Distillation

Senior Design CHE 396
Andreas Linninger

Innovative Solutions

Michael Redel
Alycia Novoa
Tanya Goldina
Michelle Englert

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Introduction

This report examines the distillation process. This will enable the reader to understand the necessary components along with distillation calculations. Distillation is a process that separates two or more components into an overhead distillate and bottoms. The bottoms product is almost exclusively liquid, while the distillate may be liquid or a vapor or both.

The separation process requires three things. First, a second phase must be formed so that both liquid and vapor phases are present and can contact each other on each stage within a separation column. Secondly, the components have different volatilities so that they will partition between the two phases to different extent. Lastly, the two phases can be separated by gravity or other mechanical means. Distillation differs from absorption and stripping in that the second phase is created by thermal means (Seader, 1998).

Flowsheet

Total Condenser
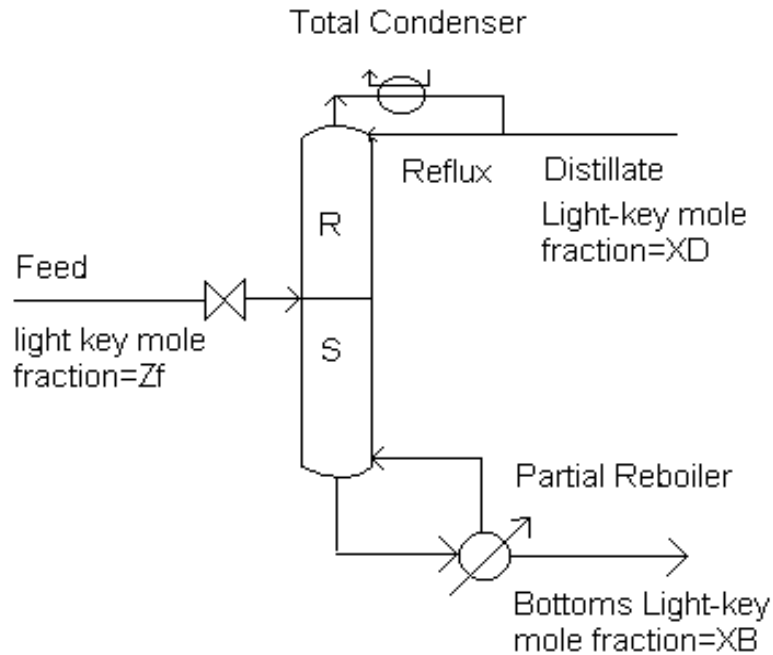
The distillation column contains one feed stream and two product streams. The feed contains a mole percent of the light component, Z_F. The product stream exiting the top has a composition of X_D of the light component. The product stream leaving the bottom contains a composition of X_b of the light component. The column is broken in two sections. The top section is referred to as the rectifying section. The bottom section is known as the stripping section.

The top product stream passes through a total condenser. This effectively condenses all of the vapor distillate to liquid. The bottom product stream uses a partial reboiler. This allows for the input of energy into our column.

Limitations

- Azeotropes: An azeotrope is a liquid mixture which when vaporized produces the same composition as the liquid. If the mixture is azeotropic, then more advanced types of separation must be considered. More information on azeotropes maybe found in Douglas, Section 7.3.

- Solids: If the material to be separated is high in solids, or contains tars or resins that could plug or foul a continuous unit, then a batch separation should be considered (Perry's, 1997).

- Optimum Pressure (King, 1980):
  1. Vacuum operation: Use of a vacuum should be considered for heat-sensitive compounds or polymerizable materials. Vacuum is usually not used unless required, e.g., a low bottoms temperature is needed to avoid thermal decomposition.
  2. Distillation column is above atmospheric pressure: Column shell should be thicker to withstand pressure of the column.
  3. If the column pressure required to accomplish overhead condensation with cooling water is less than 250 lb/in^2, then the column pressure should give an average temperature driving force of 5-15*C in the overhead condenser.
  4. If the column pressure required accomplishing overhead condensation with cooling water is greater than 250 lb/in^2, then consider an alternative of using a refrigerant on the overhead and running the column at a lower pressure.

