Adsorption 11: 579–584, 2005

Thermally Assisted Simulated Moving Bed Systems

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Abstract. The principles of simulated moving bed (SMB) and thermal swing adsorption (TSA) are combined to develop a traveling wave mode, thermally assisted SMB. The four-zone, thermal SMB and the corresponding one-column, thermal Analog to the SMB are studied for separating binary systems with linear isotherms. Design parameters and operating conditions are determined using the local equilibrium theory and detailed simulations are done with the commercially available chromatography/SMB software package Aspen Chromatography v12.1. Simulations were performed for the separation of toluene/xylene with silica gel as the adsorbent and *n*-heptane as the desorbent. The SMB and Analog are operated with a heat exchanger heating or cooling the fluid before it enters each adiabatic column. The advantage of the traveling wave mode compared to the direct mode of heat transfer is since heat transfer rates are not limiting, the SMB and Analog systems can be scaled up easily.

Keywords: adsorption, SMB, TSA

Introduction

Simulated Moving Bed (SMB) systems are an efficient method for doing large-scale chromatographic separation, particularly of binary mixtures. Specifically, SMB technology has been commercialized for the separation of enantiomers, natural and biological products, petrochemicals and fine chemicals. The isothermal four-zone SMB for binary separations has been extensively studied by many groups and is now well understood (Ruthven and Ching, 1989; Mazzotti et al., 1997; Wankat, 1986).

By changing operating conditions such as temperature or solvent composition, the performance of SMBs can be optimized by adjusting the adsorption behavior of each zone. For example, if adsorption is made more favorable in zone 4 (solvent cleaning) and less favorable in zone 1 (column regeneration) less solvent is required. Wankat (1986) proposed a traveling wave mode thermal SMB in which the fluid is heated or cooled with heat exchangers (Fig. 1). Ruthven and Ching (1989) and Migliorini et al. (2001) extended the design criteria for linear and nonlinear SMBs, respectively, to study the direct mode where the column is heated or cooled through jackets. The direct mode is difficult to scale up in TSA systems (Matz et al., 1991). Migliorini et al. (2001) found that even in a 0.46 cm i.d. column operating with a 10°C temperature swing, radial heat transfer limits the allowable fluid velocities in a direct mode thermal SMB. Since the ratio (heat transfer rate)/(volume of adsorbent to be heated) is proportional to 1/(column diameter), scale

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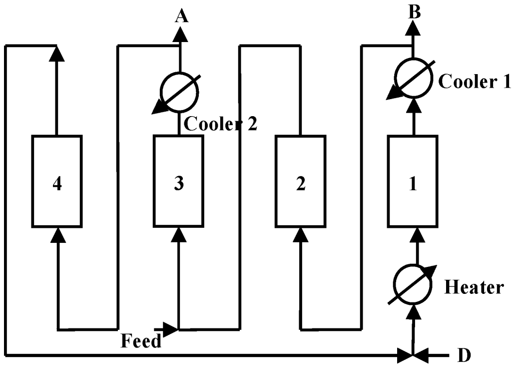

Figure 1. Thermal SMB system with traveling wave mode.

up to commercial size columns will be difficult if not impossible.

The purpose of this study is to develop thermally assisted SMBs that use heat exchangers to change the fluid temperature and thus cause a thermal wave to pass through the columns (Fig. 1). A thermally assisted SMB can be applied to the separation of mixtures that are thermally stable and have significant shifts in isotherms when the temperature changes. Although the traveling wave mode solves the serious problem of heat transfer limitations, the heat exchangers will increase the external dead volume which can increase both the lag time and external mixing. Although lag time can be adjusted for in the design of the SMB, external mixing will reduce separation. The one-column chromatograph with recycle analogous to a four-zone simulated moving bed developed by Abunasser et al. (2003), "the Analog", is also modified. The Analog has one chromatography column connected to a number of tanks equal to or greater than the number of steps in the SMB cycle (the traveling wave mode system is shown in Fig. 5). It is an inexpensive, more flexible alternative particularly when repacking the column(s) is done routinely during campaigns, but with mixed tanks it provides lower purities than SMBs.

