(\text{cycle } \theta - 1, \text{ end of step 2}) \end{cases}$ $(\theta = 2,3,4, \ldots)$	
Boundary conditions for column k	
Liquid phase: $z = 0$ $(t > 0)$:	$v_k C_{ik,o} = v_k C_{ik}\big\vert_{z=0^+} - D_k \frac{\partial C_{ik}}{\partial z}\Big\vert_{z=0^+}$
$z = L_C$ $(t > 0)$	$\frac{\partial C_{ik}}{\partial z}\Big\vert_{z=L_C} = 0$
—	Solid phase: $z = 0$ $(t > 0)$: $\frac{\partial \bar{q}_{ik}}{\partial z}\Big\vert_{z=0} = 0$
Mass balances in the nodes	
• for columns within system:	• for columns within one section and for the extract and raffinate nodes: $C_{ik+1,o} = C_{ik}$
	• for the eluent node: $C_{ik+1,o} = \frac{v_3}{v_1} C_{ik,L}$
• for the feed node: $C_{ik,o} = C_{if}$	—

*Step 1: Fixed-bed chromatography unit; Step 2: SMB unit (TMB equivalent model).

concentration variation with the time). For a larger number of columns per section in SMB, the agreement is better between the average concentration profile (and the instantaneous concentration in the half of the switching time) and the concentration profile predicted by the TMB approach.[27,28] Additionally, the CSS of an SMB operation can be visualized only if the SMB approach is used.

In this article, the process in step 2 is described as if a true flow of the stationary phase takes place in the unit: it demands lower computational time. Because the JO system works as an intermittent model—with successive change of the operational condition of the step 1 to step 2 for each new cycle—the concentration profiles of the species in each one of the cycles will always have a transient behavior. Therefore, when cyclic steady state is reached in the JO process, the concentration profiles, varying with time during a cycle of the process, will be repeated from cycle to cycle. The CSS of a JO system operation can be visualized even if the TMB approach is used in step 2 (see Figure 4b). The dynamics of the JO process will be explained later in detail under the heading Analysis of Results.

The nature of the CSS of the SMB and JO systems has different sources: whereas in the first case the CSS results from the changes in inlet and outlet ports after each switching time, in the second case the CSS comes from the switch of the steps in each cycle.

If the operation of step 2 is simulated using the SMB approach, the behavior of the exact evolution of the concentration profile of the species shown in Figure 4a will be seen in the evolution of the concentration of this species during the time t_{S2} in a cycle of the JO process.

Method of numerical solution

With respect to the numerical technique, conservation equations and boundary conditions were discretized by the method of finite volumes, applying the interpolation functions weight upstream differencing scheme.[29] They were implemented in a computational algorithm in Fortran language. The formulation is defined as totally implicit, leading to a system of algebraic equations solved by the modified strongly implicit method (MSI).[30] Convergence of the solution is evaluated by increasing the number of control volumes and decreasing the integration time until no change is observed between different runs.

The cyclic steady state of the JO process is reached when the sum of relative error was $<1\%$:

- Difference between average concentration of species in the outlet stream in current and previous iterations normalized by the current value of the variable

$$e_c = \sum_{m=Ra,Int,Ex} \sum_{i=A,I,B} \frac{|\bar{C}_{i,m}^c - \bar{C}_{i,m}^{c-1}|}{\bar{C}_{i,m}^c} \tag{1}$$

- Global mass balance for the species leaving the unit

$$e_b = \frac{\sum_{m=Ra,Int,Ex} \sum_{i=A,I,B} \bar{C}_{i,m}(Q_m t_{S\Phi})}{\sum_{i=A,I,B} C_{if}(Q_f t_{S1})} \quad (\Phi = 1 \text{ for } m = Int; \Phi = 2 \text{ for } m = Ra, Ex) \tag{2}$$

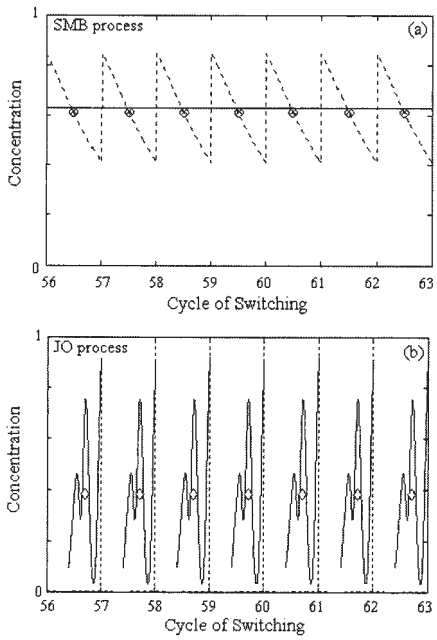

Figure 4. Evolution of concentration profiles of a more retained component in the extract stream.

(a) SMB at cyclic steady state condition: (- - -) SMB approach, (⊛) average concentration profile in the switch interval, (⊖) instantaneous concentration profile in the half of the switch interval, (—) TMB approach. (b) JO system in cyclic steady state condition: (—) TMB approach, (◇) average concentration profile in step 2.

where Q_m is the flow rate in external stream m.

Design of Four-Section JO: Ternary Separation

To achieve a good separation performance in the JO system, some criteria based on the propagation of species need to be satisfied. At the end of step 2, species A and B must have been collected in their respective enriched streams and the intermediate species propagated until a position in which, during step 1, it can be recovered without considerable contamination. Step 1 can be designed as a loading step because the feed enters the system only during step 1. If the feed conditions are known—flow rate and species concentration in the feed—for a JO system, the operation variables such as step times, internal flow rates in each section, and switching time (step 2) need to be determined to obey the required performance criteria. In the following, a sequence of definitions is presented aiming at the attainment of the base operating conditions providing a high performance for the four-section JO.

The velocities of propagating concentration (w) in steps 1 and 2 of a JO system can be given as

$$w_{i,j,S\Phi} = \frac{x_{i,j,S\Phi}}{t_{S\Phi}} = \frac{v_{j,S\Phi}\left[1 - (\Phi - 1)\upsilon\dfrac{K_i}{\gamma_{j,S2}}\right]}{(1 + \upsilon K_i)} = \frac{Q_{j,S\Phi} - (\Phi - 1)Q_S K_i}{\varepsilon A_c(1 + \upsilon K_i)} \quad (3)$$

where $\Phi = 1$ for step 1 and $\Phi = 2$ for step 2. The parameter $\gamma_{j,S2}$ is defined as the liquid to solid velocity ratio ($=v_{j,S2}/u_S$) and υ is the solid to liquid volume ratio. Each species i travels a distance $x_{i,j,S1}$ in section j during step 1 (or 2, for case of $x_{i,j,S2}$). The liquid flow rate in section j during step Φ is $Q_{j\mathrm{S}\Phi}$ and the solid flow rate is Q_S. The cross-sectional area of a JO column is A_C and the linear adsorption constant to the species i is K_i.

In step 1, the propagation of the species occurs only in the direction of the liquid phase while, in step 2, the migration of species can occur in both directions:

- A given species will propagate in direction of the liquid flow if

$$w_{i,j,S2} > 0 \Leftrightarrow \gamma_{j,S2} > \upsilon K_i \quad (4)$$

- A given species will propagate in direction of the solid flow if

$$w_{i,j,S2} < 0 \Leftrightarrow \gamma_{j,S2} < \upsilon K_i \quad (5)$$

Conditions for step 1

For a given feed flow rate and feed composition (C_{Af}, C_{If}, and C_{Bf}), the time of step 1 can be used to control the amount of species introduced into the unit as well as the breakthrough of components present in the feed. Following the literature,[17] the duration of step 1 is the time needed to feed the intermediate component only in the first column of section 3 after the feed port. In this work, this idea is extended for a time less than or equal to the time needed for the concentration front of the intermediate component to reach section 4 during step 1. The time t_{S1} can be calculated from the response to a pulse of feed in a fixed bed. In the separation of components characterized by linear adsorption isotherms, the retention time for each species is the first moment of the pulse response after p_{tS1} columns in section 3:

$$\bar{t}_i = p_{tS1}\tau[1 + \upsilon K_i] \quad (6)$$

where $\tau = \varepsilon V_C/Q_f$. The parameter p_{tS1} assumes values between zero and the number of columns in section 3 (n_{Se3}).

The intermediate species cannot be present in the first column of section 4 at the end of step 1 because it could later contaminate the raffinate. Let us keep the assumption of a previous work[17] that accepts an error $< 5\%$ in the time of step 1, given by the standard deviation σ. Thus, considering the variance of the response for species i, the time of step 1 is calculated as

$$t_{S1} = \bar{t}_i - 2\sigma = \bar{t}_i - 2\left[\frac{2\bar{t}_i^2}{\mathrm{Pe}} + \frac{2}{k_i}(\bar{t}_i - \tau)\right]^{1/2} \quad (7)$$

where i is the intermediate species I and Pe is the Peclet number ($=v_{k,S\Phi}L_C/D_k$). The parameter p_{tS1} in Eq. 7 close to zero means a low loading of the unit, whereas p_{tS1} close to the number of columns in section 3 means a maximum load of feed. The maximum value for p_{tS1} is $<n_{Se3}$ because there is

axial dispersion and mass-transfer resistances in separation processes.

In step 1, the flow rate in sections 1 and 2 controls the elution of the concentration peaks for the intermediate and the more adsorbable species. This flow rate is defined such that the intermediate species, which is located somewhere inside section 2, can be recovered without species *B* eluting from the port of the intermediate stream. This can be checked by the value of purity of the intermediate species.

An initial approximation for the flow rate in sections 1 and 2 can be obtained by assuming that the intermediate species in section 2 travels a distance equal to the number of columns in section 2 multiplied by the length of the column (L_C), that is,

$$Q_{1,S1} = \frac{\varepsilon A_c (n_{Se2})\, L_c}{t_{S1}} (1 + \upsilon K_I) \tag{8}$$

This value can be reduced by imposing a constraint on purity mentioned earlier. The situation where the intermediate species was fully recovered but the more retained species is far from the end of section 2 should be considered. In that case, the flow rate of eluent Q_{El1} (and, therefore, the flow rate in sections 1 and 2) can be reduced by saving eluent in step 1. As an example, if the concentration of species *I* in the intermediate port is, say, $<1\%$ of C_{If}, after the collection of species *I* has already been started during step 1, it means the eluent flow rate could be reduced.

