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Hybrid Simulated Moving Bed Processes for the Purification of *p*-Xylene

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Abstract: A parallel two-zone and four-zone SMB hybrid process was developed for *p*-xylene purification. By placing a high-productivity parallel two-zone SMB in front of an existing four-zone SMB, feed was enriched in the parallel two-zone SMB before it was fed to the four-zone SMB, which allows a higher feed rate to the four-zone SMB. A general design procedure for hybrid SMB-SMB process was developed. Simulations were done with Aspen Chromatography and Aspen Plus. Overall adsorbent productivity was increased by more than 100%, but with 3–5% lower overall *p*-xylene recovery. With overall recovery of the hybrid process matching the base case, the feed rate was doubled and the overall adsorbent productivity was 50% higher than the base case. The heat duties of distillation columns per unit product were similar for these hybrid processes compared to the base case. If a two-feed raffinate distillation column was used, the heat duty of distillation columns per unit product in the hybrid process was 2–4% lower than the base case. Both parallel two-zone and four-zone SMBs were also developed for use in a hybrid SMB-crystallization process for *p*-xylene purification. SMB productivity can be increased from 31% to 75% by adding additional pumps between columns to operate columns at their pressure limits. Although additional pumps are useful for both systems, the productivities of the parallel two-zone SMBs were 9% and 16% higher than the corresponding four-zone SMBs with the same number of recycle pumps. For a four-zone SMB with two columns per zone and eight recycle pumps, a 114% increase of productivity was achieved, which is 22% higher than a parallel two-zone with one column per zone and four recycle pumps.

Keywords: Hybrid process, adsorption, simulated moving bed, crystallization, *p*-xylene

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INTRODUCTION

Continuous large-scale chromatographic separations using simulated moving bed (SMB) techniques are efficient in the petrochemical, food, and pharmaceutical industries. They have been used commercially for the separation of binary and pseudo-binary liquid mixtures since their commercialization by UOP in the 1960s (1–4). A typical four-zone SMB with one column per zone for binary and pseudo-binary separation is shown in Fig. 1. This system simulates a counter current chromatographic separation process by switching the inlet and outlet ports to a closed loop of fixed bed columns. UOP's Parex for *p*-xylene purification (2) is an example of a pseudo-binary separation in which *p*-xylene is collected in the extract and other xylene isomers and ethylbenzene are collected in the raffinate. If it is desirable to achieve very high productivity and recovery, a four-zone SMB with multiple columns per zone is usually preferable (5).

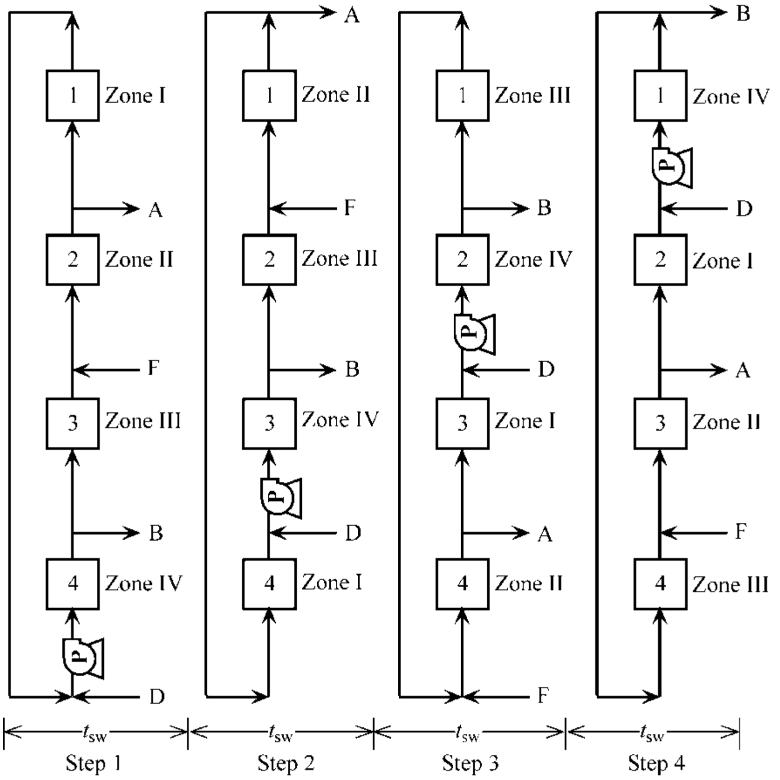

Figure 1. Complete cycle for a four-zone SMB with one column per zone and one recycle pump. A is the less retained component and B is most retained, $K_A < K_B$. A: raffinate; B: extract; F: feed; D: desorbent; P: pump.

The design of SMB systems for binary separation has been extensively studied. Because of its simplicity, the most widely adopted methods are local equilibrium methods (5–8), which includes the widely adopted triangle theory (6–8). Mass transfer effects are included in standing wave analysis (9, 10) and in scaling methods (11).

Although the most widely used scheme among simulated moving bed separation processes is the four-zone one described in Fig. 1, there are alternative schemes that may be more suited to various particular cases, such as three-zone SMBs (12, 13), two-section SMB (14), one-zone analogue (15, 16), and the VARICOL process (17–19). A discontinuous two-zone SMB system with a storage tank was developed for binary separation (20, 21) and was extended to ternary separations (22, 23). The two-zone SMB is simpler and has a lower pressure drop than the standard four-zone SMB, but its purity is lower and separation usually does not improve with additional columns per zone (20).

The two-zone SMB was made continuous by operating two systems in parallel but out of phase. The operation of a "parallel two-zone SMB" system which has continuous feed and products is shown for a complete cycle in Fig. 2 (21). In Fig. 2 during step a zone I has the same function as zone I in Fig. 1. During step b zone I has the same function as zone II in Fig. 1. Zone II in Fig. 2 does the functions of zones III and IV in Fig. 1 during steps a and b, respectively. This continuous SMB system is used in the hybrid processes. When the systems are operated with the same total pressure drop and product purities, the productivity of a parallel two-zone SMB is 30% higher than a four-zone SMB with one column per zone (21). Pressure utilization with increased velocity can be accomplished with no decrease in product purity by use of scaling rules (11, 21), which are discussed in detail later.

Hybrid Processes

To utilize the advantages of both the four-zone SMB (high purity and recovery) and the parallel two-zone SMB (high productivity), a hybrid SMB system was formed by placing a parallel two-zone SMB in front of a four-zone SMB. In general, a hybrid separation process is a specialized, optimized separation sequence using the synergy arising from the combination of unit operations (24). With very high purity and recovery requirements the single operation may be expensive. Hybrid chromatography or SMB and crystallization units have been widely studied, especially for enantioseparations (24–28). In these applications, SMBs are used to generate partially enriched fractions from which pure products are obtained by crystallization. With the features of parallel two-zone SMB (i.e., high productivity with one column per zone), we believe it serves the pre-concentration goal well in hybrid applications.

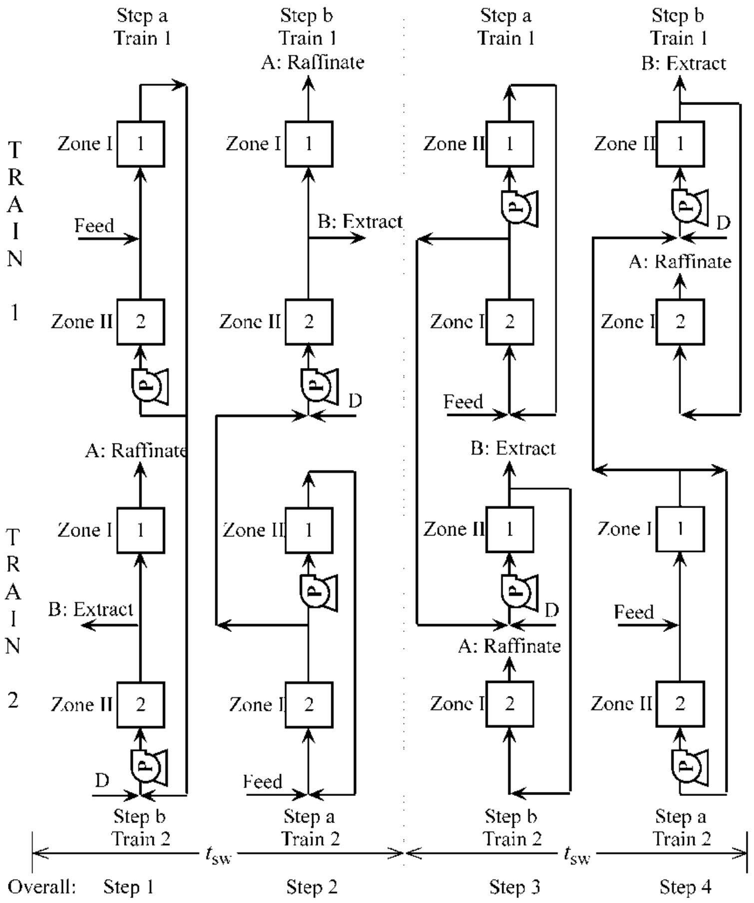

Figure 2. Complete cycle for a parallel two-zone SMB with one column per zone and one recycle pump in each train (21). This system couples two two-zone SMB systems that are operated 180° out of phase. D: desorbent input; P: pump.