- Optimum Temperature Differences in Reboilers and Condensers (King, 1980):

  1. Reboiler temperatures should be kept low enough to avoid bottoms degradation and/or fouling.

  2. Common temperature differences used for heat exchange across reboilers and condensers are shown in the following table:

	Temp, K
Condenser:	
Refrigeration	3-10
Cooling Water	6-20
Pressurized Fluid	10-20
Boiling Water	20-40
Air	20-50
Reboiler:	
Process Fluid	10-20
Steam	10-60
Hot Oil	20-60

Applicability

- Distillation is the least expensive means of separating mixtures of liquids.
- If relative volatilities of components is less than 1.1, distillation becomes very expensive (Douglas, 1988) and extraction or reactive distillation should be considered.

Theory

Section 1. Graphical Determination of a Distillation Column Design

Step 1. Determine Process Operation Variables

- Assumed feed rate, composition, purity of distillate and bottoms, and the quality of the feed are known.
- Perform overall material and component balances to determine the compositions of the distillate and bottoms.

$$F*Z_F = X_D*D + X_B*B \qquad (1)$$

$$F = D + B \qquad (2)$$

where

F	Feed rate of input stream
Z_F	Composition of light component in feed
X_D	*Mole Fraction of light in distillate
X_B	*Mole Fraction of light in Bottom
D	Total distillate amount
B	Total bottom amount

*If more than two components, these values are the light-key and heavy-key component.

Step 2. Determine the Minimum Reflux Ratio

This graphical approach is determined using the McCabe-Thiele Method for binary mixtures. The ratio of reflux flow to distillate flow is called the reflux ratio.

Assumptions

The following assumptions are implied when using this method (McCabe, 1993):

a.   Constant Molal Overflow. The molar flow rates of the vapor and liquid are nearly constant in each section of the column. This also ensures the operating lines are straight lines.

b.   Heat Effects are negligible. For example, heat losses to and from the column are small and neglected.

c.   For every mole of vapor condensed, another mole of liquid is vaporized.

d.   The liquid and vapor leaving the tray is in equilibrium with the vapor and liquid entering the tray.

Procedure

If an equilibrium curve is not given, draw a y-x diagram (y representing the vapor phase and x the liquid). The equilibrium curve can be obtained by relating the relative volatility to the composition of the liquid:

$$y = a*x/(1+x(a-1)) \qquad (4)$$

This shows the bubble-point and dew point of a binary mixture at constant pressure. An equilibrium line describes the compositions of the liquid and vapor in equilibrium at a fixed pressure. The equilibrium line crossing the forty-five degree line is an indication of an azeotropic mixture. An azeotrope is a liquid mixture which when vaporized produces the same composition as the liquid. If the mixture is azeotropic, then more advanced types of separation must be considered.

Equilibrium Curve at Minimum Reflux
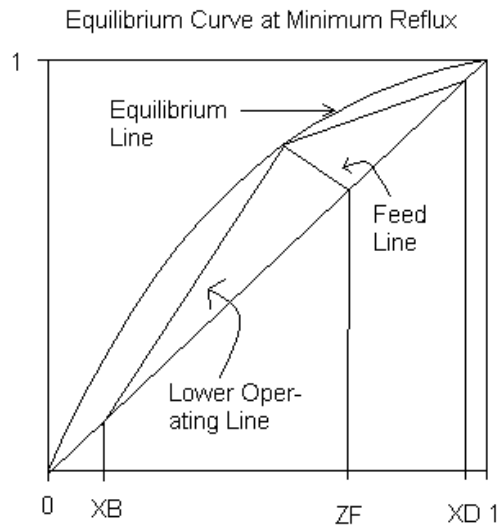
- Forty Five Degree Line