Moreover, a global mass balance in the four-section JO in step 1 is

$$Q_{Int} = Q_{1,S1} = Q_{2,S1} \tag{9}$$

$$Q_{El1} = Q_{Int} - Q_f \tag{10}$$

After defining t_{S1} and the flow rates in the unit sections during step 1 the operating conditions are set.

Conditions for step 2

For step 2, assuming that the geometry and number of sections are fixed, the design variables are: liquid flow rate in the various sections, solid flow rate (or switching time), and duration of step 2 (t_{S2}).

After the unit is charged with the feed ternary mixture in step 1, step 2 takes place to separate all three species in such a way that they can be collected individually without appreciable contamination at different ports and to allow the recovery of both the more and the less retained species. A separation in step 2 will be successful if the chromatographic peaks are located in the following way:

- The peak of species *A* is at the raffinate port, moving in the direction of the liquid flow.
- The peak of intermediate species is located in section 2, preferably near the end of section 2, moving in the direction of the solid flow.
- The peak of species *B* is at the extract port, moving in the direction of the solid flow.

The distance traveled by the species *i* in sections 2 and 3 ($x_{i,2/3,S2}$) is expressed as

$$x_{i,2/3,S2} = \frac{t_{S2}}{\varepsilon A_c (1 + \upsilon K_i)} (Q_{2/3,S2} - Q_S K_i) \quad (\text{with } i = A, I, \text{ and } B) \tag{11}$$

and must satisfy the following constraints:

$$x_{A,2/3,S2} = p_A L_C - x_{A,3,S1} \qquad \left(\text{with } \frac{x_{A,3,S1}}{L_C} \le p_A \le n_{Se3}\right) \tag{12}$$

$$x_{I,2/3,S2} = -(x_{I,3,S1} + p_I L_C) \qquad (\text{with } 0 < p_I < n_{Se2}) \tag{13}$$

$$x_{B,2/3,S2} = -(x_{B,3,S1} + p_B L_C) \qquad (\text{with } p_B = n_{Se2}) \tag{14}$$

The displacement of species *A* must be positive because it goes toward the raffinate with the liquid phase, contrary to what occurs to the other species, which move in the direction of the solid flow. The parameters p_i are used to define the position of the concentration peak of the species *i* inside the unit; n_{Se2} and n_{Se3} represent the number of columns in sections 2 and 3, respectively. In Eq. 13, we should look for a minimum eluent consumption to recover intermediate species at the end of section 2 in step 1 and therefore the peak of species *I* should be near the end of section 2. However, this choice can affect other performance criteria, such as purity in other external streams, which can eventually be more important than the eluent consumption.

To complete the set of constraints that must be verified to recover the less retained species in the raffinate and the more retained species in the extract during step 2, we need to address the rules for the regeneration sections (sections 1 and 4). In section 1, the more adsorbable species must move in direction of the liquid flow to regenerate the solid; in section 4, the less adsorbable species must move in direction of the solid phase to regenerate the eluent. The constraints considering both steps of the JO process are then

$$Q_{1,S2} + \frac{t_{S1}}{t_{S2}} Q_{Int} > Q_S K_B \tag{15}$$

$$Q_{4,S2} + \frac{t_{S1}}{t_{S2}} Q_f < Q_S K_A \tag{16}$$

The constraints given by Eqs. 12–16 constitute the basis for the calculation of flow rates in all sections of the four-section JO operating in step 2. One should notice that because there is no feed in step 2 when the JO system works as an SMB unit, the liquid flow rates in sections 2 and 3 are the same (notation 2/3 has been used in such case), differing from situation occurring in the real SMB separator. In fact, in step 2, these sections 2 and 3 outline a single section with an important role: the positioning of concentration waves for the recovery of the species. The flow rates $Q_{3,S2}$ and Q_S are obtained from Eqs. 11–14.

Strategies for Definition of $Q_{3,S2}$ and Q_S. Two strategies will be used to define the liquid flow rate in section 3 and solid flow rate. In the first strategy—strategy 1—these design parameters are obtained with Eqs. 11 ($i = I$ and *B*), 13, and 14.

In this way the conditions imposed by the migration rules for both species—*I* and *B*—are obeyed. The flow rates are

$$Q_S = \frac{\varepsilon A_c}{t_{S2}}\left(\frac{1}{K_B - K_I}\right)[x_{I,2/3,S2}(1 + \upsilon K_I) - x_{B,2/3,S2}(1 + \upsilon K_B)] \tag{17}$$

$$Q_{3,S2} = \frac{\varepsilon A_c}{t_{S2}}\left(\frac{K_B}{K_B - K_I}\right)\left[x_{I,2/3,S2}(1 + \upsilon K_I) - x_{B,2/3,S2}\frac{K_I}{K_B}(1 + \upsilon K_B)\right] \tag{18}$$

In strategy 1, Eqs. 11 ($i = A$) and 12 are used to obtain an inequality that is the condition for applying this strategy. Because the propagation of *A* (weakly adsorbed species) must be in the direction of the liquid phase, the lowest value to the variable $x_{A,2/3,S2}$ is zero. In fact, even if species *A* is kept in the same position during step 2, it can move in the right direction during step 1. Therefore, Eq. 11 ($i = A$) is used to establish the condition of maximum value for the parameter K_A (slope of the adsorption isotherm for *A*) so that species *A* goes to the raffinate port with the defined flow rates Q_S and $Q_{3,S2}$ (Eqs. 17 and 18).

$$K_A^{\max} = \frac{Q_{3,S2}}{Q_S} \Rightarrow K_A \le K_A^{\max} \tag{19}$$

If the adsorption isotherm constant K_A does not satisfy the inequality of Eq. 19, the second strategy to obtain Q_S and $Q_{3,S2}$ can be used. Now, instead of calculating those flow rates by Eqs. 11 ($i = I$ and *B*), 13, and 14, we use the system formed by Eqs. 11 ($i = A$ and *I*), 12, and 13, which leads to values enabling the separation of species *A* and *I* in section 3. In strategy 2, the flow rates of solid Q_S and liquid in section 3 (step 2) $Q_{3,S2}$ are then calculated by

$$Q_S = \frac{\varepsilon A_c}{t_{S2}}\left(\frac{1}{K_I - K_A}\right)[x_{A,2/3,S2}(1 + \upsilon K_A) - x_{I,2/3,S2}(1 + \upsilon K_I)] \tag{20}$$

$$Q_{3,S2} = \frac{\varepsilon A_c}{t_{S2}}\left(\frac{K_I}{K_I - K_A}\right)\left[x_{A,2/3,S2}(1 + \upsilon K_A) - x_{I,2/3,S2}\frac{K_A}{K_I}(1 + \upsilon K_I)\right] \tag{21}$$

Again, Eqs. 11 ($i = B$) and 14 are used to establish a condition of minimum value for the parameter K_B such that species *B* can be taken in the direction of the solid flow to the extract port, according to the migration rules. The limiting condition from Eqs. 11 ($i = B$) and 14 for species *B* obtained from strategy 2 is given by

$$K_B^{\min} = \frac{Q_{3,S2} - \varepsilon A_c w_{B,2/3,S2}}{Q_S + (1 - \varepsilon)A_c w_{B,2/3,S2}} \tag{22}$$

where Q_S and $Q_{3,S2}$ are the parameters calculated by Eqs. 20 and 21 and $w_{B,2/3,S2}$ is the propagation velocity that the concentration wave of the species *B* should travel to be at the extract port at the end of step 2:

$$w_{B,2/3,S2} = \frac{x_{B,3,S1} + n_{Se2}L_C}{t_{S2}} \tag{23}$$

The value of $w_{B,2/3,S2}$ depends on the distance traveled of *B* in step 1 and thus it would be necessary to know K_B to determine $K_B^{\min}$. To avoid this problem and to establish a condition that would be independent of the value of K_B, let us make an assumption to restrict the application of strategy 2. The most drastic condition of migration for species *B* for application of strategy 2 would be that of species *B* having the same adsorption affinity as that of the intermediate species. In this case, species *B* would be located as far as possible from the extract port at the beginning of step 2. For this reason, let us rewrite Eq. 22 using propagation velocity of species *I* instead of propagation velocity of species *B* and the new limiting condition to use strategy 2 will be conservative:

$$K_B^{\min} = \frac{Q_{3,S2} - \varepsilon A_c w_{I,2/3,S2}}{Q_S + (1 - \varepsilon)A_c w_{I,2/3,S2}} \Rightarrow K_B \ge K_B^{\min} \tag{24}$$

By observing the values obtained from Eqs. 17 and 18 and 20 and 21, one can see that both the flow rate in section 3 and the solid flow rate will always be higher when strategy 2 is used. This also means that higher flow rates in the other sections have to be used and more eluent needed. Thus, strategy 1 must be preferred for determination of the mentioned operating conditions.

The possibility in using one or another strategy for the calculation of the flow rates $Q_{3,S1}$ and Q_S in a four-section JO is managed by the adsorption constants of the components of the ternary mixture to be separate:

- *Application of strategy 1*: The linear adsorption constant of the less retained species (K_A) must be lower than $K_A^{\max}$ defined from strategy 1.
- *Application of strategy 2*: The linear adsorption constant of the more retained species (K_B) must be higher than $K_B^{\min}$ defined from strategy 2.

Definition of Other Flow Rates and t_{S2}. In all cases previously reported to calculate the flow rate in section 2 (and section 3) and the solid flow rate, we notice that the flow rates depend on the value of t_{S2} and their values are higher when t_{S2} is lower. The duration of step 2 is linked to the condition of pressure drop in fixed-bed columns of the JO system.

