Non-equilibrium modelling of simulated moving bed processes for separation of Xylenes in petrochemical industry

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Xylene is an aromatic hydrocarbon with a single ring and two methyl groups attached to this ring in positions 1-2, 1-3 and 1-4, called o-xylene, m-xylene, and p-xylene.

Xylenes are obtained as isomeric mixtures by repeated extractions or distillations of light petroleum fractions.

o-Xylene and m-Xylenes are mainly used in the production of phthalic anhydride and isophthalic acid respectively.

p-Xylene is the principal precursor to terephthalic acid and dimethyl terephthalate. PET (polyethylene terephthalate), is produced by the reaction of terephthalic acid and ethylene glycol. Amongst others, this specific example illustrates the importance of separation of pure p-Xylene from the remaining isomers.
The separation of xylene isomers is one of the most difficult separations in petrochemistry. Literature reports numerous patents and articles on the use of several principles to separate xylene isomers.

Nowadays adsorption processes are preferred because they achieve a significantly higher recovery of p-xylene.

The state-of-the art processes for xylene separation were developed by UOP, Toray, and IFP group where Simulated Moving Bed (SMB) technology is employed.

SMB processes for xylene separation systematically employ p-xylene selective adsorbents.
• The simulated moving bed (SMB) technology is an important technique for large-scale continuous separation processes.

• This technology has been applied over four decades in the petrochemical industry.

• Currently enjoying separation of sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods and enantiomers.
The reference process for simulated moving bed (SMB) is true moving bed (TMB).

Where, in a single column, counter-current flow between a solid and a liquid phase is imagined.
- In the SMB system, the solid phase is not moving like in the hypothetical TMB.

- The simulation of solid phase movement is accomplished by switching the valves of inlet/outlet lines.
Because of the complex nature of operation of SMB, generally a model-based control scheme is used for better understanding of the process.

Thus a great deal of theoretical work* has been carried out for developing useful simulation procedures for design and process development purposes.

*Some examples:
C. Migliorini, M. Mazzotti and M. Morbidelli, AIChE J., 46 (200) 1384.
There are several models to be used for chromatographic separations whether it is at the analytical scale or at the preparative/production scale, including:

- the ideal model
- the equilibrium dispersive model
- the transport dispersive model
- the general rate model
(a) the ideal model, (b) the equilibrium dispersive model, (c) the transport dispersive model, (d) the general rate model
Homogeneous Solid Diffusion

In homogeneous solid diffusion model, all solute within the particle, whether free or adsorbed, is lumped into a single quantity q.

\[
\frac{\partial q}{\partial t} = \frac{D_{\text{solid}}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
\]

particle phases

bulk fluid

Adsorption Isotherm

In the Column Governing Differential Equation, there are two independent variables (x & t) and two dependent variables (c & c*).
\[
\frac{\partial c(x,t)}{\partial t} + v \frac{\partial c(x,t)}{\partial x} + \frac{3(1-\varepsilon)}{\varepsilon r_p} k_f \left[ c(x,t) - c_s^*(x,t) \right] = D_a \frac{\partial^2 c(x,t)}{\partial x^2}
\]

**HOW DO WE EVALUATE?**

- \(q_s(x,t)\) = solid conc. at solid surface
- \(\bar{q}(x,t)\) = average solid conc.
- \(q(r,t) = A(t) + B(t) r^2\) time dependent parabolic solid conc. profile at a certain bed height

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**MAIN ASSUMPTIONS**

- In order to represent the external and internal resistances, separate “film mass transfer coefficient” and “homogeneous solid diffusion coefficient” values are used for A and B components.

- Axial dispersion of components A and B can be represented with a single constant dispersion coefficient.

- Nonlinear isotherm (multicomponent Langmuir). Instant equilibrium is only attained at the solid-liquid interphase.

- Monosized spherical particles. Columns init. conc. (mobile and stationary phase) is zero.
\[ q_{sA}^* (t) = \bar{q}_A (x,t) + \frac{Bi_A}{5} \left[ c_A (x,t) - c_{sA}^* (x,t) \right] \] (1)

\[ q_{sA}^* (x,t) = \frac{a_A c_{sA}^* (x,t)}{1 + b_A c_{sA}^* (x,t) + b_B c^*_{sB} (x,t)} \] (2)

\[ q_{sB}^* (x,t) = \frac{a_B c_{sB}^* (x,t)}{1 + b_A c_{sA}^* (x,t) + b_B c^*_{sB} (x,t)} \] (3)

\[ c_{sB}^* (x,t) = \frac{a_A q_{sB}^* (x,t) c_{sA}^* (x,t)}{a_B q_{sA}^* (x,t)} \] (4)

In the numerical solution "one time step earlier" value this ratio will be used.

