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Expanding Simulated Moving Bed Chromatography into Ternary Separations in Analogy to Dividing Wall Column Distillation

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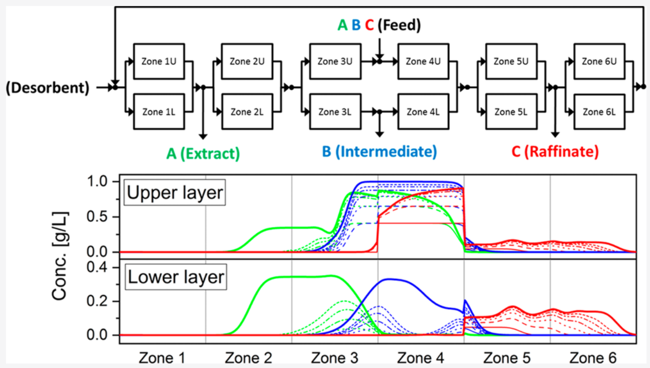
ABSTRACT: Chromatographic separation techniques are widely applied for complex separations. For binary or pseudo-binary separation problems, it is well known that continuous chromatographic separation processes, such as simulated moving bed (SMB) chromatography, are efficient and cost-effective compared to batch or semicontinuous chromatographic separation processes. However, it is still challenging to design a suitable continuous chromatographic process for ternary separations because of its operational and structural complexity. In this work, a new SMB process concept for ternary separations is introduced, considering the operational similarity between SMB chromatography and fractional distillation. Especially, dividing wall column distillation, which is nowadays well-established and widely used for multicomponent fractional distillation, is adopted for a novel continuous SMB design concept by parallelizing the zones to two layers. A modified shortcut design method for the new design concept is presented in case of linear adsorption isotherms. This new concept is validated in the simulation study and compared with alternative SMBs.



1. INTRODUCTION

In fine chemical and pharmaceutical industries, chromatographic separation techniques are widely used to isolate valuable target components from complex mixtures. The simulated moving bed (SMB) technology was introduced and developed as one of the most promising continuous separation in liquid—solid chromatography for the separation of binary and pseudo-binary.[1] The conventional four-zone SMB forms a closed ring with several packed columns. This ring is divided into four zones by two inlets (feed and desorbent) and two outlets (extract and raffinate). The positions of four ports are shifted to the next positions in the direction of the liquid-phase flow to simulate the counter-current flow of the solid phase. A feed mixture continuously enters into the process through the feed port, and desorbent—usually the same solvent composition as feed solution—enters into the process through the desorbent port. The mixture components are separated in the chromatographic columns and collected at two outlets (raffinate: less-retained components, extract: more-retained components). Although the true counter-current separation processes—such as fractional distillation—reach the steady state, the SMB process does not reach the steady state but the cyclic steady state (CSS) because of the periodic repetition of port switching.

For the ternary separation, few modified SMB configurations were introduced for continuous and semicontinuous separations. In semicontinuous separations, the feed mixture is fed into the SMB process intermittently, which means that a certain part of operation is carried out without feeding; meanwhile, separations take place in batch manner.[2−4] These configurations are simple—even simpler than the conventional four-zone SMB process—and easy to adopt the gradient elution of solvents or buffers.[5,6] In some specific applications, these semicontinuous processes are beneficial. However, the process performances, productivity, and desorbent consumption are not significantly improved compared to batch operations.

One straightforward configuration for continuous ternary separations is called "SMB-cascade", which uses two conventional four-zone SMBs in series.[7] For example (ternary separation of components A, B, and C with the elution order of C → B → A), the first sub-SMB isolates the more-retained component (A) in the extract stream while the raffinate stream that contains the intermediate component (B), and the less-retained component (C) is fed into the second sub-SMB to separate them. Even though this configuration is versatile and efficient compared to batch chromatography,[8,9] it is not widely used because of high complexity and investments.

To overcome these drawbacks, some innovative alternative configurations that can be realized in one SMB ring were

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introduced. However, these configurations are only available in restricted conditions. As an example, the more-retained component should have larger selectivity than the less-retained component in "3F-SMB".[10] The other attractive SMB configuration, which is known as "eight-zone SMB", was introduced for the ternary separation.[11] Because the second four-zone sub-SMB is consecutively integrated in one SMB ring, two sub-SMBs share the columns and are operated with the same port-switching intervals. Therefore, the performance of the eight-zone SMB cannot exceed that of the SMB cascade.

In this work, a new continuous SMB process concept, which is based on the analogy of the dividing wall column distillation process,[12] was introduced. Exploiting the shortcut design method based on the equilibrium theory, the process performance of the new SMB process was compared with the early-established continuous ternary SMB processes, the eight-zone SMB and the SMB cascade. In detailed process simulation, the new SMB process was validated for two specific separation problems.

2. NEW SMB CONCEPT APPLYING ZONE PARALLELIZATION

2.1. Analogy between SMB Chromatography and Distillation. In principle, the structure of the conventional four-zone SMB process is similar to the fractional distillation tower, so that two SMB zones, the zones 2 and 3, can correspond to the major constituents of the distillation tower, the stripping and rectifying sections, respectively, as shown in Figure 1. The

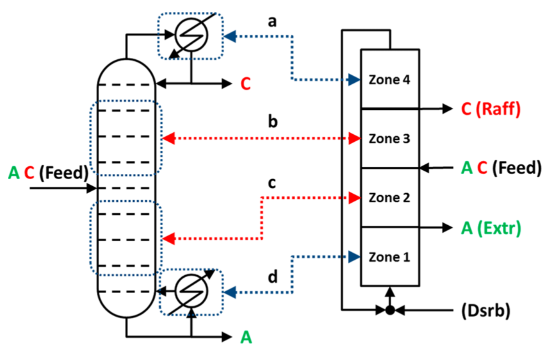

Figure 1. Schematic illustrations of similarity between the fractional distillation tower (left) and the conventional four-zone SMB (right). Strong constituent similarity: rectifying section ↔ zone 3 (b), stripping section ↔ zone 2 (c); and weak constituent similarity: condenser ↔ zone 4 (a), reboiler ↔ zone 1 (d).

roles of the zones 1 and 4 do not perfectly correspond to the reboiler and condenser, respectively. However, these are related in aspect of sustaining counter-current operation. In the SMB process, two carriers, the solid adsorbent and liquid desorbent, are regenerated in the zones 1 and 4, respectively, and recycled to the zones 4 and 1 to sustain simulated counter-current movement, whereas the component itself can move upward (vapor) or downward (liquid) without any carrier in the distillation tower. The distillation tower consumes energy to produce vapor and liquid refluxes at the reboiler and the condenser, respectively. These refluxes maintain consistent counter current for continuous separation. In the SMB process, additional desorbent is required to regenerate the column in the zone 1 with the recycled desorbent from the zone 4. Therefore, energy consumption in the distillation tower (energy-intensive) can be interpreted to desorbent consumption in the SMB process (material-intensive).

