Computer-Aided Chemical Reaction Engineering

Transient reactor modelling
Friday 9.5  8:15 – 10:00

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  - Industrial chemistry and reaction engineering, ÅA
  - TF Engineers Oy
Transient reactor modelling

- Introduction
- Dynamic reactor models
- Solving equations from dynamic systems
- Example dynamic axial dispersion model
- Example dynamic model including surface species
- Conclusions
Reasons for transient and dynamic cases

- Step and impulse response experiments
- Periodic switching of feed components
- Reverse flow
- Reactor startup and shut down
- Reactor safety (changing conditions)
- Catalyst deactivation
- Catalyst selectivity change
- Catalyst particle dynamics
Transient

Mathematical modelling can be applied to transient data. The crucial issue is to include the accumulation term \( \frac{dn_i}{dt} \) in all mass balances and to take into account the changes in surface coverages of adsorbed species.
Massbalans

\[ \dot{n}_{i,in} + \left( -D_a \frac{\partial \alpha_i}{\partial l} A_l \right)_{in} + r_i \Delta V \rho_B = \dot{n}_{i,\text{out}} + \left( -D_a \frac{\partial \alpha_i}{\partial l} A_l \right)_{out} + \frac{\partial n_i}{\partial \alpha} \]
Dynamic catalytic reactor models

Axial- and radial dispersion

\[
\dot{n}_{i,\text{in}} + \left(-D_a \frac{\partial c_i}{\partial l} A_l \right)_{\text{in}} + \left(-D_r \frac{\partial c_i}{\partial r} A_r \right)_{\text{in}} + r_i \Delta V \rho_B = 0
\]

\[
\dot{n}_{i,\text{out}} + \left(-D_a \frac{\partial c_i}{\partial l} A_l \right)_{\text{out}} + \left(-D_r \frac{\partial c_i}{\partial r} A_r \right)_{\text{out}} + \frac{\partial n_i}{\partial t}
\]

Axial dispersion only is considered here

\[
\dot{n}_{i,\text{in}} + \left(-D_a \frac{\partial c_i}{\partial l} A_l \right)_{\text{in}} + r_i \Delta V \rho_B = \dot{n}_{i,\text{out}} + \left(-D_a \frac{\partial c_i}{\partial l} A_l \right)_{\text{out}} + \frac{\partial n_i}{\partial t}
\]

\[
A_l = 2\pi r \Delta r \quad D_a = \varepsilon D_L \quad \varepsilon = V_L / V
\]

L = total reactor length
V = total reactor volume
Dynamic catalytic reactor models

The differences can be written by $\Delta$:s and we get:

$$
\Delta \left( D_a \frac{\partial c_i}{\partial l} A_l \right) + r_i \Delta V \rho_B = \Delta \dot{n}_i + \frac{\partial n_i}{\partial t}
$$

The volume element is $\Delta V = A_l \Delta l$ and the amount of substance can be written as $n_i = c_i \Delta V_L = c_i \varepsilon \Delta V$. If $D_a$ is constant and the mass balance is divided by $2 \pi r \Delta r \Delta l$ we obtain:

$$
D_a \frac{\Delta \left( \frac{\partial c_i}{\partial l} \right)}{\Delta l} + r_i \rho_B = \frac{\Delta \dot{n}_i}{2 \pi r \Delta r \Delta l} + \varepsilon \frac{\partial c_i}{\partial t}
$$
Dynamic catalytic reactor models

The following expressions for the molar flow are valid:

\[ \Delta \dot{n}_i = \Delta(c_i \dot{w}) 2\pi r \Delta r \]

\[ \frac{\Delta \dot{n}_i}{2\pi r \Delta r \Delta l} = \frac{\Delta(c_i \dot{w})}{\Delta l} \]

After inserting the above eq:s and letting \( \Delta l \to 0 \), the mass balance becomes:

\[ \varepsilon \frac{\partial c_i}{\partial \alpha} = -\frac{\partial(c_i \dot{w})}{\partial \alpha} + D_a \frac{\partial^2 c_i}{\partial \alpha^2} + r_i \rho_B \]
The dimensionless quantity \( z = l / L \) is introduced. Furthermore, the superficial velocity \( (w) \) can be regarded as a constant for isothermal liquid phase reactions. The final form of the model for a tube reactor with axial dispersion is obtained:

\[
\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon} \left( -\frac{w}{L} \frac{\partial c_i}{\partial z} + \frac{D_a}{L^2} \frac{\partial^2 c_i}{\partial z^2} + r_i \rho_B \right)
\]
Boundary conditions