The highest flow rate in step 2 is located in section 1 where the adsorbent is regenerated. Therefore, given the restriction of Eq. 15, the flow rate in section 1 can be determined by

$$Q_{1,S2} = \beta_1 Q_S K_B - \frac{t_{S1}}{t_{S2}}Q_{Int} \qquad (\text{with } \beta_1 > 1) \tag{25}$$

where β_1 is a parameter > 1 that guarantees the validity of the inequation of Eq. 15. Thus, the parameter β_1 represents a "safety margin."[31,32] Some chosen value of t_{S2} is used to calculate the solid flow rate and, then, both t_{S2} and Q_S are taken

Table 2. Performance Parameters for Ternary Separation in the JO System

Purity	Recovery	Productivity (g L^{-1} h^{-1})	Eluent Consumption (L/g)
$Pu_{i,m} = \dfrac{\bar{C}_{i,m}}{\sum_{s=A,I,B} \bar{C}_{s,m}}$	$Re_{i,m} = \dfrac{Q_m \bar{C}_{i,m}}{Q_f \bar{C}_{i,f}} \dfrac{t_{S\Phi}}{t_{S1}}$	$Pr_{i,m} = \dfrac{Q_m \bar{C}_{i,m}}{V_S} \dfrac{t_{S\Phi}}{t_{S1} + t_{S2}}$	$EC_{i,m} = \dfrac{Q_{El1} t_{S1} + Q_{El2} t_{S2}}{Q_m \bar{C}_{i,m} t_{S\Phi}}$

i, $m = I$, $Int(\Phi = 1)$; A, $Ra(\Phi = 2)$; B, $Ex(\Phi = 2)$

to evaluate the flow rate in section 1 by Eq. 25. The velocity in section 1 can not exceed the allowed maximum velocity defined by the maximum pressure drop possible in the fixed-bed columns. The last one can be verified by the Kozeny–Kárman equation:

$$\frac{\Delta P_{k,S\Phi}}{L_C} = 150 \frac{(1-\varepsilon)^2}{\varepsilon^2 d_p^2} \mu v_{k,S\Phi} \tag{26}$$

The Kozeny–Kárman equation is adequate for laminar flow in chromatographic columns, which relates the pressure drop ($\Delta P_{k,S\Phi}$) with the velocity in column k during step Φ ($v_{k,S\Phi}$), length of column (L_C), particle diameter in the stationary phase (d_p), and eluent viscosity (μ). Alternatively, one could calculate the highest allowed velocity in section 1 according to the limiting pressure drop inside the adsorption columns. This velocity would be used to define $Q_{1,S2}$. Equation 17 (or Eq.20) would be introduced in Eq. 25 and an initial value for the t_{S2} would be achieved. Because the duration of step 2 (t_{S2}) influences the value of the flow rates of the inlet and outlet streams in step 2, an analysis is necessary on this operation condition to evaluate the range of values that requirements of optimization are satisfied, although the highest productivity is obtained when the system operates with the maximum pressure drop allowed inside the columns.

Finally, the constraint in Eq. 16 provides the liquid flow rate in section 4 for step 2 of the JO process:

$$Q_{4,S2} = \beta_4 Q_S K_A - \frac{t_{S1}}{t_{S2}} Q_f \qquad (\text{with } \beta_4 < 1) \tag{27}$$

where the parameter β_4 must be <1 to guarantee inequality of Eq. 16. The flow rates of external streams are easily calculated from mass balance at the unit nodes, expressed by the following equations:

$$Q_{Ra} = Q_{3,S2} - Q_{4,S2} \tag{28}$$

$$Q_{Ex} = Q_{1,S2} - Q_{2,S2} \tag{29}$$

$$Q_{El2} = Q_{1,S2} - Q_{4,S2} \tag{30}$$

It is worth noting that such design equations are derived for the case of linear adsorption equilibrium. The design based on nonlinear adsorption becomes more complicated. The JO system performance for the separation of the ternary mixture—*A* (less adsorbed species), *I* (intermediate affinity), and *B* (more retained species)—is evaluated according to the performance parameters described in Table 2.

Analysis of Results

Ternary separation: four-section JO process

Operating conditions must be chosen to make high recovery of species with high purity and low eluent consumption, ensuring high productivity of the JO process. The aim of the research is to develop a decision-helping tool to design a four-section JO system meeting the optimization criteria required. We start with the example of ternary separation reported elsewhere,[17] where adsorption data (equilibrium and kinetics) and geometry of columns in a four-section JO are listed in Table 3. The parameters correspond to linear equilibrium isotherms, low resistance to mass transfer, and a unit with 12 columns (three per section).

Figure 5 shows the evolution of species concentration profiles in each outlet stream as a function of the cycle number. The operating parameters are described in Table 3. The liquid flow rate in section 2 (and section 3) and the solid flow rate during step 2 were calculated with strategy 1. In this separation process, species *A* has lower adsorption constant than the limiting condition for applying this strategy ($K_A^{\max}$). In Figure 5, one can see the cyclic steady state starting from the sixth or seventh cycle in the four-section JO system. It can also be seen that only during step 1 (t_{S1}) is the intermediate species collected (Figure 5b) and during step 2 (t_{S2}) species *A* and *B* are collected

Table 3. Operational Conditions Used in Separation of the Ternary Mixture in the Four-Section JO System

Step 1		Step 2		Properties of the Columns	
t_{S1}	36.90 min	t_{S2}	66.00 min	L_C	1.2 m
Q_f	350.00 cm^3/min	Q_{Ra}	221.73 cm^3/min	D_C	0.1084 m
Q_{El1}	30.57 cm^3/min	Q_{Ex}	304.60 cm^3/min	ε; Pe	0.4; 2000
Q_{Int}	380.57 cm^3/min	Q_{El2}	526.33 cm^3/min	No subsections	12
				4-section JO Configuration	3–3–3–3
$Q_{1/2,S1}$	380.57 cm^3/min	$Q_{1,S2}$	537.32 cm^3/min	Components of the Mixture	
$Q_{3/4,S1}$	350.00 cm^3/min	$Q_{2/3,S2}$	232.72 cm^3/min	K_A	0.19
C_{Af}, C_{If}, C_{Bf}	100.0 g/L each	$Q_{4,S2}$	11.00 cm^3/min	K_B	0.39
		Q_S	1120.37 cm^3/min	K_C	0.65
		(γ_1; $\gamma_{2/3}$; γ_4)	(0.719; 0.312; 0.015)	k_A, k_I, k_B	0.5 s^{-1}

*Feed condition: $p_{tS1} = 2$. Propagation condition: $p_I = 1$; $p_B = 3$.

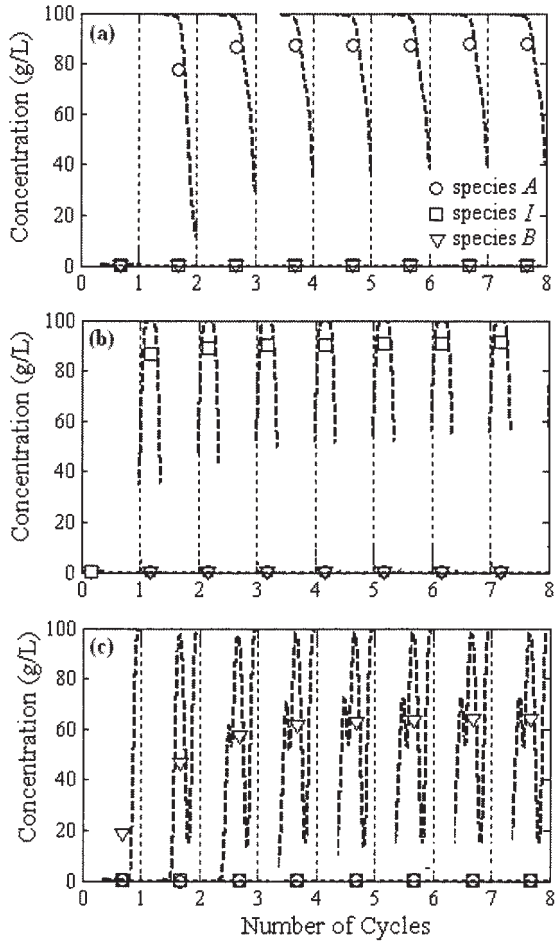

Figure 5. Concentration profiles of the species in four-section JO.

(a) Raffinate, (b) intermediate stream; (c) extract; (– – –) exact transient concentration profile; (○), (□), (▽) average concentration profiles of species *A*, *I*, and *B*, respectively, in the respective operation step.

(Figures 5a and 5c), with average concentration, in their respective enriched streams, given by

$$\bar{C}_i = \frac{\int_0^{t_{S\Phi}} C_i dt}{t_{S\Phi}} \qquad (\Phi = 1 \text{ for } i = I;\ \Phi = 2 \text{ for } i = A, B) \tag{31}$$

Figure 6 shows the concentration profiles for the three species in the sections of the JO system, at specific times of both operation intervals in cyclic steady state. One can observe that the unit is continuously fed with the mixture to be separated during the entirety of step 1. It is seen that the system works as a chromatography column in this first step of the cycle and all species travel in the direction of the liquid phase, making the withdrawal of the intermediate species at the end of section 2 possible. Of course, the final state of the concentration profiles of the species at the end of t_{S1} corresponds to the initial state of the concentration profiles at the beginning of t_{S2}. During step 2, the system operates as an SMB unit without feed stream and therefore the more (*B*) and less (*A*) retained species are directed to the respective enriched streams. Figure 6 shows that there is a propagation of intermediate species in the direction to section 2 and species *I* should be located inside this section at the end of t_{S2}. In this case, operational conditions were defined for species *I* to be located in the first column before section 3.

Effect of Feed Loading. Figure 7 shows the unit behavior for the separation with two different feed charges: one for $p_{tS1} = 1$[17] and another with $p_{tS1} = 2$ (Table 3). The concentration front of the intermediate species for the second situation is near the end of section 3 (with reference to the liquid-phase direction) at the end of step 1 and so it will not contaminate the raffinate in step 2, and at the beginning of section 2 at the end of step 2 to avoid contamination of the extract. The operational conditions described in Table 3 for the case of $p_{tS1} = 2$ were not the same as for the case of $p_{tS1} = 1$. There are changes in the following conditions: $t_{S1} = 18.17$ min, $Q_{El1} = 422.94$ cm^3/min, $Q_{El2} = 427.00$ cm^3/min, $Q_{Ra} = 172.06$ cm^3/min, $Q_{4,S2} = 110.33$ cm^3/min, and $u_S = 0.337$ cm/s. In this determination, the sequence of design criteria presented in the previous item had to be satisfied. The first strategy is used to define conditions for step 2. It can be seen that high purity and recovery of species can be achieved with higher productivity and lower eluent consumption, even for the higher loading of the system (Table 4).

Another aspect worth mentioning is related to the average concentration of species recovered. The average concentrations obtained in the outlet streams for the two different values of p_{tS1} are: (1) for $p_{tS1} = 1 - \bar{C}_A = 56.0$ g/L, $\bar{C}_I = 45.3$ g/L, $\bar{C}_B = 37.8$ g/L; (2) for $p_{tS1} = 2 - \bar{C}_A = 87.7$ g/L, $\bar{C}_I = 91.7$ g/L, $\bar{C}_B = 64.3$ g/L. In both situations, the time needed to reach the cyclic steady state is similar; the average concentrations are higher when the feed charge is higher. This leads to higher productivity and lower eluent consumption; moreover, high concentrated products will imply lower energy consumption in the following unit operations for future concentration.

