Separator Analysis
Distillation Separation
Commercial Distillation Columns (1)
Commercial Distillation Columns (2)
Commercial Distillation Columns (3)
Commercial Distillation Columns (4)
Commercial Distillation Columns (5)
Commercial Distillation Columns (6)
Simple Column

Overhead (Distillate)

\[ D = \sum_{j=1}^{C} d_j, \quad \Delta_D = \frac{d_j}{D} \]

Feed

\[ F - \sum_{j=1}^{C} f_j, \quad \varepsilon = \frac{f}{F} \]

Bottoms

\[ B = \sum_{j=1}^{C} b_j, \quad \Delta_B = \frac{b_j}{B} \]
A Typical Separation

\[ P_D = 248 \text{ psia} \]

\[ f_j, \text{ lbmole/hr} \]

- \( \text{C}_2\text{H}_6 \): 30
- \( \text{C}_3\text{H}_8 \): 200
- \( \text{nC}_4\text{H}_{10} \): 370
- \( \text{nC}_5\text{H}_{12} \): 350
- \( \text{nC}_6\text{H}_{14} \): 50

\[ \text{Total}: 1000 \]

\[ P_F = 250 \text{ psia} \]
\[ T_F = 225 \text{ °F} \]

\[ P_B = 252 \text{ psia} \]

\[ d_j, \text{ lbmole/hr} \]

- \( \text{C}_2\text{H}_6 \): 30
- \( \text{C}_3\text{H}_8 \): 191
- \( \text{nC}_4\text{H}_{10} \): 5

\[ \text{b}_j, \text{ lbmole/hr} \]

- \( \text{C}_3\text{H}_8 \): 9
- \( \text{nC}_4\text{H}_{10} \): 365
- \( \text{nC}_5\text{H}_{12} \): 350
- \( \text{nC}_6\text{H}_{14} \): 50
Multicomponent Distillation Column Design

- Approximate (Short-cut) method: Fenske-Underwood-Gilliand
- Rigorous method: Stage by stage calculations
Short-cut method

Binary system (McCabe-Thiele) indicates:

\[ N_{\text{ideal}} = Fcn(R_{\text{min}}, N_{\text{min}}, R_{\text{act}}) \]
Approximate shortcut methods

Although rigorous calculation techniques are available, it is common practice to use the so called approximate methods in order to get preliminary design and/or to optimize the design conditions for a multicomponent distillation problem.

The method, we are going to illustrate in this section, is known under the name of "Fenske-Underwood-Gilliland" (FUG), from the three guys which developed the three different parts of the method in order to get the ideal number of stages of a multicomponent distillation column.

The method follows the here below sequence of steps:

<table>
<thead>
<tr>
<th>Equation</th>
<th>Condition:</th>
<th>To calculate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fenske</td>
<td>$N_{min}$</td>
</tr>
<tr>
<td>2</td>
<td>Underwood</td>
<td>$N \rightarrow \infty$</td>
</tr>
<tr>
<td>3</td>
<td>Reflux</td>
<td>$R=1.2-1.5 \times R_{min}$</td>
</tr>
<tr>
<td>4</td>
<td>Gilland</td>
<td>ideal number of stage $N$</td>
</tr>
</tbody>
</table>
Figure 9.1 Algorithm for multicomponent distillation by FUG method.
Figure 9.3 Specifications for debutanizer.
The Fenske equation allows for the calculation of the minimum number of stage.

The final equation is here below shown in the two forms (eqs.1 and 2), to be used respectively whether composition or fractional recovery specifications of the key components in the Distillate and in the Bottoms products are given.

1) \[ N_{\text{min}} = \frac{\left(\frac{x_{\text{LK}}}{x_{\text{HK}}} \right)_D}{\left(\frac{x_{\text{LK}}}{x_{\text{HK}}} \right)_B} \alpha_{\text{LK, HK}} \]

where the constant of relative volatility \( \alpha_{\text{LK, HK}} \) is calculated with respect to the heavy key component, taken as a reference:

\[ \alpha_{\text{LK, HK}} = \frac{k_{\text{LK}}}{k_{\text{HK}}} \]

\( \alpha_{\text{LK, HK}} \) depends on the temperature, therefore it is different at every stage of the column.

However, most often, for the seek of simplicity it is possible to use a constant value valid for all the column stages.

When this is not possible an average value of \( \alpha_{\text{LK, HK}} \) among all the \( (N=N_{\text{min}}) \) values must be then calculated, e.g. average between the value at the first stage and at the reboiler:

\[ \alpha_{\text{aver.}} = \left( \alpha_1 \alpha_R \right)^{1/2} \]
Fenske equation
Derivation of the Fenske equation

The concept behind the Fenske equation is really simple.

The column schematized here beside with the hypothesis of total reflux (no feed no products) is taken into consideration. Then the equilibrium and the mass balance equation are written for the two key components starting from the reboiler stage (see envelope in the figure).

(3) Equilibrium:
\[ y_{B,\text{LK}} = k_{\text{LK}} x_{B,\text{LK}} \]
\[ y_{B,\text{HK}} = k_{\text{HK}} x_{B,\text{HK}} \]

(4) Mass balance:
\[ V' y_{B,\text{LK}} = L' x_{N,\text{LK}} \]
\[ V' = L' \]

Please for the derivation of the Fenske's equation, see the attached pdf file.
The Underwood equations allow for the calculation of the minimum reflux $R_{\text{min}}$.

where  is a particular constant of relative volatility and it is:

\begin{align*}
1) \quad 1 - q &= D \sum_{i=1}^{C} \frac{\alpha_{iHK} z_i}{\alpha_{iHK} - \phi} \quad \text{Underwood I} \\
2) \quad V_{\text{min}} &= D \sum_{i=1}^{C} \frac{\alpha_{iHK} x_{D,i}}{\alpha_{iHK} - \phi} \quad \text{Underwood II} \\
\alpha_{LK} &> \square > \alpha_{HK}
\end{align*}

For the seek of simplicity we will not explain why the value of $\square$ in the here above way fixed.

It is only important to underline that this value can be so chosen only when two key components are adjacent in the volatility scale:

\[ \alpha_{LNK} > \alpha_{LK} > \alpha_{HK} > \alpha_{HNK} \]
Underwood equations

Procedure for the calculation of the minimum reflux

**Step 1.** Apply the first Underwood equation for the calculation of $\phi$.

**Step 2.** Apply the second Underwood equation for the calculation of $R_{\text{min}}$:

\[
R_{\text{min}} = \frac{L_{\text{min}}}{D} = \frac{V_{\text{min}}}{D} - 1
\]

Please for the derivation of the Underwood's equations, see the attached pdf file.

