Adsorption Process Development

PSA and SMB design

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Outline

PSA

- Cycle and basic steps;
- Process performance parameters;
- Hydrogen purification;
- Simulation of a pilot unit for hydrogen purification.

SMB

- Xylene isomers;
- Separation processes;
- Adsorbents used for xylene isomers liquid phase separation;
- Xylene isomers liquid phase separation with MIL-53 (Al).
The operation of a Pressure Swing Adsorption process involves the definition of a **PSA cycle**: a sequential combination of elementary pre-defined steps.
The basic steps used in PSA are:

- Adsorption (production);
- Blowdown;
- Purge;
- Pressurization.
Pressure swing adsorption - Steps

Adsorption (production)

The feed stream is introduced at the column inlet.

The more adsorbed species are retained by the adsorbent while the less adsorbed species continue moving along the column until they exit it and are produced.
Pressure swing adsorption - Steps

Blowdown

The column is evacuated.

By decreasing the pressure we decrease the working capacity.

The more retained component will be desorbed and leaves the column.
Purge

Some of the product from a column that is in the production step is introduced in this column.

This reduces the partial pressure allowing a further desorption of the more retained specie.

This step also cleans the voids.
Pressurization co-current

The column is pressurized with feed at high pressure.

By increasing the pressure we increase the working capacity.
Pressure swing adsorption - Steps

Pressurization counter-current

The column is pressurized with a fraction of the light product at high pressure.
Basic Steps – **Skarstrom cycle**

For a two-bed PSA the steps may be organized as following:

<table>
<thead>
<tr>
<th>Press</th>
<th>Ads</th>
<th>Blwd</th>
<th>Purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blwd</td>
<td>Purge</td>
<td>Press</td>
<td>Ads</td>
</tr>
</tbody>
</table>
Pressure swing adsorption - Steps

The basic steps used in PSA are:

- Adsorption (production);
- Blowdown;
- Purge;
- Pressurization.

Other steps used in PSA are:

- Pressure equalization (provide and receive);
- Rinse.
Pressure equalization - provide

Before the concentration wave reaches the end of the column, the production is stopped.

The column is then connected to other at low pressure to provide gas for a partial pressurization.

This step allows for significant energy cost reduction.
Pressure equalization - receive

After the column is cleaned, it is connected to a column that ended the production step and receives gas for a partial pressurization.

Afterwards this column will be further pressurized with feed/light product.
Rinse

When a high purity heavy compound is needed a step analogous to the purge can be employed.

Prior to the blowdown, a fraction of the heavy product is fed to the bed, increasing the concentration of the product at bed inlet.
Performance parameters

Process simulation can be used to predict:

- Product purity;
- Product recovery;
- Productivity;
- Energy consumption.
Performance parameters

**Product purity** – molar fraction of the produced compound on the product stream

<table>
<thead>
<tr>
<th>A+B</th>
<th>Press CoC</th>
<th>Ads</th>
<th>Blwd</th>
<th>Purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blwd</td>
<td>Purge</td>
<td>Press CoC</td>
<td>Ads</td>
<td></td>
</tr>
</tbody>
</table>

Light product purity = \[
\frac{\int_{0}^{\text{tads}} C_B u_0|_{z=L} dt}{\left( \int_{0}^{\text{tads}} C_A u_0|_{z=L} dt + \int_{0}^{\text{tads}} C_B u_0|_{z=L} dt \right)}
\]
Performance parameters

Product recovery – ratio between the moles produced and the moles fed

<table>
<thead>
<tr>
<th></th>
<th>A+B</th>
<th>Press CoC</th>
<th>Ads</th>
<th>Blwd</th>
<th>Purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press CoC</td>
<td>Ads</td>
<td>Blwd</td>
<td>Purge</td>
<td>Ads</td>
<td></td>
</tr>
</tbody>
</table>

Light product recovery = \( \frac{\int_0^{t_{\text{ads}}} C_B u_0 \big|_{z=L} dt - \int_0^{t_{\text{purge}}} C_B u_0 \big|_{z=L} dt}{\int_0^{t_{\text{press}}} C_B u_0 \big|_{z=0} dt + \int_0^{t_{\text{ads}}} C_B u_0 \big|_{z=0} dt} \)
Performance parameters

Process simulation can be used to predict:

- Product purity;
- Product recovery;
- Productivity;
- Energy consumption.

\[
\text{Productivity} = \frac{\text{moles}}{\text{time} \times \text{mass of adsorbent}}
\]
Performance parameters

Process simulation can be used to predict:

- Product purity;
- Product recovery;
- Productivity;
- **Energy consumption** – compressors, pumps...
Four hydrogen purification technologies are widely used in industry:

- Absorption (chemical and physical);
- Adsorption;
- Membranes;
- Cryogenic processes.
Before 1980, hydrogen production and purification generally followed these steps:
Before 1980, hydrogen production and purification generally followed these steps:

1. Steam reforming of the fuel
2. Formation mainly of $\text{H}_2$, $\text{CO}_2$ and $\text{CO}$
3. For steam-methane reforming:
   - $T = 830-850 \, ^\circ\text{C}$
   - $P = 25-50 \, \text{bar}$
Before 1980, hydrogen production and purification generally followed these steps:

1. **Steam Fuel Reforming**
   - **Reformer**
   - **High Temperature Shift**
   - **Low Temperature Shift**

2. **Conversion of CO to H₂**
   - **CO₂ Wash System**
   - **Methanator**

**Conditions**:
- **20 bar**
- **315-430 °C**
- **205-230 °C**

**Conversion of CO to H₂**
Before 1980, hydrogen production and purification generally followed these steps:

Steam → Reforming → High Temperature Shift → Low Temperature Shift → CO$_2$ Wash System → Methanator → H$_2$

Removal of CO$_2$ by wet scrubbing using a weak base (potassium carbonate) or an amine (ethanolamine) at 70-95 ºC and 20-50 bar.
Before 1980, hydrogen production and purification generally followed these steps:

1. **Steam Reforming**
2. **High Temperature Shift**
3. **Low Temperature Shift**
4. **CO₂ Wash System**
5. **Methanator**

Removal of remaining CO and CO₂

- **Methanator**: 20 bar
- **Temperature**: 300-350 °C
Since the early 1980’s Pressure Swing Adsorption (PSA) has become the state-of-the-art technology for purifying hydrogen.
The hydrogen production and purification follow these steps:

Steam + Fuel $\rightarrow$ Reforming $\rightarrow$ High Temperature Shift $\rightarrow$ Pressure Swing Adsorption Unit $\rightarrow$ Tail gas with high energy value $\rightarrow$ H₂

- CH₄ = 100%
- S/C = 3.0
- F = 1

- CH₄ = 14%
- CO₂ = 37%
- CO = 7%
- H₂ = 42%
- F = 2.18

H₂ = 99-99.999%
CO = 1-50 ppm
F = 1.72

10-50 bar
20-40 °C
The first commercial PSA hydrogen purification unit was installed in conjunction with a steam reformer, in Toronto, around 1966.

Nowadays, two processes are commonly used for hydrogen purification, depending on plant capacity or size.
For capacities below 0.4 M m³N/day of hydrogen product, the three- or four-bed configuration based on Batta’s patent is used.
For larger productions, Union’s Carbide’s Polybed process, based on Fuderer and Rudelstorfer, has proved more economical.

United States Patent

Fuderer et al.

Oct. 19, 1976

3,986,849

SELECTIVE ADSORPTION PROCESS

Inventors: Andrija Fuderer; Ernst Rudelstorfer, both of Antwerp, Belgium

Assignee: Union Carbide Corporation, New York, N.Y.

Filed: Nov. 7, 1975

Applied For: 630,080

US. Cl. 55/25; 55/6; 55/68

Int. Cl. B01D 3/04

Field of Search 55/23, 26, 38, 62, 66, 56/68, 74, 76, 179

References Cited

UNITED STATES PATENTS

3,430,418 2/1969 Wagner

3 Claims, 21 Drawing Figures

Abstract

In an adiabatic pressure swing process for separation of feed gas mixtures such as H₂ containing CO₂ and N₂ impurities, at least seven adsorbent beds are employed of which at least two are receiving feed gas during the entire cycle, and with at least three pressure equalization stages.
Typically, PSA units for H₂ purification use multilayered beds with:

- A first layer of activated carbon;

Activated carbon retains preferentially the strongly adsorbed compounds such as H₂O, CO₂ and CH₄.
Typically, PSA units for $\text{H}_2$ purification use multilayered beds with:

- A first layer of activated carbon;
- A second layer of zeolite (e.g. 5A).

Zeolites retain the other species, such as CO and $\text{N}_2$ and make it easy to produce high purity hydrogen.
Hydrogen purification by PSA

Feed → Hydrogen (H₂) → Product

- CO
- N₂
- CO₂
- CH₄
- H₂O
UOP’s Polybed unit can produce high purity \( H_2 (+99.999\%) \) over 0.4 MNm\(^3\)/day.

The Polybed system normally uses between 4 to 12 beds.

