CE407 SEPARATIONS

Lecture 26

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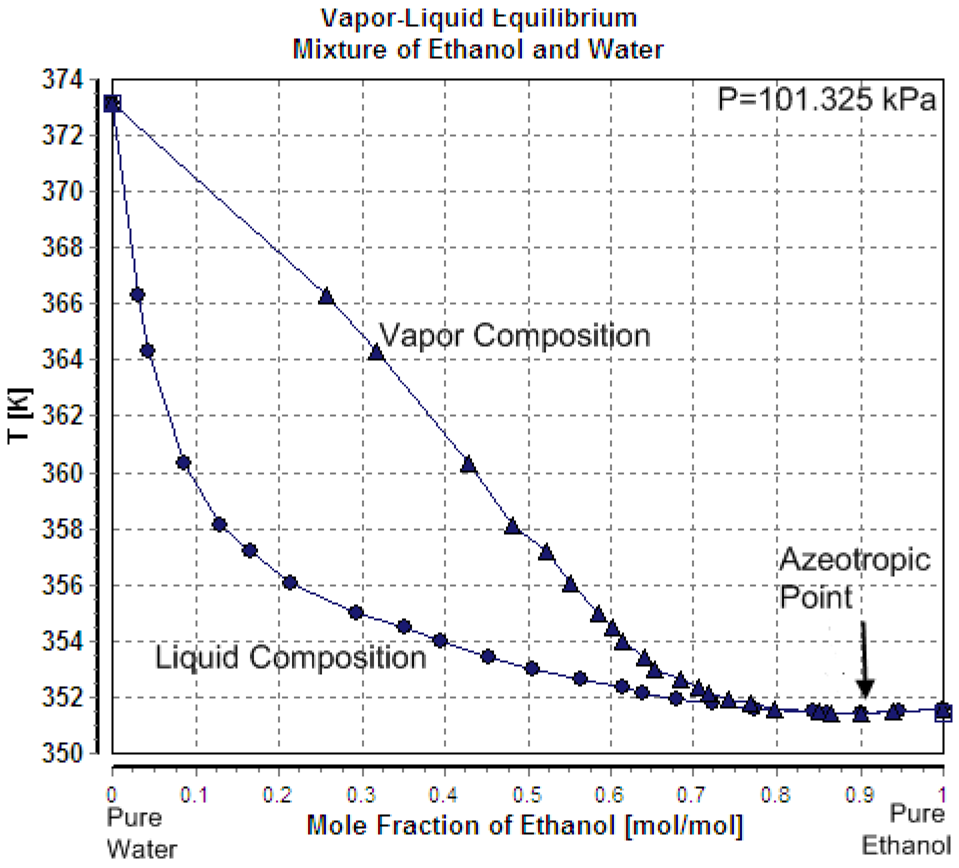
AZEOTROPIC SEPARATIONS