**Calculation of the finite reflux**

The further step is the calculation of the finite reflux. This is done, as for the binary case, using a multiplying factor, as follows:

\[
R = (1.05 - 2) \cdot R_{\text{min}}
\]
Gilliland used an empirical correlation to calculate the final number of stage $N$ from the values calculated through the Fenske and Underwood equations ($N_{\text{min}}$, $R$, $R_{\text{min}}$).

The procedure is really simple and use a diagram as the one shown here below.

One enters the diagram with the abscissa value, which is known, and read the ordinate of the corresponding point on the Gilliland curve.

The only unknown of the ordinate is the number of stage $N$. 

Other authors, besides Gilliland, have developed similar empirical correlations or have tried to find a mathematical expression for the Gilliland correlation. Here below some of the most significant result:
Rigorous Method

MESH is employed to each and every stage of the column designed

so-called

Stage by stage computation
Distillation - Rigorous Simulation Using the Unabridged MESH Equations

The models involving the unabridged MESH equations are the most accurate and flexible, when phase equilibria are assumed on the stages, but care must be exercised in their use. To obtain convergence, these nonlinear models require feasible specifications which, for highly non-ideal mixtures, can be difficult to determine. For these mixtures, the approximate methods may not give sufficiently good estimates for the number of theoretical stages and the reflux ratio needed to achieve a desired split of two key components. When this is the case, more rigorous methods may be necessary.
Since the late 1970s, many sophisticated, rigorous models have been developed. These permit multiple feed streams and sidedraws, interlinked column sections, heterogeneous operation (that is, two liquid phases on some of the trays), and chemical reaction (in reactive distillation towers).
Rigorous Column Topology
Equilibrium Stage Model
1. M equations—material balance for each component (C equations for each stage):

\[ M_{i,j} = L_{j-1}x_{i,j-1} + \sum_{i} y_{i,j+1} + F_j z_{i,j} - (L_j + U_j)x_{i,j} - (V_j + B_j)y_{i,j} = 0 \]  

(6-86)

2. E equations—phase equilibrium relation for each component, here modified to include the Murphree efficiency defined by equation 4-55 (C equations for each stage):

\[ E_{i,j} = E_{MG,i,j} m_{i,j} x_{i,j} - y_{i,j} - \left(1 - E_{MG,j,j}\right) y_{i,j+1} = 0 \]  

(6-87)

3. S equations—mole fractions summation (2 for each stage):

\[ \left(S_y\right)_j = \sum_{i=1}^{C} y_{i,j} - 1 = 0 \quad \left(S_x\right)_j = \sum_{i=1}^{C} x_{i,j} - 1 = 0 \]  

(6-88)

4. H equation—enthalpy balance (one for each stage):

\[ H_j = L_{j-1}H_{L,j-1} + V_{j+1}H_{V,j+1} + F_j H_{F,j} - (L_j + U_j)H_L - (V_j + B_j)H_V - Q_j = 0 \]  

(6-89)
Equilibrium Distillation Simulation (1)

The following feed, at 80 °C and 1,035 kPa, is to be fractionated at the rate of 1.0 kmoles/s at the given pressure so that the vapor contains 98% of the propane, but only 1% of the n-butane:

<table>
<thead>
<tr>
<th>Component</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>n-C$<em>4$H$</em>{10}$</th>
<th>n-C$<em>5$H$</em>{12}$</th>
<th>n-C$<em>6$H$</em>{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_F$, mole fraction</td>
<td>0.03</td>
<td>0.07</td>
<td>0.15</td>
<td>0.33</td>
<td>0.30</td>
<td>0.12</td>
</tr>
</tbody>
</table>

A number of simulations were carried out using the equilibrium model of ChemSep for different column configurations (number of equilibrium stages and feed stage location) and for differing operation specifications (reflux ratio and bottom product rate). Only the specifications and results of our final simulation are reported here.
Unit Specification (1)

Operation:
Simple distillation
Partial (vapor product) condenser
Partial (liquid product) reboiler
14 equilibrium stages
Feed to stage 6

Properties:
EOS $m$-model
Soave-RK Cubic EOS
Excess enthalpy from EOS

Specifications:
Column pressure 10.21 atm (constant)
Feed
Pressure 10.21 atm
Temperature 80 °C
Condenser
Reflux ratio = 1.2
Reboiler
Bottom product flow rate = 620 moles/s
A sieve-tray distillation column with a partial reboiler and a total condenser is to be designed to separate a mixture of benzene, toluene, and cumene (a common name for isopropyl benzene). The feed flows at the rate of 40 moles/s benzene, 30 moles/s toluene, and 30 moles/s cumene. It enters the column at a pressure of 1.05 atm and 50 mole% vaporized. We desire at least 98.5% recovery of the toluene in the distillate, and at least 98.5% recovery of the cumene in the bottoms. Design the column for a reflux ratio of 2.0.
Operation:
- Simple distillation
- Total (liquid product) condenser
- Partial (liquid product) reboiler
- 10 sieve trays
- Feed to stage 6 (stage 1 is the condenser; stage 12 is the reboiler)

Properties:
- DEHEMA m-model
- UNIFAC activity coefficients
- Equation of state—ideal gas law
- Vapor pressure—Antoine
- Excess enthalpy from UNIFAC model

Specifications:
- Condenser pressure—1 atm
- Column top pressure—1 atm
- Feed
  - Pressure 1.05 atm, 50 mole% vapor
  - Flowrates (moles/s)
    - Benzene: 40
    - Toluene: 30
    - Cumene: 30
- Condenser
  - Reflux ratio = 2.0
- Reboiler
  - Bottom product flow rate = 30 moles/s

Design:
- Stages
  - Section 1: 2–5
  - Section 2: 6–11
- Mass-transfer coefficient
  - Section 1: Chan Fair
  - Section 2: Chan Fair
- Vapor flow model
  - Section 1: Plug
  - Section 2: Plug
- Liquid flow model
  - Section 1: Mixed
  - Section 2: Mixed
- Fraction of flooding
  - Section 1: 0.61
  - Section 2: 0.70
- System factor
  - Section 1: 0.90
  - Section 2: 0.90
ChemCAD

Distillation
Distillation Calculations

- Distillation Principles
  - Techniques
    - Short-Cut,
    - SCDS Algorithm (Rigorous)
    - Inside-out Algorithm (Rigorous)
  - Specifications
    - Degrees-of-freedom,
    - Numerical stability,
    - Guidelines

- Workshop 1-4
Distillation Models - SHOR

ShortCut (SHOR)

◎ Fenske eqn for Nmin.

