Binary Distillation
Introduction

Dates back to 1st century AD

- first used in a batch mode (distillate changes in time)

Goal: separate “heavy key” (less volatile) from “light key” (more volatile) by exploiting $\alpha \neq 1$.

- for $\alpha \gg 1$ or $\alpha \ll 1$, this can be done very effectively unless an azeotrope exists (where $\alpha = 1$).
  - then we recover the azeotrope and the light or heavy key, depending on which side the feed lies.

- By 16th century, multiple stages were in use to improve separation.

By 1976, distillation accounted for nearly 3% of the US energy consumption!

- mostly in petroleum refineries

Binary distillation is simplest & most well-understood.

- we will limit our discussion to binary distillation

Third Law of Thermo - typically low thermodynamic efficiency.
Design Considerations

Operating pressure - “knob 1”

• below ambient pressure requires vacuum operation
• many things may influence choice of operating pressure
  ‣ Thermo: azeotrope formation, $\alpha$, etc.
  ‣ Column operating temperature range (avoiding reactions, corrosion, etc.)
• most analyses do not account for pressure variation through the column

Operating temperature - “knob 2”

• Reboiler & Condenser:
  ‣ Bottoms above ambient requires additional energy input to the reboiler
  ‣ Distillate below ambient requires energy removal from the condenser.
• Thermodynamics: critical points of fluids
Batch Distillation

- Conceptually, follows the $T$-$x$-$y$ diagram.
- More rigorous analysis in SHR chapter 13
The McCabe-Thiele Graphical Method

1925
Continuous (staged) distillation
Nomenclature

Specifications

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>total (molar) feed rate</td>
</tr>
<tr>
<td>$z$</td>
<td>LK mole fraction in feed</td>
</tr>
<tr>
<td>$P$</td>
<td>Column operating pressure</td>
</tr>
<tr>
<td>$x$</td>
<td>LK mole fraction in distillate</td>
</tr>
<tr>
<td>$x_b$</td>
<td>LK mole fraction in bottoms</td>
</tr>
<tr>
<td>R/R</td>
<td>reflux ratio</td>
</tr>
<tr>
<td>Feed phase condition</td>
<td></td>
</tr>
<tr>
<td>VLE data ($y/x$ plot)</td>
<td></td>
</tr>
<tr>
<td>Type of condenser (partial/total)</td>
<td></td>
</tr>
<tr>
<td>Type of reboiler (partial/total)</td>
<td></td>
</tr>
</tbody>
</table>

Results

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>Distillate (molar) flow rate</td>
</tr>
<tr>
<td>$B$</td>
<td>Bottoms (molar) flow rate</td>
</tr>
<tr>
<td>$N$</td>
<td>minimum number of stages</td>
</tr>
<tr>
<td>$R$</td>
<td>minimum reflux flow rate</td>
</tr>
<tr>
<td>$V$</td>
<td>Boilup ratio</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of equilibrium stages</td>
</tr>
</tbody>
</table>

Stage compositions (}

- “Light Key” (LK) - more volatile component
- “Heavy Key” (HK) - less volatile component
Preliminaries

Rectifying section - like an absorber
- Feed & reboiler supply vapor
- Condenser supplies liquid

Stripping section - like a stripper
- Feed & condenser supply liquid
- Reboiler supplies vapor

Overall mole balance:
\[ F = D + B \]

Light-key mole balance:
\[ F z_F = x_D D + x_B B \]

Combine to eliminate \( B \) & solve for \( D \):
\[ D = F \left( \frac{z_F - x_B}{x_D - x_B} \right) \]
Rectifying Section Operating Line

Overall mole balance: \( V = L + D \)

Light key mole balance: \( V y_{n+1} = Lx_n + Dx_D \)

\[ y_{n+1} = \frac{L}{V} x_n + \frac{D}{V} x_D \]

relates light-key compositions in passing streams
(streams on a stage are assumed to be in equilibrium)

If \( L \) and \( V \) are constant, then this is a straight line.

The “McCabe-Thiele Assumptions”

- Both components have equal and constant molar enthalpies of vaporization (latent heats).
- Sensible heat, \( C_p \Delta T \), is negligible compared to latent heat.
- Column is insulated (no heat loss on each stage).
- Column pressure is constant (thermodynamics can be done at a single pressure).

Big assumptions, but allow for simple analysis, since \( L \) and \( V \) are constant under these assumptions.

\[ \frac{L}{V} = \frac{L}{L + D} = \frac{L/D}{L/D + D/D} = \frac{R}{R + 1} \quad R \equiv \frac{L}{D} \text{ reflux ratio} \]

\[ \frac{D}{V} = \frac{1}{R + 1} \]

\[ y = \left( \frac{R}{R + 1} \right) x + \left( \frac{1}{R + 1} \right) x_D \]
Range of Reflux Ratios

\[ y = \frac{L}{V}x + \frac{D}{V}x_D \]

\[ R = \frac{L}{D} \]

\[ 0 \leq \left( \frac{L}{V} = \frac{R}{R+1} \right) \leq 1 \quad \text{because} \quad 0 \leq R \leq \infty \]

- What happens at \( R = 0 \)?
- What happens at \( R = \infty \)?