In the nine-bed unit, 3 beds are simultaneously producing.
Simulation of a pilot unit for H$_2$ purification

Feed composition coming from a methane steam reforming unit

<table>
<thead>
<tr>
<th>Component</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>73.3</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>16.6</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.5</td>
</tr>
<tr>
<td>CO</td>
<td>2.9</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.7</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>saturated at 30ºC</td>
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</tbody>
</table>

Pilot unit: 4 columns with activated carbon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Column length (cm)</td>
<td>44.5</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
<td>7.21</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>30</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>7</td>
</tr>
<tr>
<td>Mass of adsorbent (g)</td>
<td>855</td>
</tr>
<tr>
<td>Product flow rate (L$_N$/min)</td>
<td>3.47</td>
</tr>
<tr>
<td>Purge flow rate (L$_N$/min)</td>
<td>2.15</td>
</tr>
</tbody>
</table>
Simulation of a pilot unit for $\text{H}_2$ purification

Adsorption isotherm for AC5-KS at 30 °C

![Adsorption isotherm graph](image)

- $\text{CO}_2$
- $\text{CH}_4$
- $\text{CO}$
- $\text{N}_2$
- $\text{H}_2$
- $\text{H}_2\text{O}$
Cycle: 8-step process

- Adsorption (production);
- Provide Equalization I;
- Provide Equalization II
- Blowdown;
- Purge;
- Receive Equalization II;
- Receive Equalization I;
- Counter-current pressurization with product.

# Simulation of a pilot unit for $H_2$ purification

## Multicolumn extension

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>PEI</th>
<th>PEII</th>
<th>Bd</th>
<th>Pg</th>
<th>REII</th>
<th>REI</th>
<th>Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>PEI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>REI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Bd</td>
<td>Pg</td>
<td>REII</td>
<td>REI</td>
<td>Press</td>
<td>Adsorption</td>
<td>PEI</td>
<td>PEII</td>
</tr>
<tr>
<td>4</td>
<td>PEI</td>
<td>PEII</td>
<td>Bd</td>
<td>Pg</td>
<td>REII</td>
<td>REI</td>
<td>Press</td>
<td>Adsorption</td>
</tr>
</tbody>
</table>

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**Note:** This table represents a simulation of a pilot unit for $H_2$ purification, focusing on multicolumn extension. Each column or row typically represents a different step in the purification process, involving adsorption and various stages (PEI, PEII, Bd, Pg, REII, REI, Press). The specific details of each step (such as materials or processes) would depend on the specific application and could be further detailed in the full presentation or document.
Simulation of a pilot unit for $\text{H}_2$ purification

Model assumptions:

• Ideal gas behaviour
• No mass, heat or velocity gradients in the radial direction
• Axial dispersed plug flow
• External mass and heat transfer resistances (film model)
• Bidispersed adsorbent particle with macropore and micropore mass transfer resistances (LDF model)
• No temperature gradients inside each particle
• Constant porosity along the bed
Simulation of a pilot unit for $\text{H}_2$ purification

Mass balances

\[ \frac{\partial}{\partial Z} \left( \varepsilon D_{ax} C_{g,T} \frac{\partial y_i}{\partial Z} \right) - \frac{\partial}{\partial Z} \left( u_0 C_{g,i} \right) - \varepsilon \frac{\partial C_{g,i}}{\partial t} - (1 - \varepsilon) a_p k_f \left(C_{g,i} - C_{s,i}\right) = 0 \]

\[ \frac{\partial \mathbf{C}_{p,i}}{\partial t} = \frac{\Omega_m D_{p,i}}{R_p^2} \left(C_{s,i} - \mathbf{C}_{p,i}\right) - \frac{\rho_p}{\varepsilon_p} \frac{\partial \mathbf{q}_i}{\partial t} \]

\[ \frac{\partial \mathbf{q}_i}{\partial t} = \frac{\Omega_m D_{o,i}}{r_c^2} \left( q_i - \bar{q}_i \right) \]

Energy balances

\[ \frac{\partial}{\partial Z} \left( \lambda \frac{\partial T_g}{\partial Z} \right) - u_0 C_{g,T} C_p \frac{\partial T_g}{\partial Z} + \varepsilon R_g T_g \frac{\partial C_{g,T}}{\partial t} - (1 - \varepsilon) a_p h_r \left(T_g - T_p\right) - 4 h_{\text{wi}} \left(T_g - T_w\right) - \varepsilon C_{g,T} C_v \frac{\partial T_g}{\partial t} = 0 \]

\[ (1 - \varepsilon) \left[ \varepsilon_p \sum_{i=1}^{n} C_{g,i} C_v + \rho_p \sum_{i=1}^{n} q_i C_{v,\text{ads},i} + \rho_p \mathbf{C}_{p,\text{ps}} \right] \frac{\partial T_p}{\partial t} = \frac{\rho}{T} \left[ \frac{\partial T_p}{\partial t} \right] = \]

\[ (1 - \varepsilon) \varepsilon_p R_g T_p \frac{\partial C_{p,T}}{\partial t} + \rho_b \sum_{i=1}^{n} (-\Delta H_{\text{ads}})_i \frac{\partial \mathbf{q}_i}{\partial t} + (1 - \varepsilon) a_p h_r \left(T_g - T_p\right) \]