    1.   Draw the diagonal line connecting the points (0.0,0.0) to (1.0,1.0). This is your forty-five degree line.

- Feed Line (q-Line)

    2.   The feed line can be constructed by locating the point on the forty-five degree line that corresponds to the feed composition. This point can be extended with a slope of **q/(q-1)** where q is the feed quality. The feed line can be directly plotted through the following equation:

    $$y=q/(q-1)X - Z_F/(q-1) \qquad (5)$$

- Upper Operating Line

    3.   Draw the operating line for the enriching section. First find the desired top product composition (on the x-axis) and locate the corresponding point on the forty-five degree line. Connect this point to the point where the equilibrium cure and the feed line

intersect. This is the upper operating line. The y intercept of this line is equal to $X_D/(R+1)$. The following equation can be used to determine the minimum reflux:

$$R_{min}=(X_D/y_{intercept}) - 1 \qquad (6)$$

- Lower Operating Line

4. Draw the operating line for the stripping section. First find the desired bottom product composition (on the x-axis) and locate the corresponding point on the forty-five degree line. Draw a line from this point to the intersection of the equilibrium curve and the feed line. This is your lower operating line. The slope of this line is equal to $(Vb_{min}+1)/Vb_{min}$ where Vb is the boilup ratio. The boilup ratio is the fractional amount of liquid that is boiled back into the column to the amount of liquid leaving.

Step 3. Choose Actual Reflux Ratio:

As the reflux ratio increases, the number of trays and thus the capital cost of the column decreases. However, as a trade-off, an increase in reflux ratio will also increase the vapor rate within the tower, thus increasing expenses such as condensers and reboilers (4). Most columns are designed to operate between 1.2 and 1.5 times the minimum reflux ratio because this is approximately the region of minimum operating cost. Therefore, based on first estimates, the operating reflux ratio is equated so that (Douglas, 1988):

$$R_{actual} = R_{min} * 1.2 \qquad (7)$$

Step 4. Determine the Minimum Number of Trays

- Upper/Lower Operating Line at Actual Reflux

1. Redraw the upper and lower operating line using the actual reflux ratio. Plot the point $X_D/(R+1)$ and draw a line to the X_D. The equation of the upper operating line is:

$$y=(R/R+1)*X+X_D/(R+1) \qquad (8)$$

The equation for the lower operating line can be drawn by connecting the X_B to the intersection of the feed line and the upper operating line. The equation of the lower operating line is:

$$y=((V_B+1)/V_B)*X+X_B/V_B \qquad (9)$$

Equilibrium Curve at Theoretical Reflux Ratio
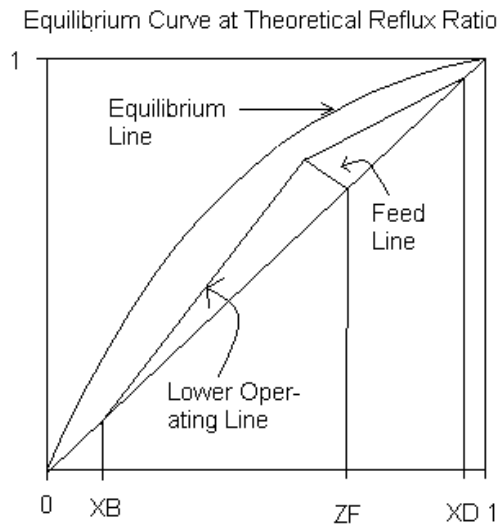
- Determine Number of Trays

2. Starting from composition of the distillate, a horizontal line is drawn to the equilibrium curve. This line demonstrates the first tray.

3. From the previous intersection, drop vertically until the upper operating line is obtained. Follow step two to determine next tray.