Theory

The local equilibrium model uses simplified forms of the mass and energy balances to enable analytical calculations. The solid and fluid are assumed to be locally in equilibrium. The mass and energy balances for non-isothermal fixed bed adsorption can be derived by writing differential balances around the solid and fluid phases. If one assumes that radial gradients are negligible, no chemical reactions, mass transfer is extremely rapid and there is no axial dispersion, the mass balances can be solved for the solute wave velocity (e.g., Wankat, 1986)

$$u_s(T) = \frac{v_j}{1 + [(1-\varepsilon_e)/\varepsilon_e]\varepsilon_p K_d + [(1-\varepsilon_e)/\varepsilon_e](1-\varepsilon_p)\rho_s \partial q_i/\partial c_i} \tag{1}$$

where K_d is the steric exclusion factor. If the isotherm is linear, $\partial q/\partial c$ is replaced by $K_{eq}(T)$.

Temperature changes force the separation. The velocity of the thermal wave can be obtained from an energy balance. If one assumes the heats of adsorption and mixing are negligible, the column is adiabatic, heat transfer is very rapid, and thermal axial dispersion is negligible, the average velocity of the thermal wave is

$$u_{th} = \frac{v_j}{1 + (1-\varepsilon_e)\varepsilon_p/\varepsilon_e + [(1-\varepsilon_e)(1-\varepsilon_p)C_{p,s}\rho_s]/(\varepsilon_e \rho_f C_{p,f})} \tag{2}$$

In a typical liquid system with $T_h > T_F > T_c$, $u_{th} > u_s(T_h) > u_s(T_F) > u_s(T_c)$. The average velocity of port movement is $u_{\text{port}} = L/t_{sw}$. The conditions to have A exit in the A product and B in the B product, respectively, are the same as for an isothermal SMB,

$$u_{A2}, u_{A3} \geq u_{\text{port}} \geq u_{A4}; \quad u_{B1} \geq u_{\text{port}} \geq u_{B2}, u_{B3} \tag{3a, b}$$

In isothermal systems Eq. (3) are satisfied by varying the velocities in each zone. In the thermal SMB the solute velocities are also functions of temperature, which adds additional degrees of freedom to satisfy these inequalities.

Local equilibrium calculations and model simulations were done for the separation of a binary mixture of toluene and xylene with silical gel as the adsorbent and n-heptane as the desorbent. Matz and Knaebel (1991) reported linear experimental isotherms that satisfy the Arrhenius form, $K_i = A_i e^{B_i/T_j}$. The isotherm parameters for toluene are $A = 0.0061$ and $B = 2175.3$ and for xylene are $A = 0.0105$ and $B = 2115.1$. The isotherms are shown in Fig. 2. The local equilibrium solution for the thermally assisted SMB system is shown in Fig. 3.

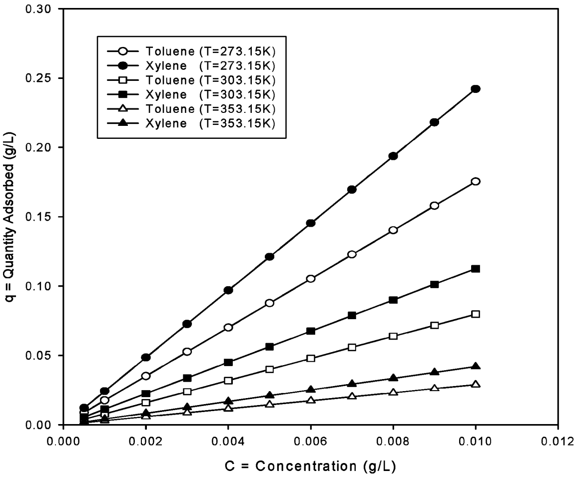

Figure 2. Adsorption isotherms for toluene-xylene on silica gel.

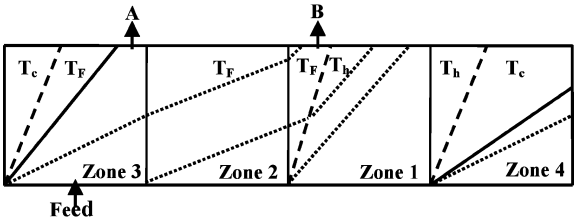

Figure 3. Local equilibrium solution for traveling wave thermal SMB. Key: - - - thermal wave;—solute A, · · · solute B.