Momentum balance

\[ - \frac{\partial P}{\partial Z} = 150 \frac{\mu (1 - \varepsilon)^2}{\varepsilon^3 d_p^2} u_0 + 1.75 \frac{(1 - \varepsilon) \rho}{\varepsilon^3 d_p} |u_0| u_0 \]

Adsorption isotherm - Virial

\[ P_i = \frac{q_i}{K_{Hi}} \exp \left( \frac{2}{3} \sum_{j=1}^{N} A_{ij} q_j + \frac{3}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} B_{ijk} q_j q_k \right) \]
Simulation of a pilot unit for H₂ purification

Performance

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Purity (%)</td>
<td>99.9992</td>
</tr>
<tr>
<td>H₂ Recovery (%)</td>
<td>62.7</td>
</tr>
<tr>
<td>Productivity</td>
<td>55.2</td>
</tr>
<tr>
<td>(mol H₂/kg ads./day)</td>
<td></td>
</tr>
</tbody>
</table>

Simulation of a pilot unit for \( \text{H}_2 \) purification

Steady state

Simulation of a pilot unit for H₂ purification

Steady state

Simulation of a pilot unit for H₂ purification

Steady state

Simulation of a pilot unit for H₂ purification

Steady state

Simulation of a pilot unit for H$_2$ purification

Simulation of a pilot unit for H$_2$ purification

Concentration profiles at the end of the feed step

Simulation of a pilot unit for H₂ purification

Concentration profiles at the end of the feed step

Simulation of a pilot unit for H₂ purification

Concentration profiles at the end of the feed step

Simulation of a pilot unit for H$_2$ purification

Temperature profile at the end of the feed step

SMB design: application to separation of xylene isomers
The name xylene was derived from the Greek word *xylon* that means wood, perhaps because xylenes occur naturally in petroleum and coal.

Aromatic isomers:
Xylene isomers

The xylene isomers are important chemical intermediates.

p-Xylene is the isomer with the most commercial importance.

It is used in the production of terephthalic acid, which is a precursor for polyethylene terephthalate (PET) production.
## Separation Processes

### Physical properties

<table>
<thead>
<tr>
<th></th>
<th>o-xylene</th>
<th>m-xylene</th>
<th>p-xylene</th>
<th>ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
</tr>
<tr>
<td>bp at 1 bar, °C</td>
<td>144.4</td>
<td>139.1</td>
<td>138.4</td>
<td>136.2</td>
</tr>
<tr>
<td>mp, °C</td>
<td>-25.2</td>
<td>-47.9</td>
<td>13.3</td>
<td>-95.0</td>
</tr>
</tbody>
</table>
Distillation

<table>
<thead>
<tr>
<th></th>
<th>o-xylene</th>
<th>m-xylene</th>
<th>p-xylene</th>
<th>ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mr</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
</tr>
<tr>
<td>bp at 1 bar, °C</td>
<td>144.4</td>
<td>139.1</td>
<td>138.4</td>
<td>136.2</td>
</tr>
<tr>
<td>mp, °C</td>
<td>-25.2</td>
<td>-47.9</td>
<td>13.3</td>
<td>-95.0</td>
</tr>
</tbody>
</table>

The small difference between the boiling points makes distillation not competitive.
Separation Processes

Crystallization

<table>
<thead>
<tr>
<th></th>
<th>o-xylene</th>
<th>m-xylene</th>
<th>p-xylene</th>
<th>ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_r )</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
<td>106.16</td>
</tr>
<tr>
<td>bp at 1 bar, (^\circ)C</td>
<td>144.4</td>
<td>139.1</td>
<td>138.4</td>
<td>136.2</td>
</tr>
<tr>
<td>mp, (^\circ)C</td>
<td>-25.2</td>
<td>-47.9</td>
<td>13.3</td>
<td>-95.0</td>
</tr>
</tbody>
</table>

The large difference between the melting points makes crystallization a viable solution.