In the SMB process, the simulated solid-adsorbent flow rate is determined by the size of column and the port-switching interval. In most cases, all ports are switched at once, and the identical columns are used, that is, most of SMB process concepts were developed with the uniform simulated solid flow. Because of this restriction, only the sequential distillation concepts were applied in the design of SMB process known as the SMB cascades. However, it is easy to manipulate the counter-current flows in the distillation tower, that is, the vapor and liquid flows can be manipulated by changing the cross-sectional area of the distillation tower. For multicomponent distillation, the dividing wall column was widely used in many applications to simplify the structure of process and reduce energy consumption.[13,14] In the following sections, a new SMB configuration is introduced to mimic the concept of dividing wall column distillation using the zone parallelization.

2.2. Parallelization of Double-Layer Zones for Ternary Mixture Separation. As introduced in Figure 2a, one simple

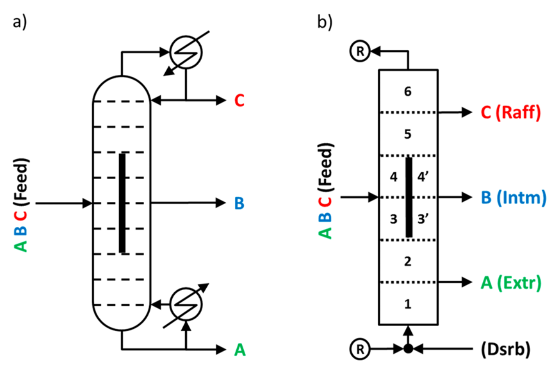

Figure 2. Schematic illustrations of the single dividing wall distillation tower (a) and the analogous SMB configuration (b). Thick vertical line: dividing wall (distillation) and isolated zone parallelization (SMB); recycle stream; feed: feed stream; Dsrb: desorbent stream; Extr: extract stream; Intm: intermediate stream; and Raff: raffinate stream.

dividing wall column distillation concept was developed for the ternary mixture distillation with a single dividing wall. The fed intermediate volatile component (B) returns at both ends of the dividing wall by modulating the vapor- and liquid-phase flows. The returned intermediate volatile component is purified and collected in the middle of the opposite side of dividing wall. A new conceptual SMB configuration analogous to this single dividing wall column distillation is shown in Figure 2b. It has eight zones including two pair of parallelized zones, the zones 3 (4) and 3′ (4′). To simulate splitting and merging solid flows in two pair of parallelized zones, the nonparallelized zones (1, 2, 5, and 6) should have two parallel sub-zones. Therefore, it is named "double-layer SMB", and at least 12 columns are required for this configuration.

3. DESIGN AND SIMULATION OF DOUBLE-LAYER SMB

One of the most well-established shortcut design method for SMB processes is the triangle theory.[15] In this method, the design parameters—the ratios of the net liquid-phase flow to the simulated counter-current solid-phase flow—are defined as

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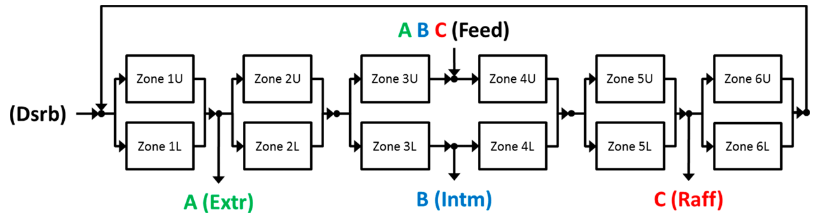

Figure 3. Schematic flow diagram and zone configuration of the double-reflux double-layer SMB process for center-cut separations. U: upper layer; L: lower layer; parallel flow expression; feed: feed stream; Dsrb: desorbent stream; Extr: extract stream; Intm: intermediate stream; and Raff: raffinate stream.

$$m_j = \frac{Q_j t_S - \varepsilon_T V_C}{(1 - \varepsilon_T) V_C} \tag{1}$$

where m is the flow-rate ratio, Q is the volumetric flow rate of the liquid phase, ε_T is the total void fraction of the column ($=\varepsilon_I + (1 - \varepsilon_I)\varepsilon_P$), ε_I and ε_P are the inter and intraparticle void fractions of the column, respectively, t_S is the port-switching interval, V_C is the column volume, and the subscript, j, denotes the zone j. If the flow-rate ratio of the zone j, (m_j), is greater than the partition coefficient of component i ($K_i = q_i/c_i$, the concentration ratio of the solid phase, q_i to the liquid phase, c_i), the component i moves toward the liquid flow direction in the zone j, and vice versa. Productivity and desorbent consumption can be obtained, corresponding to the feasible operating conditions determined with the partition coefficients and the zone flow-rate ratios. Because the triangle theory is based on the equilibrium theory, the maximum productivity and the minimum desorbent consumption obtained using the triangle theory are only theoretically feasible. Therefore, further process simulations using the detailed material balance are required. In this work, it was presumed that all components obey the linear isotherms, that is, the partition coefficients are constant.