For the boundary conditions for the axial dimension the classical approach of Danckwerts can be used:

\[ c_{0i} = c_i - \frac{D_a}{wL} \frac{dc_i}{dz} \quad \text{at } z = 0 \]

At the reactor outlet the classical closed outlet boundary condition is

\[ \frac{dc_i}{dz} = 0 \quad \text{at } z = 1 \]
Dynamic catalytic reactor models

For the adsorbed surface components, the mass balance is given by:

\[ \frac{dc_j^*}{dt} \Delta A' = r_j \Delta m_{cat} \]

where \( \Delta A' \) denotes the accessible catalyst surface area in the volume element. We denote \( \Delta m_{cat} / (\Delta A' c_0^*) = \alpha \), which gives

\[ \frac{d\Theta_j}{dt} = \alpha r_j \]

where the surface coverage of the component \( (j) \) is \( \Theta_j = c_j^* / c_0^* \) and \( \alpha \) represents the sorption capacity of the catalyst.
Summary: Dynamic catalytic reactor models

Axial dispersion model

\[ \frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon} \left( - \frac{w}{L} \frac{\partial c_i}{\partial z} + \frac{D_a}{L^2} \frac{\partial^2 c_i}{\partial z^2} + r_i \rho_B \right) \]

Dynamic plug flow reactor

\[ \frac{dc_i}{dt} = \frac{1}{\varepsilon} \left( r_i \rho_B - \frac{dc_i}{d\tau} \right) \]

Steady state plug flow reactor

\[ \frac{dc_i}{d\tau} = r_i \rho_B \]
Summary: Dynamic catalytic reactor models

Batch reactor

\[ \frac{dc_i}{dt} = \frac{1}{\varepsilon} r_i \rho_B \]

For surface components the following reactor models are valid

\[ \frac{dc^*_j}{dt} \Delta A' = r_j \Delta m_{cat} \]

\[ \frac{d\Theta_j}{dt} = \alpha r_j \]
### Numerical methods

<table>
<thead>
<tr>
<th>Dynamic packed bed</th>
<th>PDE + ODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady-state packed bed</td>
<td>ODE + (N)LE</td>
</tr>
<tr>
<td>Batch reactor</td>
<td>ODE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PDE</th>
<th>Partial differential equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODE</td>
<td>Ordinar differential equation</td>
</tr>
<tr>
<td>(N)LE</td>
<td>(Non-)linear equation</td>
</tr>
</tbody>
</table>
Solving PDEs by discretization

PDE

$$\frac{\partial c_i}{\partial \tau} = \frac{1}{\epsilon} \left( - \frac{w}{L} \frac{\partial c_i}{\partial z} + r_i \rho_B \right)$$

ODEs

$$\frac{\partial c_i}{\partial \tau} = \frac{1}{\epsilon} \left( - \frac{w}{L} c_i(z_1) + r_i \rho_B \right)$$

$$\frac{\partial c_i}{\partial \tau} = \frac{1}{\epsilon} \left( - \frac{w}{L} c_i(z_2) + r_i \rho_B \right)$$

...
Principe of numerical solving

- Different methods exist to approximate the discretized variables, e.g.:
  - Finite difference method
  - Finite element method (FEM)
  - Orthogonal collocation
  - Method of lines
Method of lines

- The PDE:s can be transformed to a set of ODEs with the method of lines.
- The strategy for solving the problem is to discretize the reactor coordinate \( (z) \) and integrate numerically the ordinary differential equations (ODEs) in time \( (t) \).
- The number of ODEs is the number of components times the number of discretization points.
Method of lines

- The derivatives which originate from plug flow should be described with backward differences,
- whereas central differences should be used for first and second derivatives originated from diffusion and dispersion
- For the first derivative (the plug flow term), for instance, the five-point backward difference formula can be used (Schiesser, 1991)
Method of lines