However, the maximum recovery of p-xylene is limited by a eutectic point.
Adsorption

Simulated Moving Bed (SMB) technology:

• UOP’s Parex
• Toray’s Aromax
• IFP’s Eluxyl
Separation Processes

PAREX process from UOP

Extract: p-xylene desorbent

Raffinate: ethylbenzene o-xylene m-xylene desorbent

“PAREX™ Process”, in “Aromatics and Derivatives”, UOP 2699C-14 899AD1M, 1999
The adsorbents most commonly used for xylene isomers separation are:

- Faujasite-type zeolites - prehydrated KY, BaKY, BaX and BaKX
- Silicates
- Polymers
- Carbon materials
- Hydrotropes
- Hydroxylated silica gel
- Metal-organic frameworks (MOFs)
MIL-53 (Al) presents lozenge-shaped pores appear with a free internal diameter of 8.5 Å

Adsorbents

MIL-53 (Al) tablets from BASF - BASOLITE (A100) – 2 × 2 mm

Separation with MIL-53 (Al)

Adsorption capacity at 313 K

\[
q_i^* = q_{s,1} \frac{b_{i,1}C_i}{1 + \sum_{j=1}^{n_c} b_{j,1}C_j} + q_{s,2} \frac{b_{i,2}C_i}{1 + \sum_{j=1}^{n_c} b_{j,2}C_j}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>m-x</th>
<th>p-x</th>
<th>o-x</th>
<th>n-hep</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_{s,1} ) [mol/kg]</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>(b_1 ) [dm³/mol]</td>
<td>1.05</td>
<td>1.80</td>
<td>6.03</td>
<td>0.00</td>
</tr>
<tr>
<td>(q_{s,2} ) [mol/kg]</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>(b_2 ) [dm³/mol]</td>
<td>0.43</td>
<td>0.33</td>
<td>0.29</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Section II

Extract

Section I

Feed

Direction of fluid flow and port switching

Section III

Extract

Feed

Section IV

Eluent

Raffinate

Raffinate

Eluent

Table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length (m)</td>
<td>1.135</td>
</tr>
<tr>
<td>Bed diameter (m)</td>
<td>4.117</td>
</tr>
<tr>
<td>Configuration</td>
<td>2-8-12-2</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Basolite A100 - MIL-53 (Al)</td>
</tr>
<tr>
<td>Feed temperature (K)</td>
<td>313</td>
</tr>
<tr>
<td>Feed composition (mol/m³)</td>
<td>p-xylene : 2.68, m-xylene : 2.68, o-xylene : 2.68</td>
</tr>
<tr>
<td>Eluents composition (mol/m³)</td>
<td>n-heptane : 6.68, m-xylene : 7.99, o-xylene : 8.14</td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Mathematical Model – TMB approach

Fluid Phase

\[ \varepsilon \frac{\partial C_{i,j}}{\partial t} = \frac{\partial}{\partial z} \left( \varepsilon D_{ax} \frac{\partial C_{i,j}}{\partial z} \right) - \frac{\partial (uC_{i,j})}{\partial z} - (1 - \varepsilon) \rho_p \frac{\partial q_{i,j}}{\partial t} + (1 - \varepsilon) \rho_p u_s \frac{\partial q_{i,j}}{\partial z} \]

Adsorbed Phase

\[ \frac{\partial q_{i,j}}{\partial t} = (1 - \varepsilon) \rho_p u_s \frac{\partial q_{i,j}}{\partial z} + k_{s,i} (q_{i,j}^* - q_{i,j}) \]
Boundary conditions

\[ z = 0 \]

\[ \varepsilon D_{ax} \frac{\partial C_{i,j}}{\partial z} = uC_{i,j} - uC_{i,j,\text{inlet}} \]

\[ z = L_j \]

\[ D_{ax} \frac{\partial C_{i,j}}{\partial z} = 0 \]

\[ q_{i,j} = q_{i,j+1} \quad j=1 \text{ to } \text{III} \]

\[ q_{i,\text{IV}} = q_{i,1} \]
Separation with MIL-53 (Al)

Mathematical Model – TMB approach

**Eluent node**

\[ u_I = u_{IV} + u_E \]
\[ u_I C_{i,I} = u_{IV} C_{i,IV} + u_E C_{i,E} \]

**Extract node**

\[ u_{II} = u_I - u_X \]
\[ C_{i,II} = C_{i,I} = C_{i,X} \]

**Feed node**

\[ u_{III} = u_{II} + u_F \]
\[ u_{III} C_{i,III} = u_{II} C_{i,II} + u_F C_{i,F} \]

**Raffinate node**

\[ u_{IV} = u_{III} - u_R \]
\[ C_{i,IV} = C_{i,III} = C_{i,R} \]