Since *p*-xylene purification requires high purity and recovery, it was selected as the model system for the development of hybrid SMB processes. In additional to being industrially important, a full set of data is available for simulations (29). The three xylene isomers, *o*-xylene (OX), *m*-xylene (MX), and *p*-xylene (PX), and ethylbenzene (EB) are C_8 aromatics, that are primarily produced by the catalytic reforming of naphtha (30, 31) in a mixed xylenes plus EB stream containing dilute *p*-xylene. The purified xylenes are used on a large scale as industrial solvents and intermediates for many products. The most important isomer, *p*-xylene, is used for the production of terephthalic acid (TPA) and dimethyl terephthalate (DMT), which are used for the production of fibers, films and polyethylene terephthalate (PET) bottles (30, 32). In these applications high purity ($>99.9\%$) *p*-xylene is required. Demand for high purity *p*-xylene has increased greatly over the past five years to meet rapidly growing markets (29). An economical method of increasing capacity is to debottleneck existing *p*-xylene production units.

Many physical properties of the individual xylene isomers are similar, such as boiling points, which makes the production of high purity xylene isomers extremely difficult by conventional distillation. Two methods are currently used commercially to separate and produce high purity *p*-xylene: adsorption and crystallization (discussed later). A third method, a hybrid adsorption/crystallization process, was successfully field-demonstrated in 1994 (30, 33).

There are three main industrial purification processes based on simulated moving bed (SMB) adsorption. In 1971 UOP commercialized the Parex process to produce high purity *p*-xylene from the isomer mixture (2). Other alternatives are IFP's Eluxyl (33) and Toray's Aromax (34) processes. Robust design and optimization of industrial-scale SMB units for *p*-xylene purification have been extensively studied (29, 33, 35–40). Typical *p*-xylene recovery per pass is over 95% in these processes, which results in less recycle and smaller isomerization units than in crystallization plants. Studies were also done to purify other xylene isomers, and to separate *p*-xylene and ethylbenzene simultaneously (30, 41, 42).

In this study, hybrid processes with a parallel two-zone SMB are developed for the separation of *p*-xylene from xylene isomers. First, a hybrid process using parallel two-zone and four-zone SMBs is developed to debottleneck existing SMB units. The impure *p*-xylene is pre-purified in the high-productivity parallel two-zone SMB with a low desorbent-to-feed ratio (D/F), and final purification is done in a four-zone SMB. Since the feed to the four-zone SMB now has a much higher *p*-xylene purity, the feed and product rates can be increased and desorbent rate can be reduced while retaining the desired *p*-xylene purity. Second, high productivity two-zone SMB units are developed for hybrid SMB-crystallization processes to debottleneck existing *p*-xylene crystallization units. The impure *p*-xylene is enriched in the high-productivity parallel two-zone SMB followed by a single stage crystallization. A pressure utilization procedure is used in both of these processes to increase the productivity of the SMB units. These methods are also applicable in the design of new plants.

THEORETICAL

Simulation Model

The published simulations of Minceva and Rodrigues for an industrial-scale SMB are used as the base case (29). The feed is a C_8 aromatics mixture with 23.6% *p*-xylene, 49.8% *m*-xylene, 12.7% *o*-xylene, and 14% ethylbenzene. The adsorbent used in this system is completely potassium-exchanged Y zeolite, the desorbent used is *p*-diethylbenzene (PDEB), and operation is at 180°C. The equilibrium data, system and operating conditions, and model parameters used for the C_8 aromatics system are listed in Table 1 (29).

The commercially available software, Aspen Chromatography v12.1, was used to simulate the adsorption process. Aspen Plus v12.1 was used to design the distillation columns for solvent recovery.

The solute mass balance for each species in the chromatographic column is (5)

$$\frac{\partial(v_s c_i)}{\partial z} + \varepsilon_e \frac{\partial c_i}{\partial t} + K_{di}(1-\varepsilon_e)\varepsilon_p \frac{\partial \bar{c}_{i,\text{pore}}}{\partial t} + \rho_s(1-\varepsilon_e)(1-\varepsilon_p)\frac{\partial \bar{q}_i}{\partial t} - \varepsilon_e E_Z \frac{\partial^2 c_i}{\partial z^2} = 0 \qquad (1)$$

This system is modeled with a variable dispersion coefficient that is estimated using the Chung and Wen correlation for each component (43):

$$Pe = \frac{v_s d_p}{E_Z} = 0.2 + 0.011(Re)^{0.48} \qquad (2)$$

The kinetic model is linear lumped resistance with constant mass transfer coefficient and the driving force is Δc. The pressure drop in a packed bed of rigid particles in laminar flow is (44)

$$\Delta P = \frac{150\mu L(1-\varepsilon)^2 v_s}{\varepsilon^3 d_p^2} \qquad (3)$$

The productivity of the system is defined as

$$\text{productivity} = (\text{mass of product/time})/(\text{total adsorbent volume}) \qquad (4)$$

The purity of *p*-xylene in the stream is

$$\frac{c_{PX}}{c_{PX} + c_{MX} + c_{OX} + c_{EB}} \times 100\% \qquad (5)$$

The recovery of *p*-xylene is

$$\frac{c_{PX,E} M_E}{c_{PX,F} M_F} \times 100\% \qquad (6)$$

Scaling Rules

Scaling rules were developed for SMB systems to predict the effect of changing operation and design variables by simple algebraic equations without requiring additional simulations or experiments (11, 21). This

Table 1. System parameters of an industrial-scale four-zone SMB for C_8 aromatics separation (29)

L	1.1 m	Column length
D_{col}	4.1 m	Column diameter
ε_{e}	0.39	External void fraction
ε_{p}	0	Internal void fraction
d_{p}	920 μm	Adsorbent particle diameter
ρ_{F}	713.7 g/L	Feed density
ρ_{D}	722.9 g/L	Desorbent density
$k_{\mathrm{m}}a_{\mathrm{p}}$ (all components)	2 1/min	Mass transfer coefficient
Number of columns	24	
SMB configuration	3,6,9,6	
Isotherm form	$q_{ij} = \frac{q_{mi}K_i c_{ij}}{1+\sum_{j=1}^{NC} K_j c_{ij}}$	
$q_{m\mathrm{PX(MX;OX;EB)}}$	130.3 g/kg	Adsorbed phase saturation concentration
K_{PX}	1.0658 m^3/kg	Adsorption equilibrium constant of *p*-xylene
K_{MX}	0.2299 m^3/kg	Adsorption equilibrium constant of *m*-xylene
K_{OX}	0.1884 m^3/kg	Adsorption equilibrium constant of *o*-xylene
K_{EB}	0.3067 m^3/kg	Adsorption equilibrium constant of ethylbenzene
$q_{m\mathrm{PDEB}}$	107.7 g/kg	Adsorbed phase saturation concentration
K_{PDEB}	1.2935 m^3/kg	Adsorption equilibrium constant

approach is particularly convenient when one wants to modify an existing design. Using the old design as a base case, the scaling rules predict the results caused by the changes in variables (including particle diameter, column length and diameter, fluid velocity and cycle time) without solving the differential equations.