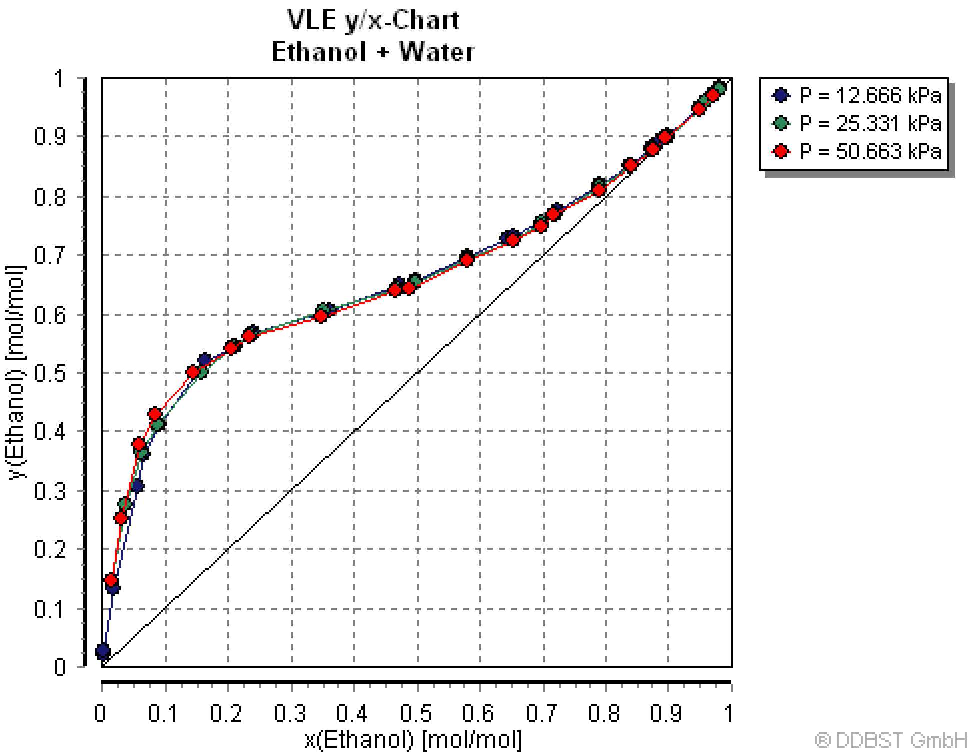
Azeotrope

- The T_{xy} diagram for Ethanol and water exhibits an azeotrope
- Around a mole fraction of 0.9 the liquid mole fraction and its equilibrium vapor mole fraction are equal



Vapor Liquid Equilibrium

- The VLE curve crosses the 45° line at x = y = 0.9
- One cannot get to an $x_D > 0.9$



Strategies for Breaking the Azeotrope

- **Extractive Distillation**
  - Using a third component to realize the separation
  - One component is preferentially soluble in the third component

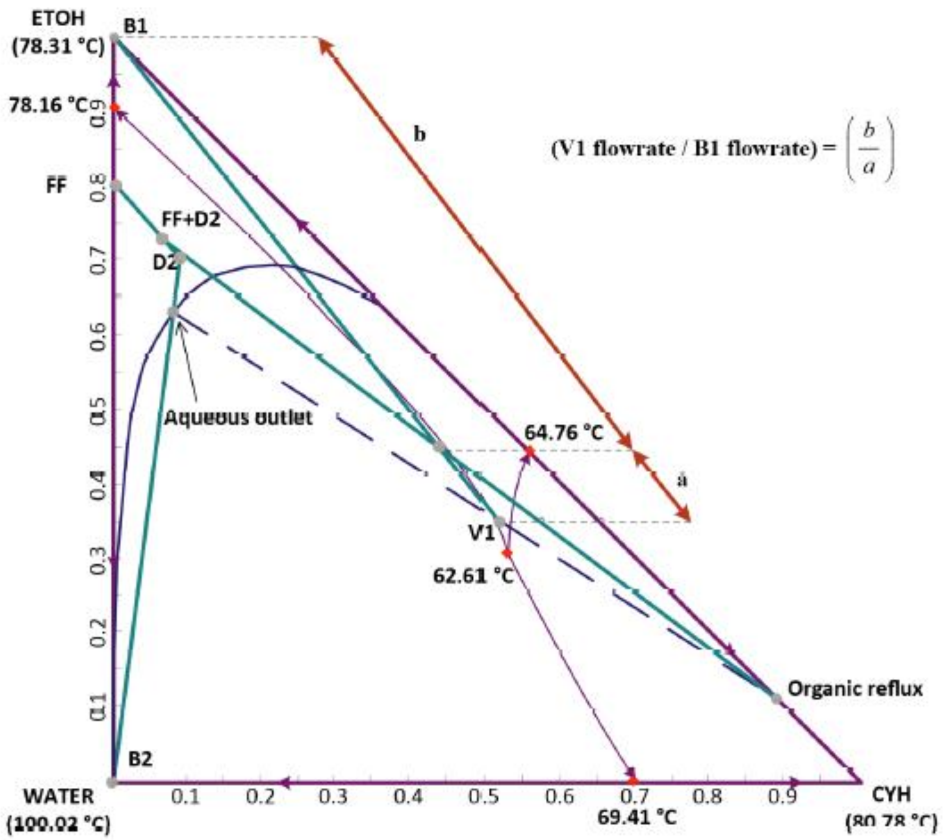
- **Pressure Swing**
  - The VLE curve is dependent on the total pressure
  - Distill the mixture up to the azeotrope at one pressure
  - Transfer to a different pressure which has an azeotropic point that is below the composition obtained in the first column