◎ Underwood for Rmin.

◎ Gilliland correlation for ideal stages.

◎ Kirkbride/Fenske for feed location.

◎ Rating:

◎ Design:

◎ One feed、two product.
Distillation Models - SCDS

Simultaneous Corrections Distillation Method (Rigorous)

◎ Plate efficiency included.
◎ Conversion: Run Time = B × (Ncomp)² × (Nstage)
◎ Good conversion for non-ideal system.
◎ w/o Side stripper, Pump around
◎ Appropriate for reactive, electrolyte system, and ternary phase distillation.
◎ Applicability: Absorbers, Reboiled Absorbers, Strippers, Fractionators
Distillation Models - TOWR

Rigorous Inside-out (TOWR)

◎ No plate efficiency selection.
◎ Conversion: Run Time = A \times (N_{comp}) \times (N_{stage})^2
◎ Not proper for non-ideal system.
◎ w/o Side stripper、Pump around
◎ Applicability : Absorbers、Reboiled Absorbers、Strippers、Fractionators.
Distillation Models (TOWR PLUS)

Rigorous Inside-out (TOWR PLUS)

◎ No plate efficiency option.
◎ Conversion: Run Time = A × (Ncomp) × (Nstage)^2
◎ Not a good choice for non-ideal system.
◎ With Side stripper、Pump around
◎ Good for crude distillation.
# Degrees of Freedom

<table>
<thead>
<tr>
<th>Equipment Item</th>
<th>D.O.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Absorber</td>
<td>0</td>
</tr>
<tr>
<td>Reboiler</td>
<td>1</td>
</tr>
<tr>
<td>Condenser</td>
<td>1</td>
</tr>
<tr>
<td>Side Exchanger</td>
<td>1</td>
</tr>
<tr>
<td>Pumparound</td>
<td>2</td>
</tr>
<tr>
<td>Side stripper</td>
<td>1</td>
</tr>
</tbody>
</table>
Distillation Specification Option

- Condenser
- Reboiler
- Heater/coolers
- Side Streams
- Pumparounds
- Tray Conditions
Usual Specifications (Typical Column)

◎ Relatively “Safe”
   One Material Bal Spec. (Dist.or Bot)
   One Heat Bal Spec. (R/D, V/B)

◎ Poor Choices
   Top and Bottom Flows
   Pure Stream Temperature

◎ Good Choices
   Pure Stream Composition
   Mixed Stream Temperature
   Known Heat Load or Split

Best Choice
Column Estimates Guidelines

- No estimate Better than Poor Estimate
- Avoid Pure Component Temperature
- Avoid Azeotrope Temperature
- Tray 2, N-1 Temps. for Unusual Problems
- Use Phase Envelopes for Guidance
- Use Material Balance for Overhead Flow
- Use Profile Options for Difficult Problems
Workshop: Distillation 1.
Short-Cut & Rigorous Distillation (SCDS)

Please design a distillation column with a partial reboiler and a total condenser to separate a mixture of benzene, toluene, and 1,2,3-trimethylbenzene. The feed, 40mol% benzene, 30% toluene, and 30% trimethylbenzene, enters the column as a sat’d vapor. A 95% recovery of benzene in the distillate and 95% Trimethyl-Benzene in the bottoms. The reflux returns as a sat’d liquidm and the operating pressure is 1 atm.

Step 1: Use Short-Cut for a preliminary design.
Step 2: Choose Rigorous model for further simulation.
Step 3: Try Equip. Sizing for internal details.
**Workshop: Distillation 2.**

**Rigorous Distillation (SCDS)**

Feed : 10 moles/hr MeOH, 90 moles/hr water, sat. at 20 psia

Thermo : 

SCDS Col : 20 stages (including condenser and reboiler) 
feed on stage 10, 15 psia top pressure, 2 psi pressure drop

Spec set 1 : Set the bottoms flow to 90 moles/hr, R/D = 20

Spec set 2 : Set the bottoms flow to 90 moles/hr, R/D = 0.5

Observe : Mole Fraction of MeOH at R/D=0.5 (Column is Pinched, see Profile)

Spec set 3 : Overhead spec set the mole fraction of MeOH at R/D=0.5

Observe : Column will not likely converge even though we solved this case.
Workshop: Distillation 3. Rigorous Distillation (SCDS)

Feed : 100 lbmoles Nitrogen and 11 lbmoles Hydrogen Chloride
SCDS Col : 10 stages, HCl/N2 feed on stage 10, water feed on stage 1
15 psia top pressure, 2psia pressure drop
Spec set 1 : No reboiler and No condenser
Thermo : 

Case 1: Heat of solution for enthalpy correction

Case 2: No Heat of solution for enthalpy correction

Compare Temperature Profiles for both cases.
Workshop Distillation 4. Atmospheric Crude Unit

COMPONENTS

<table>
<thead>
<tr>
<th>ID</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>Water</td>
</tr>
<tr>
<td>4</td>
<td>Propane</td>
</tr>
<tr>
<td>5</td>
<td>i-Butane</td>
</tr>
<tr>
<td>6</td>
<td>n-Butane</td>
</tr>
<tr>
<td>5001+</td>
<td>pseudo comps. (From Crude Characterization)</td>
</tr>
</tbody>
</table>

THERMODYNAMICS

K-VALUES - Grayson-Streed

ENTHALPY - Lee Kesler

WATER - Immiscible

STREAM 1 - CRUDE FEED

Temp, F 300
Pres, psia 100

FLASH

Mode 2 (Isothermal)
Parameter #1 410 (Temperature out)
Parameter #2 55 (Pressure out)
TOWER CONFIGURATION

No. of side strippers 2
No. of pumparounds 1
No. of side exchangers 1

MAIN COLUMN

No. of stages 16
Pres. of tower top psia 23
Col. Pres. drop psi 2
Bottom steam, lbmol/hr 83.3
Steam temp., F 335
Steam pres, psia 115
First feed stage 14

CONDENSER

Condenser type 2 (Total w/H₂O decant)
Condenser pres., psia 20
Est. cond. temp, F 100
Subcooled cond. temp, F 100 (Specification)

REBOILER

Estimated temp., F 600
Reboiler option N (No reboiler)
### SIDE STRIPPERS

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>Stripper no.</td>
<td>1</td>
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</tr>
<tr>
<td>No. of stages</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Draw stage</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Return stage</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Bottom vol., BPSD</td>
<td>3780</td>
<td>3765</td>
</tr>
<tr>
<td>Steam lbmol/hr</td>
<td>33.33</td>
<td>36.11</td>
</tr>
<tr>
<td>Temp. F</td>
<td>335</td>
<td>335</td>
</tr>
<tr>
<td>Pres. psia</td>
<td>115</td>
<td>115</td>
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### PUMPAROUNDS