4.　　Continue stepping until the liquid composition ends equals the desired bottom composition.

5.　　The total number of steps is equal to the theoretical number of trays.

Equilibrium Curve at Theoretical Reflux Ratio
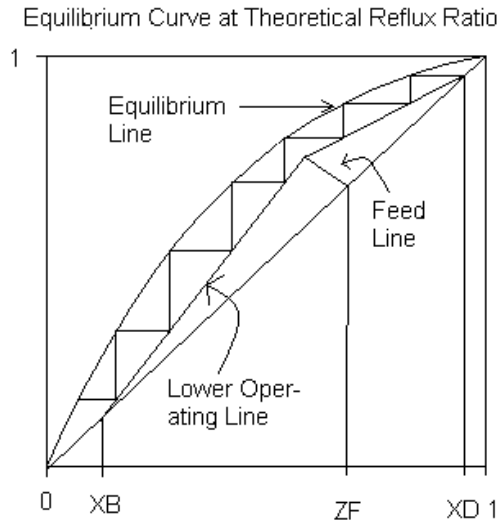
6.　　When high conversions are desired, the stepping method may cause difficulties. In these cases the Kremser equation should be used.

$$N = \ln\left[\left(1 - m\frac{V}{L}\right) * \frac{\left(y_{in} - y_{e,out}\right)}{\left(y_{out} - y_{e,out}\right)} + m\frac{V}{L}\right] \Bigg/ \ln\left(m\frac{V}{L}\right)$$

(10)

where

N	Number of trays in unreadable region
m	Slope of the line in unreadable region
V/L	R/(R+1)
y_{in}	Conveniently chosen point below unreadable region
y_{out}	X_D for rectifying section
$y_{e,out}$	$m*X_D+b$ (where b is the y intercept of new equil. line)

Step 5. Determine Actual Number of Trays

This is determined by taking the quotient of the number of theoretical trays to the tray efficiency. Typical values for tray efficiency range from 0.5 to 0.7 (Douglas, 1988). These values depend on the type of trays being used, as well as the internal liquid and vapor flow rates.

$$N_{actual} = N_{theory} /e \qquad\qquad (11)$$

Step 6. Principal Dimensions of the Column (Diameter/Height):

- A design guideline that should be used is that the height of the column should not be higher than 175 feet.
- Height-to-diameter ratio should be less than 20 to 30.
- Packed towers are used when the column has a small diameter (1.5 ft or less) or area (1.77 ft^2 or less) rather than plate towers.
- Either plate or packed towers may be used when the column diameter is between 1.5-4.5 ft (or area, 1.77- 15.9 ft^2).
- If the tower is higher than 190 ft, then a design with smaller tray spacing should be considered (Douglas, 1988).

The tower height can be related to the number of trays in the column. The following formula assumes that a spacing of two feet between trays will be sufficient including additional five to ten feet at both ends of the tower. This includes a fifteen percent excess allowance of space (Douglas, 1988).

$$H_{tower} = 2.3 \, N_{actual} \qquad\qquad (12)$$

Before we can determine the tower diameter, we need to determine the vapor velocity. The vapor velocity can be derived from the flooding velocity. To limit our column from flooding, we choose a velocity 50-80 percent of flooding velocity (Douglas, 1988):

$$V = \frac{1.2}{\sqrt{\rho_G}}$$

(13)

where

V	Vapor Velocity
ρ_G	Density of the mixture

The diameter of the tower is relatively insensitive to changes in operating temperature or pressure. The main determinant of the diameter is the vapor velocity. The desired vapor velocity is dependent on the limitations of undesired column flooding.

$$D_T = .0164\sqrt{V} * \left(\frac{M_G}{\rho_m}\right)^{0.25}$$

(14)

where

D_T	Diameter of tower
V	Vapor velocity
M_G	Molecular weight of gas
ρ_m	Molar density

Section 2. Analytically Determining the Specifications for a Distillation Column

Step 1. Determine Process Operation Variables

- Assumed feed rate, composition, purity of distillate and bottoms, and the quality of the feed are known.
- Perform overall material and component balances to determine the compositions of the distillate and bottoms.

