INTRODUCTION TO CHEMICAL PROCESS SIMULATORS

DWSIM Chemical Process Simulator

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Monday, October 3rd 2016

- Introduction to Sequential – Modular Steady State Process Simulators
- Get used to working with DWSIM and COCO

Monday, October 10th 2016

- Simulation of Chemical Reactors

Monday, October 17th 2016

- Simulation of Distillation Columns

Monday, October 24th 2016

- Case studies
Flowsheeting is a systemic description of material and energy streams in a process plant by means of computer simulation with the scope of designing a new plant or improving the performance of an existing plant. Flowsheeting can be used as aid to implement a plantwide control strategy, as well as to manage the plant operation.

Introduction to Chemical Process Simulators

Simulation

Process Flowsheet

Input streams

Operating Conditions

Unit Parameters

Output streams

Design

Process Flowsheet

Input streams

Operating Conditions

Unit Parameters

Output streams

Optimization

Process Flowsheet

Input streams

Operating Conditions

Unit Parameters

Output streams

Synthesis

Process Flowsheet

Input streams

Operating Conditions

Unit Parameters

Output streams
Architecture of Process Simulators

- **Sequential-Modular**

  Based on the concept of modularity, which extends the chemical engineering concept of the unit operation to a “unit calculation” by the computer code responsible for the calculation of single process unit. The computation of the flowsheet takes place unit by unit following a calculation sequence.

- **Equation-Oriented (Simultaneous-Nonmodular)**

  The complete model of the flowsheet is expressed in the form of one large sparse system of nonlinear algebraic equations that is simultaneously solved for all the unknowns.

- **Simultaneous-Modular**

  Combination of Sequential-Modular and Equation Oriented approaches
Commercial Steady-State Process Simulators

Sequential – Modular approach
- Aspen Plus
- Aspen Hysys
- ChemCAD
- PRO II
- UniSim

Equation – Oriented approach
- gProms
- VMGSim
- Aspen Plus in EO
- Aspen Custom Modeler

Free Steady-State Process Simulators

Sequential – Modular approach
- DWSIM
- COCO

Equation – Oriented approach
- ASCEND
Sequential – Modular Process Simulators

Graphical User Interface

Input

Output

Executive Program

Unit module library

Sizing and costing database

Numerical routines

Themodynamic methods

Physical property database

Figure reproduced from Introduction to Software for Chemical Engineers, M. Martin (2015)
Sequential – Modular Process Simulators

**Advantages**

+ Easy programming and maintenance.
+ Robustness and reliability. Specific solution methods are developed for each process unit.
+ The unit blocks can be easily added to or removed from the flowsheet.

**Disadvantages**

– SM is well suited to process simulator, but not to design or optimization, since an iterative procedure is required to satisfy the constraints.
– Need for topological analysis and systematic initialization of tear streams.
– Present difficulties with flowsheets involving a large number of recycle streams.
– Rigid direction of computation, normally outputs from inputs.
Physical Property Service Facilities

Supply estimates for a number of different physical properties while the simulation is running.

Phase equilibrium represent one of the most important physical properties, as many chemical processes simulations involve distillation, stripping, evaporation or liquid-liquid separation. Solving the mass and energy balances for these operations necessitates predicting the

- Vapor – Liquid Equilibrium (VLE)
- Liquid – Liquid Equilibrium (LLE)

Estimation of physical properties can consume up to 90% of the computation time of a simulation.

Property packages are used to predict the phase equilibrium behavior of pure components and mixture systems
Phase Equilibrium

A closed system that contains more than one phase, at constant Pressure and Temperature, is at equilibrium if:

\[ f_i^I = f_i^{II} = \ldots = f_i^F \]

Isofugacities

Where \( f_i \) is the fugacity of Component \( i \) in Phases I, II, ... F

Vapor – Liquid Equilibrium

\[ f_i^V = f_i^L \]

\( f_i^V \) is the fugacity of Component \( i \) in the vapor phase

\( f_i^L \) is the fugacity of Component \( i \) in the liquid phase
Equation-of-State Method

Vapor-phase fugacity

\[ f_i^V = y_i \varphi_i^V P \]

Liquid-phase fugacity

\[ f_i^L = x_i \varphi_i^L P \]

where

\( y_i \) and \( x_i \) are the mole fraction of Comp i in the vapor and liquid phases, respectively

\( \varphi_i^V \) and \( \varphi_i^L \) are the vapor and liquid phase fugacity coefficients, respectively

\( P \) is the system pressure

The fugacity coefficients for each phase are determined with the following expression

\[
\ln \varphi_i = \frac{1}{RT} \int_0^P \left[ \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dp
\]
Equation-of-State Method

Vapor-phase fugacity

\[ f_i^V = y_i \, \varphi_i^V \, P \]

Liquid-phase fugacity

\[ f_i^L = x_i \, \varphi_i^L \, P \]

where

- \( y_i \) and \( x_i \) are the mole fraction of Comp i in the vapor and liquid phases, respectively.
- \( \varphi_i^V \) and \( \varphi_i^L \) are the vapor and liquid phase fugacity coefficients, respectively.
- \( P \) is the system pressure.