Azeotropic Separation Method by Adding Entrainer

- Ethanol – Water system
- Typical Fermentation process generates a mole fraction of 0.04 ethanol in ethanol/water mixture
- A traditional distillation column (C_0) brings the mixture up to an EtOH mole fraction of 0.80
  - Well below the azeotrope of 0.9
  - Removes most of the water
- This is fed into the next column, C_1 …

Azeotropic Separation Method by Adding Light Entrainer

- In the reflux of column C_1 we add a stream of cyclohexane (CYH) as an entrainer
- EtOH – water mixture has an azeotrope at 0.9 mole fraction EtOH and a temperature of 78.2 C
- Addition of CYH leads to three additional azeotropes, one of which is at the system minimum temperature of 62.6 C



Azeotropic Separation Method by Adding Light Entrainer

- CYH is added to the decanter and enters the column as reflux
- The liquid going down the column is a heterogenous (two-phase) mixture
- The bottom stream can approach pure EtOH
- The vapor exiting the top stage can approach the ternary azeotrope V1 (the minimum temperature azeotrope)

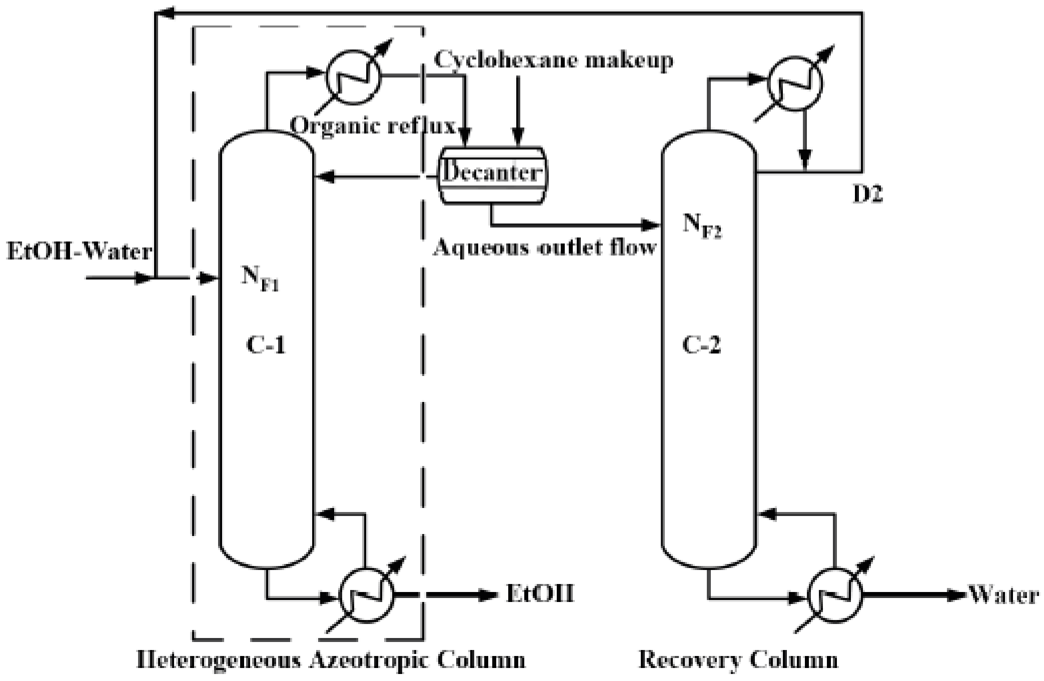


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

Azeotropic Separation Method by Adding Light Entrainer

- The vapor is condensed to 40 C and becomes a heterogenous liquid
- It separates into an organic phase (which is rich in CYH) and an aqueous phase (which still contains significant amount of EtOH)
- The decanter separates the streams
- The organic stream goes back to column C1 as reflux
- The aqueous phase goes as feed to column C2

