OPTIMIZATION OF TERNARY SIMULATED MOVING BED SEPARATION BY SUPERSTRUCTURE FORMULATION

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Abstract

Simulated moving bed (SMB) chromatography has been widely studied in past and there have been various operating schemes proposed for efficient separation of binary mixtures. SMB is a promising option of separation because of its capability to achieve efficient separation even when the components differ very little in terms of affinity towards the stationary phase. However, separation of a ternary mixture using SMB is still a major drawback of this technology. Although many different strategies have been proposed, previous studies have rarely performed comprehensive investigations for finding the best ternary separation strategy from various possible alternatives. Our study addresses this issue by adopting a systematic nonlinear programming approach. A full superstructure formulation has been proposed which encompasses numerous operating schemes proposed in the literature for ternary separation. The optimization problem, constrained by partial differential algebraic equations model, is fully discretized both in temporal and spacial domain. The resulting nonlinear programming problem is handled by IPOPT 3.0, an interior point solver. These results are obtained for linear adsorption isotherms considered in Mata and Rodrigues (2001). We demonstrate that the superstructure approach has a potential to find more advantageous operating scheme than the existing operating schemes.

Keywords

Simulated moving bed chromatography, Dynamic optimization, Multi-component separation

Introduction

Simulated Moving Bed (SMB) Chromatography developed by UOP in 1960's has emerged as a continuous and efficient separation technology. SMB systems are an efficient mean of performing large-scale chromatographic separations, particularly for separation of a binary mixture. Compared to conventional chromatography, SMB enables high throughput and low desorbent consumption and thus has been successfully applied in various areas such as sugar, petrochemical and pharmaceutical separations. The standard SMB configuration with four zones has been extensively studied by many groups and established strategies to determine the design and operation are available today (Schmidt-Traub H., 2005).

On the other hand, the application of SMB for multi-component separation is still considered one of the major challenges. Multi-component separation is a very important problem for bioseparation, such as protein purification. In such applications, the feed mixture may have a large number of components of similar chemical structures. Although there have been studies focusing on using SMB for multi-component separations, a less emphasis is given on finding best ternary separation strategy from various possible alternatives. Kim et al.

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(2003) proposed five-zone and four-zone single-cascade SMB systems for separation of ternary mixtures. Kurup et al. (2006) considered these systems to study the effectiveness of SMB by forming a multi-objective optimization problem. Mata and Rodrigues (2001) investigated a pseudo-SMB model for ternary separation referred as JO process (Masuda et al., 1993). Also, there have been nine-zone and eight-zone SMB operating schemes that require a large number of columns (Nicolaos et al., 2001). In such modified operations, by changing relative position of desorbent, feed, extract and raffinate streams, a large number of zone configurations can be created. As a consequence, we need to deal with quite a large number of choices in designing SMB. Hence, finding the best operating scheme or optimal zone configuration is a challenging problem. Kawajiri and Biegler (2006b) proposed the idea of superstructure where a number of SMB operating schemes could be incorporated in a single formulation. They also showed the potential of superstructure approach to find more advantageous operating scheme than standard SMB or PowerFeed. Nevertheless, their study is limited only to binary separations.

The objective of this study is to develop a systematic optimization approach for zone configuration by using a full superstructure formulation which encompasses a number of multi-component operating schemes such as JO process, Three-zone and Five-zone SMB. Although the emphasis of this study is on separation of a ternary mixture, our superstructure approach can be extended for any multi-component separation. Since the number of degrees of freedom is large with such formulation, the superstructure approach has a potential to find better operating scheme than the existing ones. We apply a full-discretization approach for optimization, where the spacial domains are discretized using central finite difference scheme, and the Radau collocation on finite elements is used for the temporal discretization. The discretized equations are incorporated within a large-scale Nonlinear Programming (NLP) problem, which is solved using an interior-point solver, Ipopt.