Effect of the Duration of Step 2. Figure 8 shows the behavior of the system varying when the time of step 2 is changed. The other operating conditions are those for $p_{tS1} = 1$. In this figure, the time of step 2 (t_{S2}) is decreased from 96 to 6 min. Because t_{S2} decreases, all flow rates in unit sections in step 2 and solid flow rate are increased, keeping γ ratios constant ($\gamma_1 = 0.719$; $\gamma_2 = \gamma_3 = 0.378$; $\gamma_4 = 0.148$). The larger the flow rates of both liquid and solid phases in the sections are, the more the concentration peaks of the species spread. The JO system productivity improves for lower values of t_{S2}, although at the cost of lower purity and recovery of the species, as shown in Table 5.

Performance of four-section JO for separation with different degrees of difficulty

The performance of a four-section JO for separation of a set of ternary mixtures with different combinations of linear adsorption equilibrium isotherm properties is analyzed. Separation factors α_{IA} and α_{BI} are used to classify the degree of separation difficulty[14]; however, for reduced values of Henry constant of adsorption isotherms, the separation difficulty is properly represented by the ratio of the propagation velocities of concentration.[11] A separation factor of 1.1 means a difficult

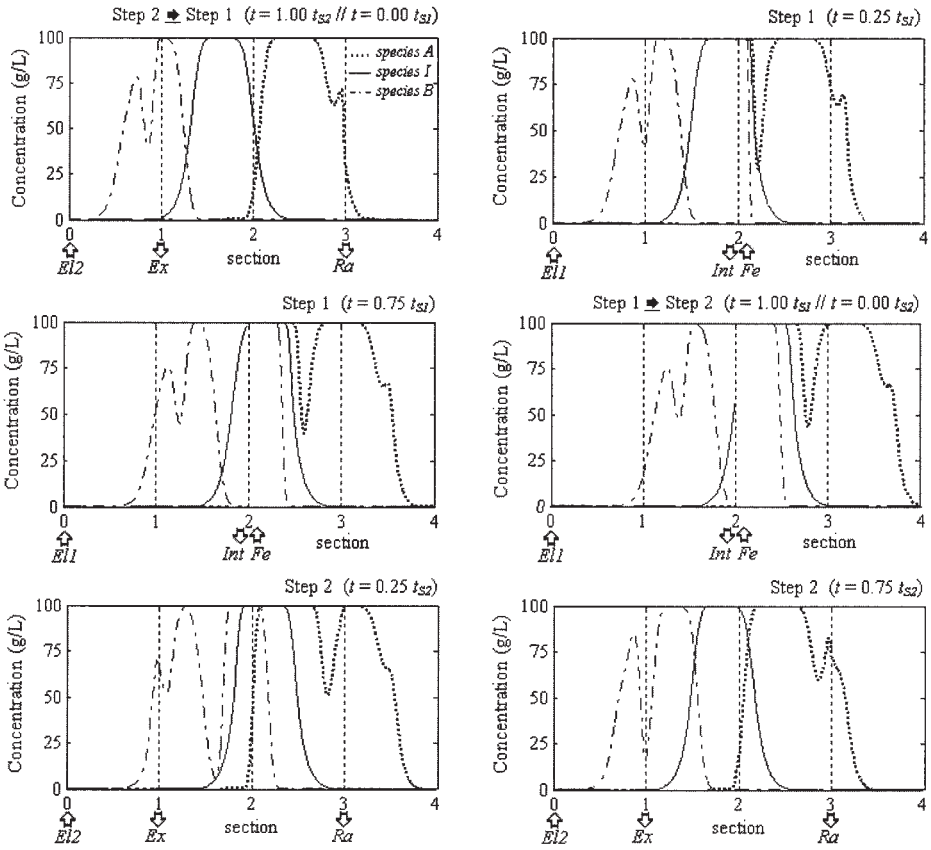

Figure 6. Concentration profiles of the ternary mixture separation in sections of the four-section JO, in different intervals of an operating cycle at the cyclic steady state; (—) species less adsorbed (*A*); (· · ·) intermediate species; and (- - -) species more adsorbed (*B*). Operating conditions: Table 3.

separation, a value of 1.5 means a moderate degree of separation, and that with $\alpha = 2.5$ is considered an easy separation. The value of K_I is kept constant and chosen equal to 0.39.

Figure 9 shows curves that establish the limits of application of the strategies for determination of the operating conditions in step 2 for the four-section JO system. Because the application of the strategies depends on the properties of equilibrium adsorption of the components of the ternary mixture, the limits are constructed according to the pair of separation factors α_{IA} and α_{BI} of a mixture.

In those ternary mixtures in which the linear adsorption constants of the components define points (α_{IA}; α_{BI}) positioned to the left of the full line (the curve related to limiting condition for application of strategy 1) the first strategy could be applied, providing a good performance from the system. One can verify that there are situations where separation factor α_{BI} is higher than α_{IA}, and even so strategy 1 can be used. On the other hand, for mixtures in which the linear adsorption constants of the three components define points (α_{IA}; α_{BI}) to the right of the dotted line (the curve related to limiting condition for application of strategy 2) it would be possible to use the second strategy to determine the operational conditions in step 2 and to operate the system properly.

If an intersection of the two indicated areas is made, it can be established that in the shaded region of Figure 9 strategy 1 could be used, whereas the remaining area is the region in which strategy 2 would have to be applied. Although there is an area in the shaded region where strategy 2 could be applied, it will be shown that the flow rates calculated by strategy 1 with the chosen parameters p_i lead to an operation with lower eluent consumption.

The regions in Figure 9 are valid only for the case of $K_I = 0.39$. Other linear adsorption constants for the intermediate species would lead to other values of flow rates (Eqs. 17 and 18 and 20 and 21) and, consequently, the limiting values—maximum and minimum—for the adsorption constants for the less and the more retained species would be different. Some combinations of ternary mixtures and some operational parameters used in the separations are listed in Table 6.

The analysis involves a series of ternary mixtures (components *A*, *I*, and *B*) in which the separation difficulty is measured by the value of the separation factors between species. Ternary mixtures are chosen such that separations with a high degree of difficulty, corresponding to values of α_{IA} and $\alpha_{BI} \leq 1.1$, and the situations of mixtures of easy separation, with values of separation factors around 2.5, are studied.

Figures 10 and 11 show the ternary separation performance of the four-section JO system. The performance is analyzed according to the average concentration of the species in their respective collected streams, the purity of the collected species, the productivity, and the eluent consumption for the separation as a function of the separation factor α_{BI}. Figure 10 shows cases of ternary mixtures that have separation factor of 1.1 to the components *A* and *I*, that is, a hard separation of these two

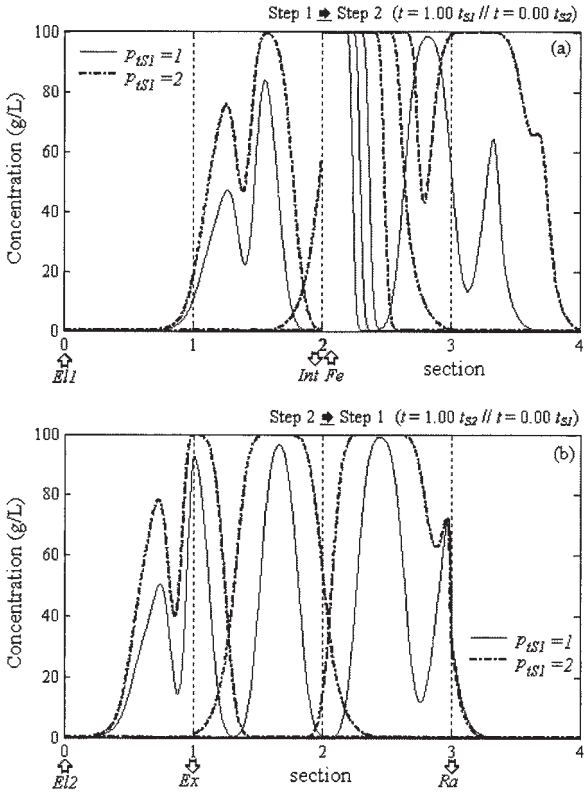

Figure 7. Concentration profiles of the ternary mixture separation in sections of the four-section JO, at the cyclic steady state.

Operation time: (a) at the end of the step 1; (b) at the end of the step 2. Feed condition: (—) $t_{S1} = 18.17$ min ($p_{tS1} = 1$); (- · -) $t_{S1} = 36.90$ min ($p_{tS1} = 2$).

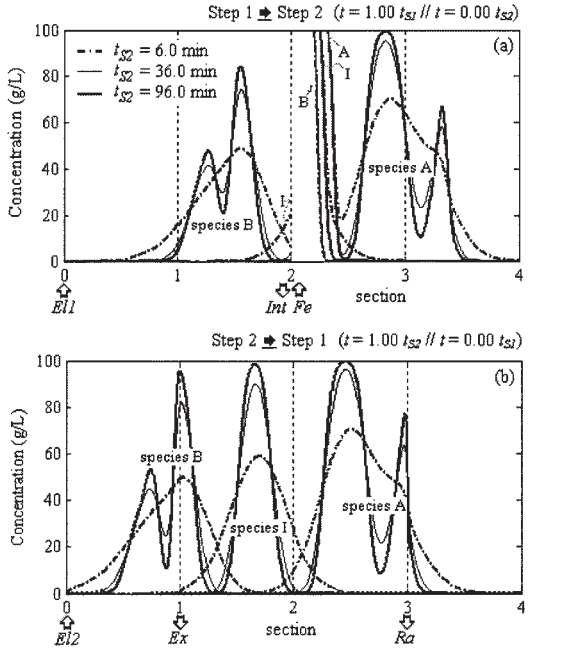

Figure 8. Concentration profiles of the ternary mixture separation in sections of the four-section JO, at the cyclic steady state.

Operation time: (a) at the end of the step 1; (b) at the end of the step 2. Different operational time to the step 2 for constant ratios γ ($\gamma_1 = 0.719$; $\gamma_2 = \gamma_3 = 0.378$; $\gamma_4 = 0.148$). (—) $t_{S2} = 96.0$ min, (—) $t_{S2} = 36.0$ min, (- · -) $t_{S2} = 6.0$ min.

species. In Figure 11, cases of ternary mixture with moderately difficult separation to species *A* and *I* ($\alpha_{IA} = 1.5$) are presented.

