INTRODUCTION TO CHEMICAL PROCESS SIMULATORS

DWSIM Chemical Process Simulator

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Introduction to Chemical Process Simulators

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Monday, October 3rd 2016

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- Get used to working with DWSIM and COCO

Monday, October 10th 2016

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Monday, October 17th 2016

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Monday, October 24th 2016

- Case studies
Tips to introduce inlet data in DWSIM

1. Introduce the composition and accept the changes

2. Introduce the rest of the inlet information by pressing **Enter** after writing each data

3. Review the thermodynamic model

4. Review the units

For any simulator!
Reactions

• **Conversion**: specify the conversion (%) of the limiting reagent as a function of temperature.

• **Equilibrium**: specify the equilibrium constant ($K$) as a function of temperature, a constant value or calculated from the Gibbs free energy reaction ($\Delta G/R$).

• **Kinetic**: specify the frequency factor ($A$) and the activation energy ($E$) for the direct reaction (optionally for the reverse reaction), including the orders of reaction of each component.

• **Heterogeneous catalytic**: specify the kinetic terms of the kinetic reaction as well as the activation energy, frequency factor, and component exponent terms of the adsorption kinetics.
Conversion Reaction

- It is assumed that the user has information regarding the conversion of one of the reactants as a function of temperature.

- By knowing the conversion and the stoichiometric coefficients, the quantities of the components in the reaction can be calculated.

- Considering the following reaction:

  \[ aA + bB \rightarrow cC \]

  where \( a, b \) and \( c \) are the stoichiometric coefficients of reactants and product, respectively. \( A \) is the limiting reactant and \( B \) is in excess. The amount of each component at the end of the reaction can be calculated from the following stoichiometric relationships:

  \[
  N_A = N_{Ao} - N_{Ao}X_A \\
  N_B = N_{Bo} - \frac{b}{a} N_{Ao}X_A \\
  N_C = N_{Co} + \frac{c}{a} N_{Ao}X_A
  \]
Conversion Reaction

DWSIM

COCO
Equilibrium Reaction

- The quantity of each component at the equilibrium is related to equilibrium constant by the following relationship:

\[
K = \prod_{j=1}^{n} (q_j)^{v_j}
\]

where \( K \) is the equilibrium constant, \( q \) is the basis of components (partial pressure in the vapor phase or activity in the liquid phase), \( v \) is the stoichiometric coefficient of component \( j \) and \( n \) is the number of components in the reaction.

- The equilibrium constant can be obtained:
  - Considering it as a constant.
  - Considering it as a function of temperature.
  - Calculating it automatically from the Gibbs free energy at the temperature of the reaction.
Equilibrium Reaction

DWSIM

COCO
Kinetic Reaction

- It is defined by the parameters of the equation of Arrhenius (frequency factor and activation energy) for both the direct order and for reverse order.

- Considering the following kinetic reaction:
  \[ aA + bB \rightarrow cC + dD \]

- The reaction rate for the A component can be defined as:
  \[ r_A = k[A][B] - k'[C][D] \]

  where:
  \[ k = A \exp(-E/RT) \quad k' = A' \exp(-E'/RT) \]

- The kinetic reactions are used in Plug-Flow Reactors (PFR) and in Continuous-Stirred Tank Reactors (CSTR).

\[ F_A = F_{Ao} + \int_{v}^{} r_A dV \]

  - \( F_A \) is the molar flow of the A component.
  - \( V \) is the reactor volume.
Kinetic Reaction

DWSIM

COCO
Heterogeneous Catalytic Reaction

- It is described the rate of catalytic reactions involving solid catalyst.
- Considering the following reaction:

\[
aA + bB \rightarrow cC
\]

- Depending on the reaction mechanism, the reaction rate expression can be generally written as:

\[
r = \frac{k_f \prod_{i=1}^{Reac} C_i^{\alpha_i} - k_r \prod_{j=1}^{Prod} C_j^{\beta_j}}{\left(1 + \sum_{k=1}^{M} \left\{K_k \prod_{g=1}^{M} C_g^{\gamma_{kg}}\right\}\right)^n}
\]

where \(k_f\) and \(k_r\) are the rate constants of the forward and reverse kinetic rate expressions, \(K\) is the absorption rate constant, and \(M\) is the number of absorbed reactants and products plus absorbed inert species.
Reactions

- Chemical reactions in DWSIM are managed through the Chemical Reactions Manager and in COCO through Settings – Reaction packages.

- The user can define various reactions which are grouped in Reaction Sets. This reaction sets list all chemical reaction, and the user must activate only those we wants to become available for one or more reactors.

- In the reaction set configuration window we define the reaction ordering.
Reactors

- Conversion Reactor
- Equilibrium Reactor
- Gibbs Reactor
- CSTR
- PFR
# Reactors

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reactor type</th>
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<tbody>
<tr>
<td>Conversion</td>
<td>Conversion</td>
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<tr>
<td>Equilibrium</td>
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<tr>
<td>Kinetic</td>
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</tr>
<tr>
<td>Heterogeneous catalytic</td>
<td>PFR, CSTR</td>
</tr>
</tbody>
</table>
Reactors

Conversion Reactor

• The conversion reaction is a vessel in which conversion reactions are performed.

• You can only attach reaction sets that contain conversion reactions.

• It should be specified the stoichiometry of all reactions and the conversion of the limiting reactant.