Step 2. Determine the Minimum Reflux Ratio

- Underwood Equation

The Underwood equation approximates the minimum reflux ratio (Douglas, 1988). The following equation can be used for multi-component systems with constant relative volatility. Relating mass balances and VLE equations, the following equation was derived for which ϕ can be calculated.

$$F*(1-q) = \sum \left((\alpha_i * z_i) / (\alpha_i - \phi) \right) \qquad (15)$$

where

F	Feed
q	Feed quality
α_i	Relative Volatility
z_i	Composition of component (i) in Feed

Through the previous expression, ϕ can be obtained in a polynomial expression. This expression can be used to solve for ϕ. Only the ϕ that falls between the relative volatilities of the components should be considered. The ϕ can be used to obtain the minimum amount of vapor (V_{min}):

$$V_{min} = \sum \left((\alpha_i * Dx_i) / (\alpha_i - \phi) \right) \qquad (16)$$

From a mass balance and the definition of reflux:

$$\mathbf{L_{min} = V_{min} - D}$$

$$\mathbf{R_{min} = V_{min} / D} \tag{17}$$

Step 3. Choose Theoretical Reflux Ratio

As the reflux ratio increases, the number of trays and thus the capital cost of the column decreases. However, as a trade-off, an increase in reflux ratio will also increase the vapor rate within the tower, thus increasing expenses such as condensers and reboilers (Douglas, 1988). Most columns are designed to operate between 1.2 and 1.5 times the minimum reflux ratio because this is approximately the region of minimum operating cost. Therefore, based on first estimates, the operating reflux ratio for the analytically method is equated so that (Douglas, 1988):

$$\mathbf{R_{Theor} = 1.2 * R_{min}} \tag{18}$$

Step 4. Determine Theoretical Number of Trays

- Modification of the Fenske Equation

A simplified approximate equation can be used to determine the number of trays (Douglas, 1988). This is an expression for the minimum number of trays, assuming total reflux and constant relative volatility. This equation takes into account the reflux ratio.

$$N = \frac{\ln SF}{\ln\left(\frac{\alpha}{\sqrt{\left(1 + \frac{1}{R} * Z_F\right)}}\right)}$$

(19)

where

$$SF = \beta * \frac{\delta}{((1-\delta)*(1-\beta))}$$

(20)

β	Fractional recovery of light in the distillate
δ	Fractional recovery of light in the bottom
α	Relative volatility
R	Reflux ratio
Z_F	Mole ratio of light component in feed

Step 5. Determine Actual Number of Trays:

This is determined by taking the quotient of the number of theoretical trays to the tray efficiency. Typical values for tray efficiency range from 0.5 to 0.7 (Douglas, 1988). These values depend on the type of trays being used, as well as the internal liquid and vapor flow rates.

$$N_{actual} = N/e \tag{21}$$

Step 6. Principal Dimensions of the Column (Diameter/Height):

- A design guideline that should be used is that the height of the column should not be higher than 175 feet.
- Height-to-diameter ratio should be less than 20 to 30.
- Packed towers are used when the column has a small diameter (1.5 ft or less) or area (1.77 ft^2 or less) rather than plate towers.
- Either plate or packed towers may be used when the column diameter is between 1.5-4.5 ft (or area, 1.77-15.9 ft^2).
- If the tower is higher than 190 ft, then a design with smaller tray spacing should be considered (Douglas, 1988).
- Height of Column

The tower height can be related to the number of trays in the column. The following formula assumes that a spacing of two feet between trays will be sufficient including additional five to ten feet at both ends of the tower. This includes a fifteen percent excess allowance of space (Douglas, 1988).