To compare the performance of thermally assisted SMB systems, the purity index (PI), the average purity of two major components in two products, and the productivity are defined as,

$$\text{Purity Index (PI)} = \frac{\text{Purity of} A(\%) \text{ in A product} + \text{Purity of} B(\%) \text{in B product}}{2} \tag{4}$$

$$\text{Productivity} = \frac{\text{Volumetric flowrate of feed}}{\text{total adsorbent volume}} \tag{5}$$

Detailed Simulation and Simulation Results

In order to examine traveling wave thermally assisted SMB and the SMB Analog, more detailed simulations are performed using the commercially available chromatography/SMB software package Aspen Chromatography version 12.1, which includes energy balances. The thermally assisted SMB system shown in Fig. 1 is simulated with two columns per zone. The flow rates are estimated from the local equilibrium theory. Dispersion is estimated and the linear lumped resistance mass transfer model is used (Wankat, 1986).

$$\frac{\partial q_i}{\partial t} = k_m a_p (c_i - c_i^*) \quad \text{and}$$
$$k_m a_p = \left[\frac{1}{k_f a_p} + \frac{d_p^2}{60 D_{mp} K (1 - \varepsilon_e) \rho_p} \right]^{-1} \tag{6}$$

where D_{mp} is the effective molecular diffusivity in the pore. The columns are assumed to be adiabatic.

First, to investigate the temperature effects under isothermal operations the simulations were run for isothermal separations at different temperatures. The base conditions and results of these simulations are summarized in Table 1. Switching times were changed to operate at the optimum port velocity based on the local equilibrium theory. If maximizing PI is desired, there is a slight advantage to operating the SMB hot.

Table 2 shows the simulation results with different heater and cooler temperatures at $D/F = 1.0$ with constant flowrates. The local equilibrium theory was used to estimate the port velocity based on the separation in zones 2 and 3 at T_F. When only the heater temperature increases (Runs 1 to 3), the extract purities go through a maximum value. The raffinate purity increases continuously with the increase in the heater temperature because $u_{B1} \gg u_{\text{port}}$. When only the temperature in cooler 2 was decreased, the raffinate and extract purities increase (compare Runs 1 and 4, 2 and 5, 3 and 6). This occurs because u_{A4} decreases as temperature drops ($u_{\text{port}} > u_{A4}$). When the feed and cooler 1 temperatures were decreased to cooler 2's temperature (compare Runs 6 and 7), the raffinate purity increased and the extract purity decreased markedly since u_{A2} decreased and $u_{A2} \geq u_{\text{port}}$ is no longer satisfied.

We also purposely ran the SMB incorrectly with a heater temperature that is less than the "cooler" temperature. As expected, the purity index (results not shown) is lower than for the base case. The purities at $D/F = 1.0$ can be improved by changing operating conditions. The flow rates in each zone were recalculated based on the values of the isotherms at the different temperatures used in the heater and coolers. Table 3 shows the simulation conditions and results. As expected, adjusting the flow rates improved the separation. The base case is Run 1 in Table 2. The highest purity is obtained in Run 5 with the hottest zone 1 and coldest zone 4.

Table 1. SMB simulation conditions and results for base cases at $D/F = 1.0$. System has two columns per zone.

	Temperature (K)				Raffinate purity (%)		Extract purity (%)		
Run	Heater	Cooler 1	Feed	Cooler 2	*A*	*B*	*A*	*B*	PI
1	273.15	273.15	273.15	273.15	**63.34**	36.66	34.35	**65.65**	64.50
2	298.15	298.15	298.15	298.15	**62.72**	37.28	32.28	**67.72**	65.22
3	323.15	323.15	323.15	323.15	**63.90**	36.10	31.58	**68.42**	66.16
4	353.15	353.15	353.15	353.15	**63.55**	36.45	31.01	**68.99**	66.27

Feed temperature is same as cooler 1. $C_{ps} = 920.0$ (J/kg/K), $C_{pf} = 2243.9$ (J/kg/K), Productivity = 0.013, $L = 100$ cm, $D_c = 2$ cm, $\varepsilon_e = 0.43$, $\varepsilon_p = 0.5$, $d_p = 0.0335$ cm, $\rho_p = 1.05$ kg/m^3, $k_m a_{p,T} \approx 4.71$ mim^{-1}, $k_m a_{p,X} \approx 5.57$ min^{-1}.
Feed = Raffinate = Extract = Desorbent:32.7518 cm^3/min, Recycle Flowrates (cm^3/min): Run 1 = 98.26, Run 2 = 102.98, Run 3 = 113.82, Run 4 = 558.99, Switch time (min): Run 1: $t_{sw} = 18.27$, Run 2: $t_{sw} = 10.00$, Run 3: $t_{sw} = 6.00$, Run 4: $t_{sw} = 0.86$.