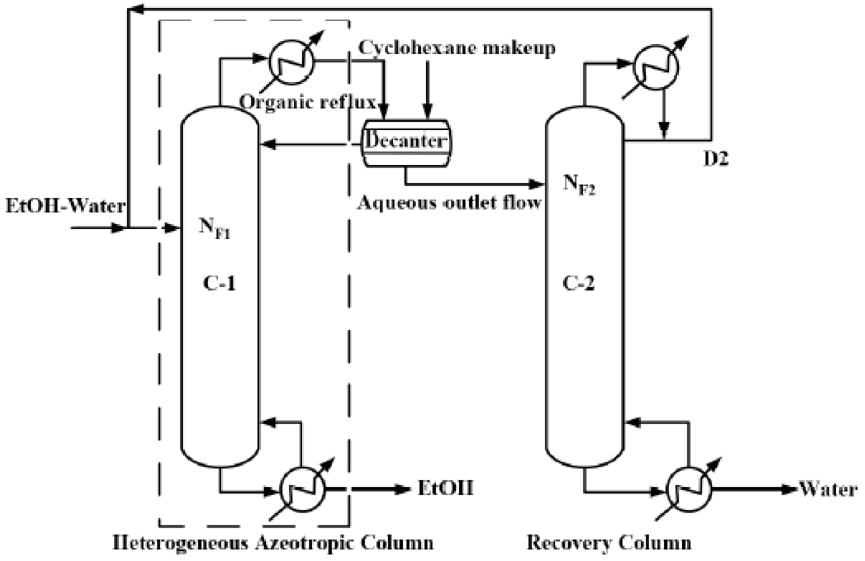


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

Azeotropic Separation Method by Adding Light Entrainer

- The aqueous feed to column C2 is homogenous
- The bottoms stream draws out the water
- The distillate stream contains significant amounts of EtOH and is recycled back to the feed of column C1

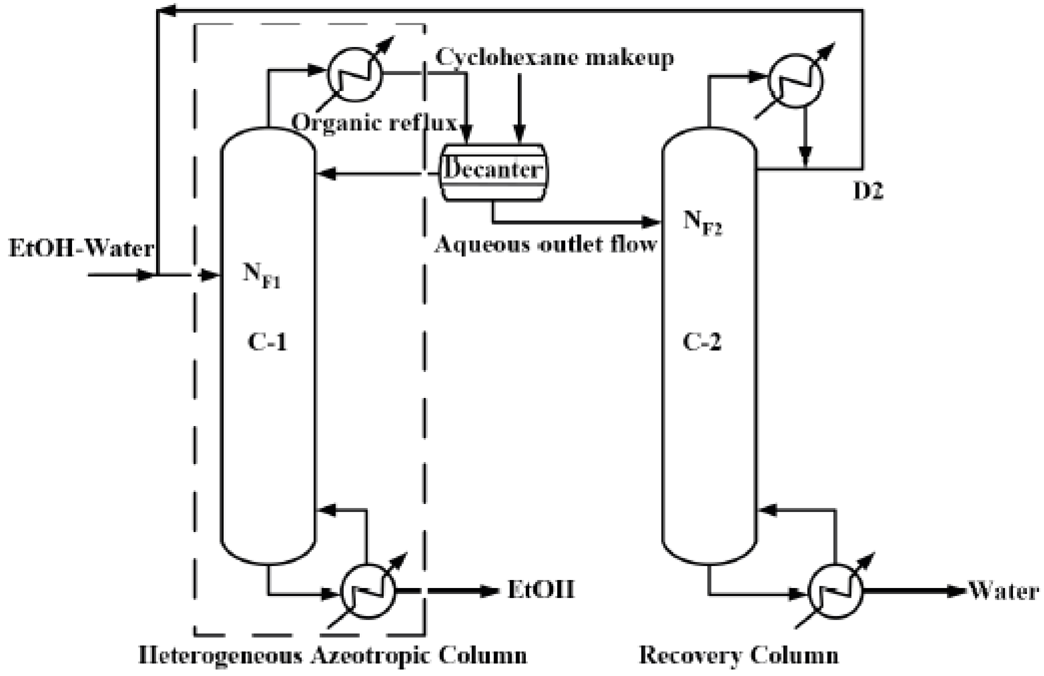


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

Azeotropic Separation Method by Adding Heavy Entrainer

- Entrainer is added above the feed
  - Ethylene glycol is one possible entrainer
- The entrainer increases the relative volatility of the water and EtOH