$$H_{tower} = 2.3 \, N_{actual} \qquad [ft] \tag{22}$$

- Vapor Velocity

Before we can determine the tower diameter, we need to determine the vapor velocity. The vapor velocity can be derived from the flooding velocity. To limit our column from flooding, we chose a velocity 60 percent of flooding velocity (Douglas, 1988). This is assumed in the following equation:

$$V = \frac{1.2}{\sqrt{\rho_G}}$$

(23)

where

        V Vapor Velocity

        ρ_G Density of the Gas

- **Diameter of Tower**

The diameter of a tower is relatively insensitive to changes in operating temperature or pressure. The main determinant of the diameter is the vapor velocity. The desired vapor velocity is dependent on the limitations of undesired column flooding. This equation allows for a twelve percent surplus in area (Douglas, 1998).

$$D_T = .0164 \ddot{O}(V) * (M_G/ r_m)^{\wedge}.25 \qquad (24)$$

where

        V Vapor Velocity
        M_G
        ρ_m Molar density

Section 3. Determining the Cost of Column and Components

All cost estimates formulas were taken from (Douglas, 1988).

Step 1. Cost of Column

- Capital Cost

  The following approximates installed cost and purchased cost for the shell and trays. This cost relates the diameter, height, and design variables of the column. The design variable is a correction used to allow specificity of the column pressure and material.

$$C_c = \left(\frac{M \& S}{280}\right) * 120 \, D_T * H^{0.8} * (218 + F_c)$$

(25)

     where

C_c	Cost of shell and trays
F_c	Design considerations for the column
D_T	Diameter of column
H	Height of column

Step 2. Cost of the Reboiler

- Capital Cost

  The installed cost of the reboiler heat exchanger is:

$$C_r = \left(\frac{M \& S}{280}\right) * 328 * \left(\frac{\Delta H_v}{11250}\right)^{0.65} * V^{0.65}$$

(26)

     where

C_r	Cost of reboiler
ΔH_v	Heat of vaporization of bottoms
V	Rate of Boilup

- Operating Cost

  If we use steam to supply the heat for the reboiler, the temperature driving force must be constrained to less than 30-45 F to prevent film boiling. We are also assuming a high value of heat transfer coefficient because the heat transfer between a condensing vapor and boiling liquid is high. The steam required is:

$$W_s = \left(\frac{\Delta H_v}{\Delta H_s} \right) * V$$

(27)

$$C_s = 8.74 * 10^{-3} * (\text{SteamCost}) * \Delta H_V * V$$

(28)

where
Ws	Amount of steam needed
Cs	Cost of steam
ΔHv	Heat of vaporization
ΔHs	Heat of saturation
V	Mass flow rate

Step 3. Cost of Condenser

- Capital Cost

    If we assume the cooling water is available at 90 F and a heat transfer coefficient
    of 100, the heat transfer area of the condenser heat exchanger is:

$$Ac=((\Delta Hv/3000)\times \ln (Tb-90/Tb-120))\times V \qquad (29)$$

    where

Ac	Area of condenser heat exchanger
ΔHv	Heat of vaporization
Tb	Bubble point of distillate
V	Mass flow rate

    The installed cost of the heat exchanger for condensing:

$$Cc=(M\&S/280)*101.3*(2.29+Fc)*Ac^{0.65} \qquad (30)$$

    where

Cc	Cost of condenser
Fc	Design considerations correction factor

- Operating Cost

    If we assume the cooling water is available at 90 F and a heat transfer coefficient
    of 100, the amount of cooling water needed for the condenser and the associated
    cost is:

$$W_c=(\Delta Hv/30)V \qquad (31)$$

$$C_c=3.26\times 10^{-4}*(Cooling\ water\ cost)(\Delta Hv)(V) \qquad (32)$$

    where

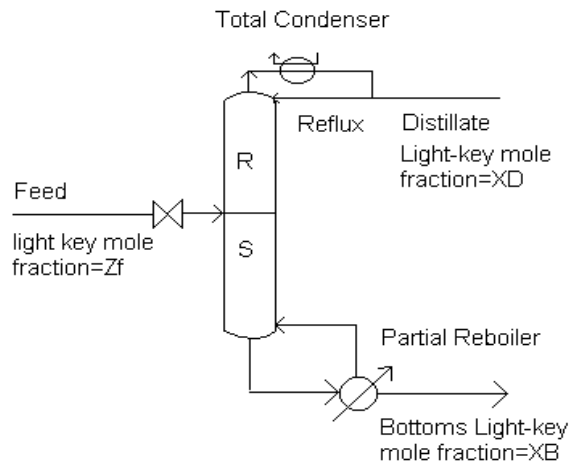 | | |
    |---|---|
    | W_c | Amount of cold water to condenser |
    | C_c | Cost of condenser |
    | ΔHv | Heat of vaporization |
    | V | Mass flow rate |

Step 4. Total Cost of Column

The total annualized cost is the sum of capital cost divided by the payback period plus the yearly operating cost.

$$\textbf{TAC = Capital Cost / Payback Period + Operating Cost} \qquad \textbf{(33)}$$

Section 4. Case Study

Feed Stream, Acetone/Acetic Acid	F=100mole/hr
Light-Key Mole Fraction,	Z_F=0.30
Percentage of Light in Distillate	X_D=0.90
Percentage of Light in Bottoms	X_B=0.10
Quality of Feed	Q=1

We can simultaneously solve equations (1) and (2), $F*Z_F=X_D*D+X_B*B$ and F=D+B, to obtain the amount of distillate and bottoms:

$$100*.3=.9*D+.1*B$$
$$100=D+B$$

B=75mole/hr   **D=25mole/hr**

The reflux ratio and number of trays were calculated graphically. These graphs can be viewed after this section. The minumum reflux ratio can be calculated through a variation of the Underwood equation. When the quality is equal to one and in a binary mixture, equation (15) reduces to: $R_{min}=(1/(\alpha-1))*((X_D/X_F)-\alpha*(1-X_D)/(1-X_F))$

$$R_{min}=(1/(4.36-1))*((.9/.7)-4.36*.1/.3)$$
$$R_{min}=.716$$

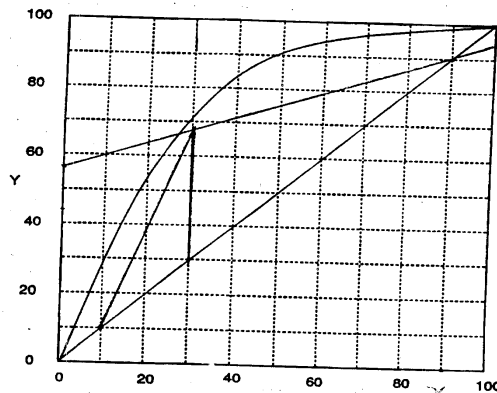The theoretical minimum reflux ratio is derived from equation (18), $R_{theory}=1.2*R_{min}$:

$$R_{theory}=.859$$

From the Fenske equation (19) we can determine the number of trays:

$$N_{min}=\ln(81)/\ln(4.36\sqrt{(1+1/(.81*.3))})$$

N=5.97 Trays

The following three graphs show how we obtain approximately the same number of trays graphically, rather than analytically (shown above).
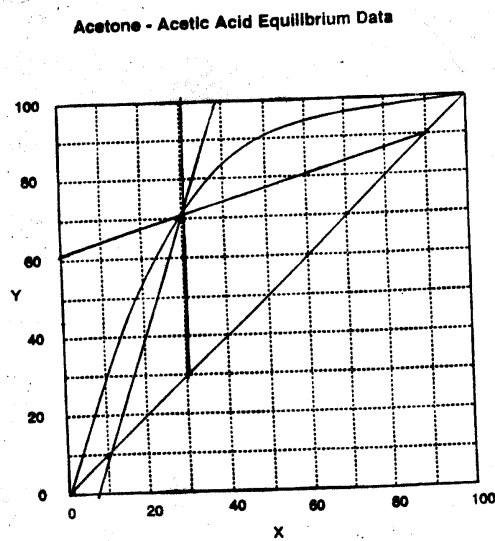