There is a limiting value of α_{BI} in which the strategy for definition of operational conditions in step 2 of the four-section JO is changed. The limiting values for any case can be verified in Figure 9 and also in Figures 10 and 11 where there is a vertical step dotted line that divides the area in two regions: one region to the right of the line where strategy 1 (called region 1 in the following analysis) can be used and another to the left of the step dotted line where strategy 2 (region 2) is used. For the limiting values, that is, on the vertical line, one can observe the separation performance achieved using conditions obtained from both strategies. In Figures 11a and 11d, another vertical line (now, in gray) is shown that is related to the limiting value for application of strategy 2 in the separation.

In Figures 10 and 11, one can verify a trend. The two cases of α_{IA} (1.1 and 1.5) close to the different values of α_{BI} show a similar behavior of the performance parameters for the separation of the three species in the four-section JO system. In region 1, the purity of species *A* and *B* (Figures 10b and 11b) increases until a maximum value when the separation of species *B* and *I* becomes easier (higher values of α_{BI}). In region 2, the performance parameter for these species is approximately constant, independent of the value of α_{BI}. The purity of species

Table 4. Performance Parameters for Different Feed Conditions in Separation of the Ternary Mixture in a Four-Section JO System

Species	t_{S1} (min)	Average Concentration (g/L)	Purity (%)	Recovery (%)	Productivity (g h^{-1} L^{-1})	Eluent Consumption (L/kg)
A	18.17*	55.9	100.00	99.94	5.68	56.4
	27.53**	74.0	100.00	99.90	7.74	37.3
	36.90†	87.7	99.97	99.39	9.38	27.9
I	18.17	45.3	100.00	100.00	5.69	56.3
	27.53	68.6	99.97	100.00	7.75	37.2
	36.90	91.7	99.48	99.71	9.41	27.9
B	18.17	37.8	100.00	100.00	5.68	56.4
	27.53	52.2	100.00	100.00	7.75	37.2
	36.90	64.2	99.92	100.00	9.45	27.8

*$p_{tS1} = 1$.
**$p_{tS1} = 3/2$.
†$p_{tS1} = 2$.

Table 5. Effect of Duration of Step 2 on Performance of the Four-Section JO for Ternary Separation

t_{S2}* (min)	Purity (%)			Recovery (%)			Productivity (g h^{-1} L^{-1})		
	A	*I*	*B*	*A*	*I*	*B*	*A*	*I*	*B*
96.0	100	100	100	100	100	100	4.19	4.19	4.19
36.0	99.99	99.98	100	99.93	100	100	8.82	8.84	8.83
6.0	99.27	94.76	98.96	97.24	99.45	97.88	19.25	19.68	19.37

*$p_{tS1} = 1$.

I has a maximum value, in region 1, and remains constant in region 2. Concerning the productivity (Figures 10c and 11c), one can see that for species *I* and *B* the productivity increases until a maximum value in region 1, whereas for species *A* this parameter decreases. In region 2, the productivity is constant for each of the species. The curves of eluent consumption show the same behavior for the three components in the cases of Figures 10d and 11d.

The average concentration of the species, in their respective enriched streams, shows different profiles for each species, although the mentioned trend for the two studied cases of α_{IA} is kept. The trend for species *A* and *I* is an increase in its average concentration when the limit of application of strategy 1 is approached; beyond this limit (strategy 2), it remains in some constant value. In region 1, the curve of average concentration of species *B* in the extract shows a trend to increase until some point (some value of α_{BI}) and then to decrease when the limiting value of α_{BI} for applying the strategy 1 is approached. In Figure 10a, this kind of behavior is not verified for this species and will be explained in the following. In region 2, the use of strategy 2 leads to a curve of average concentration of *B* that decreases smoothly from the limiting line to situations where there is easy separation of species *B* and *I*.

Effect of α_{BI} on Performance Parameters of a Four-Section JO for Separation with Different Degrees of Difficulty. Before discussing the effect of α_{BI} on performance parameters of the four-section JO shown in Figures 10 and 11, note the nomenclature "mix(α_{IA}; α_{BI})" used to represent a ternary mixture whose components have separation factors α_{IA} and α_{BI}.

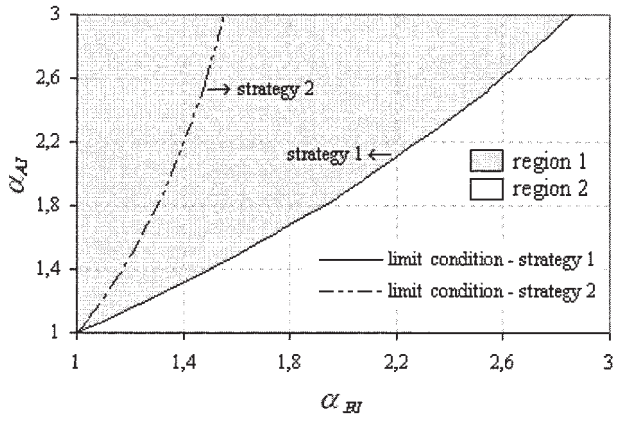

Figure 9. Regions of the plane (α_{IA}; α_{BI}), in which a point represents one ternary mixture, for limiting the use of the strategy 1 or 2 for defining operating conditions in step 2 of the four-section JO system.

Valid to $K_I = 0.39$; $p_A = 3$; $p_I = 1$; $p_B = 3$.

• *Average concentration* (Figures 10a and 11a)

In region 1 of these figures, the maximum value of average concentration of *A* is for the cases of mix(α_{IA}; $\alpha_{BI}^{\text{limit}}$), that is, mixtures that have any factor α_{IA} and a factor α_{BI} equal to the limiting value presented in Figure 9 related to the α_{IA} in question. In these cases, the values of K_A are the limiting values for application of strategy 1 (Eq. 19), and then there is no propagation of *A* toward the raffinate stream in section 3 during step 2; therefore, the mass of this species remains accumulated inside this section. Species *A* is "pushed" significantly only when the JO system works as a fixed bed in step 1. In step 1, the new loading of species *A* is joined to the previous one, and then it follows until section 4 (to the raffinate port) to be collected during step 2.

For cases of mix(α_{IA}; $\alpha_{BI} \geq \alpha_{BI}^{\text{limit}}$), one can notice that, in using strategy 1, contamination of the intermediate stream with *A* increases quickly and then strategy 2 becomes necessary. Using strategy 2, the average concentration of *A* decreases roughly 32 to 37% of the last values obtained using strategy 1. The value of this performance parameter does not depend on α_{BI} when strategy 2 is applied. This fact is already foreseen because the flow rates that are defined to separate *A* and *I*—$Q_{2/3,S2}$ and Q_S—(and also the raffinate stream) remain unchanged with any α_{BI}. This comment is also valid for the intermediate species (the flow rate of the intermediate outlet also remains constant). This statement, however, is not verified for species *B* that in region 2 has its concentration average decreased for mixtures with higher α_{BI}.

For higher values of α_{BI} (that is, larger values of K_B), the operation requires higher flow rates in section 1 and, consequently, also higher values of Q_{El2} and Q_{Ex}, leading to the larger dilution of the species collected in the extract outlet. When strategy 1 can be used, the value of average concentration of *B* in mix(1.5; $\alpha_{BI} \leq 1.61$) shows the behavior of a concave curve with a maximum point in some separation factor α_{BI}. Figure 12 shows three concentration profiles (including the average concentration) in the extract stream in some operating cycle of the system at CSS. The examples are for mix(1.5; 1.1), mix(1.5; 1.3), and mix(1.5; 1.5), in which the larger average concentration of *B* is obtained for the case of the mix(1.5; 1.3) as shown in Figure 11a. For the mix(1.5; 1.5), the concentration peaks of *B* (one coming from the previous cycle and another one from the current cycle, both identified in Figure 12) are more separated than for other mixtures. The separation of *B* and *I* is easier (lower ratios of γ_2 and γ_3 are necessary) and, then, the average is lower than that for the case of mix(1.5; 1.3). Now, for the mix(1.5; 1.1) there is a hard separation between species *B* and *I*, the concentration peak of *B* is broader (the ratios γ_2 and γ_3 are larger), and the area below the curve is smaller. For cases of mix(1.1; $\alpha_{BI} \leq 1.13$) there is just an increase in the average concentration of *B*, and not a decrease

Table 6. Set of Mixtures and Operational Parameters Used in the Ternary Separations for the Four-Section JO System*

α_{IA}	α_{BI}	K_A	K_B	Step 1	Step 2
1.1 (hard)	1.05 (hard)	0.355	0.410	t_{S1} = 18.17 min	t_{S2} = 250.0 min
	↓			p_{rS1} = 1	β_1 = 1.03
	1.5 (moderate)		0.585	Q_f = 350.00 cm^3/min	β_4 = 0.97
	↓			Q_{EI1} = 422.94 cm^3/min	
	2.5 (easy)		0.975		
1.5 (moderate)	1.1 (hard)	0.260	0.429		t_{S2} = 200.0 min
	↓				β_1 = 1.03
	1.5 (moderate)		0.585		β_4 = 0.97
	↓				
	2.5 (easy)		0.975		

*K_I = 0.39. $k_A = k_I = k_B$ = 0.5 s^{-1}. Properties of the columns: Table 3.

as in the previous case. In the case of difficult separation, the peaks of *B* show significant spreading and peaks of *B* cannot be distinguished from those coming. This is one of the reasons that the average concentration of species *B* is not decreased for hard separations (Figure 10a). These last comments can also be valid for the intermediate species. The spreading of concentration peak of *I* in sections of the system for hard separations between *B* and *I* causes a decrease of average concentration of *I* in its outlet stream.