3.1. Shortcut Design Method for Double-Layer SMB.

To implement the parallelized layers in the SMB configuration, the corresponding upper and lower layer inlet and outlet streams should be properly merged and split. Figure 3 shows the schematic flow diagram and zone configuration of the double-layer SMB by integrating the upper (U) and the lower (L) six-zone sub-SMBs. A ternary feed is fed between the zones 3U and 4U. The less-retained (C) and more-retained (A) components are collected at the raffinate and extract ports, respectively, with the same manner of the conventional four-zone SMB configuration. By manipulating the flow rates of the zones 2 and 5, it is possible to prevent the intermediate component (B) from contaminating the extract and raffinate products and concentrate the intermediate component in the zones 3L and 4L because the upper and lower layers in the zones 3 and 4 are isolated. The concentrated intermediate component is continuously collected at the intermediate port located between the zones 3L and 4L. Except the feed and intermediate ports, the upper and lower layer outlets should be merged and well mixed. Then, the merged streams split into two to enter the next upper and lower layers. In this configuration, at least five pumps for the external stream and five flow splitters for the double-layer zones (the zone 4 requires no splitter) are required. If one pump is mounted to split flow, 10 pumps are required to control the zone flows properly.

As mentioned above, the SMB zones, except the zones 3 and 4, are divided to the upper and lower layers, but they are operated as one zone, that is, they have the same flow-rate ratios. Only the upper and lower layers in the zones 3 and 4 have different flow-rate ratios, so that the complete separation and regeneration regions can be drawn on the m-value plane (Figure 4) with the following inequalities

$$K_C < m_{3U} < m_{4U} < K_A \tag{2-1}$$

$$K_C < m_{4L} < K_B < m_{3L} < K_A \tag{2-2}$$

$$K_C < m_5 < K_B < m_2 < K_A \tag{2-3}$$

$$m_6 < K_C, \qquad K_A < m_1 \tag{2-4}$$

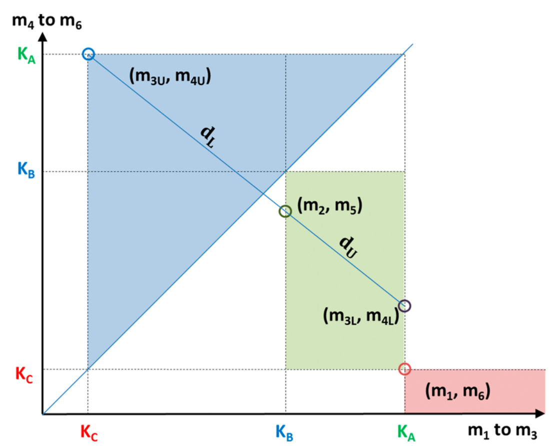

Figure 4. Complete separation (blue and green) and regeneration (red) regions of the double-layer SMB for linear adsorption isotherms. Circles: optimum operating conditions; arrows: distance of operating conditions; U: upper layer; L: lower layer; and $K_A > K_B \gg K_C$.

where the subscripts, U and L, denote the upper and the lower layers and the subscripts, respectively, A, B, and C denote the more-, intermediate-, and less-retained components, respectively. According to eq 2-1, the complete separation region for the components A and C can be decided as the blue separation region. As the same manner of the conventional four-zone SMB design, m_{4U} should be bigger than m_{3U} to have positive feed inlet flow, and they should be in between K_C and K_A to separate the less-retained and more-retained components. To maximize the feed throughput, the operating point on the blue separation region, (m_{3U}, m_{4U}), should be located far from the diagonal line. Equation 2-2 represents the condition for the complete isolation of the intermediate-retained component, B, in the lower layers of the zones 3 and 4. Contrary to the upper layer, m_{4L} should be smaller than m_{3L} to have positive intermediate-retained product outlet flow. To avoid contamination, they should be also in between K_C and K_A. For the zones 2 and 5, the same roles of the lower layers of the zones 3 and 4 should be applied, respectively, c.f. eqs 2 and 3. Therefore, two operating points, (m_{3L}, m_{4L}) and (m_2, m_5), should be on the green separation region to separate

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ternary mixture completely. Because the liquid-phase flows in the zones 2 and 5 are the summation of the liquid-phase flows in the zones 3U and d_L, 4U and 4L, respectively, the three above-mentioned operating points should be on a straight line. The distance ratio, d_L/d_U, represents the volume ratio of the lower to upper layers

$$r_{L/U} = \frac{d_L}{d_U} = \frac{m_2 - m_{3U}}{m_{3L} - m_2} = \frac{m_5 - m_{4U}}{m_{4L} - m_5} \tag{3}$$

where $r_{L/U}$ is the volume ratio of the lower to upper layers, d_L is the distance between two operating points, (m_{3U}, m_{4U}) and (m_2, m_5), and d_U is the distance between two operating points, (m_{3L}, m_{4L}) and (m_2, m_5). The productivity, which is the production rate per unit volume of system, is maximized, where $r_{L/U}$ is minimized. In the separation problem, as described in Figure 4 ($K_A > K_B \gg K_C$), $r_{L/U}$ is minimized, where $m_{3U} = K_C$, $m_{3L} = K_A$, and $m_2 = K_B$. In the opposite separation problem ($K_A \gg K_B > K_C$), $r_{L/U}$ is minimized, where $m_{4U} = K_A$, $m_{4L} = K_C$, and $m_5 = K_B$. The red region indicates the m-values of the zones 1 and 6 for the complete regeneration of adsorbent and desorbent, respectively. Desorbent consumption, which is proportional to the difference between m_1 and m_6, is minimized, where (m_1, m_6) = (K_A, K_C).