What is the minimum \( R \) that allows separation?
(We will answer this question shortly)
Stripping Section Operating Line

Overall mole balance: $\overline{L} = \overline{V} + D$

Light key mole balance: $\overline{L}x_m = \overline{V}y_{m+1} + Bx_B$

McCabe-Thiele assumptions have been applied.

The feed stage material balance relates $L$ and $V$ to $\overline{L}$ and $\overline{V}$

$y_{m+1} = \frac{\overline{L}}{\overline{V}}x_m - \frac{B}{\overline{V}}x_B$

relates light-key compositions in passing streams (streams on a stage are assumed to be in equilibrium)

$y = \left(\frac{V_B + 1}{V_B}\right)x - \left(\frac{1}{V_B}\right)x_B$

$V_B \equiv \frac{V}{B}$ boilup ratio

Mole fraction of light key in the vapor, $y$

Mole fraction of light key in the liquid, $x$
Feed Stage & the “q-Line”

rectifying section

stripping section

subcooled liquid
$q > 1$

saturated liquid
$q = 1$

partially vaporized
$q = L_F/F$

saturated vapor
$q = 0$

superheated vapor
$q < 0$

liquid flow increase across feed rate normalized by feed rate.

$q = \frac{L - L}{F} = 1 + \frac{V - V}{F}$

$q = \frac{h_{\text{sat. vapor}}}{h_{\text{sat. liquid}}} - \frac{h_F}{h_F}$

Operating lines & q-line must intersect at a single point.
∴ cannot specify $q$, $V_B$ and $R$ independently.
More on the $q$-line

rectifying section:

$$y = \frac{L}{V} x + \frac{D}{V} x_D$$

stripping section:

$$y = \frac{\bar{L}}{V} x - \frac{B}{V} x_B$$

subtract

$$y (V - \bar{V}) = x (L - \bar{L}) + D x_D + B x_B$$

$$y \left( \frac{V - \bar{V}}{F} \right) = \left( \frac{L - \bar{L}}{F} \right) x + z_F$$

$$y (1 - q) = -qx + z_F$$

$$y = \left( \frac{q}{q-1} \right) x - \frac{z_F}{q-1}$$

Typically the feed condition is known (specifying $q$). Then we can choose $V_B$ or $R$.

**Note:** specifying $R$ implies $V_B$. 
Feed Stage & Number of Stages

Locate feed stage nearest to the intersection of the operating lines & q-line as possible (just after the horizontal line on the staircase passes “P”)

too low

too high

just right
Partial Reboilers & Condensers

Total Reboiler:
- all liquid is turned back to vapor

Partial reboiler:
- bottoms product is liquid, boilup is vapor
- This is another equilibrium stage!
- very common...

Total condenser:
- all vapor is condensed back to liquid

Partial condenser:
- distillate is vapor, reflux is liquid
- This is another equilibrium stage!
Limiting Cases: $R_{\text{min}}$, $N_{\text{min}}$.

“Total reflux”
- $R = \infty$, $V_B = \infty$.
- $L = V$, $D = B = F = 0$.
- $F = 0$, $N = N_{\text{min}}$.
- $y = x$ is operating line.
- No product...

“Minimum reflux”
- $N = \infty$.

$$(L/V)_{\text{min}} = \frac{R_{\text{min}}}{R_{\text{min}} + 1}$$

$$R_{\text{min}} = \frac{(L/V)_{\text{min}}}{1 - (L/V)_{\text{min}}}$$

$$(V_B)_{\text{min}} = \left[\frac{(L/V)_{\text{max}}}{(L/V)_{\text{min}}} - 1\right]^{-1}$$

“pinch point”

higher operating costs  higher capital costs
Perfect Separation - Another “Limiting Case”

Perfect separation: \( x_B = 0, x_D = 1 \).

Pinch points form in each section of the column.

Theoretical value for minimum reflux ratio and boilup to achieve perfect separation.

To find this:

- Obtain \( x-y \) data from thermo.
- Determine \( q \)-line
- Determine slope of rectifying operating line = \( R_{\text{min}}/(R_{\text{min}}+1) \).

For saturated liquid feed, \( R_{\text{min}} = \frac{1}{Z_F(\alpha - 1)} \).
Example

We want to separate a mixture of n-heptane and n-octane using distillation at atmospheric pressure.

If the feed is 40 mole% n-heptane as a saturated vapor, determine the minimum reflux ratio and minimum number of stages required to obtain product streams with 95% and 5% n-heptane.

Known:
- $x_D = 0.95$
- $x_B = 0.05$
- $z_F = 0.4$, saturated vapor

Needed:
- $K$-values (equilibrium curve)
- $q$-line
- operating lines