- *Purity* (Figures 10b and 11b)

In region 1, there is a reduction in purity of species *A* and *B* in the raffinate and extract, respectively, when mixtures with a higher degree of separation difficulty between species *B* and *I* occur. For the separation of ternary mixtures with low α_{BI}, higher values of γ_2 and γ_3 ratios are required, which can lead to some dispersion of concentration peaks inside the system and then negatively affect the purity of the species. The main contaminant of the raffinate and of the extract is the intermediate species. The concentration peak of species *I* is between these two outlets and it can reach both streams depending on the extension of spreading. Eventually species *A* can also contaminate the extract or species *B* can contaminate the raffinate. A large mass-transfer resistance can also lead to a decrease of purity in the outlet streams.[17]

In region 1 of Figures 10b and 11b, the purity of the intermediate species shows a peculiar behavior for a mixture as mix(α_{IA}; $\alpha_{BI} \approx \alpha_{BI}^{\text{limit}}$), that is, with separation factor α_{BI} close to the limiting value for the application of strategy 1. In the limiting value of α_{BI}, it means that the linear adsorption constant of species *A* is such that, using the operational conditions from strategy 1, no displacement of the less adsorbable species occurs during step 2. In this step, although not to be carried, the left tail of the concentration peak of *A* inevitably extends from section 3 to section 2 (at least in the situations studied with a mass-transfer coefficient of 0.5 s^{-1}). Any fraction of *A* that goes to section 2 will contaminate species *I* during its recovery in step 1. The contamination is more extensive when the linear adsorption constant K_A is equal to the maximum value allowed for using strategy 1. It is thought that in an ideal situation of no mass-transfer resistance and no dispersion, this effect is minimized.

For mix(α_{IA}; $\alpha_{BI} \geq \alpha_{BI}^{\text{limit}}$), where strategy 2 is applied, the purity is almost constant for all species, except for a small variation of the purity of *B* in mixtures of difficult separation between species *A* and *I* (case of α_{IA} = 1.1). When using strategy 2, the liquid flow rates in sections 2, 3, and 4 are not changed with the linear adsorption constant of the most retained species. Only the liquid flow rate in section 1 increases for an increase in the values of K_B. This behavior is therefore expected for the purity of species in region 2 in Figures 10b and 11b. The small variation of the purity of *B* in Figure 10b (α_{IA} = 1.1) is related to the low values of flow rates required in section 1 when α_{BI} is near the limiting value. In this situation a small amount of *I* extends from section 2 to section 1 and then it contaminates the extract. The purity of the species is lower for mixtures with hard separation between species *A* and *I*.

- *Productivity and eluent consumption*

Productivity for the four-section JO, operating in conditions calculated by strategy 1, is shown in Figures 10c and 11c. The productivity of *A* decreases for cases of ternary mixtures with higher separation factor α_{BI}. Despite the increase of average concentration of the less retained species in region 1, the defined operational conditions lead to lower raffinate flow rates and lower productivity. The opposite is true for species *B*; productivity increases as a result of the greater flow rates in the extract in cases of higher α_{BI}. With respect to the productivity of the intermediate species, given that the flow rate in the intermediate outlet remains constant in this analysis, this performance parameter is influenced only by the values of the average concentration of *I*.

In region 1 of Figures 10d and 11d, for cases of ternary mixtures with higher separation difficulty between species *B* and *I*, the eluent consumption is greater, which means that greater flow rates in sections of the system are necessary to achieve an adequate separation and thus a greater flow rate of eluent.

Considering the eluent consumption for separations of mixtures with equal α_{BI} and different α_{IA}, that is, mix(1.1; α_{BI}) and mix(1.5; α_{BI}), this performance parameter is of greater magnitude when α_{IA} is higher. When there is an easy separation for species *I* and *A*, a lower liquid flow rate in section 4 becomes necessary. Because the flow rate in section 1 must be kept constant, a higher flow rate in the eluent stream is also necessary.

In region 2, the eluent consumption for recovery of the species increases linearly for mix(α_{IA}; $\alpha_{BI} \geq \alpha_{BI}^{\text{limit}}$). Using the second strategy for defining operational conditions, the eluent flow rate becomes linearly proportional to the adsorption constant of the more retained species, leading to the behavior observed in Figures 10d and 11d.

- *Strategy 1 vs. Strategy 2*

Application of both strategies in region 1 of the Figures 11a and 11d can be evaluated. As seen in Figure 9, there is some area, representing a set of mix(α_{IA}; α_{BI}), where both strategies 1 and 2

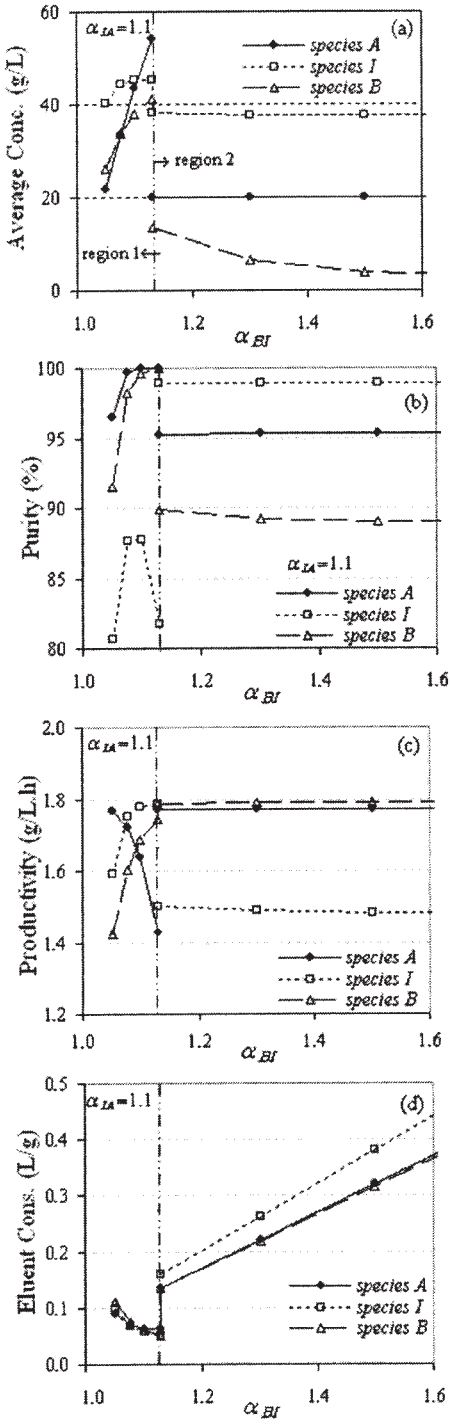

Figure 10. Performance of the four-section JO in ternary separation.

Hard separation of species *A* and *I* (that is, α_{IA} = 1.1). (a) Average concentration; (b) purity; (c) productivity; (d) eluent consumption.

could be used. In region 1, strategy 2 for defining the operational conditions of the four-section JO leads to a higher eluent consumption (Figure 11d) and lower average concentration of the recovered species (Figure 11a) compared with use of strategy 1. The gray vertical line establishes the limit of use of strategy 2 that, according to Figure 9, works to the cases of mix(1.5; $\alpha_{BI} \geq 1.2$). The values of eluent consumption and average concentration of the species in respective outlets are similar in both strategies only for the limiting case of mix(1.5; 1.2). The same behavior holds for the limiting case of mix(1.1; 1.05), not shown here.

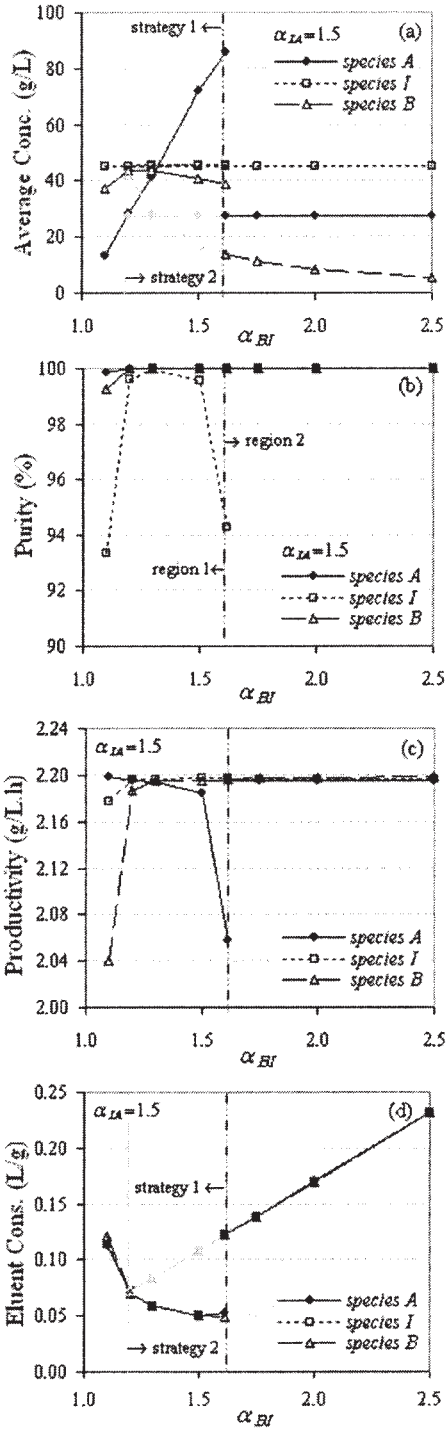

Figure 11. Performance of the four-section JO in ternary separation.

Moderate separation of species *A* and *I* (that is, α_{IA} = 1.5). (a) Average concentration; (b) purity; (c) productivity; (d) eluent consumption.

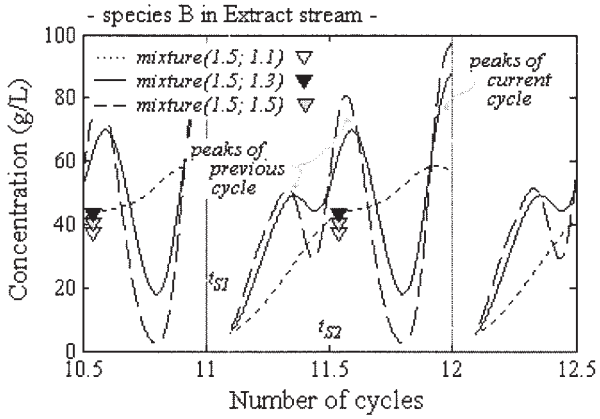

Figure 12. Concentration profiles of species *B* in extract during a cycle of a four-section JO at cyclic steady state.

Mixtures: (· · ·) mix(1.5; 1.1); (—) mix(1.5; 1.3); and (– – –) mix(1.5; 1.5).

Extension to quaternary separation: five-section JO system

An extension of the four-section JO system for ternary mixtures is developed to be used in the separation of mixtures with four components. The JO system designed for quaternary mixtures has five sections and its operation process is quite similar to that discussed previously. Figure 13 presents the new five-section JO system. One can see that a new section is introduced between the feed stream and intermediate collection stream of the four-section JO shown in Figure 3. Therefore, two intermediate species will be recovered during step 1 of an operation cycle. Species *A* and *B* are still the less and more adsorbable species, respectively. Species I_1 and I_2 have intermediate affinities with the solid phase and the adsorption affinity of component I_1 is higher. For cases of linear adsorption isotherms, it would mean the following affinity sequence: $K_A < K_{I2} < K_{I1} < K_B$.