**Initial conditions**

At \( t=0 \), the column is considered to be filled with eluent.
Dimensionless variables and parameters

\[ C_i^* = \frac{C_i}{C_{\text{Ref}}} \]
\[ x = \frac{z}{L} \]
\[ \theta = \frac{t}{\theta_{\text{Ref}}} \quad \theta_{\text{Ref}} = \frac{L}{u_{\text{Ref}}} \]
\[ u^* = \frac{u}{u_{\text{Ref}}} \]
\[ q_i^* = \frac{q_i}{q_{\text{Ref}}} \quad q_{\text{Ref}} = f(C_{\text{Ref}}) \]
\[ \text{Pe} = \frac{L u_{\text{ref}}}{D_{\text{ax}}} \]
\[ \xi_a = \frac{(1 - \varepsilon)}{\varepsilon} \rho_s \frac{q_{\text{Ref}}}{C_{\text{Ref}}} \]
\[ R_p^b = \theta_{\text{Ref}} k_{s,\text{Ref}} \]
\[ \alpha_i = k_{s,i} / k_{s,\text{Ref}} \]
Separation with MIL-53 (Al)

Dimensionless Mathematical Model – TMB approach

Considering: \( u_{Ref} = u_s \)

Fluid Phase

\[
\frac{\partial C_{i,j}^*}{\partial \theta} = \frac{1}{Pe} \frac{\partial^2 C_{i,j}^*}{\partial x^2} - \frac{\partial (v^* C_{i,j}^*)}{\partial x} - \xi_a \frac{\partial q_{i,j}^*}{\partial \theta} + \xi_a \frac{\partial q_{i,j}^*}{\partial x}
\]

Adsorbed Phase

\[
\frac{\partial q_{i,j}^*}{\partial \theta} = (1 - \varepsilon) \rho_p \frac{\partial q_{i,j}^*}{\partial x} + R_p^b \alpha_i (q_{i,j}^* - q_{i,j}^*)
\]
Separation with MIL-53 (Al)

Dimensionless Mathematical Model – TMB approach

Boundary conditions

\[ x = 0 \]
\[ \frac{1}{Pe} \frac{\partial C_{i,j}^*}{\partial x} = v^* C_{i,j}^* - v^* C_{i,j,\text{inlet}} \]

\[ x = 1 \]
\[ \frac{1}{Pe} \frac{\partial C_{i,j}^*}{\partial x} = 0 \]

\[ q_{i,j}^* = q_{i,j+1}^* \quad j=I \text{ to } III \]

\[ q_{i,IV}^* = q_{i,1}^* \]
Separation with MIL-53 (Al)

Dimensionless Mathematical Model – TMB approach

Since \( \gamma_j = v_j / u_s \)

### Eluent node

\[
\gamma_1 = \gamma_{IV} + \gamma_E \\
\gamma_1 C_{i,1}^* = \gamma_{IV} C_{i,IV}^* + \gamma_E C_{i,E}^*
\]

### Extract node

\[
\gamma_{II} = \gamma_1 - \gamma_X \\
C_{i,II}^* = C_{i,1}^* = C_{i,X}^*
\]

### Feed node

\[
\gamma_{III} = \gamma_{II} + \gamma_F \\
\gamma_{III} C_{i,III}^* = \gamma_{II} C_{i,II}^* + \gamma_F C_{i,F}^*
\]

### Raffinate node

\[
\gamma_{IV} = \gamma_{III} - \gamma_R \\
C_{i,IV}^* = C_{i,III}^* = C_{i,R}^*
\]

### Initial conditions

At \( \theta = 0 \), the column is considered to be filled with eluent.
Separation with MIL-53 (Al)

Performance parameters

\[
Pur (\%) = \frac{C_{\text{desired},X}}{\sum_{i=1}^{n} C_{i,X} \quad i \neq \text{eluvent}} \times 100
\]

\[
Rec_x (\%) = \frac{Q_x C_{\text{desired},X}}{Q_F C_{\text{desired},F}} \times 100
\]

\[
EC \left( \frac{m^3}{kg} \right) = \frac{Q_E}{Q_x C_{\text{desired},X} M} \quad \text{or} \quad \frac{Q_E}{Q_R C_{\text{desired},R} M}
\]

\[
Prod \left( \frac{kg}{m^3 \text{ads} \, h} \right) = \frac{MQ_x C_{\text{desired},X}}{V_{\text{ads}}} \quad \text{or} \quad \frac{MQ_R C_{\text{desired},R}}{V_{\text{ads}}}
\]
Separation with MIL-53 (Al)

Separation regions

Set $t^*$
- $\gamma_I$ (large value)
- $\gamma_{IV}$ (small value)

Set $\gamma_F$

Set $\gamma_{II}$

Calculate
- $\gamma_{III} = \gamma_{II} + \gamma_F$
- $\gamma_X = \gamma_I - \gamma_{II}$
- $\gamma_R = \gamma_{III} - \gamma_{IV}$

