

CE407 SEPARATIONS

Lecture 26

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University at Buffalo

Department of Chemical
and Biological Engineering

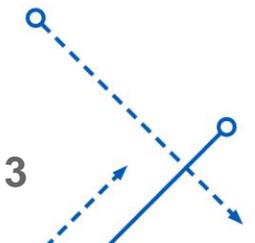
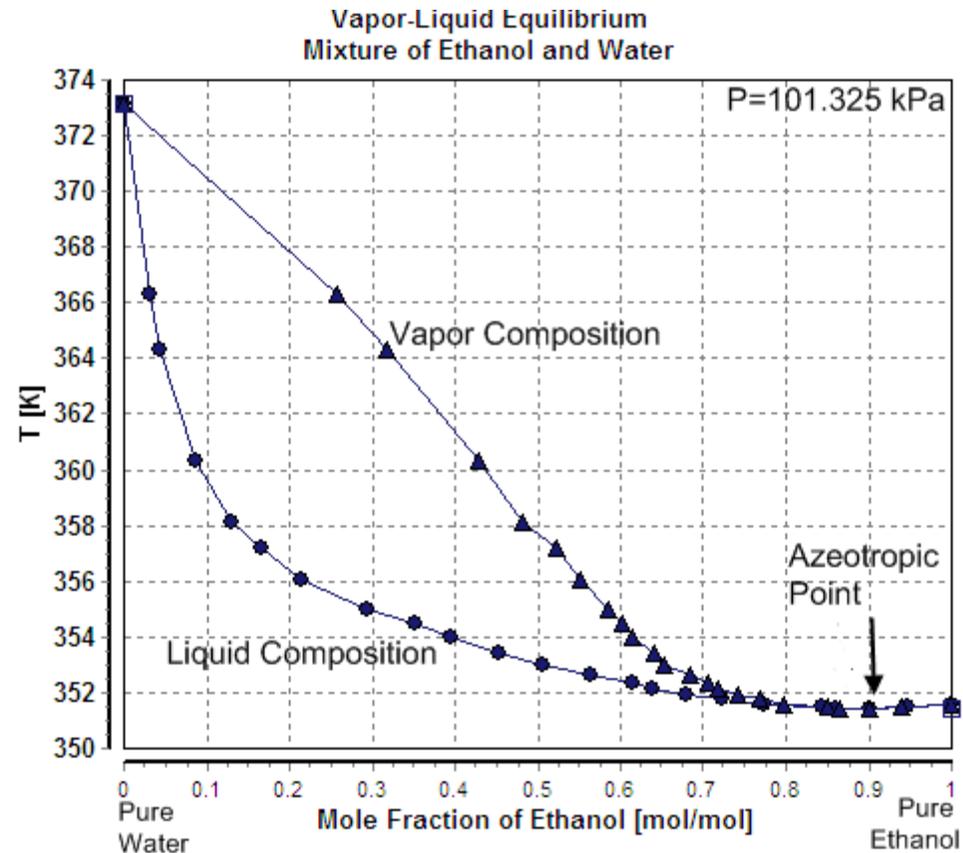
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AZEOTROPIC SEPARATIONS



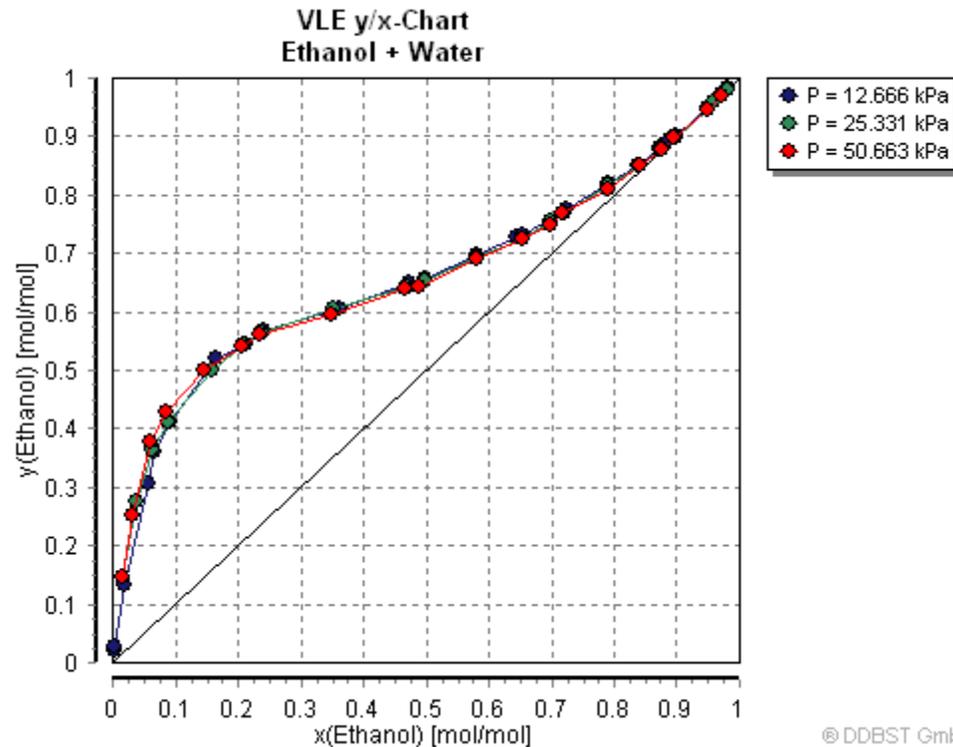
Azeotrope

- 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



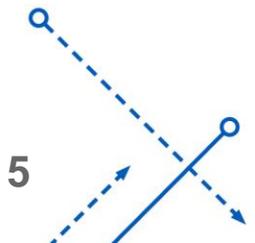
Vapor Liquid Equilibrium

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



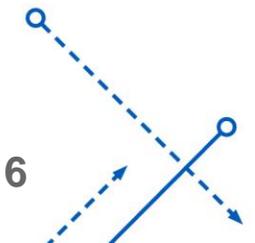
Strategies for Breaking the Azeotrope

- **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



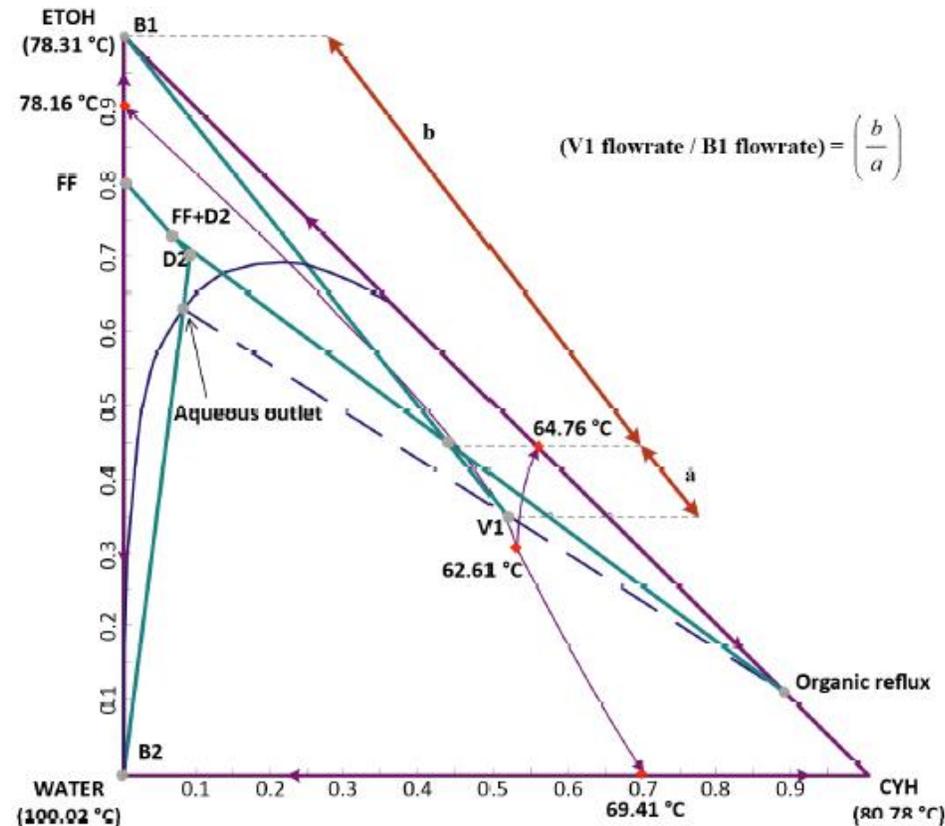
Azeotropic Separation Method by Adding Entrainer