When the five-section JO is operating in step 1, sections 1, 2, 4, and 5 are connected and work as a chromatographic column, which is fed with a quaternary mixture. The eluent stream El_{11} helps to elute the intermediate species I_1 during this time of the cycle. In this step, the elution of intermediate species I_2 occurs in section 3 and then a second eluent stream El_{12} is introduced into this JO system. Section 3 does not have any connection to the other sections and operates independently.

Once the end of step 1 is reached, step 2 takes place and the unit operates in the same way as the four-section JO system. The feed as well as the recovery of the intermediate species are stopped. The unit starts to operate according to SMB technology and then species *A* and *B* are collected in the raffinate and extract streams, respectively. The species should be separated in step 2 such that: (1) species *A* travels in the direction of liquid flow toward the raffinate outlet; (2) concentration peaks of the intermediate species I_2 and I_1 propagate in the direction of solid flow until some position in sections 3 and 2, respectively; and (3) species *B* is carried by the solid phase toward the extract outlet.

A previous set of equations was shown to determine operational conditions for the four-section JO to achieve an adequate separation of the species. For the five-section JO system some changes are needed to appropriately recover species. Such design equations are discussed in the Appendix. Here, we applied this new strategy to attain operational conditions for the five-section JO and to obtain the concentration profiles for quaternary mixtures with feed concentration of species equal to 100 g/L each. The necessary parameters and operating condi-

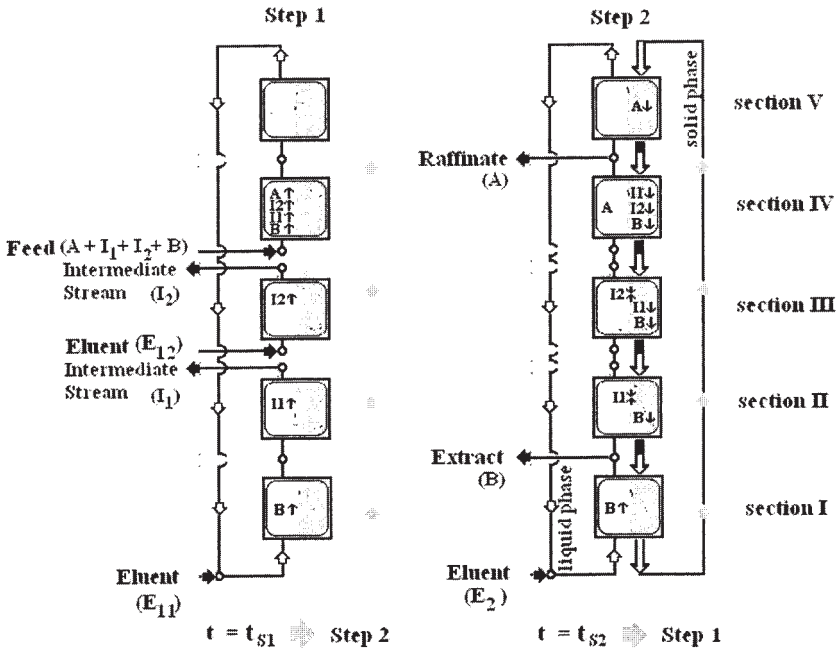

Figure 13. Scheme of operating step for "five-section JO" in which the SMB operation in step 2 is replaced by an equivalent TMB operation.

Table 7. Operational Conditions Used in Separation of the Quaternary Mixture in the Five-Section JO System*

Step 1		Step 2	
t_{S1}	27.53 min	t_{S2}	150.00 min
Q_f	350.00 cm^3/min	Q_{Ra}	217.63 cm^3/min
Q_{El11}	494.92 cm^3/min	Q_{Ex}	439.78 cm^3/min
Q_{El12}	765.25 cm^3/min	Q_{El2}	657.41 cm^3/min
$Q_{1/2,S1}$	844.92 cm^3/min	$Q_{1,S2}$	1019.46 cm^3/min
$Q_{3,S1}$	765.25 cm^3/min	$Q_{2/3/4,S2}$	579.68 cm^3/min
$Q_{4/5,S1}$	350.00 cm^3/min	$Q_{5,S2}$	362.05 cm^3/min
C_{Af}, C_{I1f}, C_{I2f}, C_{Bf}	100 g/L each	Q_S (γ_1; $\gamma_{2/3/4}$; γ_5)	1688.72 cm^3/min (0.906; 0.515; 0.322)

*Feed condition: $p_{tS1} = 3/2$. Propagation condition: $p''_{I1} = 3/2$; $p''_{I2} = 1$.

tions for model simulation are described in Table 7. According to previous definitions, the degree of separation difficulty of this example can be classified as moderate separation: mix($\alpha_{I2A} = 1.50$; $\alpha_{I1I2} = 1.28$; $\alpha_{BI1} = 1.30$). The properties and characteristics of the columns in the five-section JO are those listed in Table 3, except for the number of columns and the unit configuration that now are 15 and 3–3–3–3–3, respectively.

Figure 14 shows the liquid-phase concentration profiles of the species in the five-section JO system, at the half and the end of the two steps of a cycle. The process is already at the cyclic steady state. In Figure 14a, profiles at the end of step 1 are shown; one can see that the feed load of the mixture breaks through around the middle of the second column in section 4 according to the chosen value for p_{tS1} (=3/2). Moreover, in Figure 14d, one can verify that the intermediate species are eluted from both sections 2 and 3 and are collected in their intermediate outlet streams. Figures 15a and 15b show concentration profiles of species I_1 and I_2 in their respective enriched streams and purity of these species is >99% ($Pu_{I2} = 99.8\%$ and $Pu_{I1} = 99.9\%$). In Figure 14c, one can see that a small amount of species I_2 is still in section 4 at the end of step 2. Thus, the breakthrough curve of this species will have interference of this amount during the loading step. In Figure 14c, one can also notice the chosen values of p''_{I1} and p''_{I2} parameters (Eqs. A4 and A5) related to the migration of concentration peaks of the intermediate species during step 2 (see Table 7). The position of the species I_1 is defined in the central region of section 2 such that if some amount of I_1 exceeded the boundaries of section 2 arising from any dispersion, the left and the right rails of concentration peak could be equally distributed in the adjacent sections. With respect to species I_2 its localization is defined at the beginning of the third column of section 3 at the end of step 2, which avoids contamination of the collecting stream of species I_1 by species I_2. The liquid flow rate in section 3 in step 1 is defined to allow a total elution of I_2 from the section $p''_{I2} = n_{Se3}$.

The operating conditions described in Table 7 lead to an adequate separation process only if the inequalities shown in Eqs. A9 and A10 are fulfilled. The limiting values for application of the proposed strategy are $K_A^{\max} = 0.343$ and $K_B^{\min} = 0.532$. Figures 15c and 15d show that, once the linear adsorption constants of species A and B satisfy those inequalities, these species could be directed to their respective enriched outlets and also recovered in high purity ($Pu_A = 99.8\%$; $Pu_B = 99.1\%$). After the cyclic steady state has been reached, the outlet flows have average concentrations equal to: 29.6 g/L for species A in raffinate, 45.7 g/L for species I_2 in intermediate stream 2, 41.0 g/L for species I_1 in intermediate stream 1, and 14.7 g/L for species B in extract. The process productivity and

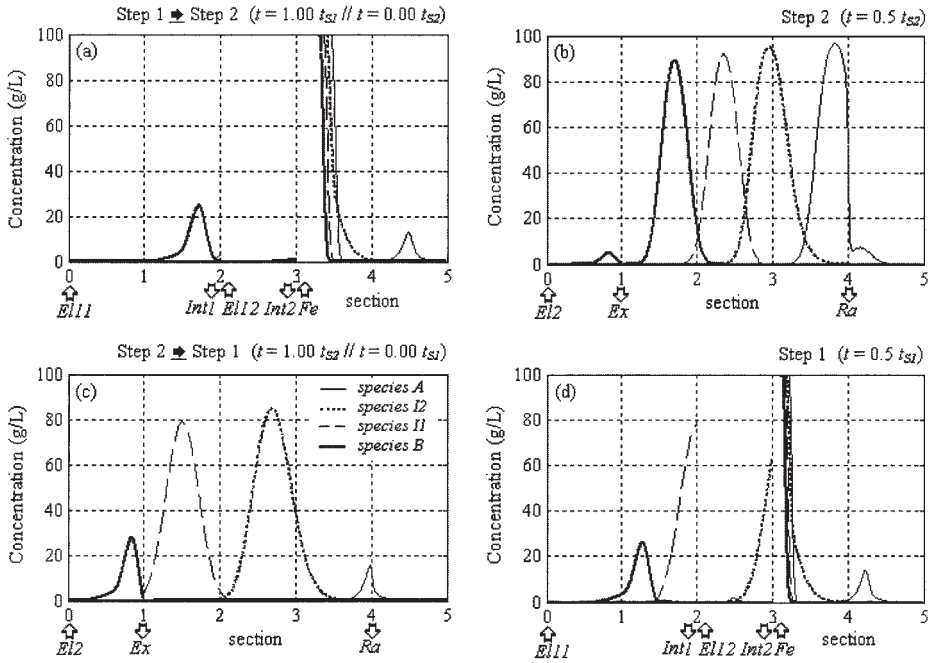

Figure 14. Concentration profiles of the species to quaternary separation in sections of a five-section JO, in different intervals of an operating cycle at cyclic steady state.

(—) Less adsorbed species A; (· · ·) intermediate species I_2; (- - -) intermediate species I_1; and (—) more adsorbed species B. Operating conditions: Table 7.