- For the first derivative (the plug flow term), for instance, the five-point backward difference formula can be used (Schiesser, 1991)

\[
\left. \frac{df}{dz} \right|_{z=z_1} = \frac{1}{\Delta z} \left[ \frac{3}{12} f(z_1) + \frac{10}{12} f(z_0) - \frac{18}{12} f(z_{-1}) + \frac{6}{12} f(z_{-2}) - \frac{1}{12} f(z_{-3}) \right]
\]
Method of lines

- For the second derivative the five-point central difference formula can be used

\[
\frac{d^2 f}{dz^2} \bigg|_{z=z_1} = \frac{1}{\Delta z^2} \left[ -\frac{1}{12} f(z_{-2}) + \frac{16}{12} f(z_{-1}) - \frac{30}{12} f(z_0) + \frac{16}{12} f(z_{+1}) - \frac{1}{12} f(z_{+2}) \right]
\]
Principle of numerical solving

- The ODEs are very often stiff, because of the large time scale difference in reaction rates and deactivation rates. Additionally, the spatial discretization increases the stiffness.

- Efficient methods for solving stiff systems of ODEs must be used: e.g.
  - Backward difference, BD, e.g. LSODE
  - Runge-Kutta, RK, e.g. SIRK

- Routines exists for estimating the various differences
Example: Method of lines

Orthogonal collocation, Colpde
Case: Conversion of epoxides in hydrogen peroxide process

\[
\text{Epoxide (A)} + \text{THAAHQ (B)} \rightarrow 2 \text{THAAQ (C)} + \text{H}_2\text{O (D)}
\]
Case: Conversion of epoxides in hydrogen peroxide process

\[ 3 \text{THAAQ (C)} \rightarrow \text{AAQ (E)} + 2 \text{THAAHQ (B)} \]
## Mechanism

<table>
<thead>
<tr>
<th>I</th>
<th>A + B → 2C + D</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>C + C ↔ C' + B</td>
</tr>
<tr>
<td>IIb</td>
<td>C' + C ↔ E + B</td>
</tr>
<tr>
<td>III</td>
<td>B + E ↔ F + C</td>
</tr>
<tr>
<td>IV</td>
<td>A + F → E + C + D</td>
</tr>
</tbody>
</table>
Kinetics

\[ r_1 = k'_{+1} \left( c_A c_B - \frac{1}{K'_1} c_C^2 c_D \right) \]

\[ r_2 = \frac{k'_{21} c_C^3}{k'_{22} c_D + c_C} \]

\[ k'_{+1} = A_1 e^{-E_1/RT} \]

\[ k'_{21} = A_2 e^{-E_2/RT} \]
Modelling results

![Graph showing Epoxide and THAAHQ weight-% over time at 70 °C.](image-url)
Modelling of continuous pilot reactor (packed bed)
Modelling of continuous pilot reactor (packed bed)

Dispersion model

\[
\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon} \left( -\frac{w}{L} \frac{\partial c_i}{\partial z} + \frac{D_a}{L^2} \frac{\partial^2 c_i}{\partial z^2} + r_i \rho_B \right)
\]

Reaction kinetics with deactivation function

\[
r_j = a(t) r_{0j}
\]

Stoichiometry

\[
r_i = \sum v_{ij} r_{0j}
\]
Semiempirical description of catalyst deactivation

\[ P + * \rightleftharpoons P^* \]

\[ r_P = k_+ c_P c_v - k_- c_{P^*} \]

\[ \frac{da}{dt} = -k' (a - a^*)^n \]

\[ a(t) = a^* + (a_0 - a^*) e^{-k't}, \quad n = 1 \]

\[ a(t) = a^* + \left[ (a_0 - a^*)^{1-n} + k'(n-1)t \right] \frac{1}{1-n}, \quad n \neq 1 \]
Reversible and irreversible deactivation

Select correct model!
Modelling of continuous pilot reactor (packed bed)
Case study, Skeletal isomerization of 1-pentene