From eqs. (1), (2) and (4)
\[
(c^*_{sA}(x,t))^2 + \left[ \frac{5}{Bi_A} \frac{q_{Am}}{\eta_A} - \frac{5}{Bi_A} \frac{q_A(x,t)}{\eta_A} + \frac{K_A}{\eta_A} - c_A(x,t) \right] c^*_{sA}(x,t) - \\
\frac{K_A}{\eta_A} \left[ \frac{5}{Bi_A} \frac{q_A(x,t)}{\eta_A} + c_A(x,t) \right] = 0
\tag{6}
\]

\[
c_{sA}^*(x,t) = \frac{-M_A + \sqrt{M_A^2 + 4 \frac{K_A}{\eta_A} \left[ c_A(x,t) + \frac{5\bar{q}_A(x,t)}{Bi_A} \right]}}{2}
\tag{7}
\]

where

\[
M_A = \left[ \frac{5}{Bi_A} \frac{q_{mA}}{\eta_A} - \frac{5}{Bi_A} \frac{q_A(x,t)}{\eta_A} + \frac{K_A}{\eta_A} - c_A(x,t) \right]
\tag{8}
\]

\[
\eta_A = 1 + \frac{q^{*}_{sB} / q_{mB}}{q^{*}_{sA} / q_{mA}}
\tag{9}
\]

\[
q_{mA} = a_A / b_A
\tag{10}
\]

\[
K_A = 1 / b_A
\tag{11}
\]
This is how we evaluate $c_{sA}^*(x,t)$.
Referring to the figure, mass balance for the control volume of $2\Delta z$ height gives stationary phase average concentration in discretization scheme as shown by Eq. (12), where $h$ and $k$ are the distance and time increments, respectively.

\[
\bar{q}_{i,j} = \bar{q}_{i,j-1} + \frac{\varepsilon k}{2(1 - s)h} \left[ \nu (c_{i-1,j} - c_{i+1,j}) - 2h \frac{\partial c(z,t)}{\partial t} + \frac{D_a (c_{i-1,j} - 2c_{i,j} + c_{i+1,j})}{h} \right]
\]

(12)


**Effect of film mass transfer coefficient**

Dp = 60 micrometers

- A, \( k_f = 1 \times 10^{-2} \) cm/s
- B, \( k_f = 1 \times 10^{-2} \) cm/s
- A, \( k_f = 1 \times 10^{-4} \) cm/s
- B, \( k_f = 1 \times 10^{-4} \) cm/s

### Common Parameters

- \( q_m \) (mg/cm³ solid): 15, 25
- \( K \) (mg/cm³): 2, 1
- \( D_s \) (cm²/s): \( 1.50 \times 10^{-8} \), \( 2.50 \times 10^{-8} \)
- \( D_a \) (cm²/s): \( 1.00 \times 10^{-3} \), \( 1.00 \times 10^{-3} \)
- \( c_0 \) (mg/cm³): 50, 50
- L (cm): 15
- \( \text{Vol}_{\text{Inject}} \) (µL): 30
- \( Q_{\text{eluent}} \) (cm³/min): 1.2
- \( D_c \) (mm): 4.6
- \( \varepsilon_c \) (-): 0.45

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### Effect of Internal Resistance

**Dp = 15 micrometers**

- **Comp. A**, $D_s = 1.50 \times 10^{-9}$ cm$^2$/s
- **Comp. B**, $D_s = 2.50 \times 10^{-9}$ cm$^2$/s

- $q_m$ (mg/cm$^3$ solid): 15, 25
- $K$ (mg/cm$^3$): 2, 1
- $k_f$ (cm/s): $5.00 \times 10^{-3}$, $5.00 \times 10^{-3}$
- $D_a$ (cm$^2$/s): $1.00 \times 10^{-3}$, $1.00 \times 10^{-3}$
- $c_0$ (mg/cm$^3$): 50, 50

### Common Parameters

- $L$ (cm): 15
- $Vol_{Inject}$ (µL): 30
- $Q_{eluent}$ (cm$^3$/min): 1.2
- $D_c$ (mm): 4.6
- $\epsilon_c$ (-): 0.45

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### Component A

- $q_m$ (mg/cm$^3$ solid): 15
- $K$ (mg/cm$^3$): 2
- $k_f$ (cm/s): $5.00 \times 10^{-3}$
- $D_s$ (cm$^2$/s): $1.50 \times 10^{-9}$
- $D_a$ (cm$^2$/s): $1.00 \times 10^{-3}$
- $c_0$ (mg/cm$^3$): 50

### Component B

- $q_m$ (mg/cm$^3$ solid): 25
- $K$ (mg/cm$^3$): 1
- $k_f$ (cm/s): $5.00 \times 10^{-3}$
- $D_s$ (cm$^2$/s): $2.50 \times 10^{-9}$
- $D_a$ (cm$^2$/s): $1.00 \times 10^{-3}$
- $c_0$ (mg/cm$^3$): 50