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\]
Activity Coefficient Method

Vapor-phase fugacity

\[ f_i^V = y_i \varphi_i^V P \]

Liquid-phase fugacity

\[ f_i^L = x_i \gamma_i f_i^0 \]

where

- \( y_i \) and \( x_i \) are the mole fraction of Comp. \( i \) in the vapor and liquid phases, respectively
- \( \varphi_i^V \) is the vapor-phase fugacity coefficient
- \( \gamma_i \) is the liquid-phase activity coefficient
- \( f_i^0 \) is the fugacity of Comp. \( i \) at standard state

In this case, thermodynamic models are required for \( \varphi_i \) (from an equation of state) and \( \gamma_i \) (from a liquid-phase activity coefficient model)
Activity Coefficient Method

At moderate pressures:

1. The vapor phase can be considered ideal \( \Rightarrow \phi_i^V = 1 \)
   
   therefore \( f_i^V = y_i \cdot P \)

2. Standard State fugacity

\[
f_i^0 = p_i^0 \phi_i^{sat} \exp \left[ \int_{p_i^{sat}}^{P} \frac{v_i^c}{RT} dP \right] \approx p_i^0
\]

therefore \( f_i^L = p_i^0 x_i \gamma_i \)

Poynting correction factor
Vapor – Liquid Equilibrium Example (Dechema Chemistry Data Series)
Decision tree for the selection of the thermodynamic property model

1. **Any polar component?**
   - Yes
     - **Under vacuum conditions?**
       - Yes
         - **Ideal**
       - No
         - **Any Electrolyte?**
           - Yes
             - Electrolyte NRTL
           - No
             - **Operating pressure low to medium ≤ 10 bar?**
               - Yes
                 - **Binary iteration coefficients available?**
                   - Yes
                     - Wilson NRTL
                   - No
                     - Liquid-liquid equilibrium?
                       - Yes
                         - UNIFAC LLE
                       - No
                         - NRTL UNIQUAC
               - No
                 - **PSRK**
                   - **PR or RKS with MHV2 mixing rules**
                     - **Schwartzentruber-Renon**
                       - PR or RKS with WS mixing rules
                         - PR or RKS with MHV2 mixing rules
                       - Wilson NRTL
                         - UNIQUAC
                       - Liquid-liquid equilibrium?
                         - Yes
                           - NRTL UNIQUAC
                         - No
                           - UNIFAC
     - No
       - **Any pseudo component?**
         - Yes
           - **Pressure**
             - Yes
               - Electrolyte NRTL
             - No
               - **Pitzer**
                 - **Bromley-Pitzer**
           - No
             - **Operating pressure low to medium ≤ 10 bar?**
               - Yes
                 - **Binary iteration coefficients available?**
                   - Yes
                     - Wilson NRTL
                   - No
                     - Liquid-liquid equilibrium?
                       - Yes
                         - UNIFAC LLE
                       - No
                         - UNIFAC
               - No
                 - **Pressure**
                   - Yes
                     - Peng-Robinson (PR)
                   - No
                     - **Soave-Redlich-Kwong (SRK)**
                       - **Lee-Kesler-Plöcker**

2. **Any Electrolyte?**
   - Yes
     - Electrolyte NRTL
   - No
     - **Under vacuum conditions?**
       - Yes
         - **Ideal**
       - No
         - **Any pseudo component?**
           - Yes
             - **Pressure**
               - Yes
                 - Electrolyte NRTL
               - No
                 - **Pitzer**
                   - **Bromley-Pitzer**
           - No
             - **Operating pressure low to medium ≤ 10 bar?**
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                 - **Binary iteration coefficients available?**
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                       - No
                         - UNIFAC
               - No
                 - **Pressure**
                   - Yes
                     - Peng-Robinson (PR)
                   - No
                     - **Soave-Redlich-Kwong (SRK)**
                       - **Lee-Kesler-Plöcker**

3. **Activity coefficient model**
   - **Pressure**
     - Yes
       - Electrolyte NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**
   - **Polarity**
     - Yes
       - Wilson NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**

4. **Equations of state model**
   - **Pressure**
     - Yes
       - Electrolyte NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**
   - **Polarity**
     - Yes
       - Wilson NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**

5. **Activity coefficient model**
   - **Pressure**
     - Yes
       - Electrolyte NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**
   - **Polarity**
     - Yes
       - Wilson NRTL
     - No
       - **Pitzer**
         - **Bromley-Pitzer**
Get used to working with Process Simulators

**FIRST STEPS**

1. Compounds
2. Property Packages
3. Flash Algorithm
4. System of Units
5. Feed inlet data
6. Units Specifications
7. Activate/recalculate all
8. Review of the results
Get used to working with Process Simulators

**DWSIM**

**COCO**

![Diagram showing DWSIM and COCO features](image-source)
Get used to working with DWSIM and COCO

Flash distillation 1
An equimolar mixture of benzene and toluene is subjected to flash distillation at a pressure of 1 bar in the separator. Determine the compositions (in mole fraction benzene) of the liquid and vapor leaving the separator when the feed is 25% vaporized. Estimate the temperature in the separator.

Sensitivity analysis
0% vaporized
50% vaporized
75% vaporized
100% vaporized
Get used to working with DWSIM and COCO

Flash distillation 1

<table>
<thead>
<tr>
<th>Vapor fraction</th>
<th>Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91.55</td>
</tr>
<tr>
<td>0.25</td>
<td>93.17</td>
</tr>
<tr>
<td>0.5</td>
<td>94.89</td>
</tr>
<tr>
<td>0.75</td>
<td>96.59</td>
</tr>
<tr>
<td>1</td>
<td>98.15</td>
</tr>
</tbody>
</table>
Get used to working with DWSIM and COCO
Vapor Liquid Equilibrium

- Dew point
- Bubble point

Benzene / Toluene
P = 1,01325 bar

Mole Fraction / Benzene

[Peng-Robinson (PR)] Bubble Points
[Peng-Robinson (PR)] Dew Points
Get used to working with DWSIM and COCO

Flash distillation 2

Calculate the composition of the final stream in the following process flowsheet.

Ethanol 41.86 kmol/h
Acetone 38.64 kmol/h

25°C
95 kPa

25°C

65°C

Use **UNIQUAC** thermodynamic package