- 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)

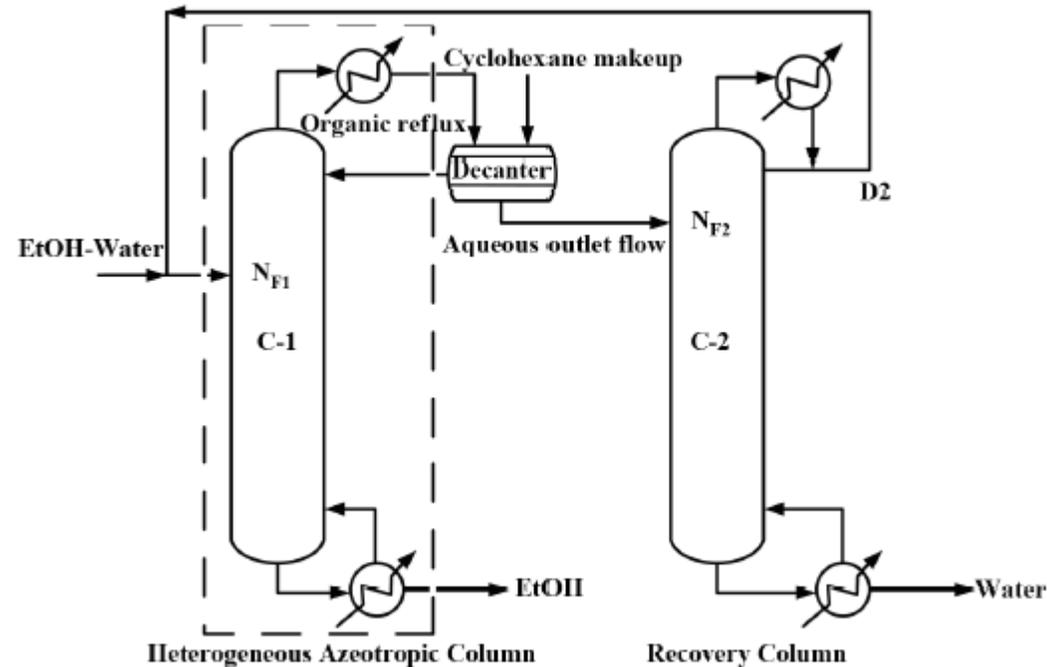


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

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

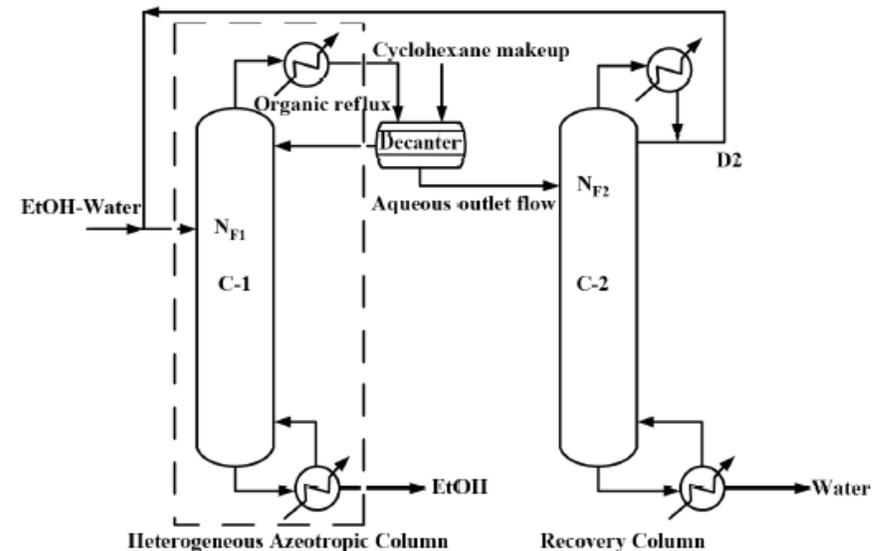


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

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

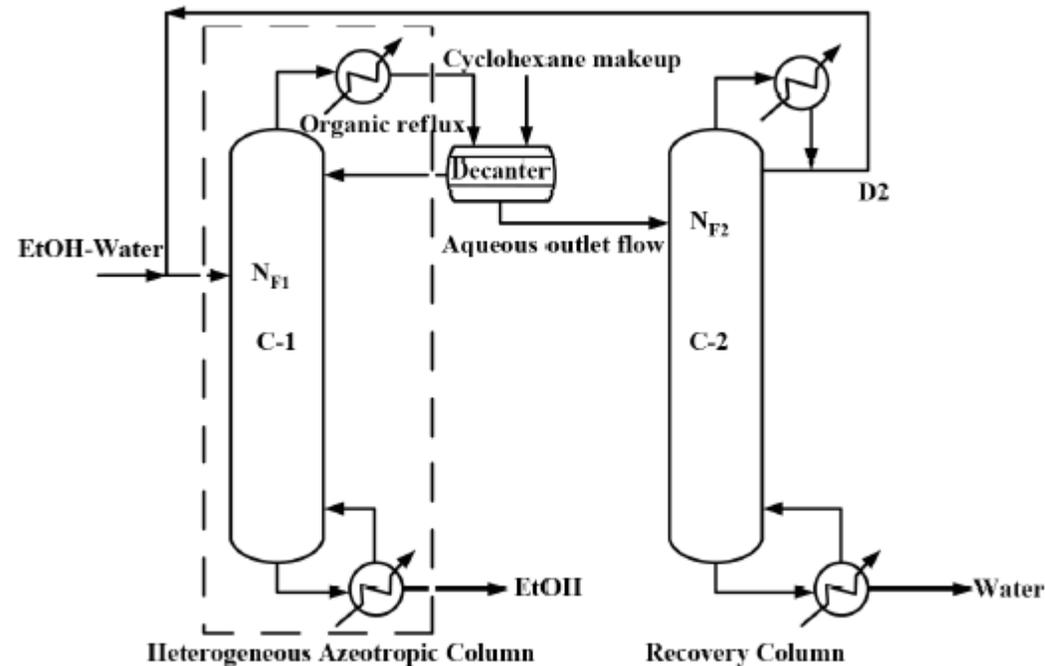


FIGURE 15.4 Azeotropic separation with heterogeneous azeotropic distillation.