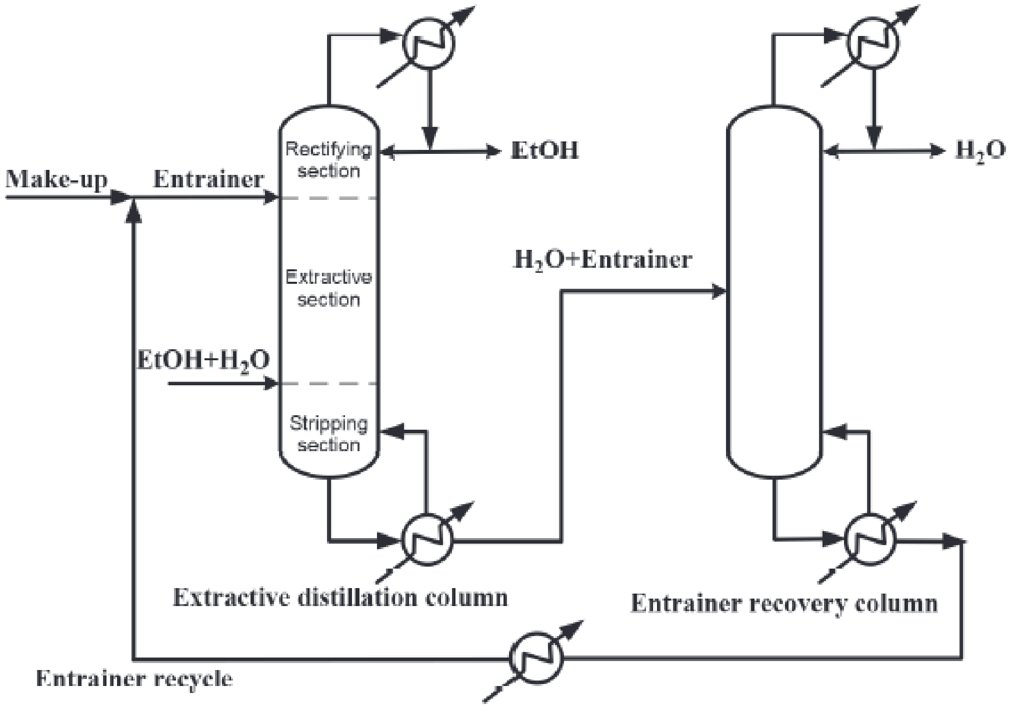


FIGURE 15.5 Azeotropic separation with extractive distillation.

Azeotropic Separation Method by Adding Heavy Entrainer

- Rectifying section separates EtOH from heavy entrainer
- Extractive Section suppresses water from going up with the vapor
- Stripping Section prevents EtOH from going down to bottom as liquid
- Second column separates water from entrainer
- Entrainer from second column bottoms is recycled to upper feed of the first column