3.2. Performance Criteria for Comparing Ternary SMB Processes. To compare the double-layer SMB with two other alternative ternary SMBs, the eight-zone SMB and the SMB cascade, two process performance parameters, productivity and desorbent consumption, were considered. In CSS, productivity (Pr) and desorbent consumption (DC) are defined as

$$\mathrm{Pr}_i = \frac{\{\text{mass of purified component i for one port switching interval}\}}{\{\text{volume of adsorbent}\}\{\text{time of one port switching interval}\}} \tag{4-1}$$

$$\mathrm{DC}_i = \frac{\{\text{volume of solvent used for one port switching interval}\}}{\{\text{mass of purified component i for one port switching interval}\}} \tag{4-2}$$

In linear isotherms, the optimal design parameters, m_j, can be assigned to the corresponding partition coefficients in the equilibrium theory-based shortcut design method. Therefore, the reduced productivity and desorbent consumption, $\widehat{\mathrm{Pr}}_i$ and $\widehat{\mathrm{DC}}_i$, at the given optimal operating conditions, can be expressed as a function of the partition coefficients.

$$\widehat{\mathrm{Pr}}_i = \frac{\mathrm{Pr}_i t_S}{c_{F,i}} = \widehat{\mathrm{Pr}}_i(K_{AB}, K_{BC}, K_{AC}) \tag{5-1}$$

$$\widehat{\mathrm{DC}}_i = c_{F,i}\mathrm{DC}_i = \widehat{\mathrm{DC}}_i(K_{AB}, K_{BC}, K_{AC}) \tag{5-2}$$

where K_{ij} is the partition coefficient difference between the components i and j ($=K_i - K_j$), and $c_{F,i}$ is the feed concentration of the component i. The shortcut design methods for the eight-zone SMB and the SMB cascades are described in Appendixes A.1 and A.2.

3.3. Process Description and Detailed Simulation Study. For a detailed simulation study, the process and model parameters were chosen and are listed in Table1.[10] For the chromatographic column simulation, the linear driving force model for mass transfer and constant dispersion model were chosen. The mass balance equations for the chromatographic column are

$$\varepsilon_T \frac{\partial c_i}{\partial t} + (1 - \varepsilon_T)\frac{\partial q_i}{\partial t} + v_L \frac{\partial c_i}{\partial z} = \varepsilon_I D_L \frac{\partial^2 c_i}{\partial z^2} \tag{6-1}$$

Table 1. Process and Model Parameters of the Double-Reflux Double-Layer SMB for Detailed Simulation Study[10]

parameters	values
Process	
column dimensions[a] [cm]	1.0 (I.D.), 15 (length)
column configurations	1 column per zone
column void fraction, ε_I and ε_P	0.4, 0.667
Model Mixture (dA, dT, dG, dC)	
isotherm model	linear
isotherm parameters, K_i	27.7, 9.6, 7.4, 3.15
mass transfer coefficient, $k_{eff,i}$ [1/min]	6.0, 30, 30, 60
axial dispersion coefficient, D_L [cm^2/min]	0.225
Design Constraints	
feed concentration, $c_{F,i}$	1.0, 1.0, 1.0, 1.0
port-switching interval, t_S [min]	10
margin for separation region	10%
margin for regeneration region	20%

[a]The column dimensions in the upper layer of the double-layer SMB and the first sub-SMB of the SMB cascade.

$$\frac{\partial q_i}{\partial t} = k_{eff,i}(q_i^* - q_i) \tag{6-2}$$

$$q_i^* = K_i c_i \tag{6-3}$$

where c and q are the concentrations in the mobile and the stationary phases, respectively, q^* is the equilibrium concentration of the solid film, D_L is the axial dispersion coefficient, k_{eff} is the mass transfer coefficient, v_L is the linear velocity of the mobile phase, and the subscript, i, denotes the component i. In this simulation study, no system void volume and no hold-up volume between sub-SMBs, such as a buffer tank between two SMBs in the SMB cascade, were considered.

Two ternary mixtures (dA/dT/dG and dT/dG/dC) were arbitrary chosen for different separation problems. In the former model mixture, the retention of the intermediate-retained component (dT) is extremely biased toward the retention of the less-retained component (dG). In the latter model mixture, the intermediate-retained component (dG) is more or less in the middle of two more- and less-retained components, dT and dC, respectively.

As described in Section 3.1 and Appendix A.2, the columns with different volumes can be used in the double-layer SMB and the SMB cascade, and the size ratios can be decided from the design parameters. Therefore, the column dimensions of the upper layer in the double-layer SMB and the first sub-SMB in the SMB cascade were fixed to 1.0 cm × 10 cm as the column dimensions of the eight-zone SMB. To hold the same length, the inner diameter of the columns in the lower zones or the second sub-SMB was correspondingly changed to satisfy the size ratios.

The port-switching interval, t_S, and the feed concentrations, $c_{F,I}$, were fixed to 10 min and 1.0 g/L, respectively. The operating conditions were obtained with 10 and 20% of margins of the separation and regeneration regions, respectively. Aspen Chromatography (Aspen Tech Inc., USA, Ver. 8.8) was used to simulate the SMB processes. For the PDE solver, BUDS scheme and Gear integration algorithm were used with 100 spatial nodes. To reach CSS, the simulation was carried out up to 80 port-switching intervals.

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Table 2. Comparisons of the Optimal Productivities and Desorbent Consumptions of the Double-Layer SMB, the Eight-Zone SMB, and the SMB Cascade for the Complete Ternary Separation

	DoF[a]	$\widehat{\mathrm{Pr}}_{\mathrm{B}}$[b]	$\widehat{\mathrm{DC}}_{\mathrm{B}}$[b]
double-layer SMB	8	$\dfrac{\min(K_{AB}, K_{BC})}{6}$	$1 + \dfrac{K_{AC}}{\min(K_{AB}, K_{BC})}$
eight-zone SMB	8	$\dfrac{K_{AB}K_{BC}}{8K_{AC}}$	$\dfrac{2(K_{AC})^2}{K_{AB}K_{BC}}$
SMB-cascade	9	$\dfrac{K_{AB}K_{BC}}{4(\min(K_{AB}, H_{BC}) + K_{AC}r_{ts})}$	$1 + \dfrac{K_{AC}(1 + r_{ts})}{\max(K_{AB}, K_{BC})}$

[a]DoF = Degree of Freedom. [b]Reduced productivity and desorbent consumption with respect to the key component, B.

4. RESULTS AND DISCUSSION

The shortcut design method based on the equilibrium theory is often used to assess the process feasibility in the early stage of process design. For the feasibility of the double-layer SMB, two early-established alternative ternary SMB processes, the eight-zone SMB and the SMB cascade, were compared, exploiting the shortcut design method.