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

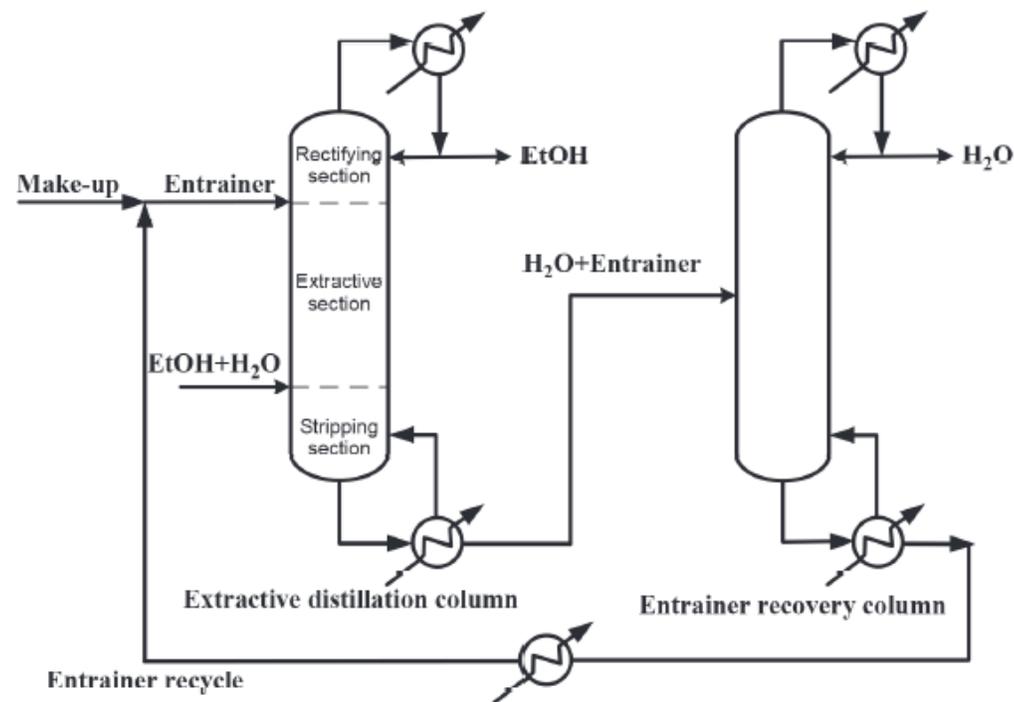


FIGURE 15.5 Azeotropic separation with extractive distillation.

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

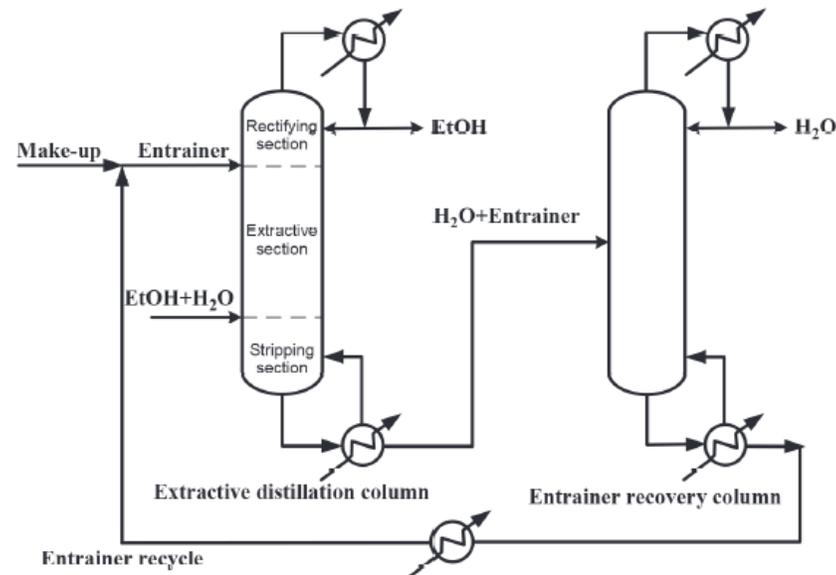
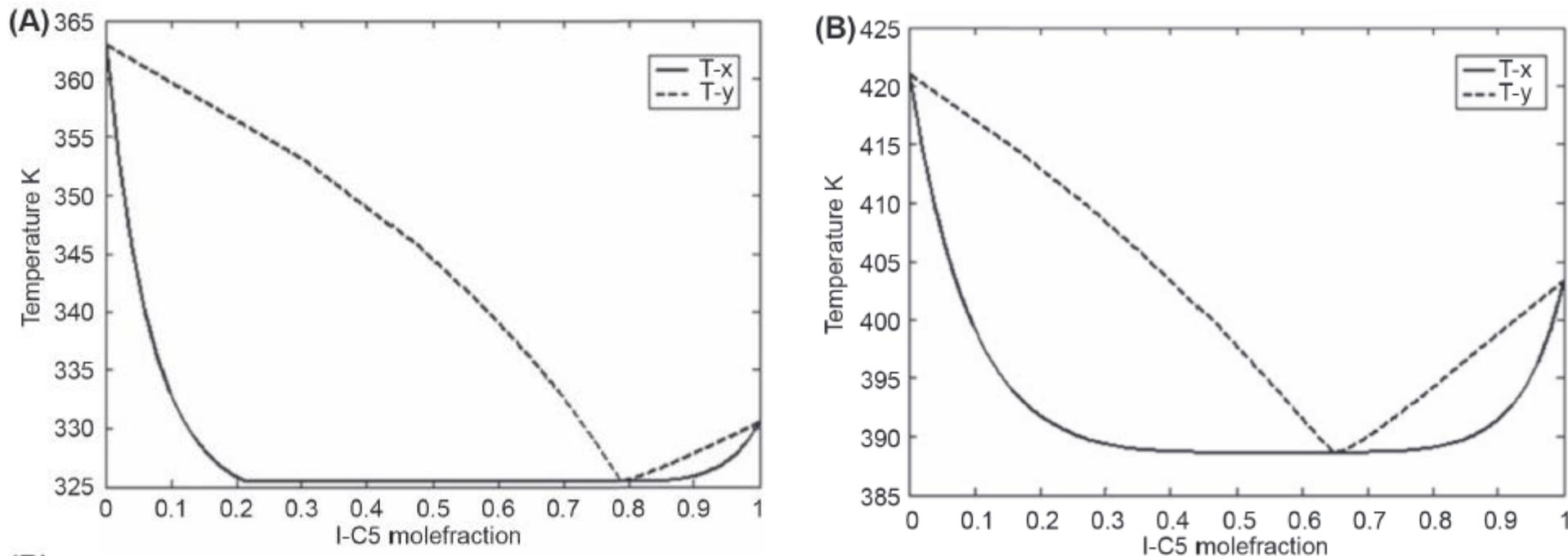


FIGURE 15.5 Azeotropic separation with extractive distillation.

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

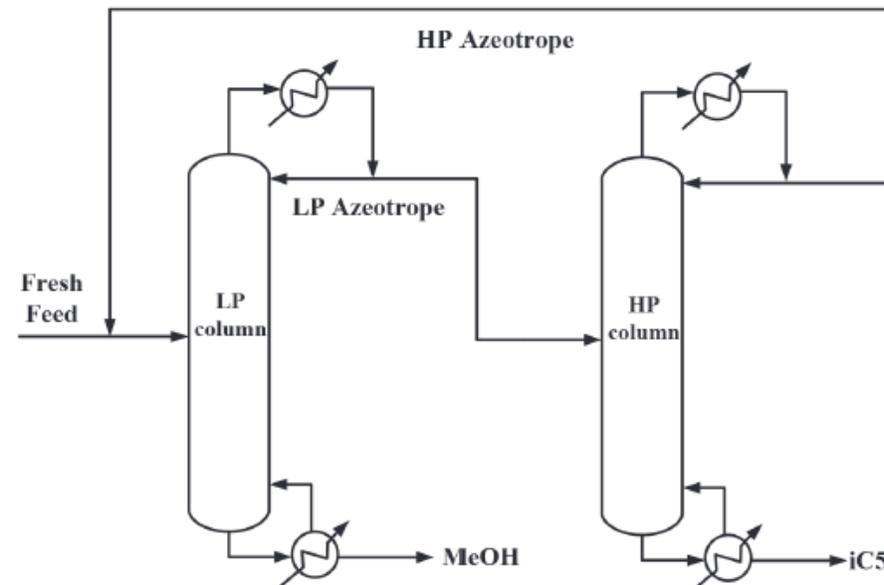


FIGURE 15.2 Azeotropic separation with pressure-swing distillation. *HP*, high pressure; *LP*, low pressure.