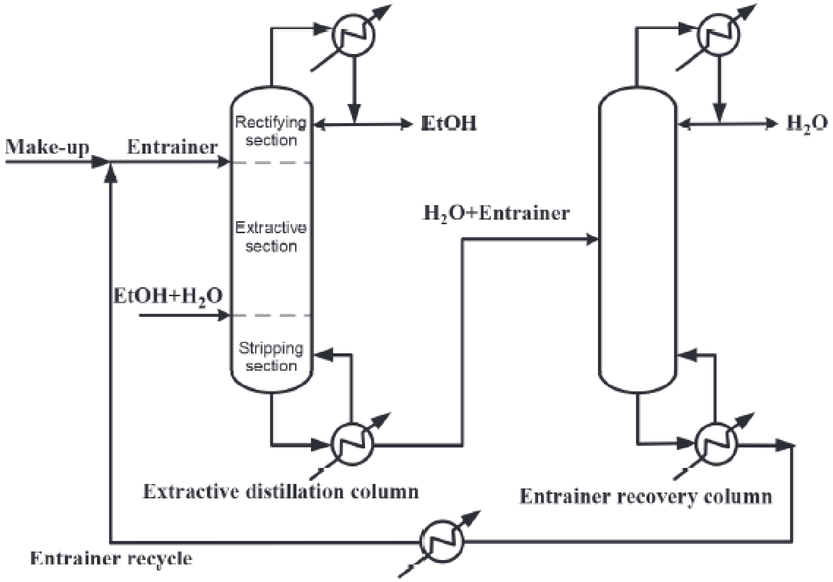
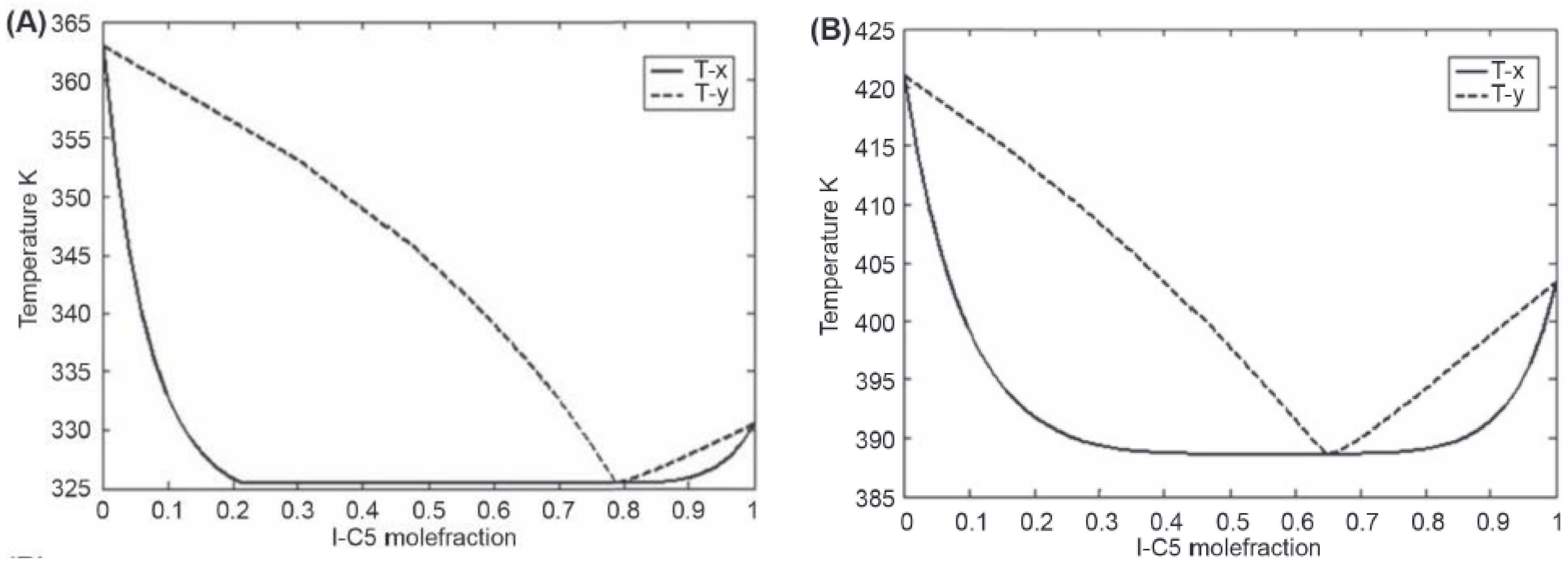


FIGURE 15.5 Azeotropic separation with extractive distillation.

Pressure Swing Method

- Methanol (MeOH) and Isopentane (iC5)
- Obviously you cannot get past 0.8 mole fraction iC5 at either pressure using just one column

FIGURE 15.1 T-xy plots of methanol-isopentane system at (A) 2.5 atm, and (B) 13 atm.