Defining the scaling factors as

$$a = \frac{d_{\mathrm{p,new}}}{d_{\mathrm{p,old}}}, \quad b = \frac{L_{j,\mathrm{new}}}{L_{j,\mathrm{old}}}, \quad c = \frac{D_{\mathrm{col,new}}}{D_{\mathrm{col,old}}}, \quad g = \frac{Q_{j,\mathrm{new}}}{Q_{j,\mathrm{old}}} \tag{7a–d}$$

the following scaling equations are then easily derived for liquid SMB systems when pore diffusion controls (11, 21).

$$R_{\mathrm{tsw}} = \frac{t_{\mathrm{sw,new}}}{t_{\mathrm{sw,old}}} = \frac{(L_j/v_{\mathrm{s},j})_{\mathrm{new}}}{(L_j/v_{\mathrm{s},j})_{\mathrm{old}}} = \frac{bc^2}{g} \tag{7e}$$

$$R_{\mathrm{p}} = \frac{\Delta P_{j,\mathrm{new}}}{\Delta P_{j,\mathrm{old}}} = \frac{bg}{a^2c^2} \tag{7f}$$

$$\begin{aligned} R_{\mathrm{N}} &= \frac{(L/L_{\mathrm{MTZ}})_{j,\mathrm{new}}}{(L/L_{\mathrm{MTZ}})_{j,\mathrm{old}}} = \left(\frac{v_{\mathrm{s},j,\mathrm{old}}}{v_{\mathrm{s},j,\mathrm{new}}}\right)\left(\frac{L_{j,\mathrm{new}}}{L_{j,\mathrm{old}}}\right)\frac{(k_{\mathrm{m}}a_{\mathrm{p}})_{\mathrm{new}}}{(k_{\mathrm{m}}a_{\mathrm{p}})_{\mathrm{old}}} \\ &= \left(\frac{v_{\mathrm{s},j,\mathrm{old}}}{v_{\mathrm{s},j,\mathrm{new}}}\right)\left(\frac{L_{j,\mathrm{new}}}{L_{j,\mathrm{old}}}\right)\left(\frac{d_{\mathrm{p,old}}}{d_{\mathrm{p,new}}}\right)^2 = \frac{bc^2}{a^2\,g} \end{aligned} \tag{7g}$$

R_{N} is a surrogate for $R_{\mathrm{purity}} = (\mathrm{Purity})_{\mathrm{new}}/(\mathrm{Purity})_{\mathrm{old}}$. When $R_{\mathrm{N}} = 1$, the fractional bed use will be constant in the two designs and the product purities and recoveries will be identical.

RESULTS AND DISCUSSION

Hybrid System: Parallel Two-Zone SMB + Four-Zone SMB

Base Case

In this study, the base case operating condition (Fig. 3) for an industrial-scale SMB was obtained from the literature (29). The operating conditions of four-zone SMB and distillation columns are shown in Tables 2 and 3, respectively. The streams' flow rates, compositions, and *p*-xylene purities and recoveries calculated from Eqs (5) and (6) are shown in Table 4. Note that, in Table 4, *p*-xylene recovery is for each individual step only. For example, the recovery of *p*-xylene in stream S7 (>99.99%) is calculated based on the feed to the distillation column (stream S3). Bottom streams of the distillation columns are basically pure PDEB, and are not included in the tables.

Feed is introduced directly to the SMB unit, a 24-column four-zone SMB with (3, 6, 9, 6) configuration, which is close-to-optimum (39). Raffinate and extract streams are sent to separate distillation columns. The bottom products of the two distillation columns are almost pure PDEB that is recycled to the SMB unit (recycle is not shown in the figure). The distillate from the extract distillation column is 99.99% pure *p*-xylene. The distillate from the raffinate column contains xylene isomers other than *p*-xylene that are recycled to the isomerization reactor, where a close-to-equilibrium mixture of xylenes is produced (30). To prevent the buildup of EB in the recycle loop, the catalysts are also designed to convert EB to either xylenes, benzene and lights, or benzene and diethylbenzene.

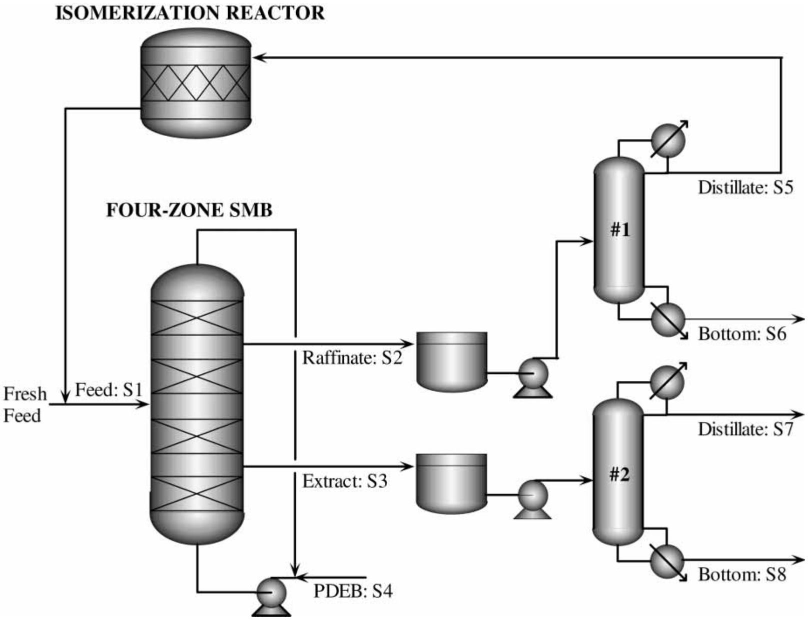

Figure 3. Flow chart of base case (29): stand-alone SMB unit with distillation columns.

The distillation columns were designed with the RADFRAC block of Aspen Plus. The feeds to the distillation columns are saturated liquids. The columns are operated at 5 bar. We specify the external reflux ratio as $R_{\text{reflux}} = 1.15 \times R_{\text{reflux,min}}$ for the column, which is reasonable in engineering practice (45). Sieve trays are used with a 2 ft tray spacing; operating at 80% flooding based on Fair's method (45), and the downcomer area is assumed to be 10% of the column cross-section area. Desorbent (PDEB) purity and recovery are both set to >99.99% in the bottoms of the columns. The dimensions and heat duties of the distillation columns are listed in Table 3.

Table 4 lists the flow rates and purities of streams in the processes. *p*-Xylene in the final product stream (stream S7 in Fig. 3) is 99.99% as desired, and the overall recovery is 97.29%. The feed and final *p*-xylene product rate are 62,100 and 14,300 kg/h, respectively. The productivity of the system is 39.35 kg/h PX/m^3 adsorbent. The heat duty of the reboilers per unit product is 1,409 kcal/kg. The result shows that a stand-alone SMB unit can produce high purity *p*-xylene with high recovery.

Debottlenecking: Hybrid Version 1.0

Figure 4 shows a generic parallel two-zone and four-zone hybrid SMB-SMB process. It is assumed that the desired product is enriched in the extract stream,

Table 2. Operating conditions for four-zone SMBs in base and hybrid processes

		Hybrid processes				
	Base case	Hybrid version 1.0	Hybrid version 1.1	Hybrid version 1.2	Hybrid version 2.0	Hybrid version 2.1
Feed rate (m^3/min)	1.45 (S1)	2.50 (S7)	2.50 (S7)	1.85 (S7)	2.50 (S5)	1.85 (S5)
Fresh desorbent rate (m^3/min)	2.89 (S4)	2.89 (S11)	2.60 (S11)	2.60 (S11)	2.60 (S2)	2.60 (S9)
Raffinate (m^3/min)	2.69 (S2)	3.44 (S9)	3.40 (S9)	2.75 (S9)	3.40 (S7)	2.75 (S7)
Extract (m^3/min)	1.65 (S3)	1.95 (S10)	1.70 (S10)	1.70 (S10)	1.70 (S8)	1.70 (S8)
Recycle rate (m^3/min)	5.39	5.00	4.95	4.95	4.95	4.95
Switching time (min)	1.15	1.24	1.27	1.265	1.27	1.265

Table 3. Operating conditions for distillation columns in base and hybrid processes. Flow rates and compositions are listed in Table 4

	Column number	Number of plates	Feed position	Reflux ratio	Column diameter (m)	Condenser heat duty (10^6 kcal/h)	Reboiler heat duty (10^6 kcal/h)
Base case	#1	54	27	2.0	4.4	−12.59	13.24
	#2	56	22	3.4	3.1	−6.58	6.84
Hybrid version 1.0	#1	53	23	2.6	5.0	−16.67	17.32
	#2	54	24	2.9	6.1	−24.06	25.25
	#3	53	29	1.9	4.7	−14.32	15.01
	#4	54	24	2.8	3.7	−9.23	9.68
Hybrid version 1.1	#1	54	29	1.9	4.6	−14.42	14.87
	#2	54	24	2.8	5.4	−20.06	20.86
	#3	52	23	2.6	4.7	−14.40	15.07
	#4	53	24	2.9	3.5	−8.30	8.68
Hybrid version 1.2	#1	54	28	1.5	3.5	−8.55	8.85
	#2	54	24	1.6	4.5	−14.38	14.95
	#3	56	25	2.1	3.9	−10.74	11.28
	#4	56	25	2.3	3.2	−6.73	7.11
Hybrid version 2.0	#1	54	24	2.8	5.4	−20.06	20.86
	#2	57	27/31	1.6	6.3	−26.31	27.42
	#3	53	24	2.9	3.5	−8.30	8.68
Hybrid version 2.1	#1	54	24	1.6	4.5	−14.38	14.95
	#2	56	27/31	1.6	5.3	−18.19	19.02
	#3	56	25	2.3	3.2	−6.73	7.11