References

- Arit, W; Azeotropic Distillation, 2014, Gorak, A; Olujić, Z; Distillation: Equipment and Processes, Academic Press, London, 247-258
- Chien, I; Yu, B; Ai, Z, 2017; Design of Azeotropic Distillation Systems, Elsevier Inc, Boston
- Lei, Z; Chen, B; Ding, Z; 2005; Special Distillation Processes; Elsevier, Boston
- Luybe, W; 2013; More Complex Distillation Systems, John Wiley & Sons, Inc, Hoboken



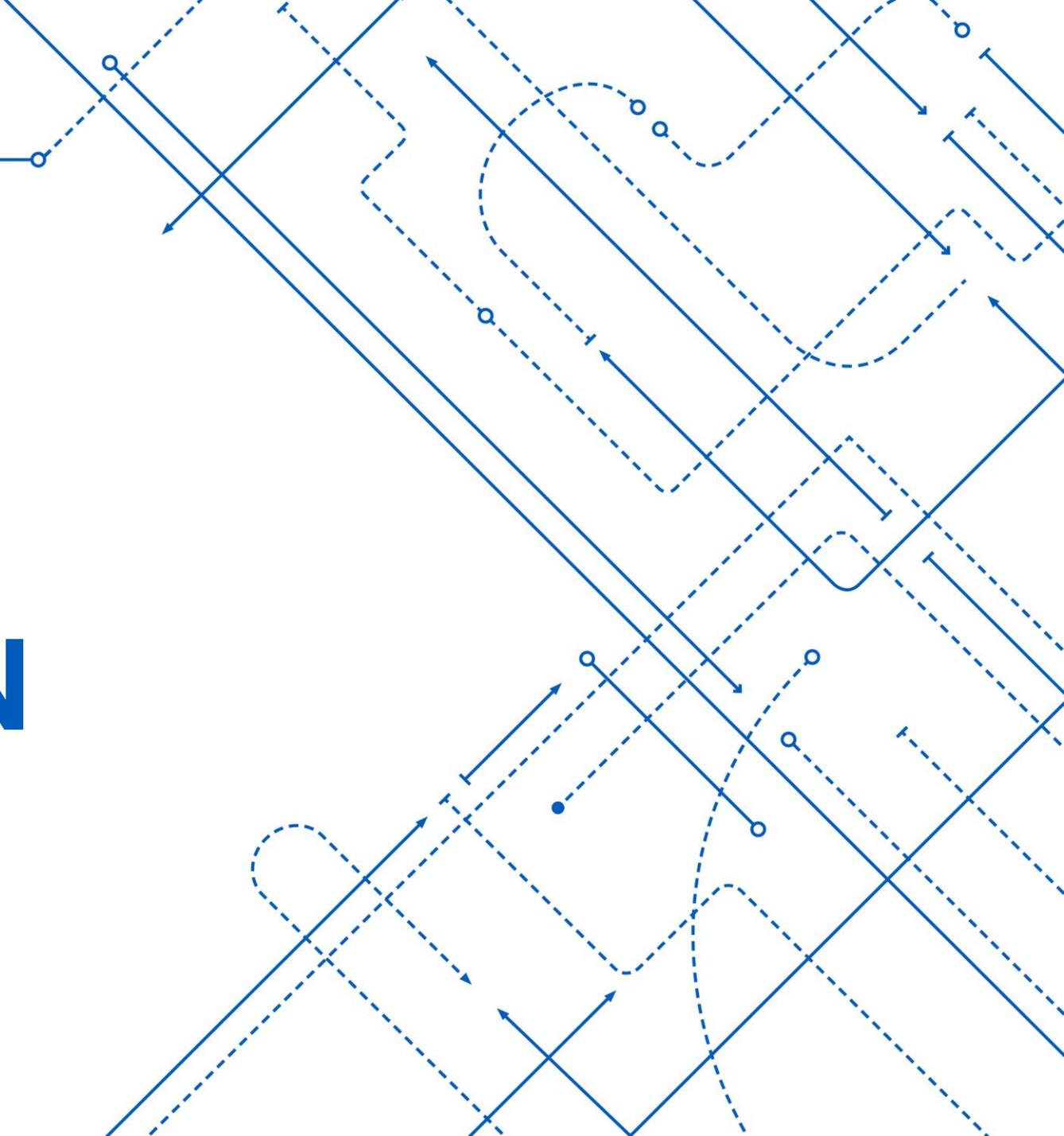


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CRYOGENIC DISTILLATION



Cryogenic Fractional Distillation

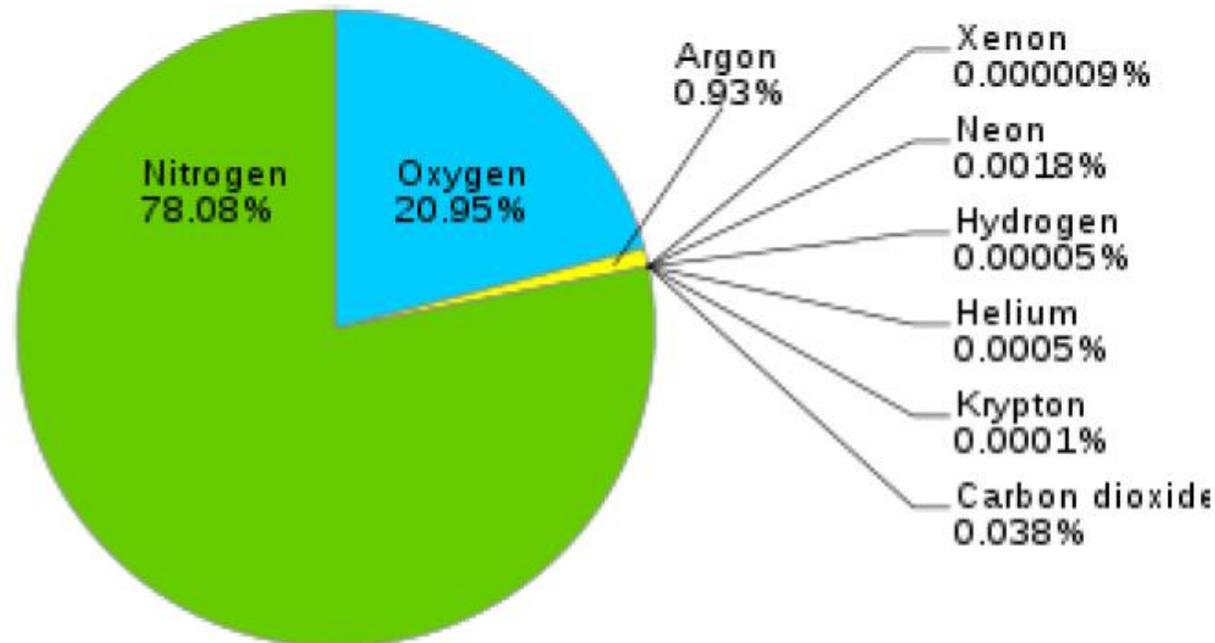
There are many process that require large amounts of relatively pure oxygen or nitrogen

- Steel making
 - Basic Oxygen Steelmaking
 - Uses almost two tons of O_2 per ton of steel produced
- Ammonia
 - N_2 used in the Haber Process to make ammonia
- Coal Gasification
 - Coal, O_2 , and water used to make Syngas
 - Syngas is mixture of CO , CH_4 , H_2 , CO_2 , and H_2O
- Inert Gas
 - N_2 used to blanket tanks containing flammable liquids



Cryogenic Fractional Distillation

- So how do we get large quantities of the constituents of air?
- Air can be cooled until it is liquified
- The liquid air can then be distilled into pure components
- No surprise – there are a lot of details to be covered in order to make this work!
- Composition of dry atmospheric air:



Cryogenic Fractional Distillation

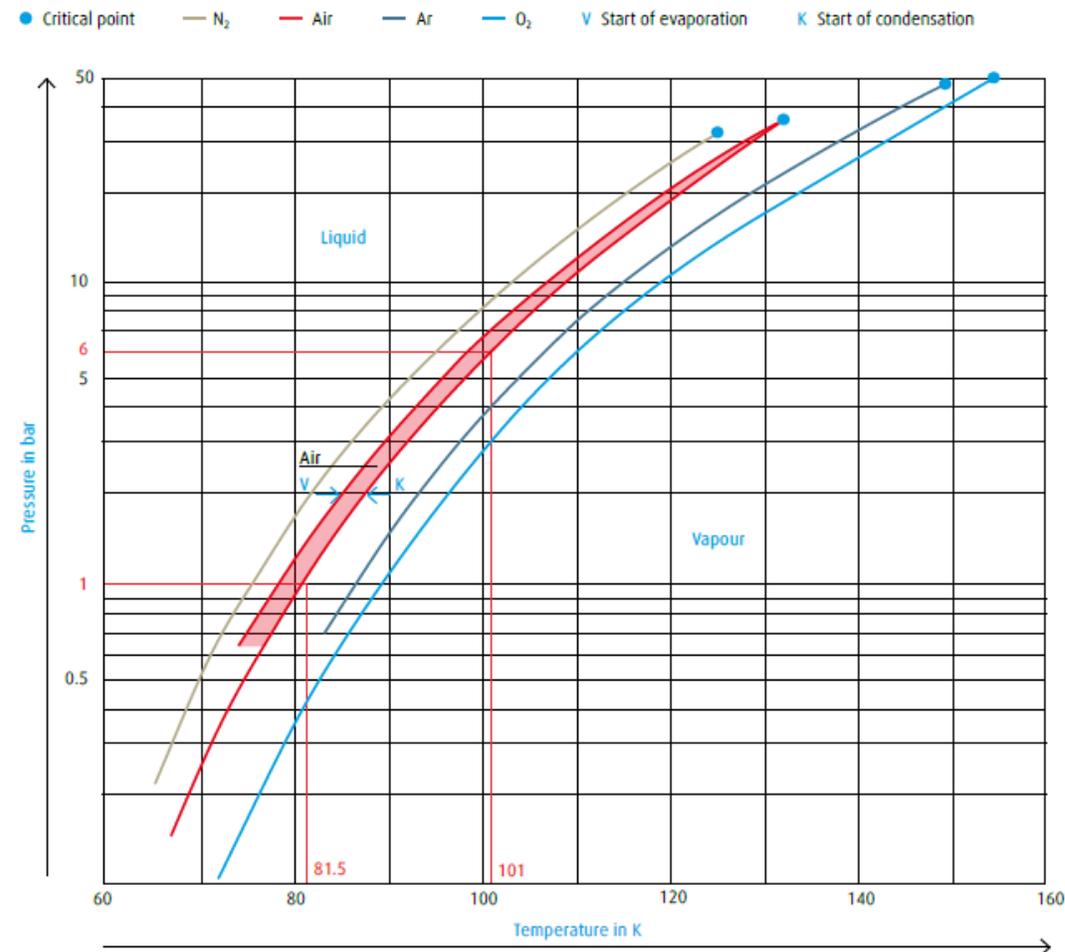
- First developed by Carl von Linde in 1895
- Industrial applications began in 1902
- Can produce high purity gases
- Very energy intensive!



Cryogenic Fractional Distillation

- Air at or below a pressure of 1 bar must be cooled to $-192\text{ }^{\circ}\text{C}$ (81.5 K) before condensation begins
- Air at or below a pressure of 6 bar must be cooled to $-172\text{ }^{\circ}\text{C}$ (101 K) before condensation begins
- This is quite cold...

Vapour pressure curves of atmospheric gases



Cryogenic Fractional Distillation

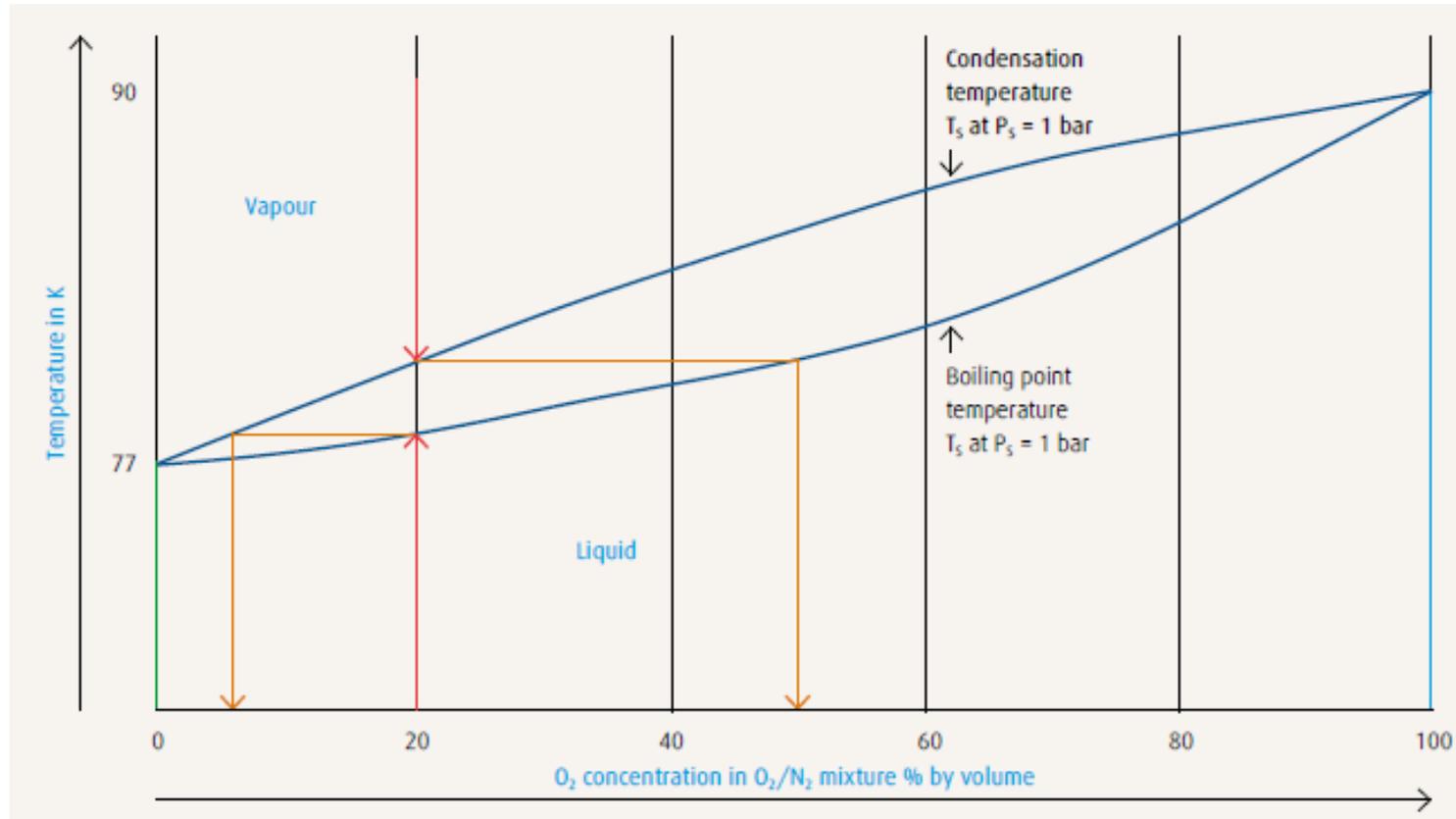
- **Joule-Thomson Effect**

- At ordinary temperatures and pressures all real gases except hydrogen and helium cool upon expansion
- The cooling occurs because work must be done to overcome the long-range attraction between gas molecules as they move further apart
 - H_2 and He have unusually weak long-range forces
- A refrigeration cycle utilizes this phenomena to reduce the temperature of the gas