Mathematical Modeling of an SMB

Modeling of a chromatographic column

We employ the linear driving force (LDF) model which is used extensively in many studies (Schmidt-Traub 2005, Kawajiri and Biegler 2006b). The mass balance in the liquid phase is given by

$$\epsilon_b \frac{\partial C_i^j(x,t)}{\partial t} + (1-\epsilon_b)\frac{\partial q_i^j(x,t)}{\partial t} + u^j(t)\frac{\partial C_i^j(x,t)}{\partial x} = 0 \quad (1.1)$$

The mass balance in the adsorbent phase is modeled as:

$$(1-\epsilon_b)\frac{\partial q_i^j(x,t)}{\partial t} = K_{appli}(C_i^j(x,t) - C_i^{j,eq}(x,t)) \quad (1.2)$$

The equilibrium between the liquid and adsorbent phase is given by isotherms, which can be linear or nonlinear. In this study, only linear isotherms are considered.

$$q_i^j(x,t) = K_i C_i^{j,eq}(x,t) \quad (1.3)$$
$$i = 1,\ldots,N_{Comp}, \quad j = 1,\ldots,N$$

where $C_i^j(x,t)$ is the concentration in the liquid phase, $q_i^j(x,t)$ is the concentration in the solid phase, $C_i^{j,eq}(x,t)$ is the equilibrium concentration in the liquid phase, $q_i^{j,eq}(x,t)$ is the equilibrium concentration in the solid phase, $u^j(t)$ is the superficial velocity in j^{th} column, ε_b is the void fraction, K_{appli} is the liquid phase mass transfer coefficient of i^{th} component, x is the distance from the beginning of the column. The subscript i corresponds to the chemical compound, superscript j to the component index, N_{comp} is the total number of components and N is the total number of columns.

We further consider a ternary mixture consisting 'A', 'B' and 'C' with 'A' as least adsorbable component, 'B' as intermediate and 'C' as most adsorbable component. Hence, components A, B and C would be dominating in raffinate, intermediate and extract stream outlets respectively.

Operating Schemes

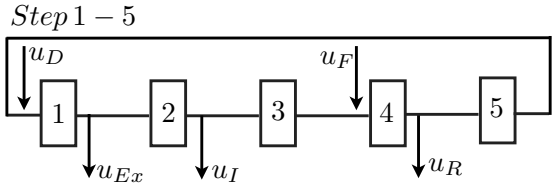

Figure 1: Five-zone SMB for separation of a ternary mixture (Kim et al., 2003).

Existing operating schemes

We started with the modeling of five-zone SMB system (see Figure 1) which is a slight modification of conventional four-zone SMB system (Kim et al., 2003) The five columns are connected with each other in a cyclic manner resulting in five zones due to the separation by feed, desorbent inlets and extract, raffinate and intermediate stream outlets. Although both inlet and outlet streams are switched in every step, in the direction of liquid flow, the amount of liquid velocities is kept

unchanged. Hence, there are six independent parameters (five column velocities and one switching time).

The JO process (see Figure 2) is also modeled which is described as a pseudo SMB model by Mata and Rodrigues (2001). In the first step, the feed and desorbent streams enter the system and the component B, rich in the intermediate stream outlet, is recovered, respectively. In the second, third and the fourth step, there are only desorbent, raffinate and extract streams considered. The more retained component (C) is recovered in the extract outlet and less adsorbed component (A) is recovered in the raffinate outlet. The important difference in the JO process from a conventional SMB is that the circuit, between column 2 and 3, is cut in the first step to separate out the intermediate component. As a consequence, feed stream flows through columns 3 and 4 and the sum of feed and desorbent stream flows through columns 1 and 2. The liquid flows are switched in the direction of liquid flow in every step as shown in the Figure 2. The amount of both inlet and outlet streams is kept same throughout the cycle except the desorbent stream whose amount is allowed to be different in the first step from rest of the steps. The switching time of the first step is also allowed to be different from rest of the steps. Hence, the total number of independent parameters (two desorbent, two steptimes, feed, extract and a column velocity in step 2) is seven.