4.1. Comparisons of Three Ternary SMB Configurations in the Equilibrium Theory. According to the short-design methods of the double-layer SMB and two alternative ternary SMBs, these SMB processes were compared with respect to productivity and desorbent consumption. Table 2 shows the productivity and desorbent consumption of three ternary SMB processes at the optimal operating conditions obtained from the equilibrium theory-based shortcut design methods. As described in Section 3.1 and Appendixes A.1 and A.2, the shortcut design methods do not consider any band-broadening effect, such as axial dispersion and mass transfer resistance. The detailed computational procedures are described in Appendix A.3. The optimal operating conditions were chosen to maximize productivity and minimize desorbent consumption. It means that they are the theoretically achievable maximum productivity and minimum desorbent consumption.

In the eight-zone SMB and the double-layer SMB, two SMBs—two consecutive four-zone SMBs and two parallelized six-zone SMBs, respectively—are integrated in one SMB ring, so that both SMB systems have the same eight degrees of freedom, seven zone flow-rate ratios, and one port-switching interval (or the size of system). On the other hand, the SMB cascade consists of two sequential and independent four-zone SMBs. Therefore, it has nine degrees of freedom, seven zone flow-rate ratios, and two port-switching intervals (or the sizes of two sub-SMB systems). It seems that the SMB cascade can provide better performance than others, and the double-layer SMB performance is in between the SMB cascade and the eight-zone SMB.

In ternary separation of SMB processes, the key component is the intermediate-retained. If the intermediate-retained component can be completely isolated with no contamination of more- and less-retained components by recycling, ternary mixture can be completely separated. Therefore, the productivity and desorbent consumption with respect to the intermediate-retained component (B) were compared at the optimal complete separation conditions. In the eight-zone SMB process, a certain ratio of the internal recycle stream is drained because the second sub-SMB that shares the same columns with the first sub-SMB cannot take entire amount of recycled product stream from the first sub-SMB. Because of a certain loss in the internal recycle stream, the eight-zone SMB provides the worst performance among three compared ternary SMB processes. In the case, where $K_{AB} = K_{BC}$, the double-layer SMB can provide 2.67 times higher productivity and consume 62.5% less desorbent consumption than the eight-zone SMB.

The productivity and desorbent consumption of the SMB cascade are changed by the ratio of the port-switching intervals, r_{ts}. In Figure 5, the double-layer SMB was compared with the SMB cascades with various port-switching interval ratios. In the case, where the SMB cascade holds $r_{Size} = 1$, that is, the second sub-SMB size is the same as the first sub-SMB size but has shorter port-switching interval than the first sub-SMB, and the double-layer SMB provides better productivity and lower desorbent consumption in the narrow range, $0.42 < K_{AB}/K_{AC} < 0.58$. The productivity is 1.3 times higher, and desorbent is 25% less consumed, where $K_{AB} = K_{BC}$. As the SMB cascade has bigger size of the second sub-SMB than that of the first sub-SMB, the double layer provides better process performances than the SMB cascade in the wider range of K_{AB}/K_{AC}. The double-layer SMB provides better productivity than the SMB cascade in the entire range of K_{AB}/K_{AC}, where $r_{tS} \geq 1.5$. In the SMB cascade, the productivity increases as the port-switching interval of the second sub-SMB is shorter, that is, the size of sub-SMB is smaller. However, it means that the second sub-SMB should be operated under the conditions of faster zone flow rates in smaller zone volumes, which is not practically preferable. In the case, where $r_{ts} = 1$, that is, the second sub-SMB size is greater than the first sub-SMB size, and the linear velocity of liquid phases in both sub-SMBs is similar. The double-layer SMB provides two times higher productivity and consumes 40% less desorbent compared to the SMB cascade, where $K_{AB} = K_{BC}$.

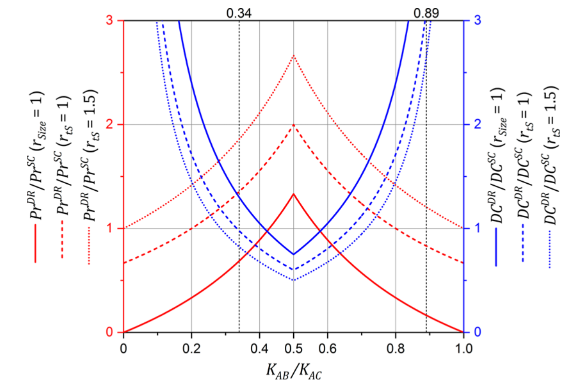

Figure 5. Comparisons of the double-layer SMB and SMB cascades in terms of productivity and desorbent consumption. The superscripts, DR and SC, denote the double-layer SMB and the SMB cascade, respectively. The black dotted grids indicate K_{AB}/K_{AC} = 0.34 and 0.89.

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Table 3. Design Parameters and Performances of Three Ternary SMBs

process	mixture	case	m_1	m_2	m_{3U}	m_{4U}	m_{3L}	m_{4L}	m_5	m_6	$r_{L/U}$	purity [%] A	purity [%] B	purity [%] C	yield [%] A	yield [%] B	yield [%] C	$Pr_B \times 10^{-2}$ [g/L–h]	$DC_B \times 10^1$ [L/g]
double-layer SMB	dA/dT/dG	1	33.2	24.4	8.14	24.9	24.9	8.14	8.64	5.92	33.6	100	88.0	100	88.8	99.7	97.5	9.68	5.74
		2	33.2	10.6	8.14	24.9	10.6	8.14	8.64	5.92	33.6	100	98.6	99.9	99.6	100	98.8	9.69	5.73
	dT/dG/dC	3	11.5	8.14	3.47	8.64	8.64	3.47	3.92	2.52	10.4	100	93.8	100	97.2	100	96.0	9.99	1.90
		4	11.5	8.14	3.47	8.64	8.64	6.47	6.66	2.52	10.4	100	98.0	100	98.2	100	99.7	9.99	1.90