Cryogenic Fractional Distillation

- T_{xy} diagram for Oxygen / Nitrogen Mixture



Cryogenic Fractional Distillation

Typical Process Steps

1. Removal of Dust Particles

- Mechanical Filter removes dust at the inlet to the compressor

2. Air Compression

- Multi-stage turbo compressor raise air pressure to approximately 6 bar

3. Air Cooling and Purification

- Air is cooled by direct contact with cooling water which also removes soluble air impurities

4. Adsorption

- Water, Carbon dioxide, and other hydrocarbons are removed via adsorption in periodically loaded/regenerated molecular sieve adsorbers
- Without this step these materials would freeze at the cryogenic temperatures and blind over the column



Cryogenic Fractional Distillation

Typical Process Steps, continued

5. Low-Temperature Heat Exchange

- Process air is cooled nearly to liquefaction temperatures by means of countercurrent heat exchange with nitrogen waste gas from the rectification process

6. Cold Production and Internal Product Compression

- Air is further compressed and then passed through an expansion turbine whereby it is cooled to liquid temperatures

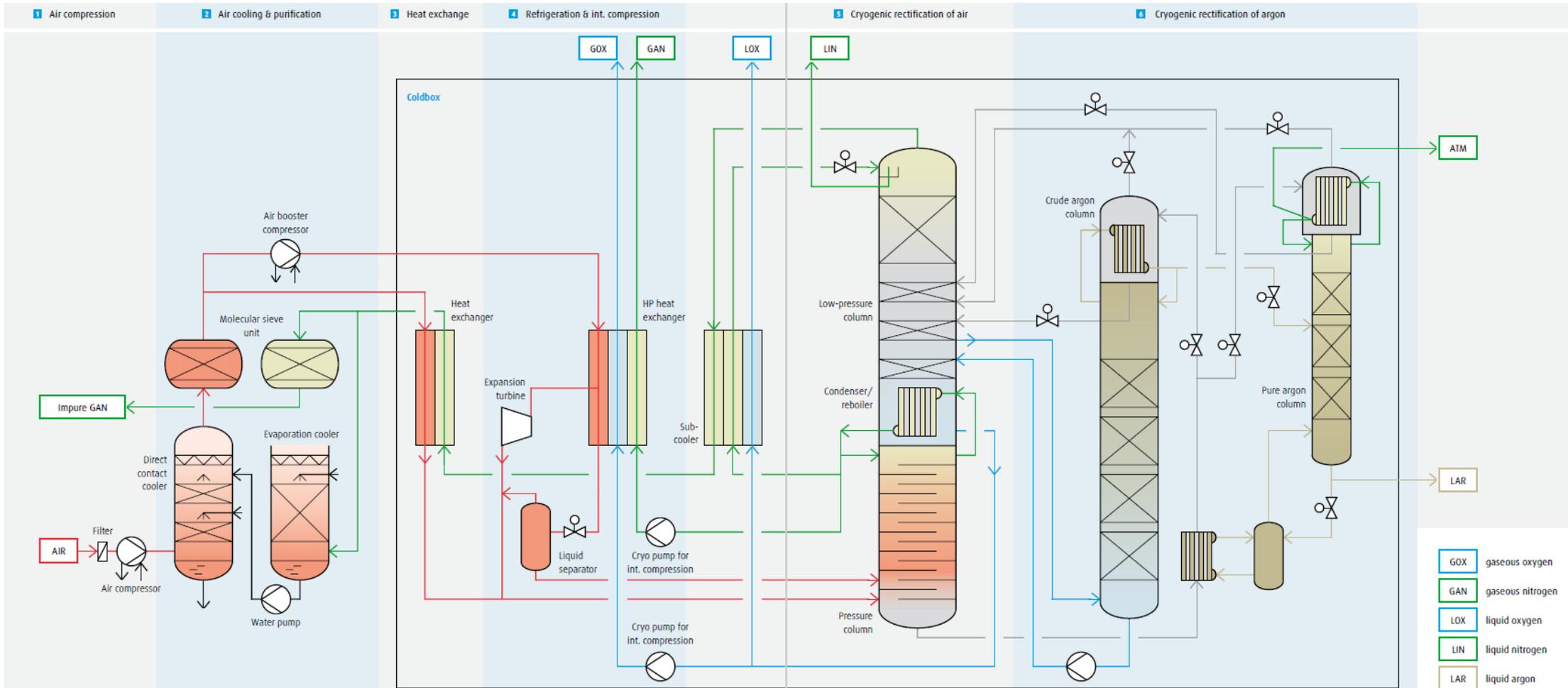
7. Cryogenic Rectification of Air

- Low pressure column produces Pure Oxygen (bottoms) and nitrogen waste gas (distillate)
- High pressure column produces pure nitrogen gas (distillate) and oxygen enriched liquid (bottoms)

8. Cryogenic Rectification of Argon

- Sidestream of argon enriched gas from low pressure column goes to series of two columns to produce pure argon

Cryogenic Fractional Distillation





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PARTIAL CONDENSORS REVISITED



Partial Condensers McSH pp 674-675

- A total condenser converts the total vapor flow to liquid flow
 - Therefore the entering vapor and exiting liquid have the same composition

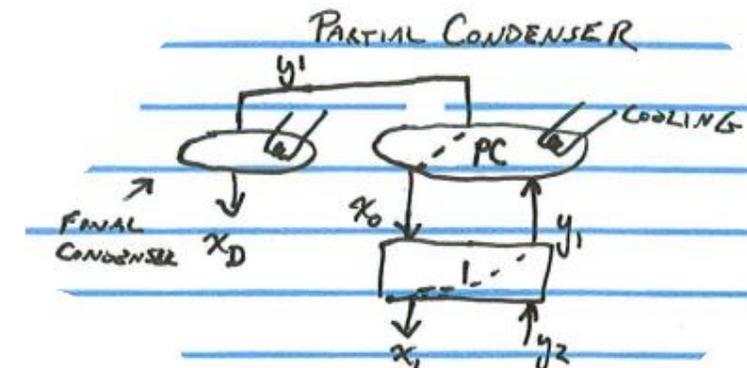
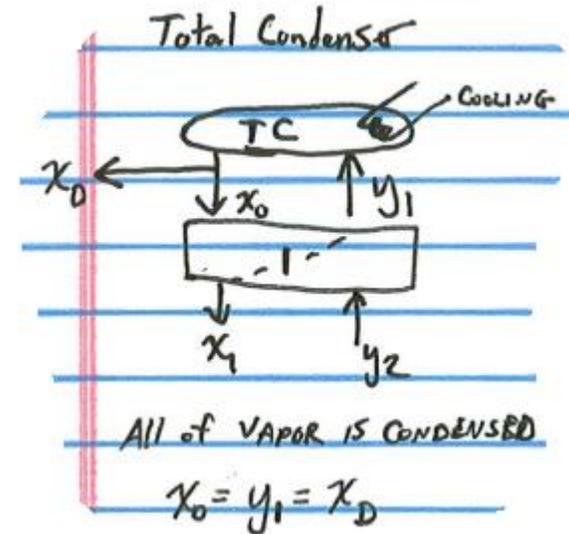
$$x_D = x_0 = y_1$$

- A partial condenser only converts a portion of the vapor flow to liquid
 - The composition of the vapor and liquid exiting are in equilibrium with one another and differ from the composition of the entering vapor.