Table 4. Stream conditions with flow rate, composition and *p*-xylene purity and recovery

	Stream	Flow rate (10^3 kg/h)	OX (%)	MX (%)	PX (%)	EB (%)	PDEB (%)	PX purity (%)	PX recovery (%)
Base case	S1	62.1	12.7	49.7	23.6	14.0	0.0		
	S2	114.0	6.93	27.18	0.36	7.69	57.86		
	S3	73.5	<0.01	<0.01	19.40	<0.01	80.59	99.99	97.29
	S4	125.4	0	0	0	0	100		
	S5	48.0	16.46	64.48	0.86	18.19	0.008		
	S7	14.3	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99
Hybrid version 1.0	S1	198.0	12.7	49.7	23.6	14.0	0.0		
	S2	152.7	10.64	38.56	1.16	9.22	40.42		
	S3	245.9	3.62	16.09	18.28	5.55	56.45	41.99	96.21
	S4	200.6	0	0	0	0	100		
	S5	90.9	17.85	64.72	1.95	15.47	0.0098		
	S7	107.1	8.31	36.94	41.99	12.75	0.007	41.99	>99.99
	S9	141.3	6.31	28.06	0.66	9.70	55.26		
	S10	91.2	<0.01	<0.01	48.24	51.76	<0.01	99.99	97.83
	S11	125.4	0	0	0	0	100		
	S12	63.2	14.10	62.73	1.48	21.68	0.01		
	S14	44.0	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99

Hybrid version 1.1	S1	191.0	12.7	49.7	23.6	14.0	0.0		
	S2	123.7	11.70	43.54	1.66	10.96	32.15		
	S3	183.4	5.34	22.40	23.47	7.19	41.60	40.18	95.47
	S4	116.1	0	0	0	0	100		
	S5	83.9	17.24	64.17	2.44	16.15	0.003		
	S7	107.1	9.14	38.36	40.18	12.32	0.003	40.18	>99.99
	S9	139.9	7.01	29.43	0.86	9.46	53.24		
	S10	80.0	<0.01	<0.01	52.25	47.75	<0.01	99.99	97.14
	S11	112.8	0	0	0	0	100		
	S12	65.4	14.98	62.93	1.84	20.23	0.008		
	S14	41.8	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99
Hybrid version 1.2	S1	128.7	12.7	49.7	23.6	14.0	0.0		
	S2	75.6	11.61	42.86	0.45	10.51	34.57		
	S3	131.3	5.77	24.04	22.87	7.67	39.65	37.89	98.89
	S4	78.2	0	0	0	0	100		
	S5	49.4	17.74	65.50	0.68	16.06	0.008		
	S7	79.2	9.55	39.84	37.89	12.71	0.005	37.89	>99.99
	S9	113.0	6.70	27.93	0.40	8.91	56.07		
	S10	79.0	<0.01	<0.01	37.45	62.55	<0.01	99.99	98.50
	S11	112.8	0	0	0	0	100		
	S12	49.7	15.24	63.56	0.9	20.28	0.005		
	S14	29.6	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99

(*continued*)

Table 4. Continued

	Stream	Flow rate (10^3 kg/h)	OX (%)	MX (%)	PX (%)	EB (%)	PDEB (%)	PX purity (%)	PX recovery (%)
Hybrid version 2.0	S1	191.0	12.7	49.7	23.6	14.0	0.0		
	S2	123.7	11.70	43.54	1.66	10.96	32.15		
	S3	183.4	5.34	22.40	23.47	7.19	41.60	40.18	95.47
	S4	116.1	0	0	0	0	100		
	S5	107.1	9.14	38.36	40.18	12.32	0.003	40.18	>99.99
	S7	139.9	7.01	29.43	0.86	9.46	53.24		
	S8	80.0	<0.01	<0.01	52.25	<0.01	47.75	99.99	97.14
	S9	112.8	0	0	0	0	100		
	S10	149.3	16.25	63.63	2.18	17.94	0.006		
	S12	41.8	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99
Hybrid version 2.1	S1	128.7	12.7	49.7	23.6	14.0	0.0		
	S2	75.6	11.61	42.86	0.45	10.51	34.57		
	S3	131.3	5.77	24.04	22.87	7.67	39.65	37.89	98.89
	S4	78.2	0	0	0	0	100		
	S5	79.2	9.55	39.84	37.89	12.71	0.005	37.89	>99.99
	S7	113.0	6.70	27.93	0.40	8.91	56.07		
	S8	79.0	<0.01	<0.01	37.45	62.55	<0.01	99.99	98.50
	S9	112.8	0	0	0	0	100		
	S10	99.2	16.46	64.42	0.8	18.13	0.008		
	S12	29.6	<0.01	<0.01	99.99	<0.01	<0.01	99.99	>99.99

which is the case for *p*-xylene. Hybrid processes are easily developed for raffinate product. Tanks are included between the SMB units and the distillation columns to provide a constant feed to the distillation units.

In the hybrid process, the impure *p*-xylene is pre-purified in the high-productivity parallel two-zone SMB, and the PDEB is removed by distillation. This intermediate solvent recovery step is required since a dilute feed stream to the four-zone SMB will limit the throughput. The pre-purified extract product is fed to the four-zone SMB for final purification. Since the feed to the four-zone SMB now has a higher *p*-xylene purity, the feed and extract rates can be increased, which increases the productivity, and the desorbent rate can be reduced while retaining the desired *p*-xylene purity. The raffinate product streams from both parallel two-zone and four-zone SMBs are fed to the raffinate distillation columns. Note that the distillation columns for the streams exiting the parallel two-zone SMB will have high energy loads unless a low desorbent-to-feed ratio (D/F) is used.

We first simulated debottlenecking in an existing four-zone SMB unit. To simplify the simulation process, the following steps outline the general procedures for the hybrid process:

1. Design a parallel two-zone SMB (21) with a total of four columns to have adequate separation (*p*-xylene recovery $>90\%$ with considerably higher *p*-xylene purity than the feed). We use the same column dimensions, particle diameter, and feed rate as for the four-zone SMB but at a lower D/F.
2. Assume that complete separation occurs in the distillation column, which is close to valid.
3. Run the simulation for the four-zone SMB with a feed composition that matches the overhead composition of the distillation column. With higher feed concentrations of *p*-xylene and higher feed rates, the operating conditions of the four-zone SMB have to be changed. If the separation in the four-zone SMB is inadequate (*p*-xylene purity $>99.99\%$ with *p*-xylene recovery $<97\%$) or overkill (*p*-xylene purity $>99.99\%$ with *p*-xylene recovery $>98\%$), scale the parallel two-zone SMB by changing the fractional bed use, R_N, using the scaling rules. This is accomplished by changing the adsorbent volume while keeping the feed rate and particle diameter constant ($g = 1$ and $a = 1$). Equation 7g simplifies to $R_N = bc^2$. The relationship between purity and R_N can be established with a few additional simulations. Repeat steps 2 and 3 until the *p*-xylene purity and recovery of the four-zone SMB are satisfactory.
4. Scale the parallel two-zone SMB from step 3 to match the flow rates required for the feed to the four-zone SMB while keeping purity constant ($R_N = 1$), and determine the feed rate of the parallel two-zone SMB. Column length and diameter are kept constant ($b = c = 1$), while particle diameter is changed following Eq 7g, $R_N = 1/(a^2g) = 1$,