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Pumparound no.</td>
<td>1</td>
</tr>
<tr>
<td>Draw stage</td>
<td>12</td>
</tr>
<tr>
<td>Return stage</td>
<td>10</td>
</tr>
<tr>
<td>Vol. flow rate, BPSD</td>
<td>4700</td>
</tr>
<tr>
<td>Heat duty, MMBTU/HR</td>
<td>-7.31</td>
</tr>
</tbody>
</table>

### SIDE EXCHANGERS

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Side exchanger no.</td>
<td>1</td>
</tr>
<tr>
<td>Location</td>
<td>14</td>
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</table>

### TRAY CONDITIONS

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Tray no.</td>
<td>16</td>
</tr>
<tr>
<td>Tray no.</td>
<td>13</td>
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</tbody>
</table>
CRUDE CHARACTERIZATION - STREAM 1

CORRELATION METHODS

<table>
<thead>
<tr>
<th>Molecular Wt. Equation</th>
<th>1</th>
<th>(Coade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Properties</td>
<td>1</td>
<td>(Cavett)</td>
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</table>

CUT BREAKDOWN

<table>
<thead>
<tr>
<th>Temp. Range</th>
<th>No. Cuts</th>
</tr>
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<tbody>
<tr>
<td>50- 150 F</td>
<td>4</td>
</tr>
<tr>
<td>150- 550 F</td>
<td>16</td>
</tr>
<tr>
<td>550- 750 F</td>
<td>4</td>
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<tr>
<td>750-1250 F</td>
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STREAM #1 ASSAY INFORMATION

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<thead>
<tr>
<th>Assay type</th>
<th>3</th>
<th>(TBP)</th>
</tr>
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<tbody>
<tr>
<td>Gravity type</td>
<td>1</td>
<td>(API)</td>
</tr>
<tr>
<td>Bulk gravity</td>
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<td></td>
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<tr>
<td>Flow units</td>
<td>1</td>
<td>(BPSD)</td>
</tr>
<tr>
<td>Total flow rate</td>
<td>25000</td>
<td></td>
</tr>
<tr>
<td>Light ends unit</td>
<td>1</td>
<td>(Vol %)</td>
</tr>
<tr>
<td>Volume</td>
<td>Temp</td>
<td>Volume</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>%</td>
<td>F</td>
<td>%</td>
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<tr>
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<td>5.00</td>
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<td>100.00</td>
<td>1440</td>
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</table>

**LIGHT-END ANALYSIS**

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<th>ID</th>
<th>Name</th>
<th>Volume %</th>
</tr>
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<tbody>
<tr>
<td>62</td>
<td>Water</td>
<td>.00</td>
</tr>
<tr>
<td>4</td>
<td>Propane</td>
<td>.18</td>
</tr>
<tr>
<td>5</td>
<td>i-Butane</td>
<td>.30</td>
</tr>
<tr>
<td>6</td>
<td>n-Butane</td>
<td>.69</td>
</tr>
</tbody>
</table>
ChemCad

Absorption and Stripping
Contents

• Typical absorption and striping process

• General design consideration

• Thermodynamic consideration

• Simulate absorption and stripping by using CHEMCAD
  • Physical absorption (stripping)
  • Chemical absorption

• Absorber and stripper Sizing
**Typical absorption process**

**In this case**

- Feed gas - from dryer
- Remove 99.5% of acetone or acetone <100 PPM in Exit gas
- Liquid absorbent: pure water
- The exit gas is almost saturated with water vapor
- The exit liquid is almost saturated with air
- 3 deg C decrease because of some water vaporization
Typical stripping process

In this case

• Waste Water from process
• Remove 99.9% of VOC or VOC < 10 PPM in exit liquid
• Stripped by air
• the exit gas is almost saturated with water vapor
• the exit liquid is almost saturated with air
• the temperature of exit liquid decrease because of some water vaporization
General design considerations

- Entering gas flow rate, composition, temperature and pressure (Feed)
- Desired degree of recovery of one or more solutes (Spec.)
- Choice of absorbent (stripping agent)
- Operating pressure and temperature, and allowable gas pressure drop (constrain)
- Minimum absorbent (stripping agent) flow rate and actual absorbent (stripping agent) flow rate as a multiple of the minimum rate needed to make the separation
- Number of equilibrium stages
- Heat effects and need for cooling (heating)
- Type of absorber (stripping) equipment
- Height of absorber (stripping)
- Diameter of absorber (stripping)
The ideal absorbent

- Have a high solubility for the solute
to minimize the need for absorbent
- have a low volatility
to reduce the lose from vent and to facilitate separation of absorbent and solute
- be stable to maximize absorbent life
to reduce absorbent makeup requirement
- be non-corrosive
to permit user of common materials of construction
- have a low viscosity
to provide low pressure drop and high mass and heat transfer rates
- be non-foaming when contact with the gas
to make it unnecessary to increase absorber dimensions
- be nontoxic and nonflammable
to facilitate its safe use
- be available, if possible, within the process
to make it unnecessary to provide an absorbent from external sources
Absorption column

\[ X \rightarrow L' \rightarrow Y_1' \rightarrow G' \]

Operating line

Equilibrium curve

- fraction of a component absorbed = \( f(\text{no of stages, absorption factor}) \)
- Absorption factor, \( A = \frac{L}{KG} \)
- if \( A > 1 \), any degree of absorption can be achieved.
- The larger the value of \( A \), the fewer the no. of stages required, however the larger absorbent flow rate required
Operating line for an Absorber - absorbent flow rate

\[ Y_{N+1} = X_N \left( \frac{L'}{G'} \right) + Y_1 - X_0 \left( \frac{L'}{G'} \right) \]

Operating line 1: no. of stages = 0; but infinite absorbent rate
Operating line 4: minimum absorbent rate; but no. of stages = infinite
Actual operating absorbent flow rate = \((1.1 \sim 2.0) \times \text{minimum absorbent flow rate}\)
Graphical determination of the no. of stages for absorber
**Stripping column**

- the fraction of a component stripped = $f$(no of stages, stripping factor)
- stripping factor, $S = \frac{(KG)}{L}$
- if $S > 1$ then any degree of stripping can be achieved.
- The larger the value of $S$, the fewer the no. of stages required, however the larger stripping gas required
Operating line for a Stripper - stripping agent flow rate

\[ Y_N = X_{N+1}(L'/G') + Y_0 - X_1(L'/G') \]

Operating line 1: minimum stripping agent rate; but no. of stages = infinite
Operating line 4: no. of stages = 0; but infinite stripping agent flow rate
Actual operating stripping agent flow rate = (1.1 ~ 2.0) * minimum stripping agent flow rate
Graphical determination of the no. of stages for stripper

Equilibrium curve

Stage 1 (bottom)

Stage 2

Stage 3 (top)

Operating line

$X_{N+1}$

$Y_N$

$Y_N$

$Y_0$

$X_1$

$X_{N+1}$

$Y_0$

$X_1$
Why Computer simulation needed?