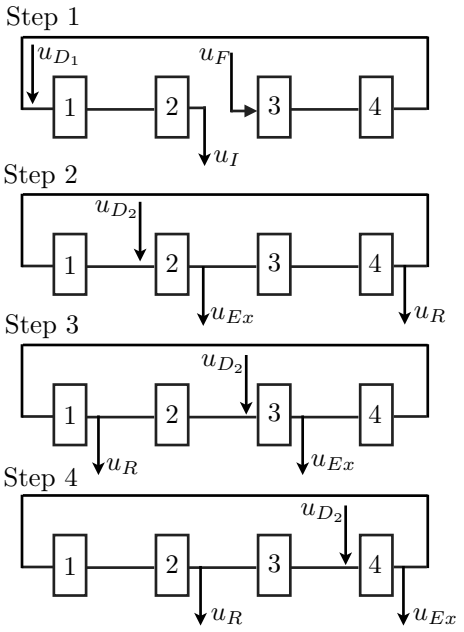

Figure 2: Pseudo-SMB JO process (Mata et al., 2001).

SMB Full Superstructure

As discussed before, the rationale behind developing the full superstructure is to find best ternary separation strategy among various possible alternatives of SMB. A schematic of the SMB full superstructure formulation has been shown in Figure 3. The symbols $u_F^j(t)$ and $u_D^j(t)$ refer to the feed and desorbent inlet velocities of the j^{th} column respectively. The symbols $u_{Ex}^j(t)$, $u_R^j(t)$ and $u_I^j(t)$ refer to extract, raffinate and intermediate stream outlet velocities of j^{th} column respectively. The full superstructure consists of multiple columns connected to each other in a cycle and divided into multiple numbers of zones by various inlet and outlet streams. Clearly, the full superstructure considers a large number of possibilities of supplying desorbent/feed as well as separating out ternary components.

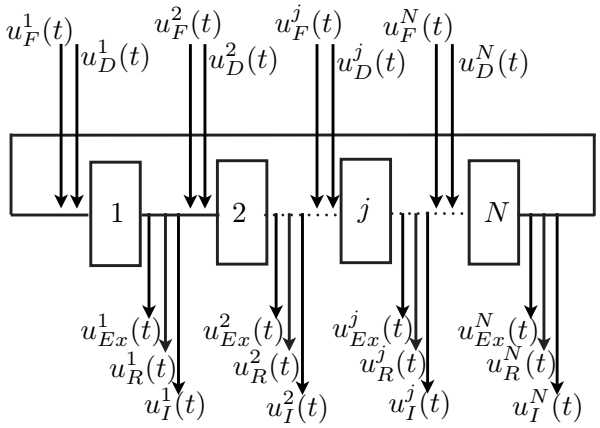

Figure 3: SMB full superstructure formulation for ternary separation

Referring to Figure 3, the volume and component balance equations between the j^{th} and $(j+1)^{th}$ column are written as follows:

$$u^{j+1}(t) = u^j(t) - u_R^j(t) - u_{Ex}^j(t) - u_I^j(t) + u_D^{j+1}(t) + u_F^{j+1}(t). \quad (1.4)$$

$$C_i^{j+1}(0,t)u^{j+1}(t) = C_i^j(L,t)\left(u^j(t) - u_{Ex}^j(t) - u_R^j(t) - u_I^j(t)\right) + C_{F,j}u_F^{j+1}(t). \quad (1.5)$$

where $C_{F,i}$ is the concentration of i^{th} component in the feed inlet and L is the length of the column. Here, the supply of feed and desorbent stream should not drain into product streams without passing through a column. To prevent this situation, the following constraint is implemented. A graphical illustration of this constraint has been presented in a previous study (Kawajiri and Biegler, 2006b).

$$u^j(t) - u_D^j(t) - u_F^j(t) \geq 0 \quad j \in J \quad (1.6)$$

This constraint is crucial for optimization as it restricts the over-dilution of product streams with desorbent. Without this constraint, the optimizer would loose the sensitivity of desorbent velocity, $u_D^j(t)$, unless desorbent consumption appears in the objective function. Furthermore, logic constraints could be imposed in the SMB formulation to avoid

feed/desorbent supply or extract/raffinate/intermediate stream outlets at multiple locations in the same step, which would restrict the number of pumps. In this study however, we do not impose any such logic constraints thus inviting numerous possibilities to operate SMB.