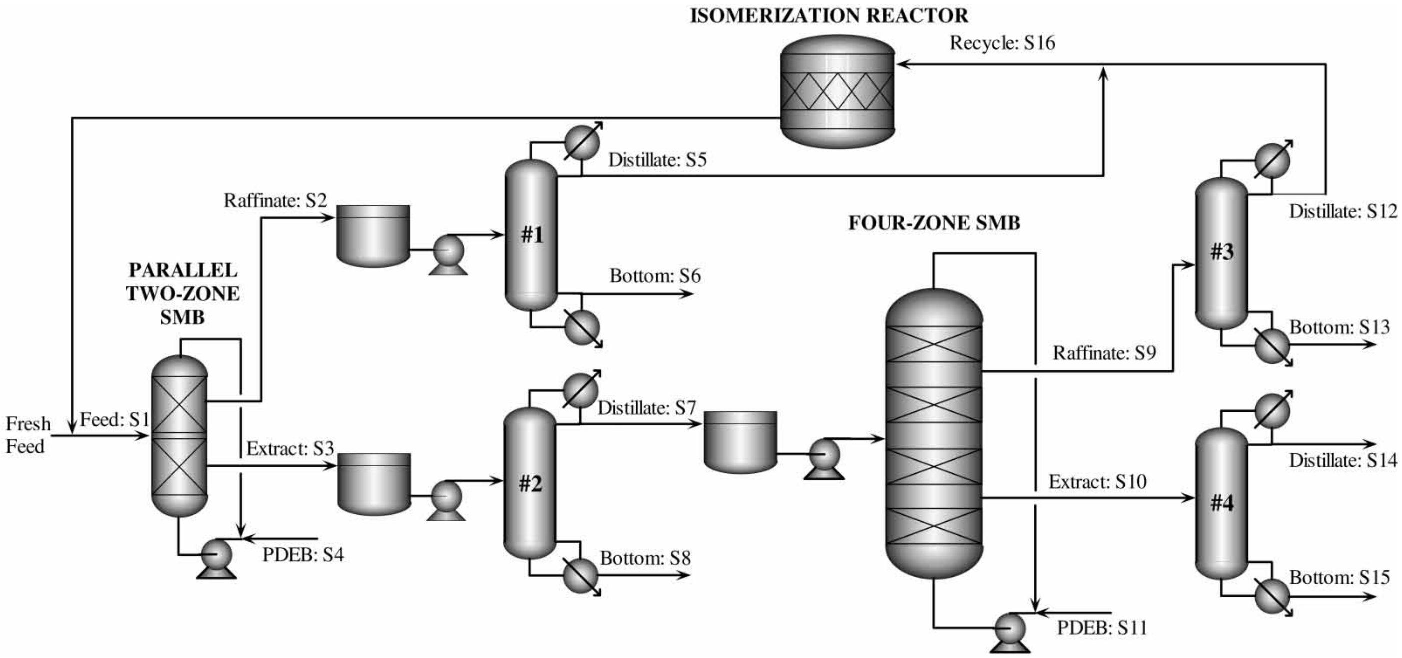

Figure 4. Flow chart of hybrid SMB-SMB process version 1: parallel two-zone SMB, four-zone SMB, and distillation columns. Two separate distillation columns are used for raffinate streams.

where g is the scaling factor for all the flow rates. Since $a = g^{-1/2}$, we can calculate the new particle size. Simulate the parallel two-zone SMB with the new system and operating parameters.

5. Simulate the entire process to validate the design determined with the scaling rules.

Steps 2 and 3 are trial-and-error, and many different parameters can be varied to optimize the process. The objectives are to increase the feed rates and productivity.

For hybrid version 1.0, the parallel two-zone SMB used $D/F = 1.0$. The desorbent flow rate of the four-zone SMB was kept at the original value, 2.89 m^3/min. The operating conditions of the four-zone SMBs are listed in Table 2; the dimensions and heat duties of distillation columns are in Table 3; the stream flow rates, composition, *p*-xylene purities, and recoveries are in Table 4; and the system and operating parameters of the parallel two-zone SMB are in Table 5. The feed rate is increased from 62,100 kg/h to 198,000 kg/h and the final product rate is increased to 44,000 kg/h. The recycle rate to the isomerization reactor is 149,000 kg/h, tripled from 48,000 kg/h in the base case, which will require additional reactors (not shown in Fig. 4).

The overall *p*-xylene recovery of the hybrid system is 94.12%, less than 3% lower than that of the stand-alone system. The overall productivity is 90.90 kg/h PX/m^3 adsorbent, 131% higher than the base case. The heat duty of the reboilers per unit product is 1,529 kcal/kg, 8.5% higher than that of the stand-alone system. In particular, the energy loads of the distillation columns for the streams exiting the parallel two-zone SMB are high. Reducing the desorbent use of this SMB will reduce the heat duty in the distillation columns, but *p*-xylene purity or recovery will drop.

Table 5. Operating conditions for parallel two-zone SMBs in the hybrid SMB-SMB processes

	Hybrid version 1.0	Hybrid version 1.1	Hybrid version 1.2	Hybrid version 2.0	Hybrid version 2.1
Column length (cm)	160.5	160.5	160.5	160.5	160.5
Column diameter (cm)	489.6	489.6	489.6	489.6	489.6
Particle diameter (μm)	520	520	520	520	520
Feed rate (S1) (m^3/min)	4.62	4.46	3.00	4.46	3.00
D/F	1	0.6	0.6	0.6	0.6
Raffinate (S2) (m^3/min)	3.83	3.08	1.89	3.08	1.89
Extract (S3) (m^3/min)	5.42	4.06	2.92	4.06	2.92
$Q_{\text{zone II,step a}}$ (m^3/min)	1.59	0.77	0.50	0.77	0.50
Switching time (min)	2.20	2.93	4.21	2.93	4.21

Debottlenecking: Hybrid Version 1.1

The hybrid process version 1.1 is the same as shown in Fig. 4, except conditions are changed. D/F of the parallel two-zone SMB is reduced from 1.0 to 0.6. We also follow the guidelines described previously except in step 3, the desorbent rate of the four-zone SMB is reduced if more separation is achieved than needed. Since the parallel two-zone SMB has a large feed rate, the desorbent rate of this unit is reduced more.

Tables 2 to 5 list the system and operating conditions for this design. From these results, we can see that with reduced desorbent for both parallel two-zone and four-zone SMBs, the overall productivity is reduced from 90.90 (hybrid 1.0) to 86.57 kg/h PX/m^3 adsorbent, which is still 120% higher than the base case. The heat duty of the reboilers per unit product is 1,423 kcal/kg, only 1% higher than that of the stand-alone system. The trade-off for the lower heat duty is that the overall *p*-xylene recovery is reduced from 94.12% in version 1.0 to 92.73%.

These results show that the hybrid system is capable of producing high purity *p*-xylene with reasonable overall recovery. The product rate can be tripled, and the productivity of the system can be doubled, with a less than 5% decrease in the recovery. However, there is a balance between the overall productivity and recovery. If we reduce the feed flow rates to both SMBs, according to the scaling rules, with constant column length, column diameter, and particle diameter, R_N and therefore the product purity and recovery, will be increased, but the productivity drops. High productivity can be achieved if one is willing to accept lower overall recovery. Lowering D/F reduces the *p*-xylene recovery while keeping desired purity; however, it has the advantage of lower heat duty per unit product.

Debottlenecking: Hybrid Version 1.2

Hybrid version 1.2 (Fig. 4) was developed to match the overall *p*-xylene recovery of the base case. We start with the conditions in hybrid version 1.1.

1. Reduce the feed rate of the parallel two-zone SMB to increase R_N and hence the *p*-xylene recovery. The column dimensions and particle size are kept constant ($a = b = c = 1$). From Eq. (7g), $R_N = 1/g$, reducing g increases R_N, hence the product purity and recovery. Simulate the parallel two-zone SMB with these new conditions.
2. Assume that complete separation occurs in the distillation columns.
3. Simulate the four-zone SMB with the reduced feed. The column dimensions, particle size, and desorbent rate are kept constant. The SMB unit needs to be reoptimized.
4. If the separation in the four-zone SMB is adequate and overall *p*-xylene recovery is satisfactory, the new hybrid process design is determined.

If not, adjust the flow rates for the parallel two-zone SMB and repeat steps 1–4.

5. Scale the parallel two-zone SMB to match the feed flow rate of the four-zone SMB. This step is similar to step 4 for hybrid version 1.0. Simulate the parallel two-zone SMB to check the result.
6. Simulate the entire process to check the design.

This process is also a trial-and-error. To simplify the analysis, we kept $D/F = 0.6$ for the parallel two-zone SMB and desorbent rate $= 2.6\ \mathrm{m}^3/\mathrm{min}$ for the four-zone SMB.