Pressure Swing Method

- The low pressure column (LP) can produce distillate approaching the low pressure azeotrope of 0.78 mole fraction iC5 and can go no further
- The feed of the high pressure column (HP) has a mole fraction that is greater than the high pressure azeotrope of 0.65 mole fraction iC5
- We can therefore get to any desired purity specification

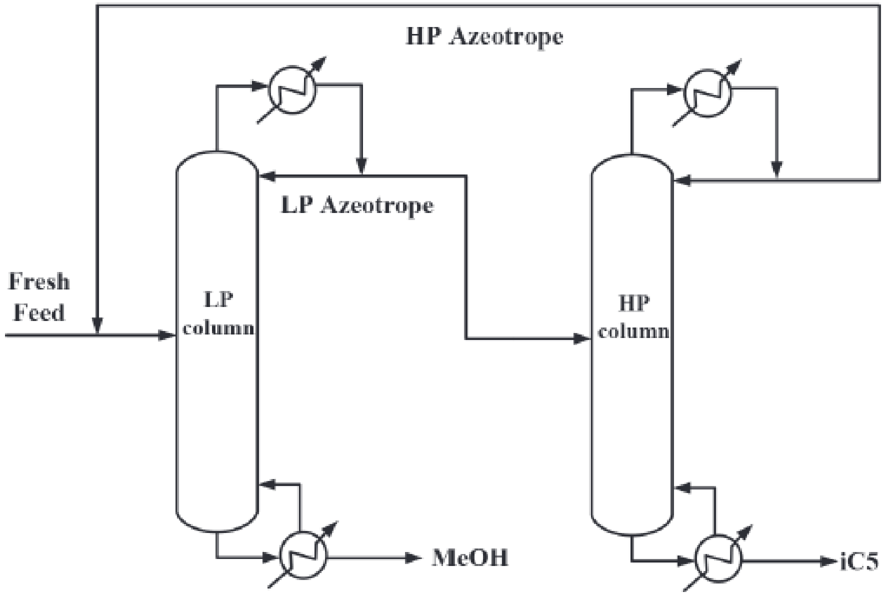


FIGURE 15.2 Azeotropic separation with pressure-swing distillation. *HP*, high pressure; *LP*, low pressure.

References

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PACKED TOWERS

COMPLICATIONS WITH NON-DILUTE CASES

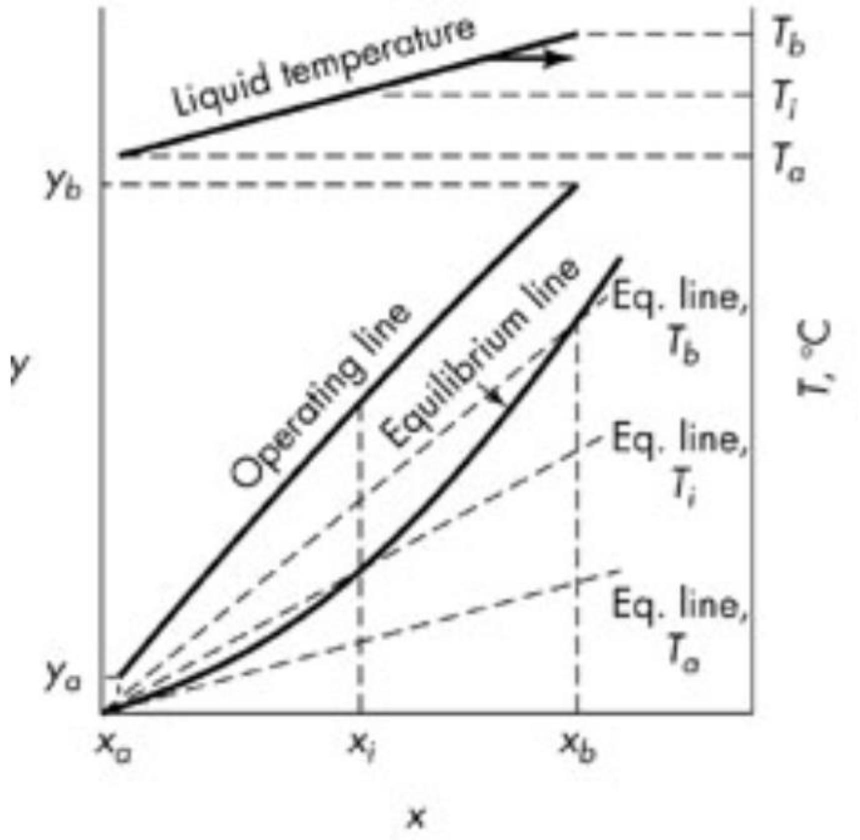
Temperature Variations in Packed Towers

- Heat of Absorption
  - Solute Molecule is at a lower energy state in solution than it was as a gas
    - It has condensed
  - Energy is released which raises the liquid temperature
- Evaporation of solvent lowers the temperature
- In general temperature increases as liquid progresses through the tower