### Common Parameters

- $L$ (cm): 15
- $Vol_{Inj}$ (µL): 30
- $Q_{eluent}$ (cm$^3$/min): 1.2
- $D_p$ (µm): 15
- $D_c$ (mm): 4.6
- $\varepsilon_c$ (-): 0.45

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Component A
L = 10 cm

Component A
L = 20 cm

$\mathbf{Comp. A}$
$q_m$ (mg/cm$^3$ solid) 15 25
$K$ (mg/cm$^3$) 2 1
$k_f$ (cm/s) $5.00 \times 10^{-3}$ $5.00 \times 10^{-3}$
$D_s$ (cm$^2$/s) $1.50 \times 10^{-9}$ $2.50 \times 10^{-9}$
$D_a$ (cm$^2$/s) $1.00 \times 10^{-3}$ $1.00 \times 10^{-3}$
$c_0$ (mg/cm$^3$) 50 50

$\mathbf{Comp. B}$
$q_m$ (mg/cm$^3$ solid) 15 25
$K$ (mg/cm$^3$) 2 1
$k_f$ (cm/s) $5.00 \times 10^{-3}$ $5.00 \times 10^{-3}$
$D_s$ (cm$^2$/s) $1.50 \times 10^{-9}$ $2.50 \times 10^{-9}$
$D_a$ (cm$^2$/s) $1.00 \times 10^{-3}$ $1.00 \times 10^{-3}$
$c_0$ (mg/cm$^3$) 50 50

$\mathbf{Common Parameters}$
$Vol_{Inject}$ (µL) 30
$Q_{eluent}$ (cm$^3$/min) 1.2
$D_p$ (µm) 15
$D_c$ (mm) 4.6
$\varepsilon_c$ (-) 0.45
Component B
L = 10 cm

Component B
L = 20 cm

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<thead>
<tr>
<th>Parameter</th>
<th>Comp. A</th>
<th>Comp. B</th>
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<tbody>
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<td>( q_m ) (mg/cm³ solid)</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>( K ) (mg/cm³)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>( k_f ) (cm/s)</td>
<td>( 5.00 \times 10^{-3} )</td>
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<td>( 1.00 \times 10^{-3} )</td>
<td>( 1.00 \times 10^{-3} )</td>
</tr>
<tr>
<td>( c_0 ) (mg/cm³)</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

**Common Parameters**

- \( V_{\text{Inject}} \) (µL): 30
- \( Q_{\text{eluent}} \) (cm³/min): 1.2
- \( D_p \) (µm): 15
- \( D_c \) (mm): 4.6
- \( \varepsilon_c \) (-): 0.45

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The node model

**Desorbent Node:** \( Q_1 = Q_D + Q_4 \)
\[ c_1^{in} = \frac{(c_D Q_D + c_4^{out} Q_4)}{(Q_D + Q_4)} \]

**Extract Node:** \( Q_2 = Q_1 - Q_E \)
\[ c_E = c_1^{out} = c_2^{in} \]

**Feed Node:** \( Q_3 = Q_2 + Q_F \)
\[ c_2^{in} = \frac{(c_F Q_F + c_2^{out} Q_2)}{(Q_F + Q_2)} \]

**Raffinate Node:** \( Q_4 = Q_3 - Q_R \)
\[ c_R = c_3^{out} = c_4^{in} \]

**Overall:** \( Q_E + Q_R = Q_F + Q_D \)

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Node model - Cyclic port switching - Assigning new values for column inlet flow rates and inlet concentrations at each switch.

The General Rate Model

Non-linear adsorption isotherm (multicomponent Langmuir)

Switching time: 4 minutes

Time = 12 switching time + the time shown on the x axis

\[ Q_{\text{Des}} = 5.30 \text{ mL/min}; \quad Q_{\text{F}} = 1.20 \text{ mL/min}; \quad Q_{\text{Ext}} = 3.00 \text{ mL/min}; \quad Q_{\text{Raf}} = 3.50 \text{ mL/min}; \]

\[ q_{\text{mA}} = 15 \text{ mg/cm}^3_{\text{solid}}; \quad q_{\text{mB}} = 25 \text{ mg/cm}^3_{\text{solid}}; \quad K_A = 2 \text{ mg/cm}^3; \quad K_B = 1 \text{ mg/cm}^3; \]

\[ D_{Aa} = D_{Ba} = 1 \times 10^{-3} \text{ cm}^2/\text{s}; \quad k_{fA} = k_{fB} = 5 \times 10^{-3} \text{ cm/s}; \quad D_{sA} = 1.5 \times 10^{-3} \text{ cm}^2/\text{s}; \quad D_{sB} = 2.5 \times 10^{-3} \text{ cm}^2/\text{s}; \]

\[ L = 15 \text{ cm}; \quad D_c = 4.6 \text{ mm}; \quad D_p = 15 \mu\text{m} \]
Thank you for your attention.