The design and operating conditions for hybrid version 1.2 are delineated in Tables 2 to 5. From these results, we see that with reduced feed rates for both parallel two-zone and four-zone SMBs, the overall productivity is reduced to 61.26 kg/h PX/m^3 adsorbent, which is still 55% higher than the base case. The heat duty of the reboilers per unit product is 1,425 kcal/kg, 1% higher than that of the base case. The overall *p*-xylene recovery is 97.4%, which matches the recovery of the base case.

New Designs: Hybrid Version 2.0 and 2.1: Two-feed Raffinate Distillation Column

For retrofitting, it is probably easier to reuse the base case raffinate distillation column if two distillation columns are used as shown in Fig. 4. For a new design, a single raffinate distillation column with two feeds can be used. In hybrid version 2.0, we modify hybrid version 1.1 to use a two-feed distillation column (Fig. 5). Because this process uses the SMB units designed for hybrid version 1.1, only the new two-feed distillation column has to be designed. The design and operating parameters are in Tables 2–5. The heat duty of reboilers is 1,363 kcal/kg, which is 4% lower than the base case. With a two-feed raffinate distillation column, the new system has an energy advantage over the base case in addition to a higher feed rate and higher productivity.

Hybrid version 2.1 (Fig. 5) corresponds to hybrid version 1.2, which has a similar overall recovery and 50% higher productivity compared to the base case, but uses a two-feed distillation column. The design and operating parameters are in Tables 2–5. The heat duty of reboilers is 1,387 kcal/kg, which is 1.5% lower than the base case.

Discussion and Conclusions for Hybrid SMB-SMB Processes

Hybrid parallel two-zone and four-zone SMB processes were developed for the separation of *p*-xylene. With less than 5% lower overall *p*-xylene recovery, the product rate can be tripled and overall productivity doubled. With matched overall *p*-xylene recovery, the product rate can be doubled

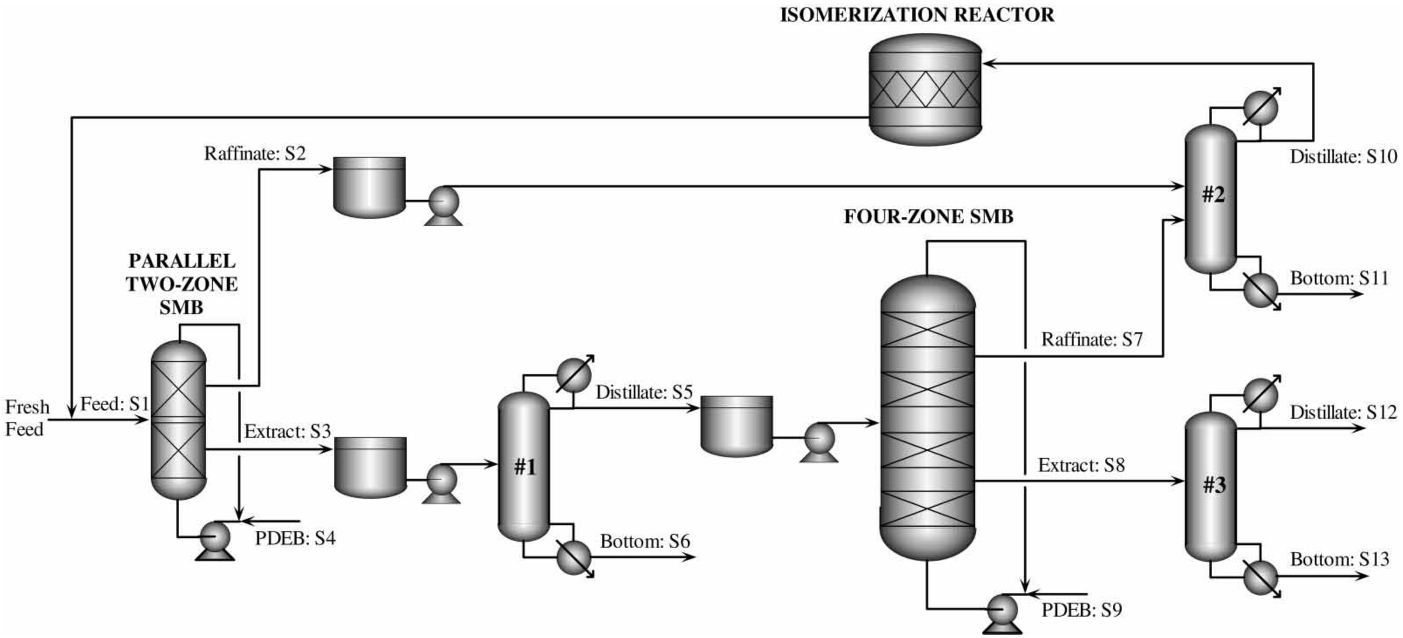

Figure 5. Flow chart of hybrid SMB-SMB process version 2: parallel two-zone SMB, four-zone SMB, and distillation columns. One distillation column with two feeds is used for raffinate streams.

with overall productivity 50% higher than the base case. Energy loads in the reboilers of the distillation columns per unit product are similar in these processes. By reducing the desorbent use for both SMBs, lower energy loads can be obtained in the distillation columns but with a slight decrease in overall *p*-xylene recovery. These results show that the hybrid system can produce high purity *p*-xylene with high recovery and productivity. Different designs of hybrid processes that balance productivity and recovery are also discussed. We can obtain very high productivity with trade-off of lower recovery, or vice versa. With the help of scaling rules, the operating conditions of new SMBs can be readily determined. Since significantly more feed is processed, all of these designs will require increased reactor capacity.

Hybrid System: SMB + Crystallization

Crystallization Processes

Low temperature fractional crystallization was the first and for many years the only commercial technology for separating *p*-xylene from C_8 aromatics. The xylene system is an extremely favorable system for melt crystallization. The melting points of PX, MX, OX, and EB are 13.3°C, −47.9°C, −25.2°C, and −95.0°C respectively (30), and the system does not form solid solutions. Thus, the crystals are essentially pure *p*-xylene. Several commercial crystallization processes have been developed to separate *p*-xylene from its isomer mixture, such as Chevron, Krupp, Arco (Lyondell), Amoco, Phillips, and Exxon processes (30, 46). *p*-Xylene crystals are typically produced in two or more crystallization stages, with *p*-xylene recovery of about 60–65% per pass (30). In commercial practice, *p*-xylene crystallization is carried out at a temperature just above the eutectic point. At all temperatures above the eutectic point, *p*-xylene is soluble in the remaining C_8 aromatics liquid (mother liquor). This limits the efficiency of the crystallization process. The solid *p*-xylene crystals are typically separated from the mother liquor by filtration or centrifugation. In the last stage, the crystals are reslurried with the high purity *p*-xylene product. After a final liquid-solid separation, *p*-xylene purity $>99.9\%$ is achieved.

These processes are based on suspension crystallization. Recently, static (layer) crystallization processes based on progressive freezing have been developed (46–48). Compared at the same unit capacity, the overall production cost of *p*-xylene using modern crystallization designs is claimed to be lower than adsorption processes (31).

SMB Processes

In this section, the SMB parts of the hybrid SMB-crystallization processes are developed for the separation of *p*-xylene. After the feed is enriched in the

SMB unit and the desorbent is removed by distillation, the SMB extract stream is sent to the crystallizer. With higher *p*-xylene purity in the feed, a single stage crystallizer may be used. In a retrofit system the other crystallizer stages would be operated in parallel to increase throughput. Since the design of the crystallizer is beyond the scope of this paper, our efforts are focused on developing the SMB units. A *p*-xylene purity of 75–98% is required for one-stage crystallization (33, 49, 50). The previously developed pressure utilization procedure (21) is applied to the SMBs (either four-zone or parallel two-zone) in the hybrid processes.

Standard four-zone SMBs use only one pump in the recycle line (Fig. 1). With one pump in the recycle line (Fig. 1), $\Delta P_{\text{total}} = \sum(\Delta P)_i$. The feed end of zone IV is designed to operate at the pressure limit, but none of the other columns is operated at the maximum pressure. Adding more pumps between columns allows the SMB systems to more efficiently use the available pressure drop, and thus operate at higher flow rates. With two pumps the total pressure drop of zones II plus III and the total pressure drop of zones I plus IV are each provided by one pump. With four pumps zone IV can operate at $\Delta P_{\max}$.