process	mixture	case	m_1	m_2	m_3	m_4	m_5	m_6	m_7	m_8	r_{Loss}[a]	purity [%] A	purity [%] B	purity [%] C	yield [%] A	yield [%] B	yield [%] C	$Pr_B \times 10^{-2}$ [g/L–h]	$DC_B \times 10^1$ [L/g]
eight-zone SMB	dA/dT/dG	5	33.2	8.14	8.64	5.92	33.2	10.6	24.9	7.68	0.43	100	95.9	99.3	98.6	55.8	56.7	4.16	19.2
		6	33.2	10.5	24.9	5.92	11.5	8.14	8.64	5.92	0.97	99.6	95.3	95.9	96.1	2.6	2.6	5.60	12.7
	dT/dG/dC	7	11.5	3.47	6.66	2.52	11.5	8.14	8.64	5.92	0.94	99.8	98.8	99.1	6.1	6.1	99.0	2.93	9.11
		8	11.5	8.14	8.64	2.52	8.88	3.47	6.66	2.52	0.48	99.3	98.2	100	98.8	51.9	51.8	3.86	6.15

process	mixture	case	m_1	m_2	m_3	m_4	m_5	m_6	m_7	m_8	r_{Size}[b]	purity [%] A	purity [%] B	purity [%] C	yield [%] A	yield [%] B	yield [%] C	$Pr_B \times 10^{-2}$ [g/L–h]	$DC_B \times 10^1$ [L/g]
SMB cascade	dA/dT/dG	9	33.2	8.14	8.64	5.92	33.2	10.6	24.9	7.68	1.75	99.9	96.6	99.3	97.7	99.0	98.6	5.37	14.7
		10	33.2	10.6	24.9	5.92	11.5	8.14	8.64	5.92	38.0	99.6	97.3	98.3	96.1	99.5	99.3	11.0	1.78
	dT/dG/dC	11	11.5	3.47	6.66	2.52	11.5	8.14	8.64	5.92	16.1	99.7	98.6	99.1	99.1	99.1	99.0	5.54	3.24
		12	11.5	8.14	8.64	2.52	8.88	3.47	6.66	2.52	1.92	99.3	98.2	99.9	98.8	99.4	99.2	5.08	4.39

[a]The ratio of loss in the internal recycle stream: $r_{Loss} = (Q_{E,1} - Q_{F,2})/Q_{E,1} = 1 - (m_7 - m_6)/(m_1 - m_2)$ in nos. 5 and 7 and $r_{Loss} = (Q_{R,1} - Q_{F,2})/Q_{R,1} = 1 - (m_7 - m_6)/(m_3 - m_4)$ in nos. 6 and 8. [b]The size ratio where $r_{tS} = 1$: $r_{Size} = (m_1 - m_2)/(m_7 - m_6)$ in nos. 9 and 11 and $r_{Size} = (m_3 - m_4)/(m_7 - m_6)$ in nos. 10 and 12.

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4.2. Validation of the Principle of Double-Layer SMB in Detailed Simulation Study. The equilibrium theory does not take into account the band-broadening effect that is mostly caused by axial dispersion and finite mass transfer between two phases. For detailed approach, the double-layer SMB was validated in the simulation study with the model parameters obtained from the literature. Two ternary mixtures, dA/dT/dG and dT/dG/dC, were chosen for the validations of different separation problems (dA/dT/dG: K_{AB}/K_{AC} = 0.89 and dT/dG/dC: K_{AB}/K_{AC} = 0.34). The operating conditions were obtained from the 10% of the separation region margin. To prevent the contamination caused by bad regeneration of the liquid and solid phases, the regeneration region margin was set to 20%. For example, the design parameters for the upper layer of the zones 2 and 3 are 1.1K_C and 0.9K_A, respectively, and the design parameter for the zones 1 is 1.2K_A. In the upper tier of Table 3, the selected operating conditions and the process performances were described. In this work, no further optimization of the operating conditions was performed for three SMB processes considered. However, the safety margins applied in the separation and regeneration regions were arbitrary chosen to demonstrate the performance of double-layer SMB.

To investigate the development of the internal concentration profiles, the double-layer SMB simulation was observed with the operating conditions of case 4 (Figure 6). At the beginning of the port-switching interval, the fresh feed enters into the zone 4U, and then, the front end of intermediate- and less-retained component profiles penetrates the zone 2 while the more-retained component remains in the zone 4U. At the end of the port-switching interval, two columns in the zone 2—they are operated as a single column—split and move to the upper and lower layers in the zone 3 correspondingly. On the opposite side, the less-retained component is eliminated in the zone 3U, and the column that contains only the more- and intermediate-retained components moves to the zone 5 at the end of port-switching interval. In the next port-switching interval, the more- and intermediate-retained components penetrate the zone 3L. Therefore, the intermediate-retained component turns around at the zones 2 and 5. After further separation in the zones 3 and 4L, the purified intermediate-retained component is collected at the intermediate product stream. As shown in Figure 6a, the development of lower layer internal concentration profile of the intermediate-retained component starts at the inlet of the zone 3L and the outlet of the zone 4L. At the CSS, the internal concentration profiles of all three components are well developed around the designated product ports. Figure 6b shows the concentration histories of three product streams. In four complete SMB cycles—24 port-switching intervals in one column per zone configuration—the double-layer SMB can reach the CSS.

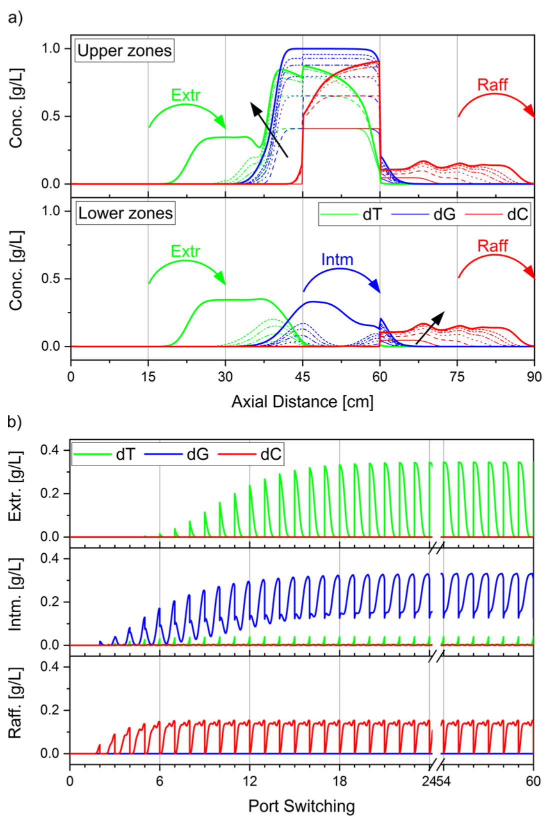

Figure 6. Development of internal concentration profiles at the end of the port-switching interval (a) and the product stream concentration histories (b) of the double-layer SMB with the operating conditions of case 4 in Table 3. The black arrows indicate the direction of internal concentration profile development from the first to sixth port-switching intervals and the CSS (thick profiles). The colored arrows indicate the port switching of corresponding ports for the next cycle operation.