Table 2. SMB simulation conditions and results at $D/F = 1.0$. System has two columns per zone. All flowrates are constant.

					Purity (%)				
	Temperature (K)				Raffinate		Extract		
Run	Heater	Cooler 1	Feed	Cooler 2	*A*	*B*	*A*	*B*	PI
1	298.15	298.15	298.15	298.15	**62.72**	37.28	32.28	**67.72**	65.22
2	323.15	298.15	298.15	298.15	**69.64**	30.36	29.09	**70.91**	70.28
3	353.15	298.15	298.15	298.15	**69.75**	30.25	29.13	**70.87**	70.31
4	298.15	298.15	298.15	273.15	**66.23**	33.77	19.23	**80.77**	73.50
5	323.15	298.15	298.15	273.15	**73.79**	26.21	16.47	**83.53**	78.66
6	353.15	298.15	298.15	273.15	**73.81**	26.19	16.45	**83.55**	78.68
7	353.15	273.15	273.15	273.15	**84.18**	15.82	48.15	**51.85**	68.02

Flowrate (cm^3/min): Feed: 32.7518, Raffinate: 32.7518, Extract: 32.7518, Desorbent: 32.7518, Recycle: 102.98,
Feed temperature is same as cooler 1 temperature. $t_{sw} = 10$ min.

Table 3. SMB simulation conditions and results with adjusted flow rates with constant productivity at $D/F = 1.0$, $t_{sw} = 10$ min.

	Temperature (K)				Raffinate purity (%)		Extract purity (%)		
Run	Heater	Cooler 1	Feed	Cooler 2	*A*	*B*	*A*	*B*	PI
1	323.15	298.15	298.15	298.15	**70.29**	29.71	24.19	**75.81**	73.05
2	353.15	298.15	298.15	298.15	**70.76**	29.24	17.34	**82.66**	76.71
3	298.15	298.15	298.15	273.15	**68.27**	31.73	19.68	**80.32**	74.30
4	323.15	298.15	298.15	273.15	**71.88**	28.12	13.70	**86.30**	79.09
5	353.15	298.15	298.15	273.15	**72.27**	27.73	13.21	**86.79**	79.53

Parameter		Run 1	Run 2	Run 3	Run 4	Run 5
Flowrate (cm^3/min)	Feed	32.7518	32.7518	32.7518	32.7518	32.7518
	Raffinate	37.9008	46.1391	28.0558	46.0018	46.0017
	Extract	27.6028	19.3645	37.4478	19.5018	19.5019
	Desorbent	32.7518	32.7518	32.7518	32.7518	32.7518
	Recycle	97.8306	89.5922	107.6756	89.7296	89.7296

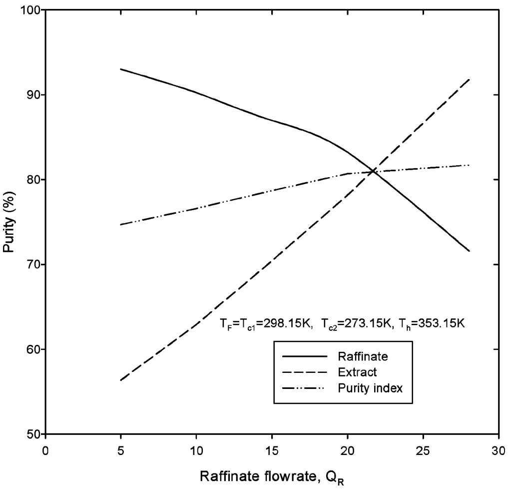

Figure 4. Influence of raffinate and extract flowrates at $D/F = 0.0$. Constraint: $Q_R + Q_E = Q_F = 32.7518$ cm^3/min.