- The temperature and equilibrium profiles in the tower will depend on many variables, including:
  - Incoming temperature of liquid
  - Incoming temperature of gas
  - Heat of absorption
  - Heat of evaporation
  - Heat transfer rate

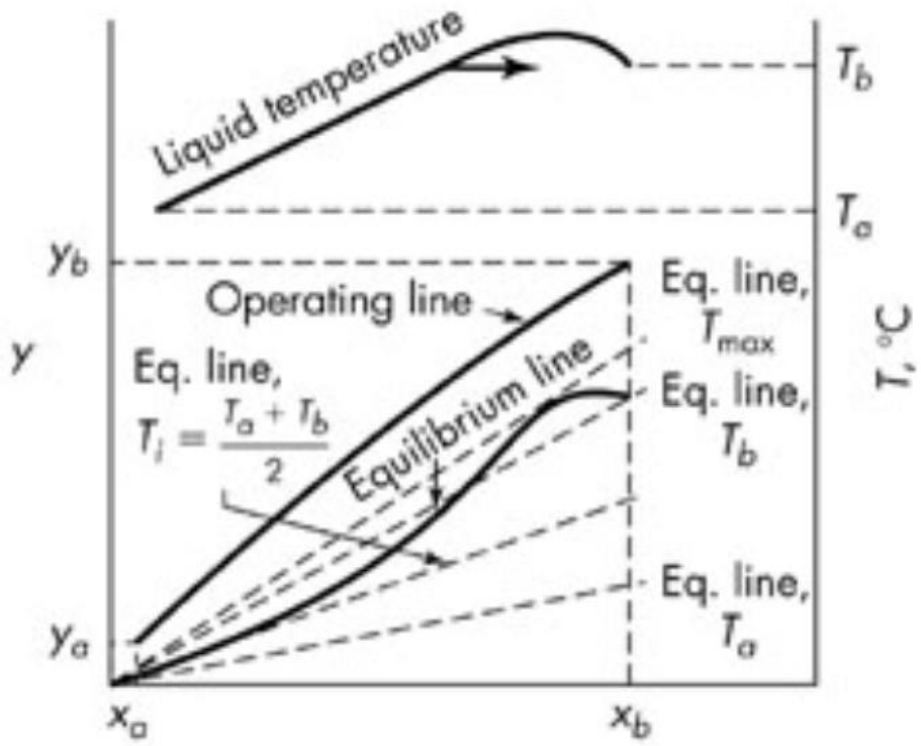
Profiles

- Low solvent evaporation with gas inlet temperature near the liquid exit temperature



Profiles

- Significant solvent evaporation or gas inlet temperature 10 – 20 C below liquid exit temperature



Determining the Minimum Liquid Flow

- Complicated because:
  - The liquid exit temperature is dependent on the flow rate
  - The equilibrium liquid concentration, x_b^*, is dependent on the liquid temperature

Absorption from Rich Gases

- When the gas is not dilute enough the changes in gas and liquid flows throughout the tower become significant
- The mass transfer coefficients depend on G_x and G_y so they are not constant
- Temperature gradients can be significant

- Numerical Integration is needed:

$$Z_T = \frac{V_A}{S} \int_{y_a}^{y_b} \frac{1}{k_y\, a\, (1 - y)^2 (y - y_i)}\, dy$$

Absorption Design Variables

- G_x
  - Liquid flow - chosen based on minimum requirement
  - Diameter of tower
- G_y
  - Vapor flow – process specification
  - Diameter of tower
- Pressure
  - $y_i = \frac{P^{sat}}{P} x_i$
- Temperature
  - $P^{sat} = P^{sat}(T)$
- Packing
- Solvent
- Diameter of Column

Your first design may not be acceptable!