We make some assumptions before:

- Carrier gas is insoluble
- Solvent is nonvolatile
- The system is isothermal and isobaric
- The heat of absorption is negligible

The problems:

- **fixes the no. of stages** rather than recover the percent of solute
- **more than one solute**
- when the best operating conditions of temperature and pressure are to be determined so that the location of the **equilibrium curve is unknown**
- **very low or very high concentrations** force the graphical construction to the corners of the diagram so that **multiple y-x diagrams** of varying sizes and dimensions are needed
Phase equilibrium $\hat{f}_i^v = \hat{f}_i^L$ where $\hat{f}_i^v = P_y \phi_i^v = y_i x_i \phi_i^v$ and $\hat{f}_i^L = P_x \phi_i^L = x_i \gamma_i \phi_i^L$

\[ K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^v} \]

\[ P y_i \phi_i^v = x_i \gamma_i \phi_i^L \]

\[ K_i = \frac{y_i}{x_i} = \frac{\gamma_i \phi_i^L}{P \phi_i^v} \]

\[ f_i^L = P_i^{sat} \phi_i^{sat} \exp \left[ \int_{P_{sat}}^{P} \left( \frac{V_i^L}{RT} \right) dP \right] \]

Poynting Factor

\[ K_i = \frac{\gamma_i P_i^{sat} \phi_i^{sat}}{P \phi_i^v} \] (medium pressure)

\[ K_i = \frac{\gamma_i P_i^{sat}}{P} \] (low pressure) modified Raoults law

\[ K_i = \frac{P_i^{sat}}{P} \] (ideal solution) Raoults law

Note: Dissolved non-condensable gases:

1. Henry's Gas Law - light gases dissolved in water
2. TSRK method - light gases dissolved in methanol
Thermodynamic consideration for absorber

For Absorption
- Acetone - modified Raoults law
- N₂, O₂ - Henry law
- Argon - Henry law

For Absorption simulation
- Acetone, Water - NRTL, UNIQUAC,...
- N₂, O₂, Argon - Henry law
Thermodynamic consideration for stripper

For stripper
- benzene - modified Raoult’s law
- Toluene - modified Raoult’s law
- Ethylbenzene - modified Raoult’s law
- Water - Raoult’s law
- air - Henry law

For stripper simulation
- benzene - NRTL, UNIQUAC,...
- Toluene - NRTL, UNIQUAC,...
- Ethylbenzene - NRTL, UNIQUAC,...
- Water - NRTL, UNIQUAC,...
- air - Henry law
Chemical absorption (reactive absorption)

Non-electrolyte approach
- **Amine** - for the removal of *sour gases (H2S, CO2)* from hydrocarbon streams using MEA, MDEA or DEA.
- **Sour** - for modeling systems with CO2, NH3, H2S, and other compounds dissolved in water.
- **PPAq** - used for the modeling of ionic type compounds, such as HCl or HNO3, which dissolve in water and disassociate.

Electrolyte approach
- **Ideal**
- **Pitzer**
- **NRTL for electrolyte 1982**
- **NRTL for electrolyte 1986**
Amine Model

The chemical reactions in an H2S-CO2-Amine system are described by the following reactions:

1. $RR'NH_2^+ \rightleftharpoons H^+ + RR'NH \quad K_1$
2. $RR'NCOO + H_2O \rightleftharpoons RR'NH + HCO_3^- \quad K_2$
3. $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad K_3$
4. $HCO_3^- \rightleftharpoons CO_3^{--} + H^+ \quad K_4$
5. $H_2S \rightleftharpoons HS^- + H^+ \quad K_5$
6. $HS^- \rightleftharpoons S^{--} + H^+ \quad K_6$
7. $H_2O \rightleftharpoons H^+ + OH^- \quad K_7$

where $R$ and $R'$ represent alcohol groups. The reaction equations are solved simultaneously to obtain the free concentration of H2S and CO2. The partial pressure of H2S and CO2 are calculated by the Henry's constants and free concentration in the liquid phase. Reference: Kent, R. L. and Eisenberg, Hydrocarbon Processing, Feb. 1976, p. 8’
SOUR WATER Model

The chemical reactions in \textit{H2S-CO2-NH3} systems are represented by the following reactions:

1. \[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \] \(K_1\)
2. \[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \] \(K_2\)
3. \[ \text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \] \(K_3\)
4. \[ \text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{NCOO}^- + \text{H}_2\text{O} \] \(K_4\)
5. \[ \text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+ \] \(K_5\)
6. \[ \text{HS}^- \rightleftharpoons \text{S}^{2-} + \text{H}^+ \] \(K_6\)
7. \[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \] \(K_7\)

The addition of \textit{NaOH} or \textit{Carbolic acid} is also considered in CHEMCAD. The dissociation of \textit{Phenol} and \textit{Hydrogen Cyanide} is also included in the program.

Reference: EPA-600/2-80-067 A New Correlation of NH2, CO2, and H2S Volatility Data from Aqueous Sour Water Systems by Grant M, Wilson EPA Grant No. R804364010.
Partial Pressures of Aqueous mixtures Model (PPAQ)

1. The K-value of the solute is calculated by the following equation,

   \[ K = \frac{PP}{XP_T} = \frac{PP}{P_T}/X \]

   \( PP = \) the solute partial pressure, calculated by interpolating the user-provided table
   \( P_T = \) the system pressure
   \( X = \) the liquid molar concentration of the solute

2. The K-value of water is calculated using the partial pressure data given in the .PPA file.

3. K-values for all other components are calculated using Henry's Gas Law.

4. If the HGL data is not present for a given compound, the program will fall back to the MSRK method. If the MSRK parameters for a given compound are not present, the program will use the SRK method.
   - using partial pressures to calculate the equilibrium of the solute.
   - HCl or HNO3 is already considered in CHEMCAD.
Simulate absorber using ChemCAD