A

1-pentene

trans-2-pentene

cis-2-pentene

B

3-methyl-1-butene

2-methyl-2-butene

2-methyl-1-butene

\[
\begin{array}{ccc}
1 & 2 & 5 \\
A + * & \leftrightarrow & A^* \rightarrow B^* \leftrightarrow B + *\\
\downarrow 3 & \downarrow 4 & \\
C^* & C^* & \\
\end{array}
\]
Semi-empirical model

Mechanism reduces to

\[ A \rightarrow B \]

Kinetics

\[ r_{\text{Isom}} = k'' c_A a \]
Semi-empirical model

Deactivation functions

\[ a = e^{-k_d t} \]

\[ a = \frac{1}{1 + k_d t} \]

Mass balance

\[ \frac{d c_i}{d \tau} = r_{\text{Isom}} \rho_B \]
Results, semi-empirical model

50% olefins in feed

- ■ = n-C5 olef.
- ♦ = i-C5 olef.
- ++ = exponential
- -x- = hyperbolic

Concentration (wt-%)

Time (h)
Results, semi-empirical model

15% olefins in feed

-■- = n-C5 olef.
-◇- = i-C5 olef.
-+- = exponential
-×- = hyperbolic

Concentration (wt-%)

Time (h)
Problem

Empirical model deactivation = fkt of time

\[ r_{\text{Isom}} = k'' c_A a \]

\[ a = e^{-k_d t} \]

Actual case deactivation = fkt of deposit

\[ a = f(\text{coke}) \]
CFB reactor for skeletal isomerization

Reactor 2 regeneration
Reactor 1 isomerisation

Flue gas

Products

TC = temperature control
LC = level control
LI = level indication
Pdl = pressure difference indication

Air
Feed
Mechanistic model

Mechanism

\[ \text{A}^* \rightarrow \text{B}^* \quad \text{II} \]

\[ 2\text{A}^* \rightarrow \text{C}^* \quad \text{IV} \]

\[
\begin{align*}
    r_{\text{Isom}} &= k'_+ c_A K_A \Theta_V \\
    r_{\text{Deact}} &= k'_+ 4 \left( c_A K_A \Theta_V \right)^2
\end{align*}
\]
Mechanistic model

Kinetics

\[ r_{Isom} = \frac{k'_{+2}c_A (1 - \Theta_{C^*})}{1 + K(c_A + c_B)} \]

\[ r_{deact} = \frac{k'_{+4}c_A^2 (1 - \Theta_{C^*})^2}{(1 + K(c_A + c_B))^2} \]
Mechanistic model

Mass balance

\[ \frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon} \left( - \frac{w}{L} \frac{\partial c_i}{\partial z} + r_i \rho_B \right) \]

\[ \frac{d \Theta_{c^*}}{dt} = \alpha r_{deact} \]
Results, mechanistic model

50% olefins in feed

- □ = n-C5 olef.
- ◆ = i-C5 olef.
- = mechanistic

Concentration (wt-%)

Time (h)
Results, mechanistic model

15% olefins in feed

- ■ = n-C5 olef.
- ◊ = i-C5 olef.
- = mechanistic

Concentration (wt-%)

Time (h)
Investigate deactivation mechanisms

Isomerization

\[ A^* \rightarrow B^* \] II

Deactivation mechanisms

\[ 2A^* \rightarrow C^* \] IVa

\[ A^* \rightarrow C^* \] IVb

\[ B^* \rightarrow C^* \] IVc

\[ A^* \leftrightarrow C^* \] IVd
Investigate mechanism

Outlet, Model II a, pp=0.5

2A* → 2C*

Outlet, Model I a, pp=0.5

A* → C*

Outlet, Model II c, pp=0.5

2B* → 2C*

Outlet, Model V a, pp=0.5

A* → C*
Estimate coke yield

Discretization point 10 (Outlet), Model II a, pp=0.5

- = model estimate
♦ = coking at 180 °C
● = coking at 300 °C
■ = kinetic experiment
Conclusions

- Deactivation can be accounted for in many ways.
- If understanding of the deactivation phenomenon is desired a more rigorous model is needed.
- Time-on-stream is not always a good variable for catalyst deactivation.
- A dynamic mechanism model is solvable with modern computational tools.
- The coke on catalyst was modelled and compared to experimental data.