Simulate for obtaining
- $Pur_X$
- $Pur_R$

Increase $\gamma_{II}$

Increase $\gamma_F$
Separation with MIL-53 (Al)

Separation regions

The points that form the triangle have:

\[ \text{Pur}_X > 99\% \]
and

\[ \text{Pur}_R > 99\% \]

Separation with MIL-53 (Al)

Operating conditions from separation regions

- Select operating point: \( (\gamma_{III}, \gamma_{III}) \)
- Calculate \( \gamma_F = \gamma_{III} - \gamma_{II} \)
- For a given \( \frac{Q_F}{\varepsilon A} \), \( u_s = \frac{Q_F}{\varepsilon A \gamma_F} \)
- For a given \( \frac{L}{u_s} \), \( t^* = \frac{L}{u_s} \)
- Estimate \( \gamma_{IV} \)
- Get \( Q_R = \varepsilon A u_s (\gamma_{III} - \gamma_{IV}) \)
- Get \( Q_E = \varepsilon A u_s (\gamma_I - \gamma_{IV}) \)
- Get \( Q_X = \varepsilon A u_s (\gamma_I - \gamma_{II}) \)
Separation with MIL-53 (Al)

Adsorption capacity at 313 K

Case 1: Separation of o-x from p-x/m-x with n-heptane as eluent
Separation with MIL-53 (Al)

Case 1: Separation of o-x from p-x/m-x with n-heptane as eluent

![Graph showing separation with MIL-53 (Al)]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ax}$</td>
<td>3.83×10^{-6}</td>
<td>m²/s</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>1400</td>
<td>kg/m³</td>
</tr>
<tr>
<td>$k_i$</td>
<td>0.1</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$t^*$</td>
<td>115</td>
<td>s</td>
</tr>
<tr>
<td>$\gamma_I$</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma_{IV}$</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Case 1: Separation of o-x from p-x/m-x with n-heptane as eluent

![Graph showing the separation process with key parameters and values listed in a table.]

**Table: Operating Conditions and Dimensionless Parameters**

<table>
<thead>
<tr>
<th>SMB unit geometry</th>
<th>Operating conditions</th>
<th>Dimensionless parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c = 1.135 \text{ m}$</td>
<td>$T = 313 \text{ K}$</td>
<td>$\eta_1 = 4.32$</td>
</tr>
<tr>
<td>$d_c = 4.117 \text{ m}$</td>
<td>$t^* = 10.32 \text{ min}$</td>
<td>$\eta_{II} = 0.70$</td>
</tr>
<tr>
<td>$V_c = 15.1 \text{ m}^2$</td>
<td>$Q_f = 87.0 \text{ m}^2/\text{h}$</td>
<td>$\eta_{III} = 0.89$</td>
</tr>
<tr>
<td>$Q_x = 1657.6 \text{ m}^3/\text{h}$</td>
<td>$Q_A = 237.9 \text{ m}^3/\text{h}$</td>
<td>$\eta_{IV} = 0.37$</td>
</tr>
<tr>
<td>Number of columns: 24</td>
<td>$Q_B = 1808.5 \text{ m}^2/\text{h}$</td>
<td></td>
</tr>
<tr>
<td>Configuration: 2-8-12-2</td>
<td>$Q_I = 2436.0 \text{ m}^3/\text{h}$</td>
<td></td>
</tr>
</tbody>
</table>
Case 1: Separation of o-x from p-x/m-x with n-heptane as eluent
Case 2: Separation of o-x/p-x from m-x with n-heptane as eluent
Separation with MIL-53 (Al)

Case 2: Separation of o-x/p-x from m-x with n-heptane as eluent

![Graph showing separation with MIL-53 (Al)]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ax}$</td>
<td>3.83×10^{-6}</td>
<td>m²/s</td>
</tr>
<tr>
<td>ε</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>1400</td>
<td>kg/m³</td>
</tr>
<tr>
<td>$k_i$</td>
<td>0.1</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$\tau^*$</td>
<td>115</td>
<td>s</td>
</tr>
<tr>
<td>$\gamma_I$</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma_{IV}$</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Case 2: Separation of o-x/p-x from m-x with n-heptane as eluent

\[ \begin{align*}
\gamma_I & = 0.6 \\
\gamma_{III} & = 0.7 \\
\gamma_{II} & = 0.8 \\
\gamma_{IV} & = 0.9 \\
\gamma_I & = 1.0 \\
\end{align*} \]