If the flow rates are increased with no other adjustment, purities will plummet. The scaling rules can be used to keep purity constant ($R_{\text{N}} = 1$) by repacking existing columns ($b = 1$ and $c = 1$) with smaller ($a < 1$) adsorbent particles, which decrease mass transfer resistance (51). The increased pressure drop made available by adding pumps makes $R_{\text{p}} > 1$, and R_{p} is known. This extra available pressure drop is used to compensate for the increased velocity and the smaller particles. From Eqs (7)f and (7)g,

$$R_{\text{p}} = \frac{bg}{a^2c^2} = \frac{g}{a^2} \Longrightarrow g = R_{\text{p}}a^2 \qquad \text{(8a,b)}$$

$$R_{\text{N}} = \frac{bc^2}{a^2\, g} = 1 \Longrightarrow a^2\, g = 1 \Longrightarrow g = a^{-2} \qquad \text{(9a,b,c)}$$

Combining Eqs (8b) and (9c), we obtain

$$R_{\text{p}}a^4 = 1 \Longrightarrow a \equiv \frac{d_{\text{p,new}}}{d_{\text{p,old}}} = (R_{\text{p}})^{-1/4} \qquad \text{(10a,b)}$$

Combining Eqs (10b) and (8b),

$$g \equiv \frac{Q_{j,\text{new}}}{Q_{j,\text{old}}} = (R_{\text{p}})^{1/2} \qquad \text{(11)}$$

Since existing columns are used, $b = c = 1$, and combining Eqs (7e) and (11) gives

$$R_{\text{tsw}} = \frac{1}{g} \Longrightarrow t_{\text{sw,new}} = t_{\text{sw,old}}(R_{\text{p}})^{-1/2} \qquad \text{(12a,b)}$$

This procedure increases productivity at constant purity without exceeding the pressure limit of the columns. Since parallel two-zone SMBs have lower flow rates, larger increases in the velocities are possible with the same pressure limits. A similar procedure of balancing maximum allowed pressure drop and mass transfer resistance (but without the use of additional pumps) was recently used for SMB protein separation (51).

Since two-zone and parallel two-zone SMBs are not improved with multiple columns per zone, we start with a four-zone SMB with one column per zone. To produce $>85\%$ pure *p*-xylene with $>90\%$ recovery, D/F has to be increased. Table 6 shows the system and operating conditions for a four-zone SMB with one column per zone. The pressure limit of the columns is arbitrarily set to 6 bar, and the minimum pressure in the system is 1 bar (maximum $\Delta P = 5$ bar). The simulation results for a four-zone SMB are shown in Table 7. The total ΔP of these four columns is 0.284 bar for the original case, which has not reached the pressure limit. This design is easily scaled to operate with a total ΔP of the columns of 5 bar (basis case). Then two (case 1) and four (case 2) pumps are used between the columns, which increases the ΔP of zones I plus IV (case 1) and the ΔP of zone IV (case 2) to 5 bar. With more pumps for a four-zone SMB, the throughput and productivity can be greatly increased; however, the columns need to be repacked with smaller particles. The productivities are 31% and 51% higher than the base case with two and four recycle pumps operated at their pressure limits, respectively.

In order to match the purity of the four-zone SMB, the design for the parallel two-zone SMB requires an extra step. We start with the same feed rate and column dimensions as the base case of the four-zone SMB (Table 7). The system and operating parameters for the parallel two-zone system are shown in Table 6. Initially, the product purity and recovery

Table 6. Operating conditions of original cases for four-zone and parallel two-zone SMBs in the hybrid SMB-crystallization processes

	Four-zone SMB	Parallel two-zone SMB
Column length (m)	1.1	1.1
Column diameter (m)	4.1	4.1
Particle diameter (μm)	920	449
Feed rate (m^3/min)	1.45	6.09
D/F	4	4
Raffinate (m^3/min)	1.92	9.95
Extract (m^3/min)	5.33	20.29
Recycle rate (m^3/min)	3.0	3.99 ($Q_{\text{zone II,step a}}$)
Switching time (min)	2.17	2.56

Table 7. Pressure scaled design for four-zone SMBs with one column per zone in the hybrid SMB-crystallization processes[a]

Case	Original	Basis	Case 1	Case 2
d_p (μm)	920	449	393	365
Feed (m^3/min)	1.45	6.09	7.96	9.22
$g = Q_{new}/Q_{old}$	—	1	1.31	1.51
R_p	—	1	1.71	2.29
ΔP in zone I (bar)	0.042	0.74	1.27	1.71
ΔP in zone II (bar)	0.069	1.22	2.09	2.80
ΔP in zone III (bar)	0.049	0.86	1.47	1.97
ΔP in zone IV (bar)	0.124	2.18	3.73	5.00
Total ΔP in II & III (bar)	0.118	2.08	3.56	4.77
Total ΔP in I & IV (bar)	0.166	2.92	5.00	6.71
Total ΔP (bar)	0.284	5.00	8.56	11.47
p-Xylene purity (%)	87.4	87.4	87.4	87.3
p-Xylene recovery (%)	90.2	90.2	90.2	90.2
% of basis productivity	—	100	131	151

[a] Original: one pump in recycle line (pump not at pressure limit, Fig. 1); basis: one pump in recycle line (pump at pressure limit, Fig. 1); case 1: two pumps in recycle line (pumps at pressure limit); case 2: four pumps in recycle line (pumps at pressure limit).

obtained in a parallel two-zone SMB (Table 8, original case) is not as high as in a four-zone SMB (Table 7, basis). The new basis for the two-zone SMB (Table 8) was established with an identical *p*-xylene product purity, and the same D/F as the four-zone SMB by scaling to increase R_N and hence product purities by decreasing g while keeping $a = b = c = 1$. In the new basis the feed rate was reduced from 6.09 to 4.45 m^3/min, which reduced the productivity to 73%.

Table 8 shows that the productivity of the parallel two-zone SMBs can be increased by operating at the 5 bar ΔP limit. With one recycle pump in each train (two total, case 1), the productivity is 143% of the base case of the four-zone SMB (Table 7), and 9% higher than a four-zone SMB with two pumps (case 1 in Table 7). With two recycle pumps in each train (four total, case 2), the productivity is 175% of the base case of the four-zone SMB (Table 7), and 16% higher than a four-zone SMB with four recycle pumps (case 2 in Table 7). The parallel two-zone SMB with one column per zone can achieve higher productivity than the four-zone SMB with one column per zone with the same number of recycle pumps, identical column dimensions, same maximum ΔP, D/F, *p*-xylene purity and recovery but smaller particles.

One advantage of the four-zone SMB is that with multiple columns per zone it can achieve higher product purity and recovery. With additional

Table 8. Pressure scaled design for parallel two-zone SMBs with one column per zone in the hybrid SMB-crystallization processes[a]

Case	Original	New basis	Case 1	Case 2
d_p (μm)	449	449	320	290
Feed (m^3/min)	6.09	4.44	8.72	10.65
$g = Q_{new}/Q_{old}$	—	1	1.96	2.39
R_p	—	1	3.85	5.72
ΔP in zone I Train 1 (bar)	0.60	0.44	1.67	2.48
ΔP in zone II Train 1 (bar)	0.23	0.17	0.66	0.98
ΔP in zone I Train 2 (bar)	0.58	0.42	1.65	2.45
ΔP in zone II Train 2 (bar)	1.20	0.88	3.35	5.00
Total ΔP in Train 1 (bar)	0.83	0.61	2.33	3.47
Total ΔP in Train 2 (bar)	1.78	1.30	5.00	7.45
p-Xylene purity (%)	84.9	87.4	87.4	87.4
p-Xylene recovery (%)	88.9	90.1	90.1	90.1
% of basis, table 7 productivity	100	73	143	175

[a] Original and new basis: one pump in each train (pumps not at pressure limit, Fig. 2); case 1: one pump in each train (two total, pumps at pressure limit, Fig. 2); case 2: two pumps in each train (four total, pumps at pressure limit).

columns in the system, one can also add more pumps to increase utilization of available pressure drop (21). A four-zone SMB with two columns per zone was studied for this hybrid process. The maximum ΔP is again set to 5 bar. For the base case of a four-zone SMB with two columns per zone there is one pump operated at the pressure limit in the recycle line. The feed rate, column diameter, and particle diameter are the same as those of the base case for a four-zone SMB with one column per zone. To keep the same productivities, the column length and switching time of the four-zone SMB with two columns per zone are half those of the four-zone SMB with one column per zone. Cases 1, 2, and 3 have two, four, and eight recycle pumps, respectively.