Finally, it should be noted that the full superstructure encompasses the two existing operating schemes, Five-zone SMB and the JO process. These existing operating schemes can be extracted from the full superstructure formulation by enforcing constraints.

Optimization Strategy

Treatment of CSS

The dynamics of a SMB process are characterized by a cyclic steady state (CSS), where the same concentration profiles are created repeatedly in every cycle. In other words, the concentration profiles inside SMB are identical at the beginning and at the end of a cycle. Unlike the study by Kawajiri and Biegler (2006b), we consider the full cycle formulation where the operation during all the four steps is considered:

$$C_i^j(x,0) = C_i^j(x,t_{cycle}), \quad i = 1,\ldots,N_{Comp}, \quad j = 1,\ldots,N_{Column} \tag{1.7}$$

$$q_i^j(x,0) = q_i^j(x,t_{cycle}), \quad i = 1,\ldots,N_{Comp}, \quad j = 1,\ldots,N_{Column} \tag{1.8}$$

Problem Formulation

With the SMB model and CSS constraints, we formulate a single-objective maximization problem, referred as throughput maximization problem, subject to the product specifications. These product specifications are often described in terms of desired purity and recovery. The overall optimization problem is:

$$\min_{u^j(t),u_D^j(t),u_F^j(t),u_{Ex}^j(t),u_R^j(t),u_I^j(t),t_{cycle}} \Phi(t)\left(= \sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_F^j(t)\,dt \right)$$

subject to: Eqs. (1.1)-(1.8),

Raffinate stream product purity:

$$\frac{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_R^j(t) C_{A,R}^j(L,t)\,dt}{\sum_{j=1}^{N_{Column}} \sum_{i=1}^{N_{Comp}} \int_0^{t_{cycle}} u_R^j(t) C_{i,R}^j(L,t)\,dt} \geq Pur_{A,R}^{min}, \tag{1.9}$$

Raffinate stream product recovery:

$$\frac{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_R^j(t) C_{A,R}^j(L,t)\,dt}{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_F^j(t) C_{A,F}^j(t)\,dt} \geq Rec_{A,R}^{min}, \tag{1.10}$$

Intermediate stream product purity:

$$\frac{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_I^j(t) C_{B,I}^j(L,t)\,dt}{\sum_{j=1}^{N_{Column}} \sum_{i=1}^{N_{Comp}} \int_0^{t_{cycle}} u_I^j(t) C_{i,I}^j(L,t)\,dt} \geq Pur_{B,I}^{\min} \tag{1.11}$$

Intermediate stream product recovery:

$$\frac{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_I^j(t) C_{B,I}^j(L,t)\,dt}{\sum_{j=1}^{N_{Column}} \int_0^{t_{cycle}} u_F^j(t) C_{B,F}^j(t)\,dt} \geq Rec_{B,I}^{min}, \tag{1.12}$$

$$u_L \leq u^j(t) \leq u_U \tag{1.13}$$

where Φ is the objective functions corresponding to throughput fed to the SMB process, $C_{A,R}^j(L,t)$ is the concentration of component A in the raffinate stream outlet from the j^{th} column, $C_{B,I}^j(L,t)$ is the concentration of component B in the intermediate stream outlet from the j^{th} column and L is the length of a column. The symbols $Pur_{A,R}^{\min}$ and $Rec_{A,R}^{\min}$ refers to the desired purity and recovery of component A in the raffinate stream. Similarly, $Pur_{B,I}^{\min}$ and $Rec_{B,I}^{\min}$ refers to the desired purity and recovery of component B in the intermediate stream. It is to be noted that we have assumed all the extract outlets, throughout the cycle, are combined together and collected into one extract port. Similarly, raffinate and intermediate streams are also collected into raffinate and intermediate port respectively. The parameters u_U and u_L are the upper and lower bound on zone velocities.