In Figure 7, the key design parameters for the ternary separation (m_2−m_5) used in cases 1−4 were drawn on the m-plane with the complete separation regions obtained from the shortcut design method. For the separation of dA/dT/dG mixture (Figure 7a), the region for complete isolation of the intermediate-retained component (dT) is narrow because the intermediate-retained component retention is extremely biased toward the less-retained component (dG). In this case, two operating points for the zones 2 and 5, and the zones 3L and 4L are very close. It means that the size of lower zones is much greater than the size of upper layer ($r_{L/U}$ = 33.6). In the other separation problem (Figure 7b), the intermediate-retained component is not extremely biased, so that it is possible to separate the ternary mixture with a small size ratio ($r_{L/U}$ = 10.4) compared to the former separation problem. As discussed in the previous section (Table 2), the productivity of the double-layer SMB is proportional to min(K_{AB},K_{BC}). Because the minimum partition coefficient difference is K_{dTdG}, and the same design constraints were applied in both separation cases, the productivities of cases 1−4 are very close. However, the partition coefficient differences of the more- and less-retained components, K_{AC}, are K_{dAdG} and K_{dTdC} for former and latter model mixtures, respectively, so that the desorbent consumption of the dA/dT/dG separation cases (cases 1 and 2) is higher than the other separation cases (cases 3 and 4).

Maintaining the same size ratio $r_{L/U}$, the operating points on the region for complete isolation of the intermediate-retained component can move horizontally (Figure 7a) or vertically (Figure 7b). As the operating points are far from the diagonal line (cases 1 and 3), the difference between m_{4L} and m_{3L} increases, that is, the flow rate of the intermediate stream increases. Because the feed throughput ($m_{4U} - m_{3U}$) is fixed, the intermediate product concentration decreases. On the contrary, the extract stream in case 1 and the raffinate stream in case 3 decrease correspondingly. Therefore, the double-layer SMB can provide various enrichment of intermediate product while maintaining other process performances, productivity and desorbent consumption. Table 4 shows the product stream enrichments of cases 1−4. In case 1, the zone 2 flow rate (m_2) is

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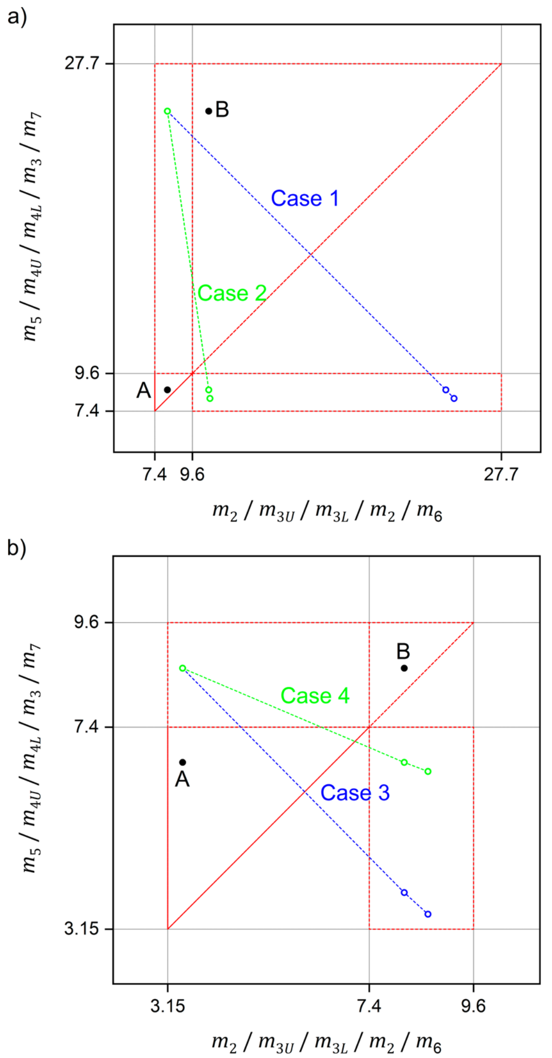

Figure 7. Separation regions and key design parameters for dA/dT/dG mixture (a) and dT/dG/dC mixture (b). Cases 1−4 represent the operating conditions of the double-layer SMB. The points A and B represent the operating conditions of the eight-zone SMB and the SMB cascade. Complete design parameters are listed in Table 3.

Table 4. Product Enrichment of the Double-Layer SMB in Various Operating Conditions

mixture	case	enrichment[a] Extr.	Intm.	Raff.
dA/dT/dG	1	0.049	0.030	0.175
	2	0.021	0.200	0.177
dT/dG/dC	3	0.144	0.107	0.332
	4	0.145	0.255	0.120

[a]{the average target component concentration in the product stream}/{the target component concentration in the feed stream}.

much greater than case 2. It means that the more-retained component can leave the zone 2 and penetrate the zone 3L, so that the purity of the intermediate-retained component in case 1 is lower than in case 2. Because of the similar effect, the purity of the intermediate-retained component in case 3 is lower than in case 4. For both separation problems tested in this work, the operating conditions for enriched intermediate products (cases 2 and 4) provide better purities and recovery yields than others (cases 1 and 3).