\begin{table}
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{SMB unit geometry} & \textbf{Operating conditions} & \textbf{Dimensionless parameters} \\
\hline
L_c = 1.135 m & T = 313 K & \gamma_I = 10 \\
\hline
d_\phi = 4.117 m & \epsilon^* = 0.31 min & \gamma_{II} = 0.67 \\
\hline
V_c = 15.1 m^2 & Q^I = 87.0 m^3/h & \gamma_{III} = 0.71 \\
\hline
Q^x = 18045.7 m^3/h & Q^A = 1277.9 m^3/h & \gamma_{IV} = 0.05 \\
\hline
Number of columns: & Q^B = 19236.7 m^3/h & \\
24 & Q^I = 21266.7 m^3/h & \\
\hline
Configuration: & 2-8-12-2 & \\
\hline
\end{tabular}
\end{table}
Case 2: Separation of o-x/p-x from m-x with n-heptane as eluent
Separation with MIL-53 (Al)

Adsorption capacity at 313 K

Case 3: Separation of p-x using o-x as eluent
Separation with MIL-53 (Al)

Case 3: Separation of p-x using o-x as eluent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ax}$</td>
<td>$3.83\times10^{-6}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>1400</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\kappa_i$</td>
<td>0.1</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$t^*$</td>
<td>115</td>
<td>s</td>
</tr>
<tr>
<td>$\gamma_I$</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma_{IV}$</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Case 3: Separation of p-x using o-x as eluent

<table>
<thead>
<tr>
<th>SMB unit geometry</th>
<th>Operating conditions</th>
<th>Dimensionless parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c = 1.135 \text{ m}$</td>
<td>$T = 313 \text{ K}$</td>
<td>$\gamma_T = 0.702$</td>
</tr>
<tr>
<td>$d_c = 4.117 \text{ m}$</td>
<td>$t^* = 0.14 \text{ min}$</td>
<td>$\gamma_{II} = 0.256$</td>
</tr>
<tr>
<td>$V_c = 15.1 \text{ m}^3$</td>
<td>$Q_p = 87.0 \text{ m}^3/\text{h}$</td>
<td>$\gamma_{III} = 0.276$</td>
</tr>
<tr>
<td></td>
<td>$Q_{\delta} = 1940.1 \text{ m}^3/\text{h}$</td>
<td>$\gamma_{IV} = 0.09$</td>
</tr>
<tr>
<td>Number of columns: 24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Configuration: 2:8:12:2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Case 3: Separation of p-x using o-x as eluent

![Diagram showing separation of xylene isomers](image)

<table>
<thead>
<tr>
<th>Performance Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pur_X (%)</td>
<td>99</td>
</tr>
<tr>
<td>Rec_X (%)</td>
<td>99</td>
</tr>
<tr>
<td>Pur_R (%)</td>
<td>98</td>
</tr>
<tr>
<td>Rec_R (%)</td>
<td>97</td>
</tr>
<tr>
<td>Prod (kg/h m^3 ads.)</td>
<td>129</td>
</tr>
<tr>
<td>EC (m^2/kg)</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Separation with MIL-53 (Al)

Adsorption capacity at 313 K

Case 4: Separation of p-x using m-x as eluent
Case 4: Separation of p-x using m-x as eluent

<table>
<thead>
<tr>
<th>SMB unit geometry</th>
<th>Operating conditions</th>
<th>Dimensionless parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c = 1.135 \text{ m}$</td>
<td>$T = 313 \text{ K}$</td>
<td>$\gamma_1 = 2.43$</td>
</tr>
<tr>
<td>$d_c = 4.117 \text{ m}$</td>
<td>$t^* = 2.15 \text{ min}$</td>
<td>$\gamma_II = 0.40$</td>
</tr>
<tr>
<td>$V_c = 15.1 \text{ m}^3$</td>
<td>$Q_R = 87.0 \text{ m}^3/\text{h}$</td>
<td>$\gamma_III = 0.71$</td>
</tr>
<tr>
<td></td>
<td>$Q_X = 569.7 \text{ m}^3/\text{h}$</td>
<td>$\gamma_IV = 0.22$</td>
</tr>
</tbody>
</table>

Number of columns: 24

Configuration: 2-8-12-2

$Q_R = 136.9 \text{ m}^3/\text{h}$

$Q_X = 619.6 \text{ m}^3/\text{h}$

$Q^*_R = 962.6 \text{ m}^3/\text{h}$
Separation with MIL-53 (Al)

Case 4: Separation of p-x using m-x as eluent

Performance Parameter | Value
--- | ---
Pur\(_R^p-x\) (%) | 100
Rec\(_R^p-x\) (%) | 97
Prod\(_R^p-x\) (kg / h m\(^2\) ds) | 197
Ec\(_R^p-x\) (m\(^2\) / kg) | 0.026