$$y' = y^*(x_0) = x_D \neq y_1 \neq x_0$$

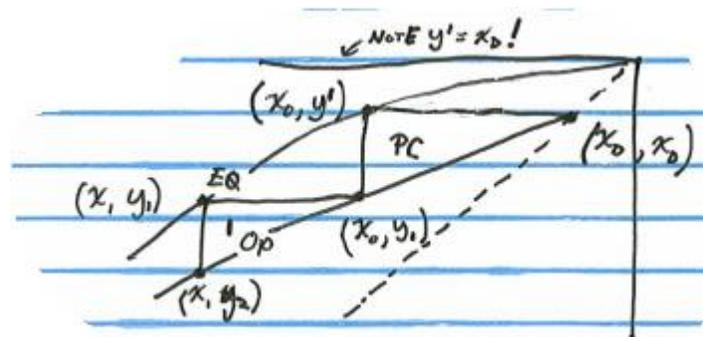
$$x_0 = x^*(y')$$

- A secondary condenser then converts the rest of the vapor to a liquid



Partial Condensers and McCabe-Thiele

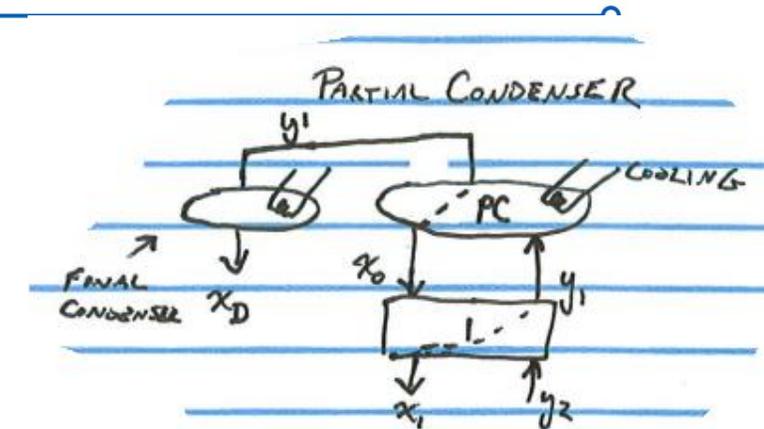
- Because of the equilibrium relationship between the vapor and liquid exiting the partial condenser there is separation being accomplished
- The first step on the McCabe-Thiele is the partial condenser
 - This step does NOT count as a stage
 - Stages are actual trays in the column



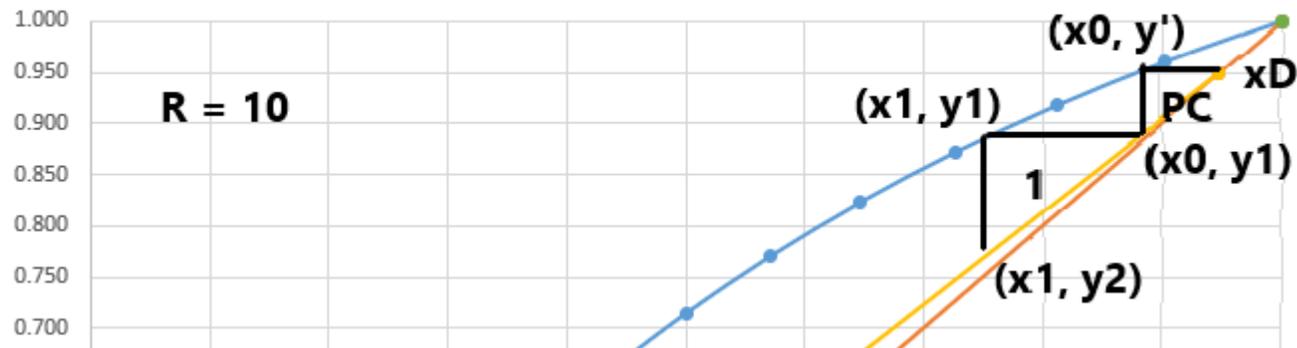
- Make sure you know whether the condenser is a Total Condenser or a Partial Condenser

Partial Condensers and McCabe-Thiele

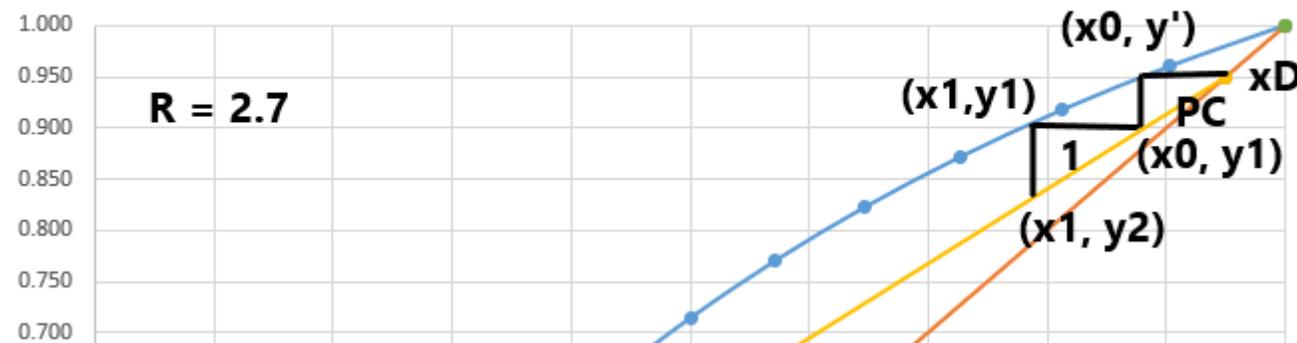
- Note that the same y' is equal to x_D no matter what Reflux ratio is used
- Note that the required x_0 is NOT dependent on the Reflux Ratio
 - It is the liquid mole fraction in equilibrium with vapor x_D
- Note that the required y_1 is dependent on the Reflux Ratio



Benzene and Toluene at Atmospheric Pressure



Benzene and Toluene at Atmospheric Pressure



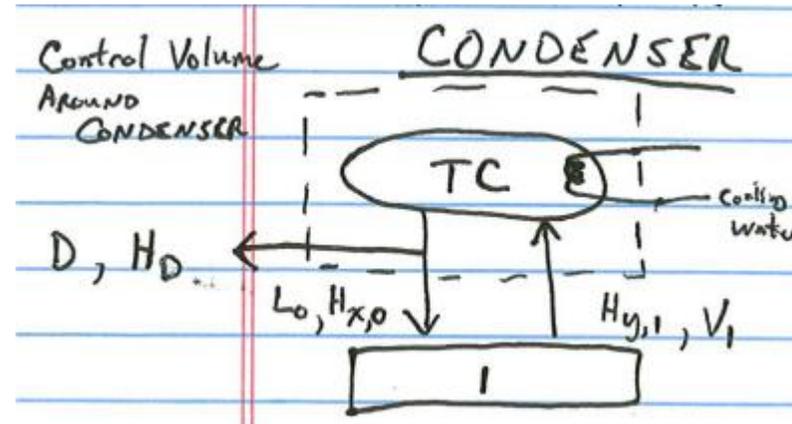
Continuous Distillation – Enthalpy Balances with Total Condenser

McSH pp 694-701, pp 679, 682 eq 21.1 and 21.2

- How much energy does one need to remove via condenser?

Total Condenser

- Control Volume
around condenser



- Heat added = Enthalpy out – enthalpy in

$$\begin{aligned}
 -q_c &= DH_D + L_0H_{x,0} - V_1H_{y,1} \\
 &= (D + L_0)H_{x,0} - V_1H_{y,1}
 \end{aligned}$$