4.3. Comparisons of Three Ternary SMB Configurations in Detailed Simulation Study.

In Section 4.1, the feasibility of the double-layer SMB process was accessed by comparing with two alternative ternary SMB processes, exploiting the equilibrium theory-based shortcut design method. In this section, these three ternary SMB processes were compared for the specific separation problems tested in Section 4.2. Under the same design constraints applied in the design of the double-layer SMB process, the design parameters and process performances were listed in the middle and lower tiers of Table 3. Both alternative ternary SMB processes should be designed corresponding to the specific separation order—more- and intermediate-retained component separation first or intermediate- and less-retained component first, so that each separation problem can have two alternative conditions. For dA/dT/dG mixture separation, the design parameters of cases 5 and 9 (the eight-zone SMB and the SMB cascade, respectively) were determined to conduct relatively difficult separation (dT and dG separation) in the first sub-SMBs, and then the second sub-SMBs were carried out to determine relatively easy separation (dA and dT separation). The design parameters of cases 6 and 10 were determined for the opposite separation order. On the contrary, the design parameters of cases 7 and 11 were determined to conduct easy-to-difficult separation, and the design parameters of cases 8 and 12 were determined to conduct difficult-to-easy separation for the eight-zone SMB and the SMB cascade, respectively.

The general rule of thumb for the SMB cascade design is the easy-to-difficult separation order. Therefore, case 10 provides much higher productivity and consumes less desorbent compared to case 9 for the dA/dT/dG separation. In the aspect of process size, case 10 requires quite different sizes of two sub-SMBs (r_{Size} = 38.0) while case 9 can be realized with similar sizes of two sub-SMBs (r_{Size} = 1.75). However, the separation difficulties are similar in the dT/dG/dC separation. Both separation order cases (cases 11 and 12) provide similar productivities and desorbent consumptions with different size ratios of sub-SMBs—the easy-to-difficult separation order still provides better performance, and the size ratios of sub-SMBs are 16.1 and 1.92. In the eight-zone SMB, it is not always profitable conducting the easy-to-difficult separation order because of a certain loss in the internal recycle stream. As the separation difficulties are quite distinct (cases 5 and 6), the easy-to-difficult separation order can provide slightly better productivity and desorbent consumption even though the ratio of loss in the internal recycle stream, r_{Loss}, is close to 1. In the opposite case (cases 7 and 8; the separation difficulties are not significantly distinct), the easy-to-difficult separation order cannot provide better process performances compared to the difficult-to-easy separation order because r_{Loss} dominantly affects the process performance.

For the comparisons with the double-layer SMB process, the separation orders that can provide better process performances were chosen—cases 6 and 8 for the eight-zone SMB and cases 10 and 11 for the SMB cascades. In Figure 8, four process performances, the purity, recovery yield, productivity, and desorbent consumption, were compared for one target component, the intermediate-retained component. All performances were normalized with respect to the maximum performance value among three processes. Because the margins for the design parameters are applicable to produce pure products, all three processes can provide high purity products—the eight-zone SMB provides the lowest product purity, 95.3% for dA/

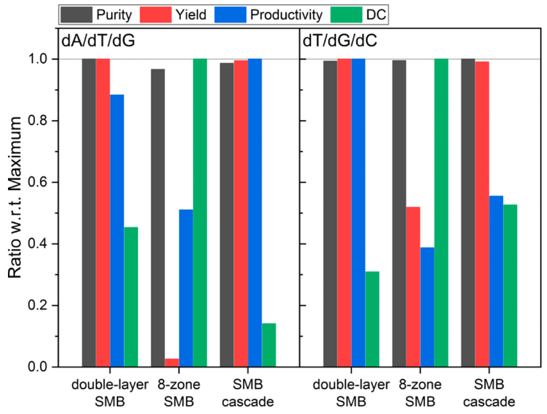

Figure 8. Comparisons of the double-layer SMB, eight-zone SMB, and SMB cascade for the separation of different K_{AB}/K_{AC} mixture systems. dA/dT/dG: K_{AB}/K_{AC} = 0.89; dT/dG/dC: K_{AB}/K_{AC} = 0.34.

dT/dG mixture separation. As expected, the eight-zone SMB cannot recover the target component, so that it provides the worst process performances except the purity. As discussed in Section 4.1, the process performances of the double-layer SMB and the SMB cascade are complementary, according to the separation difficulty, K_{AB}/K_{AC}. Because the SMB cascade processes were designed with r_{tS} = 1, the SMB cascade may provide better productivity for dA/dT/dG mixture separation (K_{AB}/K_{AC} = 0.89), and the double-layer SMB may provide better productivity for dT/dG/dC mixture separation (K_{AB}/K_{AC} = 0.34), c.f. Figure 5. In the detailed simulation study, similar results were obtained. The SMB cascade provides slightly (1.1 times) higher productivity and consumes 69% less desorbent than the double-layer SMB for dA/dT/dG mixture separation, and the double-layer SMB provides 1.8 times higher productivity and consumes 41% less desorbent than the SMB cascade.

5. CONCLUSIONS

In this work, the double-layer SMB, a new SMB process concept for complete separation of ternary and pseudo-ternary mixtures, and its shortcut design method based on the equilibrium theory were introduced. The double-layer SMB, which mimics the splitting and merging of the counter-current flows of dividing wall distillation to separate ternary mixtures continuously, was demonstrated in simulation study with simple safety margin approaches. To assess the feasibility of the new process concept, the early-established ternary SMB processes, the eight-zone SMB, and the SMB cascade were compared with the double-layer SMB, exploiting the equilibrium-based shortcut design method and the process simulations of two separation problems. For a specific separation problem, in which the retention of the intermediate-retained component is not extremely biased one of other components, the double-layer SMB can provide higher productivity and consume less desorbent than the SMB cascade. The double-layer SMB has the same degrees of freedom of the eight-zone SMB (one less than the SMB cascade). Because the double-layer SMB requires four more zones than two other ternary SMBs, it has complex internal flows and requires more flow control unit, such as pumps and valves. To realize this process concept, further investigation is required to reduce the process complexity, to optimize the operating conditions, and to assess process feasibility regarding various separation problems, such as low column efficiency and nonlinear adsorption isotherm systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c00572.

Shortcut design methods for alternative ternary SMBs, shortcut design method for the eight-zone SMB, shortcut design method for the SMB cascade, and computation of reduced productivity and desorbent consumption for the considered ternary SMBs (PDF)

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Notes

The author declares no competing financial interest.

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