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Tutorial Chemical Reaction Engineering:

\textbf{11. Real reactors, residence time distribution and selectivity / yield for reaction networks}

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Tutorial CRE: Residence time distribution

- Ideal: no mixing (PFTR) or perfect mixing (CSTR)
- Technical reality is in between those cases!

- For technical / real reactors:
  - Measurements and modeling of the mixing state
  - Calculation of e.g. conversion for the mixing state

![Diagram of CSTR and PFTR with bypass flow and dead zones]

Fluid elements take different ways through packed bed
Radial flow velocity profile because of bypass flows at low $d_T/d_P (<10)$
Tutorial CRE: Residence time distribution

\[ Da = \frac{(-v_{\text{reactant}}) \cdot r_0(T) \cdot \tau}{c^0_{\text{reactant}}} \]

= "time given"

= "time needed"
Characterization of residence time distribution with measurement of pulse or step responses

Description of pulse response with statistical moments

- Normalized pulse response: \( E(t) = S(t) \left( \int_{t=0}^{\infty} S(t) \, dt \right)^{-1} \)
- 1. moment: \( \tau = \int_{t=0}^{\infty} t \, E(t) \, dt \) mean residence time
- 2. moment: \( \sigma^2 = \int_{t=0}^{\infty} (t - \tau)^2 \, E(t) \, dt \) variance
Tutorial CRE: Residence time distribution

- Ideal reactors vs. cascade model (N CSTR’s)

PFTR:
\[ \tau = \frac{V_R}{V} \quad \sigma^2 = 0 \]

CSTR:
\[ \tau = \frac{V_R}{V} \quad \sigma^2 = \tau^2 \]

Cascade:
\[ \tau = \frac{V_C}{V} = \frac{V_R N}{V} = \tau_R N \quad \sigma^2 = \frac{\tau^2}{N} \]
Tutorial CRE: Residence time distribution

- Dispersion model: Tubular reactors

- Introduction of an axial dispersion term in the mass balance

\[
\frac{\partial c_i}{\partial t} = -\text{div} \, \bar{j}_i + \sum_{j=1}^{M} \nu_{i,j} r_j = -\frac{\partial}{\partial z} \left( \frac{\dot{V}}{A} c_i + J_i \right) + \sum_{j=1}^{M} \nu_{i,j} r_j = 0
\]

\[
J_i = -D_{\text{ax}} \frac{dc_i}{dz}
\]

- Characterization possible with Bodenstein–Number Bo:

\[
Bo = \frac{\dot{V} L}{AD_{\text{ax}}} = \frac{\nu L}{D_{\text{ax}}} = \frac{\text{"convective mass transfer"}}{\text{"diffusive mass transfer"}}
\]

- PFTR assumption is reasonable if Bo > 100 and \(d_T/d_p > 10\)

\[
\tau = \frac{V_R}{\dot{V}}, \quad \sigma^2 = \frac{2\tau^2}{Bo} + \frac{8\tau^2}{Bo^2} + \text{THO}
\]
Tutorial CRE: Residence time distribution

- Segregation model: Tubular reactors

- Splitting of a tubular reactor into parallel PFTR‘s with different length (residence time, conversion)

- Calculation of the mean conversion from the residence time distribution possible:

\[
\bar{X} = \int_{t=0}^{\infty} X(t) E(t) \, dt
\]
Tutorial CRE: Real tubular reactor

- 10.1 Real tubular reactor: Tracer experiment

<table>
<thead>
<tr>
<th>$(t - \tau)^2/\text{min}^2$</th>
<th>$t/\text{min}$</th>
<th>$c_{\text{tracer}}/\text{mol l}^{-1}$</th>
<th>$E/\text{min}^{-1}$</th>
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\[
E(t) = S(t) \left( \int_{t=0}^{\infty} S(t) \, dt \right)^{-1} \approx S(t) \left( \sum_i S(t_i) \Delta t \right)^{-1}
\]

\[
\tau = \int_{t=0}^{\infty} t \, E(t) \, dt \approx \sum_i t_i \, E(t_i) \Delta t = 12 \text{ min}
\]

\[
\sigma^2 = \int_{t=0}^{\infty} (t - \tau)^2 \, E(t) \, dt \approx \sum_i (t_i - \tau)^2 \, E(t_i) \Delta t = 30.4 \text{ min}^2
\]

$A \xrightarrow{r} B$

$r = k_c A$

$k = 0.045 \text{ min}^{-1}$
Tutorial CRE: Real tubular reactor

- Part b: Number of STR for equivalent cascade

\[ N = \frac{\tau^2}{\sigma^2} = 4.74 \approx 5 \]

- Part c: Conversion for cascade model

\[ X_{\text{cascade}} = 1 - \frac{c_A^N}{c_A^0} = 40\% \]