Figure 4 shows simulations optimized at $D/F = 0.0$. All desorbent enters with the feed. Only the raffinate and extract flow rates were adjusted, while everything else is kept constant ($T_h = 353.15$ K, $T_F = T_{c1} = 298.15$ K, $T_{c2} = 273.15$ K). The raffinate purity increases and the extract purity decreases with decreasing raffinate flow rate. The results show that with no additional desorbent, a traveling wave, thermally assisted SMB system separating a dilute feed can achieve a higher purity index than an isothermal SMB at $D/F = 1.0$ (Table 1).

Thermal Wave Operation of Analog to SMB

The Analog corresponding to the traveling wave thermal SMB with one column per zone is shown in Fig. 5. Simulations are run for the Analog with two columns per zone (i.e. total 8 tanks) for the same binary system used in the SMB. The results for both traveling wave thermally assisted SMB and Analog for this configuration are shown in Table 4. As expected, the purities in the analog increase when it is operated non-isothermally and the percent increase in purities are close to that seen in the SMB. The extract purity in the last run decreases because at the low temperature solute velocity u_{A2} violates Eq. (3a). A thermally operated analog will be relatively easy to scale-up, simple to control because the temperatures in well-mixed tanks are easily controlled, and quite flexible.

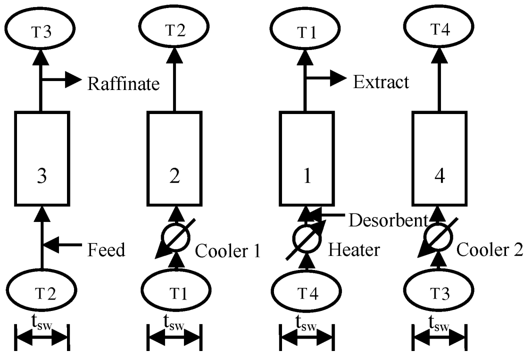

Figure 5. Steps for one-column traveling-wave mode thermal Analog to a four-zone SMB with one column per zone.

Higher Purity Runs

There are several methods that can be used to obtain higher purities. Among these are increasing the D/F value, increasing the number of columns per zone and decreasing the productivity. Some of these methods were investigated using Run 5 in Table 3 as the base case. First D/F was increased to 3.30 without changing the number of columns used. This resulted in the

Table 4. Comparison of results for both SMB and Analog at *D/F* = 1.0. System has two columns per zone.

Temperature (K)				SMB				Analogue			
Heater	Cooler 1	Feed	Cooler 2	Raffinate		Extract		Raffinate		Extract	
298.15	298.15	298.15	298.15	**62.72**	37.28	32.28	**67.72**	**59.59**	40.41	37.29	**62.71**
298.15	298.15	298.15	273.15	**66.23**	33.77	19.23	**80.77**	**63.52**	36.48	27.29	**72.71**
323.15	298.15	298.15	273.15	**73.79**	26.21	16.47	**83.53**	**71.82**	28.18	24.41	**75.59**
353.15	298.15	298.15	273.15	**73.81**	26.19	16.45	**83.55**	**72.39**	27.61	24.53	**75.47**
353.15	273.15	273.15	273.15	**84.18**	15.82	48.15	**51.85**	**82.23**	17.77	48.28	**51.72**

Flowrates (cm^3/min): Feed: 32.7518, Raffinate: 32.7518, Extract: 32.7518, Desorbent: 32.7518, Recycle: 102.98, $t_{sw} = 10$ min.

raffinate and extract purities increasing to 86.68 and 88.82% respectively in the SMB and to 83.35 and 77.86% in the Analog. Next the number of columns per zone was increased to 3 while keeping $D/F = 3.3$ and productivity constant. This caused a further increase in the raffinate and extract purities to 94.76% and 93.01 in the thermal SMB and to 91.99 and 83.45% in the thermal Analog.

Discussion and Conclusions

Thermally assisted SMBs and their Analogs operated in the traveling wave mode can significantly reduce the amount of desorbent required while improving the purity if the isotherms are temperature dependent. This study is preliminary since SMBs are restricted to dilute feeds with linear isotherms, and the design of the heat exchangers was not studied. Future work will study linear and nonlinear systems including the design of the heat exchangers and optimization of the temperature levels to produce higher purity products.

Acknowledgments

Supported by NSF Grant CTS-0211208 and the ERC for Advanced Bioseparation Technology, KOSEF.

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