Remove acetone down to 100 ppm

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Overall</td>
<td>Overall</td>
<td>Overall</td>
<td>Overall</td>
</tr>
<tr>
<td>Molar flow kmol/h</td>
<td>484.2522</td>
<td>702.5000</td>
<td>691.5662</td>
<td>495.1859</td>
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<tr>
<td>Mass flow kg/h</td>
<td>8723.8021</td>
<td>20596.9013</td>
<td>19989.6598</td>
<td>9331.0409</td>
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<tr>
<td>Temp C</td>
<td>25.0000</td>
<td>25.0000</td>
<td>27.5198</td>
<td>38.6127</td>
</tr>
<tr>
<td>Pres kPa</td>
<td>101.3000</td>
<td>101.3000</td>
<td>590.0000</td>
<td>601.3000</td>
</tr>
<tr>
<td>Vapor mole fraction</td>
<td>0.0000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Enth kcal/h</td>
<td>-3.3065E+007</td>
<td>-8.2339E+005</td>
<td>-2.9296E+005</td>
<td>-3.3596E+007</td>
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<tr>
<td>Actual vol m3/h</td>
<td>8.7526</td>
<td>17182.7439</td>
<td>2927.1054</td>
<td>9.5782</td>
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<tr>
<td>Std liq 0 C m3/h</td>
<td>8.7252</td>
<td>23.7343</td>
<td>22.9770</td>
<td>9.4825</td>
</tr>
<tr>
<td>Std vap 0 C m3/h</td>
<td>10853.8570</td>
<td>15745.5861</td>
<td>15500.5215</td>
<td>11098.9225</td>
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<tr>
<td>Component mole fractions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>0.000000</td>
<td>0.009822</td>
<td>0.009976</td>
<td>0.000001</td>
</tr>
<tr>
<td>O2</td>
<td>0.000000</td>
<td>0.205409</td>
<td>0.208641</td>
<td>0.000022</td>
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<tr>
<td>N2</td>
<td>0.000000</td>
<td>0.762989</td>
<td>0.775023</td>
<td>0.000041</td>
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<td>H2O</td>
<td>1.000000</td>
<td>0.007117</td>
<td>0.006260</td>
<td>0.979275</td>
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<td>Acetone</td>
<td>0.000000</td>
<td>0.014662</td>
<td>0.000100</td>
<td>0.020661</td>
</tr>
</tbody>
</table>

Exit gas, 25°C, 90 kPa
- Argon: 6.9 kmole/h
- O₂: 144.291 kmole/h
- N₂: 535.983 kmole/h
- Water: 22.0 kmole/h
- Acetone: 0.05 kmole/h

Liquid absorbent, 25°C, 101.3 kPa
- Water: 194.3 kmole/h

Feed gas, 25°C, 101.3 kPa
- Argon: 6.9 kmole/h
- O₂: 144.3 kmole/h
- N₂: 536.0 kmole/h
- Water: 5.0 kmole/h
- Acetone: 10.3 kmole/h

Exit liquid, 22°C, 101.3 kPa
- O₂: 0.009 kmole/h
- N₂: 0.017 kmole/h
- Water: 1926.0 kmole/h
- Acetone: 10.25 kmole/h
Using sensitivity analysis to explore major variables
Simulate absorber using ChemCAD

97% EtOH must be removed

find:  1. Lmin

2. no. of stages when 1.5* Lmin

Liquid absorbent, 30°C, 110 kPa

Water

Feed gas
25°C, 110 kPa

CO₂ 176.4
EtOH 3.6

kmole/h

kmole/h
Simulate stripper using ChemCAD

Exit gas 70°F, 15 psia

- Waste Water, 500 gpm
  - 70°F, 15 psia
  - Mass fraction
    - Bzn: 0.000150
    - Tol: 0.000050
    - Eth-bzn: 0.000020
    - Water: 0.999780

- Air, 60°F, 1 atm
  - 3400 scfm
Simulate Sour water stripper using ChemCAD (SOUR)

Remove H2S and NH3 from wastewater down to 5 ppm

**Stream No.** 1 2 3
---
**Name**
**Molar flow lbmol/h** 3854.5125 15.4541 3839.0581
**Mass flow lb/h** 69503.8516 343.2190 69160.6250
**Temp °F** 148.0000 147.9073 218.7682
**Pres psia** 148.0000 147.9073 218.7682
**Vapor mol fraction** 0.0000 1.0000 0.0000
**Enth MMBtu/h** -468.44 -0.56860 -462.24
**Actual vol ft3/hr** 1165.9974 6971.4404 1212.2500
**Std 1iq ft3/hr** 1115.3810 7.3525 1108.0283
**Std vap 60F scfh** 1462705.1250 5864.5171 1456840.5000
**Component mass fractions**
- **Hydrogen Sulfide** 0.002194 0.444269 0.000000
- **H2O** 0.996045 0.199916 0.999996
- **Ammonia** 0.001761 0.355815 0.000004
### MEA sour Gas Treatment Plant