Solution Strategy

The system of equations governing the cyclic steady state of SMB involves both spacial and time domains. There have been two kinds of methodology applied to solve this system of equations: (1) full-discretization, and (2) single-discretization. The full-discretization approach considers discretization of both temporal and spacial domains while single-discretization approach considers only the discretization of spatial domain. The efficacy of full-discretization approach has already been demonstrated with a case study on linear isotherms (Kawajiri and Biegler, 2006a). Hence, in this study, we implement the full discretization approach where the spacial domains are discretized using the central finite difference scheme, and the temporal domain is discretized using Radau collocation on finite elements.

The liquid velocities at all the ports are kept constant in each step of the cycle. This is to ensure that optimal operating scheme obtained from full superstructure does not involve frequent flow rate

changes and could be easily implemented on SMB. Also, the resulting problem has large number of variables and linearized KKT condition tends to have a sparse structure (Kawajiri and Biegler, 2006b). Hence, it is crucial to choose a solver which can handle large number of variables and at the same time exploit the problem structure. To satisfy these requirements, we choose Ipopt 3.0, an interior-point solver, which also utilizes exact second derivative information (Wachter and Biegler, 2006).

Results and Discussion

The optimization problem was solved using Ipopt 3.0 within the AMPL modeling environment. The details of the corresponding modeling parameters are described in Table 1. It is to be noted that five-zone SMB is the only operating scheme where identical operations are repeated while shifting inlet and outlet flows in the direction of liquid flow. This symmetry could be exploited easily to reduce the problem size (Kawajiri and Biegler, 2006a). In all other operating schemes of SMB discussed in this paper, we have considered the full cycle formulation discussed in the previous section.

Table 1: SMB Modeling Parameters

Parameter	Value	Parameter	Value
ε_b	0.389	K_{appl1} (1/s)	6.84×10^{-3}
K_{appl2} (1/s)	6.84×10^{-3}	K_{appl3} (1/s)	6.84×10^{-3}
L (m)	*1.5*	$C_{F,A}$(%)	*33.33*
$C_{F,B}$ (%)	33.33	$C_{F,C}$ (%)	33.33
u_l(m/h)	0	u_u (m/h)	10
K_1	0.19	N_{Comp}	3
K_2	0.39	N	4#
K_3	0.65	$Pur_{A,R}^{min}$	98
$Rec_{A,R}^{min}$	98	$Pur_{B,I}^{min}$	80
$Rec_{B,I}^{min}$	94		

The number of columns considered in five-zone SMB cascade is five.