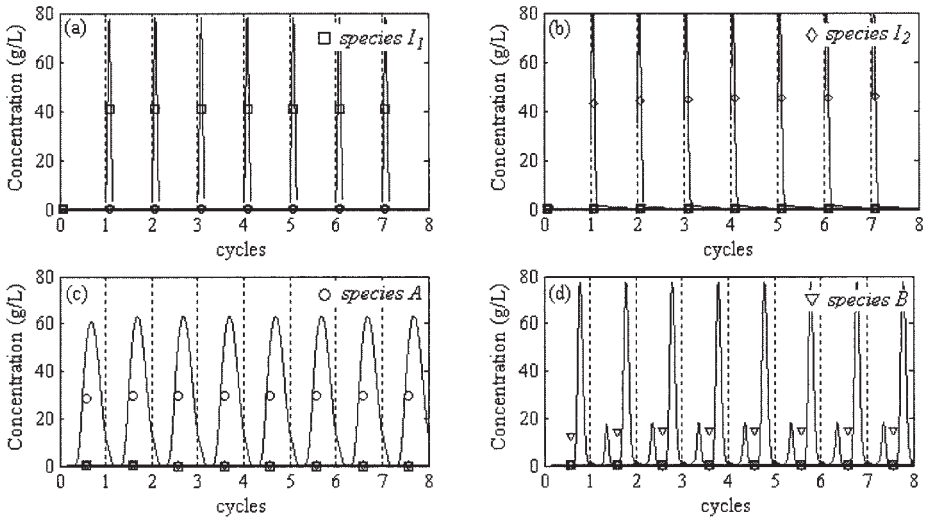

Figure 15. Concentration profiles of the species in a five-section JO.

Species in: (a) intermediate stream 1; (b) intermediate stream 2; (c) raffinate; (d) extract; (—) exact transient concentration profile; (○), (□), (◇), (▽) average concentration profile of species A, I_1, I_2, and B, respectively, in the respective operation step.

the eluent consumption for separation of the species are 3.2 g/L h and 0.13 L/g, respectively.

Conclusions

Separation systems operating according to JO technology have been proven useful in continuous separation of multicomponent mixtures. A four-section JO system for purification of components from ternary mixture feeds has been proven effective even for cases classified according to this article as hard separation. Integration of the fixed bed and the SMB processes at the four-section JO has been modeled using a lumped mass-transfer model and simulated by computational algorithm. The SMB model used to predict the behavior of the JO system during step 2 has been based on the equivalent TMB model approach. The developed algorithm can be identified as a decision-helping tool to aid in dimension analysis and determination of favorable operating conditions in units based on this technology.

Criteria to design a JO system operation have been defined that allow evaluating operation conditions for separation of ternary mixtures with species characterized by linear isotherms. Two strategies have been suggested in this design procedure to determine operating conditions in the four-section JO system when it operates in step 2—SMB technology—to achieve high-purity products. Application of one or the other strategy is linked to the adsorption constant of components in the mixture.

Considering several ternary mixtures, strategy 2 has a broader range of applications than strategy 1 for the defined parameters p_i. Despite this, it has been demonstrated that strategy 2 leads to an operation with higher eluent consumption. Thus, in those situations in which one could use both strategies, strategy 1 should always be chosen when process requirements are high purity and high average concentration in outlets close to the minimum eluent consumption.

The new five-section JO system has been proposed for quaternary separations. Some design criteria for the operation of the four-section JO were revised and new migration rules were used to obtain operational conditions for the five-section JO. It has been possible to separate a mixture of four components, classified as moderate separation, achieving high-purity products in their enriched outlets.

Acknowledgments

E. A. Borges da Silva gratefully acknowledges financial support from Fundação para a Ciência ea Tecnologia (FCT Grant SFRH/BPD/19701/2004), Ministry of Science and Technology of Portugal.

Notation

A_C = cross-sectional area of a JO column, m^2
C = liquid-phase concentration, g/L
$\bar{C}$ = average concentration, g/L
d_p = particle diameter, m
D = axial dispersion coefficient, m^2/s
e_b; e_c = mass balance error (%); iteration error (%)
EC = eluent consumption, L/g
k_i = mass transfer coefficient, s^{-1}
K = linear adsorption constant, dimensionless
L_C = column length, m
n_{Se2} = number of columns in section 2
n_{Se3} = number of columns in section 3
p = parameter to position of concentration wave—step 2 (four-section JO)
p'' = parameter to position of concentration wave—step 2 (five-section JO)
p_{iS1} = operational parameter used in Eq. 6—step 1
Pe = Peclet number
$\bar{q}$ = average adsorbed phase concentration, g/L
q^* = adsorbed concentration in equilibrium with liquid concentration, g/L
Pu = purity, dimensionless
Pr = productivity, g L^{-1} h^{-1}
Q = liquid flow rate, m^3/s
Q_S = solid flow rate, cm^3/min
Re = recovery, dimensionless
t^* = switching time, s
t = time, s
$\bar{t}$ = retention time, s
t_{S1} = operation time of step 1, s
t_{S2} = operation time of step 2, s
u_S = interstitial solid velocity, m/s

v = interstitial liquid velocity, m/s
V_C = column volume, m^3
w = velocity of propagation of a concentration wave, m/s
x = distance traveled by a concentration wave, m
z = axial coordinate, m

Greek letters

α = separation factor, dimensionless
β = safety margin for linear systems, dimensionless
ε = bed porosity, dimensionless
Φ = step index
γ = ratio of the liquid and solid velocities, dimensionless
θ = related to the cycle in JO process
σ = standard deviation, dimensionless
τ = parameter defined in Eq. 6, dimensionless
υ = adsorbent/liquid volume ratio, dimensionless

Subscripts and superscripts

A, B = less and more retained species, respectively
Ex, *Ra*, *Int* = extract, raffinate, and intermediate outlets, respectively
f, *El* = feed and eluent inlets, respectively
i = chemical species
I, I_1, I_2 = intermediate species
j = JO sections
k = JO columns
m = in- and outlet streams in JO system
S1, *S2* = related to step 1 and step 2, respectively

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Appendix: Determination of Operational Conditions for the Five-Section JO

To determine operational conditions for the five-section JO, some changes are needed in previous design methodology derived for the four-section JO. In step 1, t_{S1} is any time such that the concentration front of the intermediate species I_2 does not move to section 5; otherwise, it will contaminate the product in the raffinate stream during step 2. During this time, species I_1 and I_2 must be eluted from sections 2 and 3, respectively.

The liquid flow rates in sections 1 (and 2) and 3 for step 1 are

$$Q_{1,S1} = Q_{2,S1} = Q_{El11} + Q_{Fe} = \frac{\varepsilon A_c (p'_{I1}) L_C}{t_{S1}} (1 + \upsilon K_{I1}) \qquad (\text{with } 0 < p'_{I1} \le n_{Se2}) \quad \text{(A1)}$$

$$Q_{3,S1} = \frac{\varepsilon A_c (p'_{I2}) L_C}{t_{S1}} (1 + \upsilon K_{I2}) \qquad (\text{with } 0 < p'_{I2} \le n_{Se3}) \quad \text{(A2)}$$

where the parameters p'_{I1} and p'_{I2} must be defined to allow the elution of the species I_1 and I_2 from their respective sections to their intermediate withdrawals. The liquid flow rates in sections 4 and 5 are defined according to feed flow rate of the process.

For step 2, the migration rules to the species can be mathematically expressed as

$$\frac{t_{S2}}{\varepsilon A_c(1+\upsilon K_A)}(Q_{4,S2}-Q_S K_A)=p''_A L_C - x_{A,4,S1} \quad \left(\text{with } \frac{x_{A,4,S1}}{L_C} \le p''_A \le n_{Se4}\right) \tag{A3}$$

$$\frac{t_{S2}}{\varepsilon A_c(1+\upsilon K_{I2})}(Q_{4,S2}-Q_S K_{I2})=-(x_{I2,4,S1}+p''_{I2}L_C) \quad (\text{with } 0<p''_{I2}<n_{Se3}) \tag{A4}$$

$$\frac{t_{S2}}{\varepsilon A_c(1+\upsilon K_{I1})}(Q_{4,S2}-Q_S K_{I1})=-(x_{I1,4,S1}+p''_{I1}L_C) \quad (\text{with } n_{Se2}<p''_{I1}<(n_{Se2}+n_{Se3})) \tag{A5}$$

$$\frac{t_{S2}}{\varepsilon A_c(1+\upsilon K_B)}(Q_{4,S2}-Q_S K_B)=-(x_{B,4,S1}+p''_B L_C) \quad (\text{with } p''_B=n_{Se2}+n_{Se3}) \tag{A6}$$

where $Q_{4,S2}=Q_{3,S2}=Q_{2,S2}$. The parameters p''_i is used to define the position of concentration wave of species i in sections of the five-section JO.

Given the specified aim of strategy 1 to define flow rates $Q_{3,S2}$ and Q_S in the four-section JO, let us consider Eqs. A4 and A5 to calculate the liquid flow rate in section 4 and solid flow rate in the five-section JO. Thus, the intermediate species I_1 and I_2 will be directed to the right positions in sections of the JO system. Solving the equations above for flow rates, we will find

$$Q_S=\frac{\varepsilon A_c}{t_{S2}}\left(\frac{1}{K_{I2}-K_{I1}}\right)[x_{I1,2/3/4,S2}(1+\upsilon K_{I1}) - x_{I2,2/3/4,S2}(1+\upsilon K_{I2})] \tag{A7}$$

$$Q_{4,S2}=\frac{\varepsilon A_c}{t_{S2}}\left(\frac{K_{I2}}{K_{I2}-K_{I1}}\right)\left[x_{I1,2/3/4,S2}(1+\upsilon K_{I1}) - x_{I2,2/3/4,S2}\frac{K_{I1}}{K_{I2}}(1+\upsilon K_{I2})\right] \tag{A8}$$

For the five-section JO system, Eqs. A3 and A6 are used to establish the limiting conditions for applying the flow rates Q_S and $Q_{4,S2}$ ($=Q_{3,S2}=Q_{2,S2}$) expressed in Eqs. A7 and A8, respectively. A procedure similar to that used before when limiting conditions were achieved for strategies 1 and 2 is carried out again. As a result, two inequalities related to the linear adsorption constant of the species A and B must be satisfied for proper operation of the JO system:

$$K_A^{\max}=\frac{Q_{4,S2}}{Q_{S,S2}} \Rightarrow K_A \le K_A^{\max} \tag{A9}$$

$$K_B^{\min}=\frac{Q_{4,S2}-\varepsilon A_c w_{I1,2/3/4,S2}}{Q_S+(1-\varepsilon)A_c w_{I1,2/3/4,S2}} \Rightarrow K_B \ge K_B^{\min} \tag{A10}$$

Once Eqs. A9 and A10 are valid for a given quaternary mixture, this strategy can be used to obtain adequate operational conditions for the five-section JO system.

Manuscript received Nov. 22, 2005, and revision received Aug. 1, 2006.