$$y_{int} = x_D / (R_{min} + 1)$$

$$60.5 = 90 \Big/ (R_{min} + 1)$$

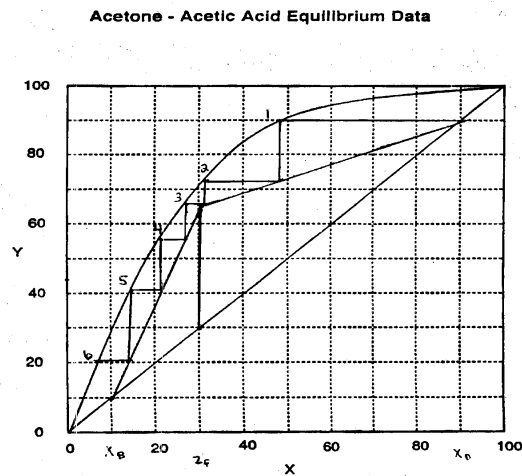$$R_{min} = 0.4876$$

Graph A, Acetone- Acetic Acid Equilibrium Data

Acetone - Acetic Acid Equilibrium Data

$$R = 1.2 * R_{min} = 1.2 * 0.4876 = 0.5861$$

$$y_{int} = 90 \Big/ (0.5851 + 1) = 56.78$$

Graph B, Acetone- Acetic Acid Equilibrium

Acetone - Acetic Acid Equilibrium Data

Graph C, Acetone- Acetic Acid Equilibrium Curve. We can see that the number of trays is six. This can be seen from the stepping on the above graph. We note here that the analytical method stated the number of trays to be 5.97, which is close to our graphical method of 6 trays.

Alternatives

- Extraction: A process where one or more solutes are removed from a liquid by transferring the solute(s) into a second liquid phase. Liquids must be immiscible or partially immiscible. Vaporization is not required, thus extraction can be done at low temperatures and is a gentle process suitable for unstable molecules (Wankat, 1988).

- Adsorption: Involves the transfer and equilibrium distribution of one or more solutes between a fluid phase and particles. Liquid mixture is brought into contact with a microporous solid allowing adsorption of certain components in the mixture takes place on the internal surface of the solid. The adsorbent (solid) is insoluble in the liquid, and the components being adsorbed are called solutes (Perry's, 1997).

- Condensation: Occurs when a saturated vapor comes in contact with a surface whose temperature is below the saturation temperature. Film-type condensation occurs when a film layer of condensate is formed on the surface. Dropwise condensation occurs when appears in many small droplets at various points on the surface (Perry's, 1997).

- Reactive Distillation: Works by adding an entrainer that reacts with one component in a mixture that is difficult to separate if relative volatilities of two components are very close (less than 1.1). In the first column, the entrainer will react with one component to increase the relative volatility so that it may be separated while in a second column, the reaction can be reversed so that the entrainer can be recycled (King, 1980).

- Extractive Distillation: This operation requires two distillation columns. A heavy nonvolatile component is added near the top of the tower to modify the activity coefficients between two components. A pure component in the overhead in the first column is obtained while the other component is recovered in the overhead in the second column (King, 1980).

References

1.   Seader, J. and Henley, E. *Separation Process Principles*. John Wiley & Sons, 1998, Chapters 7 and 8.

2.   McCabe, Warren. *Unit Operations of Chemical Engineering, Fifth Edition*. McGraw-Hill, Inc, 1993, Chapters 18 and 19.

3.   Distillation Column Design. Copyright 1997. http://lorien.ncl.ac.uk/ming/distil/distil0.htm

4.   Douglas, James. *Conceptual Design of Chemical Processes*. McGraw-Hill, Inc., 1988, Section A.3.

5.   King, C. Judson. *Separation Processes, Second Edition.* McGraw-Hill, Inc., 1980, Chapters 4-6.