**Diagram: MEA sour Gas Treatment Plant**

**Table: Stream Data**

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Sour</td>
<td>Sweet</td>
<td>Coldrich</td>
<td>Warmrich</td>
<td>Offgas</td>
<td>Hotlean</td>
<td>Warmlean</td>
<td>Coldlean</td>
<td>Pumpout</td>
<td>Makeu p</td>
<td>Absrfeed</td>
<td></td>
</tr>
<tr>
<td>Molar flow lbmol/h</td>
<td>3535.6250</td>
<td>3840.1001</td>
<td>3759.9153</td>
<td>3615.8804</td>
<td>3615.8804</td>
<td>96.6456</td>
<td>3519.2346</td>
<td>3519.2346</td>
<td>3519.2346</td>
<td>3519.2346</td>
<td>16.3905</td>
<td>3535.6250</td>
</tr>
<tr>
<td>Mass flow lb/h</td>
<td>71356.3281</td>
<td>64100.8828</td>
<td>60612.6836</td>
<td>74846.1563</td>
<td>74846.1563</td>
<td>3785.1079</td>
<td>71061.0547</td>
<td>71061.0547</td>
<td>71061.0547</td>
<td>71061.0547</td>
<td>295.2743</td>
<td>71356.3281</td>
</tr>
<tr>
<td>Temp F</td>
<td>127.7411</td>
<td>90.0000</td>
<td>133.7256</td>
<td>141.7256</td>
<td>230.0000</td>
<td>125.0000</td>
<td>252.7791</td>
<td>160.5412</td>
<td>125.0000</td>
<td>127.7536</td>
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<td>127.7411</td>
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<tr>
<td>Pres psig</td>
<td>1000.0000</td>
<td>900.0000</td>
<td>900.0000</td>
<td>900.0000</td>
<td>897.0000</td>
<td>12.6000</td>
<td>15.4000</td>
<td>12.4000</td>
<td>12.4000</td>
<td>1000.0000</td>
<td>1000.0000</td>
<td>1000.0000</td>
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<tr>
<td>Vapor mole fraction</td>
<td>0.0000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.0000</td>
<td>0.0001553</td>
<td>1.000</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Enthal MMBtu/h</td>
<td>-431.32</td>
<td>-134.93</td>
<td>-122.53</td>
<td>-443.72</td>
<td>-437.50</td>
<td>-12.302</td>
<td>-420.93</td>
<td>-427.16</td>
<td>-429.53</td>
<td>-429.32</td>
<td>-2.0013</td>
<td>-431.32</td>
</tr>
<tr>
<td>Actual vol ft³/hr</td>
<td>1174.2444</td>
<td>22547.0566</td>
<td>24580.8759</td>
<td>1299.5634</td>
<td>1357.9508</td>
<td>22033.3965</td>
<td>1227.2813</td>
<td>1181.5676</td>
<td>1168.5450</td>
<td>1169.4530</td>
<td>4.7920</td>
<td>1174.2444</td>
</tr>
<tr>
<td>Std liq ft³/hr</td>
<td>1142.5914</td>
<td>3286.5100</td>
<td>3215.8374</td>
<td>1213.2896</td>
<td>1213.2896</td>
<td>75.4288</td>
<td>1137.8608</td>
<td>1137.8608</td>
<td>1137.8608</td>
<td>1137.8608</td>
<td>4.7306</td>
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</tr>
<tr>
<td>Std vap 60F scfh</td>
<td>1341694.1250</td>
<td>1457235.8750</td>
<td>1426807.5000</td>
<td>1372149.2500</td>
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<td>36674.9570</td>
<td>1335474.2500</td>
<td>1335474.2500</td>
<td>1335474.2500</td>
<td>1335474.2500</td>
<td>6219.8330</td>
<td>1341694.1250</td>
</tr>
</tbody>
</table>

**Flowrates in lbmol/h**

- Monoethanol amine: 166.0833
- H₂O: 3349.9563
- Hydrogen Sulfide: 0.0120
- Carbon Dioxide: 19.5734
- Methane: 0.0000

**Flowrates in lb/h**

- Water: 3860.1001
- Monoethanol amine: 166.0833
- H₂O: 3349.9563
- Hydrogen Sulfide: 0.0120
- Carbon Dioxide: 19.5734
- Methane: 0.0000

**Pressure and Temperature**

- Pressure (psig): 1000.0000
- Temperature (F): 127.7411

**Enthalpy and Volume**

- Enthalpy (MMBtu/h): -431.32
- Volume (ft³/hr): 1174.2444
Selective H2S Removal with MDEA
CO2 removal by hot carbonate /Benfield/ Process (K2CO3)

Stream No. | 1 | 12 | 3 | 5
---|---|---|---|---
Name | GAS FEED | Purified gas | Purge | CO2
---|---|---|---|---
Temp C | 33.00 | 83.70 | 86.35 | 93.70
Press bar | 22.20 | 21.50 | 1.50 | 1.30
Actual vol m³/h | 1888.10 | 2197.02 | 129.59 | 7191.99
Std vap 0 °C m³/h | 38668.52 | 36527.86 | 146.48 | 6925.29
Component mole fractions
- Ethylene | 0.1959 | 0.2060 | 0.3009 | 0.0007
- Oxygen | 0.0453 | 0.0479 | 0.0166 | 0.0000
- Carbon Dioxide | 0.0682 | 0.0000 | 0.0503 | 0.3792
- Water | 0.0006 | 0.0170 | 0.2708 | 0.6198
- Nitrogen | 0.0248 | 0.0263 | 0.0054 | 0.0006
- Argon | 0.0609 | 0.0643 | 0.0394 | 0.0006
- Methane | 0.6008 | 0.6347 | 0.3151 | 0.0002
- Ethane | 0.0036 | 0.0038 | 0.0016 | 0.0000

Stream No. | 11 | 4
---|---|---
Name | Lean | Rich
---|---|---
Molar flow kmol/hr | 6923.38 | 6895.30
Mass flow kg/hr | 163428.61 | 168079.00
Temp C | 83.49 | 86.35
Press bar | 28.50 | 1.50
PH value | 11.19 | 10.03
Flowrates in kmol/hr
- Ethylene | 0.00 | 0.22
- Oxygen | 0.00 | 0.00
- Carbon Dioxide | 0.01 | 0.16
- Water | 5550.93 | 5407.40
- Nitrogen | 0.00 | 0.00
- Argon | 0.00 | 0.01
- Methane | 0.00 | 0.07
- Ethane | 0.00 | 0.00
Wet Desulfurization of Flue Gas

Reactive ionic absorption of SO2 in aqueous CaCO3
Absorber and Stripper Sizing by using ChemCAD

• Tray tower
  • Sieve tray
  • Valve tray
  • Bubble cap

• Pack column
  • Sherwood-Eckert for Random Packing
  • Mackowiak for Structure/Random Packing
  • Billet and Schultes Correlation for Structure/Random Packing
ChemCAD

VLE, LLE data regression
and
Extractor Simulation
ChemCAD Regression

- Properties of Pure Components
- BIP Regression (VLE, LLE)
  - Vapor-Liquid Equilibrium (VLE)
  - Liquid-Liquid Equilibrium (LLE)
  - Regression VLE, LLE data
  - VLE, LLE Phase Diagram
  - Flash Calculation (VLE, VLLE)
  - Extractor Calculation
- Electrolyte Regression
- Rate Equation Regression
Regression of Pure Components Properties

◎ Antoine Vapor Pressure
◎ Library Vapor Pressure
◎ Heat of Vaporization
◎ Liquid Density
◎ Liquid Heat Capacity
◎ Liquid Viscosity
◎ Liquid Thermal Conductivity
◎ Liquid Surface Tension
◎ Ideal Gas Heat Capacity
◎ Vapor Viscosity
◎ Vapor Thermal Conductivity
BIP Regression

◎ Act. Model from UNIFAC VLE
◎ TPXY data VLE
◎ TPX data VLE
◎ TXX data LLE
◎ Regression Gamma data
◎ Act. Model from UNIFAC LLE
Workshop Regression 1. Ternary VLE Regression