• This reactor calculates the composition of the outlet streams.
Reactors

**Equilibrium Reactor**

- The equilibrium reactor is a vessel which models equilibrium reactions.
- The outlet streams of the reactor are in a state of the chemical and physical equilibrium.
- The reaction set can contain an unlimited number of equilibrium reactions, which are simultaneously or sequentially solved.
Gibbs Reactor

- Gibbs reactors can work with equilibrium reactions or without any reaction information (Gibbs minimization mode).
- In this case, it will respect the element mass balance and try to find a state where the Gibbs free energy will be at a minimum.
Reactors

CSTR

- The CSTR (Continuous-Stirred Tank Reactor) is a vessel in which Kinetic and Heterogeneous catalytic reactions can be performed.
- The conversion in the reactor depends on the rate expression of the reactions associated with the reaction type.
- The inlet stream is assumed to be perfectly (and instantaneously) mixed with the material already in the reactor, so that the outlet stream composition is identical to that of the reactor contents.
- To simulate the CSTR we need to know the volume of the reactor.
Reactors

PFR

• The PFR (Plug Flow Reactor, or Tubular Reactor) generally consists of a bank of cylindrical pipes or tubes.

• The flow field is modeled as plug flow, implying that the stream is radially isotropic (without mass or energy gradients). This also implies that axial mixing is negligible.

• To simulate the PFR we need to know the volume and the length of the reactor.
Butyl Acetate Production

The following system is used to produce Butyl-acetate from Methyl acetate and Methanol.

\[ \text{MeAC} + \text{BuOH} \rightleftharpoons \text{MeOH} + \text{BuAc} \]

Use Peng-Robinson (PR) thermodynamic package

BuOH Feed
100 kmol/h
T = 305 K
P = 15 atm

MeAc Feed
150 kmol/h
T = 305 K
P = 15 atm

Reactor
\[ \Delta P = 0 \text{ atm} \]
Liquid phase reaction

R in
P = 5 atm

R out
T = 305 K
P = 5 atm
Butyl Acetate Production

The following system is used to produce Butyl-acetate from Methyl acetate and Methanol.

\[
\text{MeAC} + \text{BuOH} \rightleftharpoons \text{MeOH} + \text{BuAc}
\]

Use Peng-Robinson (PR) thermodynamic package

The reaction follows the next kinetic law:

\[
\begin{align*}
    r &= k_F C_{\text{MeAc}} C_{\text{BuOH}} - k_R C_{\text{MeOH}} C_{\text{BuAc}} \\
    k_F &= 7 \cdot 10^6 \exp \left( \frac{-71960}{RT} \right) \\
    k_R &= 9.467 \cdot 10^6 \exp \left( \frac{-72670}{RT} \right)
\end{align*}
\]
Butyl Acetate Production

The following system is used to produce Butyl-acetate from Methyl acetate and Methanol.

\[
\text{MeAC} + \text{BuOH} \rightleftharpoons \text{MeOH} + \text{BuAc}
\]

Use Peng-Robinson (PR) thermodynamic package

Molar flow and composition of the reactor outlet stream, for different types of reactors:

- Conversion reactor, assuming 10% of methyl acetate
- Gibbs reactor.
- Plug Flow Reactor (PFR), 4 m length and 0.5 m diameter.
- Continuous-Stirred Tank Reactor (CSTR), 2 m³ volume.
Ethylene Glycol Production

Diagram showing the production process with the following steps:

1. Oxidation of ethylene
2. Water
3. Recycled monoethylene glycol
4. Diethylene glycol
5. Triethylene glycol
6. Heavy products

The process involves reaction vessels and distillation columns to separate the glycols and water.
Ethylene Glycol Production

Simulate with COFE (COCO) a reactor to produce ethylene glycol considering that we know the conversion for each reaction.

Reactions:

\[ W + \text{EtO} \xrightarrow{k_1} \text{MEG} \]

\[ \text{MEG} + \text{EtO} \xrightarrow{k_2} \text{DEG} \]

\[ \text{DEG} + \text{EtO} \xrightarrow{k_3} \text{TEG} \]

Use Peng-Robinson (PR) thermodynamic package
Ethylene Glycol Production
Parametric study varying length of the PFR

\[ W + \text{EtO} \xrightarrow{k_1} \text{MEG} \]

\[ \text{MEG} + \text{EtO} \xrightarrow{k_2} \text{DEG} \]

\[ \text{DEG} + \text{EtO} \xrightarrow{k_3} \text{TEG} \]

**Kinetics**

\[ k_1 \left[ \text{L/(mol} \cdot \text{min)} \right] = \exp(13.62 - \frac{8220}{T}) \]

\[ k_2 \left[ \text{L/(mol} \cdot \text{min)} \right] = \exp(15.57 - \frac{8700}{T}) \]

\[ k_3 \left[ \text{L/(mol} \cdot \text{min)} \right] = \exp(16.06 - \frac{8900}{T}) \]

**Kinetics in COCO**

\[ R1 = \exp(13.62-8220/T)/60/1000\times C(\text{Water}) \times C(\text{Ethylene oxide}) \]

\[ R2 = \exp(15.57-8700/T)/60/1000\times C(\text{Monoethylene glycol}) \times C(\text{Ethylene oxide}) \]

\[ R3 = \exp(16.06-8900/T)/60/1000\times C(\text{Diethylene glycol}) \times C(\text{Ethylene oxide}) \]
Ethylene Glycol Production
Parametric study varying length of the PFR