The simulation results for scaling a four-zone SMB with two columns per zone and constant D/F are shown in Table 9. As expected, at the same D/F the product purity and recovery for the four-zone SMB with two columns per zone are higher than for the four-zone SMB with one column per zone. Note that the productivity increases for the four-zone SMB with two columns per zone and two and four recycle pumps are the same as for corresponding cases for a four-zone SMB with one column per zone (Table 7). For the scaled SMB design with eight pumps (case 3 in Table 9), the productivity is 214% of the base case in Table 7, 22% higher than a parallel two-zone SMB with one column per zone and four recycle pumps (case 2 in Table 8). If the four-zone SMB has more than two columns per zone, an even higher productivity can be expected with higher *p*-xylene purity and recovery.

Table 9. Pressure scaled design for four-zone SMBs with two columns per zone in the hybrid SMB-crystallization processes[a]

Case	Basis	Case 1	Case 2	Case 3
d_p (μm)	449	393	365	307
Feed (m^3/min)	6.09	7.96	9.22	13.04
$g = Q_{new}/Q_{old}$	1	1.31	1.51	2.14
R_p	1	1.71	2.29	4.59
ΔP in zone I (bar)	0.74	1.27	1.71	3.41
ΔP in zone II (bar)	1.22	2.09	2.80	5.59
ΔP in zone III (bar)	0.86	1.47	1.97	3.94
ΔP in zone IV (bar)	2.18	3.73	5.00	10.00
Total ΔP in II & III (bar)	2.08	3.56	4.77	9.53
Total ΔP in I & IV (bar)	2.92	5.00	6.71	13.41
Total ΔP (bar)	5.00	8.56	11.47	22.94
p-Xylene purity (%)	88.0	88.0	88.0	87.9
p-Xylene recovery (%)	91.3	91.3	91.3	91.3
% of basis, table 7 productivity	100	131	151	214

[a]Basis: one pump in recycle line (pump at pressure limit); case 1: two pumps in recycle line (pumps at pressure limit); case 2: four pumps in recycle line (pumps at pressure limit); case 3: eight pumps in recycle line (pumps at pressure limit).

The four-zone SMB with multiple columns per zone is superior to a parallel two-zone SMB with one column per zone in terms of product purity, recovery, and productivity, but it is significantly more complex.

The *p*-xylene purities (~87%) obtained in the SMB units are within the range of purity from the first stage of crystallization in a two-stage crystallizer, which indicates that single stage crystallization is sufficient in the hybrid process. The *p*-xylene recoveries of the SMBs are above 90%, 30% higher than the recovery of one–stage crystallization, which will reduce the isomerization reactor size significantly.

With equal numbers of pumps the parallel two-zone SMB can obtain 10–15% higher productivity than a four-zone SMB with one column per zone. However, the four-zone SMB has the advantage that multiple columns per zone increase purity and recovery, which allows one to simultaneously obtain high *p*-xylene purity and recovery with relatively low D/F. The productivity of four-zone SMB systems with multiple columns per zone can be increased by adding additional pumps between columns to fully utilize the maximum pressure drop while repacking with smaller diameter packing to retain product purity and recovery (21). As the number of columns increases more pump arrangements and options are available. A four-zone SMB with two or more columns per zone has higher *p*-xylene purity and recovery, and with eight pumps has a higher capacity than either of the one column per zone systems. The price for this increase performance is increased complexity.

Discussion

To simplify already complicated analyses and comparisons, only one pump in each train is considered in the SMB-SMB hybrid process (as shown in Fig. 2), and the pump may not be operated at pressure limit. Using the pressure utilization procedure with multiple pumps for either the parallel two-zone SMB and/or the four-zone SMB, smaller SMB units could be expected with the same throughput.

Economic factors have not been considered in this study. From the results of the hybrid SMB-SMB processes, we can see that there are balances between desorbent use, energy load, and overall recovery. High desorbent use results in a higher energy load for the distillation columns and higher overall recovery, which increases the operation cost and decreases the size of the isomerization reactor. Low desorbent use decreases the energy load of distillation columns and overall recovery. A complete economic analysis is required to determine the optimum design of these processes.

CONCLUSIONS

Hybrid processes with parallel two-zone and four-zone SMBs, and SMB plus crystallization were developed, and general design procedures were discussed. Simulations were done for retrofitting a p-xylene purification unit. A productivity increase of more than 100% was achieved with hybrid processes compared to the base case, with the trade-off of 3–5% lower overall recovery. With matched overall recovery, a more than 50% increase of productivity was obtained. For a hybrid SMB-SMB process using a two-feed raffinate distillation column, the total reboiler heat duty per unit product was 2–4% lower than the base case. Hybrid SMB-SMB processes can produce high p-xylene purity with high recovery and productivity.

A hybrid SMB-crystallization process was also developed, with focus on the SMB unit. A pressure utilization procedure was applied in this development by adding additional pumps between columns to operate columns at their pressure limits. A parallel two-zone SMB with one column per zone has a 10–15% higher productivity than a four-zone SMB with one column per zone with similar product purity and recovery. However, a four-zone SMB with two columns per zone and eight recycle pumps has a higher p-xylene purity and recovery and 22% higher productivity than a parallel two-zone SMB with one column per zone and four pumps. Four-zone SMBs with multiple columns per zone and multiple recycle pumps have the advantages of higher productivity, product purity and recovery, but they are more complex.

NOMENCLATURE

a	ratio of particle diameters in two designs, $d_{\mathrm{p,new}}/d_{\mathrm{p,old}}$
b	ratio of column lengths in two designs, $L_{\mathrm{new}}/L_{\mathrm{old}}$
c	ratio of column diameters in two designs, $D_{\mathrm{col,new}}/D_{\mathrm{col,old}}$
c_i	solute concentration of component i, kg/m^3
$\bar{c}_{i,\mathrm{pore}}$	volume average solute concentration in the liquid phase inside the porous particles, kg/m^3
c_{EB}	ethylbenzene concentration, kg/m^3
c_{F}	feed concentration, kg/m^3
c_{MX}	*m*-xylene concentration, kg/m^3
c_{OX}	*o*-xylene concentration, kg/m^3
c_{PX}	*p*-xylene concentration, kg/m^3
$c_{\mathrm{PX,E}}$	*p*-xylene concentration in extract, kg/m^3
$c_{\mathrm{PX,F}}$	*p*-xylene concentration in feed, kg/m^3
d_{p}	particle diameter, μm
D_{col}	column diameter, m
D	desorbent flow rate, m^3/min
D/F	desorbent-to-feed ratio, volume basis
E_{Z}	axial dispersion coefficient, based on superficial velocity, m^2/s
EB	ethylbenzene
F	feed flow rate, m^3/min
g	ratio of volumetric flow rate, $Q_{j,\mathrm{new}}/Q_{j,\mathrm{old}} = F_{\mathrm{new}}/F_{\mathrm{old}}$
$k_{\mathrm{m}}a_{\mathrm{p}}$	mass transfer resistance, 1/min
$K_{\mathrm{d}i}$	the fraction of the interparticle volume species can penetrate
L	column length, m
L_{MTZ}	length of mass transfer zone, m
M_{E}	extract flow rate, kg/h
M_{F}	feed flow rate, kg/h
MX	meta-xylene
OX	ortho-xylene
P	pressure drop, bar
Pe	Peclet number, Eq 2
PX	para-xylene
q	solute concentration on the solid phase, g/(cm^3 of adsorbent)
$\bar{q}_i$	the volume average solute concentration on the solid phase inside the porous particles, g/(cm^3 of adsorbent)
Q_j	volumetric flow rate in zone j, m^3/min
$Q_{\mathrm{zone\ II,step\ a}}$	volumetric flow rate in zone II step a in a two-zone SMB, m^3/min
Re	Reynolds number, $Re = v_{\mathrm{s}}d_{\mathrm{p}}\rho/\mu$
R_{N}	ratio of the fractional bed use in two designs, $(L/L_{\mathrm{MTZ}})_{j,\mathrm{new}}/(L/L_{\mathrm{MTZ}})_{j,\mathrm{old}}$

R_p	ratio of pressure drop in two designs, $\Delta P_{j,\text{new}}/\Delta P_{j,\text{old}}$
R_{reflux}	reflux ratio of distillation column
$R_{\text{reflux,min}}$	minimum reflux ratio of distillation column
R_{tsw}	ratio of switching time of two designs, $t_{\text{sw,new}}/t_{\text{sw,old}}$
t_{sw}	switch time, min

Greek Letters

ε_e	external void fraction
ε_p	internal void fraction
μ	liquid viscosity, cP
ρ_F	feed density, kg/m^3
ρ_D	desorbent density, kg/m^3
ρ_s	solid density, kg/m^3

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