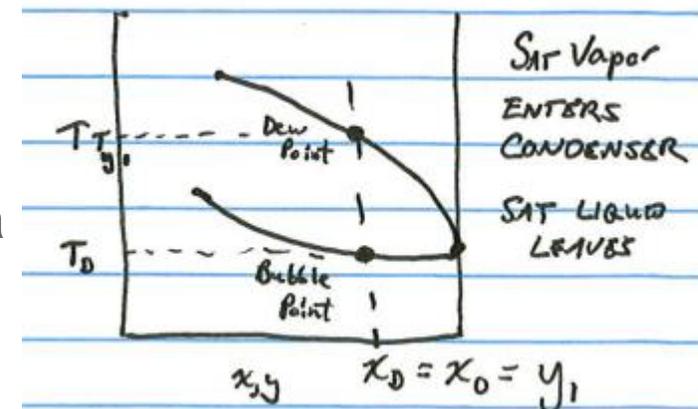
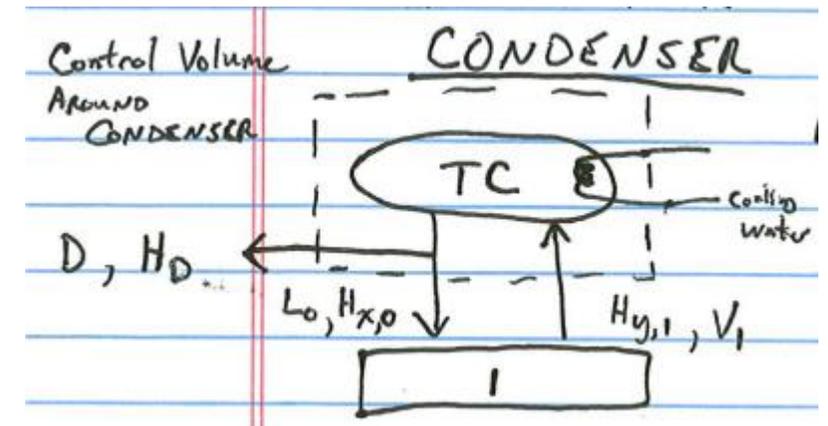
- Note: q_c is defined as the amount of heat **REMOVED** via the condenser and is a positive number. The enthalpy balance is the amount of heat added, therefore the term appears as $-q_c$ in the equation. The fact that $-q_c$ is therefore a negative term is consistent with the fact that we are removing heat to affect a phase change from vapor to liquid

Enthalpy Balances: Total Condenser, continued

- $-q_c = (D + L_0)H_{x,0} - V_1H_{y,1}$
- But from mass balance we know that $V_1 = D + L_0$
- $-q_c = (D + L_0)H_{x,0} - (D + L_0)H_{y,1}$
- And from definition of reflux ratio $L_0 = D R$

$$-q_c = D(1 + R)(H_{x,0} - H_{y,1})$$

- It's not as simple as just looking at Heats of Vaporization
- You have the temperature changing from Dew Point to Bubble Point
- Heats of Vaporization are defined for a pure material at a given temperature (usually the normal boiling temperature for pure material) and we are condensing over a range of temperatures



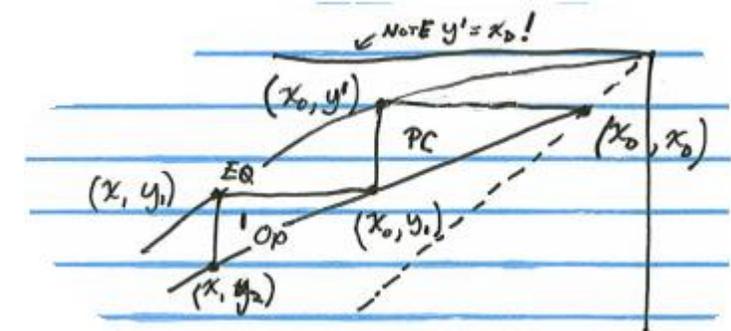
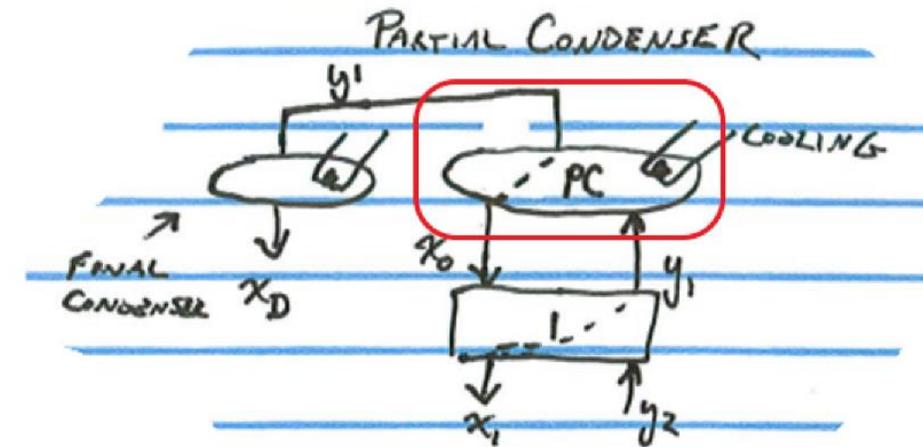
Continuous Distillation – Enthalpy Balances with Partial Condenser

- Heat added = Enthalpy out – enthalpy in

$$-q_c = DH_D + L_0H_{x_0} - V_1H_{y_1}$$

$$-q_c = DH_y(x_D) + L_0H_x(x_0) - V_1H_y(y_1)$$

- From definition of reflux ratio $L_0 = D * R$
- From mass balance we know that $V_1 = D + L_0 = (1 + R)D$
- $$-q_c = DH_y(x_D) + (DR)H_x(x_0) - (1 + R)DH_y(y_1)$$
- Note that $H_y(x_D)$ is a saturated VAPOR Phase Enthalpy at x_D
- $H_x(x_0)$ is a saturated LIQUID Phase enthalpy at x_0
- x_0 is the liquid mole fraction in equilibrium with vapor having a mole fraction equal to x_D
- They are NOT at the same temperature
- y_1 is the mole fraction of the vapor exiting stage 1
- y_1 is dependent on the reflux ratio, which sets the operating line!



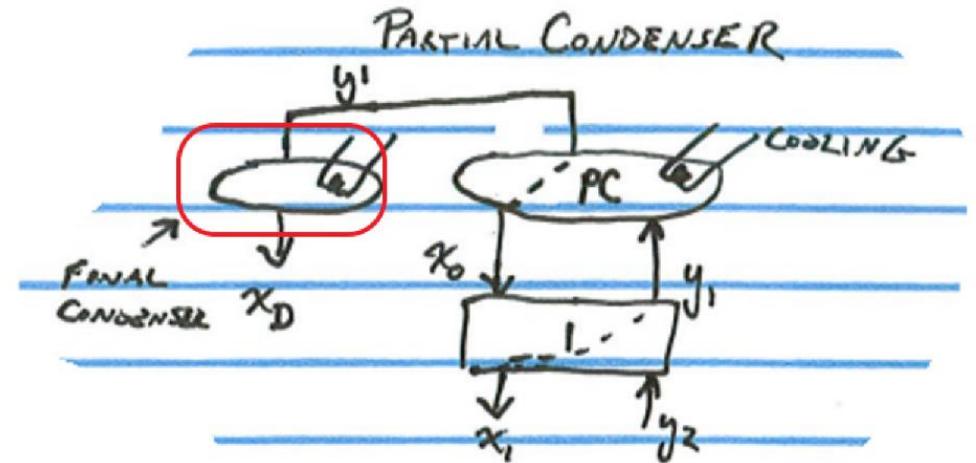
Partial Condensers Revisited

- Final Condenser Enthalpy Balance
 - Heat added = Enthalpy out – enthalpy in

$$-q_{fc} = DH_D - DH_{y'}$$

$$-q_{fc} = DH_x(x_D) - DH_y(x_D)$$

- $$-q_{fc} = D[H_x(x_D) - H_y(x_D)]$$



Partial Condensers Revisited

- Both condensers together
- Looks somewhat similar to the Total Condenser case...
 - Heat added = Enthalpy out – enthalpy in

$$-q_c = DH_D + L_0H_{x,0} - V_1H_{y,1}$$

- But, of course, $x_D \neq x_0 \neq y_1$

- $-q_c = DH_x(x_D) + L_0H_x(x_0) - V_1H_y(y_1)$

- $-q_c = DH_x(x_D) + RDH_x(x_0) - (R + 1)DH_y(y_1)$

- Note difference from Partial Condenser Enthalpy Balance is that the exiting distillate stream is now liquid phase whereas when evaluating the partial condenser by itself it was vapor phase