- Mass balances of all CSTR's in cascade

\[ \frac{dc_A^i}{dt} = \frac{1}{\tau_R} \left( c_A^0 - c_A^i \right) - kc_A^i = 0 \]

\[ \vdots \]

\[ \frac{dc_A^i}{dt} = \frac{1}{\tau_R} \left( c_A^{i-1} - c_A^i \right) - kc_A^i = 0 \quad \Rightarrow \quad c_A^i = \frac{c_A^{i-1}}{1 + \tau_R k} \]

\[ \vdots \]

\[ \frac{dc_A^N}{dt} = \frac{1}{\tau_R} \left( c_A^{N-1} - c_A^N \right) - kc_A^N = 0 \quad \Rightarrow \quad c_A^N = \frac{c_A^{N-1}}{1 + \tau_R k} \]

\[ \frac{c_A^N}{c_A^0} = \frac{1}{\left(1 + \frac{\tau}{N} k\right)^N} \]
Tutorial CRE: Real tubular reactor

- Part d: Conversion for segregation model
  
  \[ X_{\text{seg}} = \int_{t=0}^{\infty} X(t) E(t) \, dt \approx \sum_i X(t_i) E(t_i) \Delta t = 40\% \]

- Conversion as function of time? Analogy between PFTR and batch reactor!

  \[ \frac{dc_A}{d\tau} = -kc_A \rightarrow c_A(t_i) = c_A^0 \exp(-kt_i) \]

  \[ X_A(t_i) = 1 - \frac{c_A}{c_A^0} = 1 - \exp(-kt_i) \]

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Cascade model and segregation model give the same result!
10.2: Yield and selectivity for series reactions $A \xrightarrow{r_1} B \xrightarrow{r_2} C$

- **Part a: Maximum yield of B for CSTR**

\[
0 = \frac{1}{\tau} (c_A^0 - c_A) - k_1 c_A \\
0 = -\frac{c_B}{\tau} + k_1 c_A - k_2 c_B \\
0 = -\frac{c_C}{\tau} + k_2 c_B
\]

\[
c_A = \frac{c_A^0}{(1 + \tau k_1)}
\]

\[
c_B = \frac{k_1 c_A^0}{(1 + \tau k_1) \left( \frac{1}{\tau} + k_2 \right)}
\]

\[
Y_B = \frac{c_B}{c_A} = \frac{k_1}{(1 + \tau k_1) \left( \frac{1}{\tau} + k_2 \right)}
\]

**Maximum yield → 1. derivative = 0 (product rule)**

\[
\frac{dY_B}{d\tau} = 0 = \frac{k_1}{\left(1 + \tau k_1\right) \left( \frac{1}{\tau} + k_2 \right)^2 \tau^2} - \frac{k_1^2}{\left(1 + \tau k_1\right)^2 \left( \frac{1}{\tau} + k_2 \right)^2}
\]

\[
\tau_{Y_{B,\text{max}}} = \sqrt{\frac{1}{k_1 k_2}}
\]
Tutorial CRE: Selectivity / yield for networks

- 10.2: Yield and selectivity for series reactions $A \xrightarrow{r_1} B \xrightarrow{r_2} C$
- Part b: Maximum yield of B for BR/PFTR

\[
\frac{\mathrm{d}c_A}{\mathrm{d} \tau} = -k_1 c_A \quad \Rightarrow \quad c_A = c_A^0 \exp(-k_1 \tau)
\]
\[
\frac{\mathrm{d}c_B}{\mathrm{d} \tau} = k_1 c_A - k_2 c_B
\]
\[
\frac{\mathrm{d}c_C}{\mathrm{d} \tau} = k_2 c_B
\]
\[
c_B = k_1 c_A^0 \left( \frac{\exp(-k_1 \tau) - \exp(-k_2 \tau)}{k_2 - k_1} \right)
\]
\[
Y_B = \frac{c_B - c_B^0}{c_A^0} = \frac{c_B}{c_A^0}
\]

- Maximum yield $\Rightarrow$ 1. derivative $= 0$

\[
\frac{\mathrm{d}Y_B}{\mathrm{d} \tau} = 0 = k_1 \left( \frac{k_2 \exp(-k_2 \tau) - k_1 \exp(-k_1 \tau)}{k_2 - k_1} \right) \quad \Rightarrow \quad \tau_{Y_B, \text{max}} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1}
\]
Tutorial CRE: Selectivity / yield for networks

- More than one reaction: Reaction network!
  - Series reaction: \( A \xrightarrow{r_1} B \xrightarrow{r_2} C \)
  - Parallel reaction: \( A \xrightarrow{r_1} B \quad A \xrightarrow{r_2} C \)

- High selectivity to desired product!
- Differential selectivity:

\[
\begin{align*}
  dS &= \frac{\text{produced product}}{\text{consumed reactant}} \\
  dS_{B,\text{series}} &= \frac{r_1 - r_2}{r_1} = 1 - \frac{k_2 c_B}{k_1 c_A} \quad \text{PFTR, low conversion} \\
  dS_{B,\text{parallel}} &= \frac{r_1}{r_1 + r_2} = \frac{1}{1 + \frac{k_2}{k_1}} \quad \text{PFTR or CSTR}
\end{align*}
\]