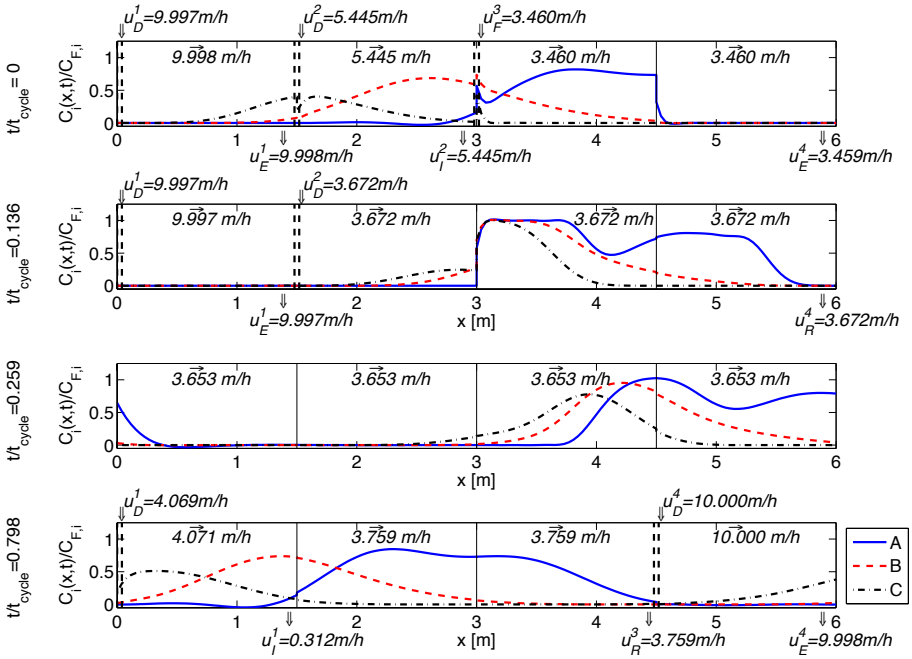

Figure 2: Optimal operating scheme obtained from the full superstructure formulation. The two vertical dashed lines, closely spaced to each other, indicate the breaking of the circuit.

The full superstructure as discussed in the subsection 2.2 of this paper has the potential to find the best ternary separation strategy as it considers numerous possibilities to operate SMB. The number of independent parameters has been drastically increased to 84 (four column velocities, four intermediate, four extract, four raffinate stream outlets and four desorbent inlets in each step, four step times) in the throughput optimization problem. Despite the increase in the number of variables, the full superstructure formulation was successfully optimized. This demonstrates the efficacy of Ipopt solver in handling large-scale optimization problems.

The optimal operating scheme obtained from the full superstructure formulation is shown in Figure 4 along with the normalized concentration profiles at the beginning of each step. The four SMB columns are connected in a cyclic manner separated by the solid vertical lines. The two vertical dashed lines, closely spaced to each other, indicate the breaking of the circuit,

i.e., stopping the liquid flow into the next column from the previous one. The fraction of the beginning of the steps time are also shown vertically to the left side of the figure. In the first step, both columns 1 and 2 are isolated by breaking the circuit and then components B and C are purged into their respective outlet streams forcefully by feeding desorbent at the inlet of first and second column. Hence, we obtain column 4 to be dominating in terms of component A in the beginning of second step. The pure component A and B are recovered through the raffinate and intermediate stream outlets during the second step. The discontinuity in the concentration profiles at the end of second column arises due to the isolation of column 2 in the first step. The third step, on the other hand, is a complete recycle with no inlet and outlet streams. This step takes the longest time, which is required for the concentration profiles to get separated from each other inside the SMB columns. Any removal stream in the third step would result in the contamination of products. In the fourth step, again purging is performed by isolating column 4 and pure components B and C are recovered. This optimal operating scheme although results in high throughput, consumes a larger amount of desorbent because of high amount of purging. Hence, such operating scheme of SMB could be very useful in situations where desorbent is inexpensive compared to overall profit obtained from the purification of products.

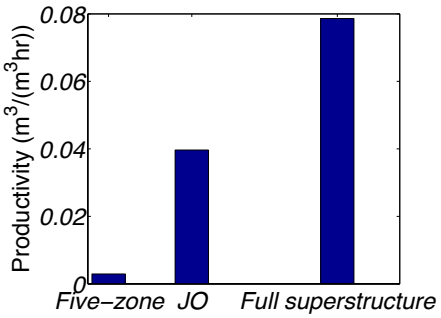

Figure 3: Comparison of optimal productivities.

To compare Five-zone, JO and full superstructure operating schemes together, we show a bar plot depicting productivities obtained in the SMB process (see Figure 5). The throughput obtained is translated in terms of productivity, which is defined as the volume fed to the SMB process per unit volume of the adsorbent per unit time. As can be seen from the figure, the five-zone SMB would be least preferred for ternary separation because of its low productivity. The result obtained from the full superstructure outperforms various operating schemes considered in the literature. There is up to 100 percent increase in the productivity obtained from the full superstructure compared to the JO process.

Conclusions and Future Work

A fully discretized NLP formulation with an SMB full superstructure and interior-point solver has been used to determine best ternary separation strategy. The performance obtained from the full superstructure achieves a considerably higher throughput. In our future work, we would be exploring this study to incorporate nonlinear isotherms considering reduction of desorbent usage as a multi-objective optimization study. An experimental validation of SMB full superstructure would also be performed.

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