Comps.: 1. Sec-Butanol (450)
   2. MEK (153)
   3. Water (62)

Literature  2-3 azeotrope at 73.86 °C (homogeneous)
            2 (MEK) boiling at 79.63 °C
            1-3 azeotrope at 87.00 °C (heterogeneous)
            1 (2- butanol) boiling at 99.54 °C
            3 (Water) boiling at 100.0 °C

◎ Set K-model: Wilson and Regression the BIPs of 1-2, 1-3, 2-3 (VLE data from literature)
◎ Set K-model: NRTL and Regression the BIPs of 1-2, 1-3, 2-3 (VLE data from literature)
◎ Reset k-model: UNIFAC, predict binary VLE and compare it with Know data (azeotrope temp. and compositions)
◎ Set K-model: NRTL and Regression the ternary system of 1-2-3 (VLE data from literature)
## 2-Butanol(1) / Water(2) VLE data

<table>
<thead>
<tr>
<th>Temp C</th>
<th>Press mmHg</th>
<th>X</th>
<th>Y</th>
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### MEK(1) / H₂O(2) VLE data

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## MEK(1) / 2-Butanol(2) VLE data

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# 2-Butanol(1) / MEK(2) / Water(3) VLE data

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MEK(1) / Sec-Butanol(2) at 760.00 mmHg By NRTL

Y1 Mole Frac

X1 Mole Frac

XY Data
Sec-Butanol(1) / Water(2) at 760.00 mmHg By NRTL
Extractor Calculations

1. Liquid-Liquid Equilibrium (LLE)

2. Regression LLE data

3. LLE Phase Diagram

4. Three Phase Equilibrium (Three Phase Flash)

5. Extractor Calculation
## Regression LLE data

Toluene(1)/Acetone(2)/Water(3)  Experimental Data (mole fraction)

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<th>X21</th>
<th>X12</th>
<th>X22</th>
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<td>0.1537</td>
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Toluene/Acetone/Water at 30.00 C

Mole Percent of (2)

Mole Percent of (3)
NRTL Model

The NRTL equation has the following form:

\[
\ln \gamma_i = \frac{\sum_{j}^{N} \tau_{ji} G_{ji} X_j}{\sum_{k}^{N} G_{ki} X_k} + \sum_{j}^{N} \frac{X_j G_{ij}}{\sum_{k}^{N} G_{kj} X_k} \left[ \tau_{ij} - \frac{\sum_{k}^{N} X_k \tau_{ki} G_{kj}}{\sum_{k}^{N} G_{kj} X_k} \right]
\]

where

\( \tau_{ji} = A_{ji} + B_{ji} / T \)

\( G_{ji} = \exp (-\alpha_{ji} \cdot \tau_{ji}) \)

\( \alpha_{ij} = \alpha_{ji} \)

\( T = \) Temperature in degrees Kelvin
UNIQUAC Model

UNIQUAC equation

$$\ln \gamma_i = \ln \frac{\Phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i$$

$$- \frac{\Phi_i}{X_i} \sum_j x_j l_j - q_i \ln \left[ \sum_j \theta_i \tau_{ji} \right] + q_i$$

$$- q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}$$

Where

$$\Phi_i = x_i * \chi_i / (\Sigma x_i * \chi_j)$$

$$\Theta_i = x_i * q_i / (\Sigma x_i * q_j)$$

$$t_{ij} = \exp [A_{ij} - (U_{ij} - U_{jj}) / RT]$$

$$a_{ij} + b_{ij} / T = A_{ij} + (U_{ij} - U_{jj}) / RT$$

$$- (U_{ij} - U_{jj}) / R = b_{ij}$$

$$A_{ij} = a_{ij}$$

$$T = \text{Temperature in degrees Kelvin}$$

$$l_i = (z/2) * (\chi_i - q_i) - \chi_i + 1$$

$$z = 10 \text{ (coordination number)}$$

$$q_i = \text{van der Waals area parameter} (A_{Wi} / (2.5 * 10E9)) \text{ where } A_{Wi} \text{ is the van der Waals area}$$

$$\chi_i = \text{van der Waals volume parameter} (V_{Wi}/15.17) \text{ where } V_{Wi} \text{ is the van der Waals volume}$$
WILSON Model

WILSON equation

\[
\ln \gamma_i = - \ln \left[ \sum_{j=1}^{N} x_j \Lambda_{ij} \right] + 1 - \sum_{k=1}^{N} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}}
\]

where

\[
\Lambda_{ij} = \frac{V_j}{V_i} \cdot \exp\left[\frac{-(\kappa_{ij} - \kappa_{ii})}{RT}\right]
\]

\[V_i\] = liquid molar volume of component i

\[\kappa_{ij} - \kappa_{ii}\] = an empirically determined energy term in cal/g mol.

\[X_i\] = mole fraction of component i

\[T\] = temperature in degrees Kelvin

The user may provide either \(\Lambda_{ij}\) and \(\Lambda_{ji}\) or \((\kappa_{ij} - \kappa_{ii})\) and \((\kappa_{ji} - \kappa_{jj})\). If the absolute value of any parameter is greater than 10, the program will assume that you are using \((\kappa_{ij} - \kappa_{ii})\)'s.
Rules for Successful Regression

1. Suggestion: Use mole fractions for VLE and LLE data input.

2. Use the VLLS option if two liquid phase are likely to be present.

3. When doing ternary VLE regression, the third NRTL parameter, alpha, will have a default value of 0.3 if there is no value in the BIP list. You can define the alpha with the BIP command.

3. When doing ternary LLE regression, the third NRTL parameter, alpha, will have a default value of 0.2 if there is no value in the BIP list. You can define the alpha with the BIP command.
4. Choose regression data in the range of process requirements.

5. Plot the model fit with the data points. Reasonable curve or not?

6. If the model looks good but a better fit is required, reduce the relative and absolute tolerances.

7. Parameter sets are not unique. Once you have minimized error, you may try a different set of starting estimates.

8. Certain systems are better fit specific models. Wilson for strong hyperbolic characteristics (i.e. HCN-H2O). Data with strong inflections bordering on or including immiscibility may be better fit with 3-parameter (or higher) model such as NRTL.
### Conversion of DECHEMA Parameters to ChemCAD

<table>
<thead>
<tr>
<th>Model</th>
<th>Model</th>
<th>(a_{ij}), units</th>
<th>(a_{ij}), units</th>
<th>DECHEMA (\rightarrow) ChemCAD</th>
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<td>-</td>
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<tr>
<td></td>
<td>NRTL</td>
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