

CE407 SEPARATIONS

Lecture 27

Instructor: David Courtemanche



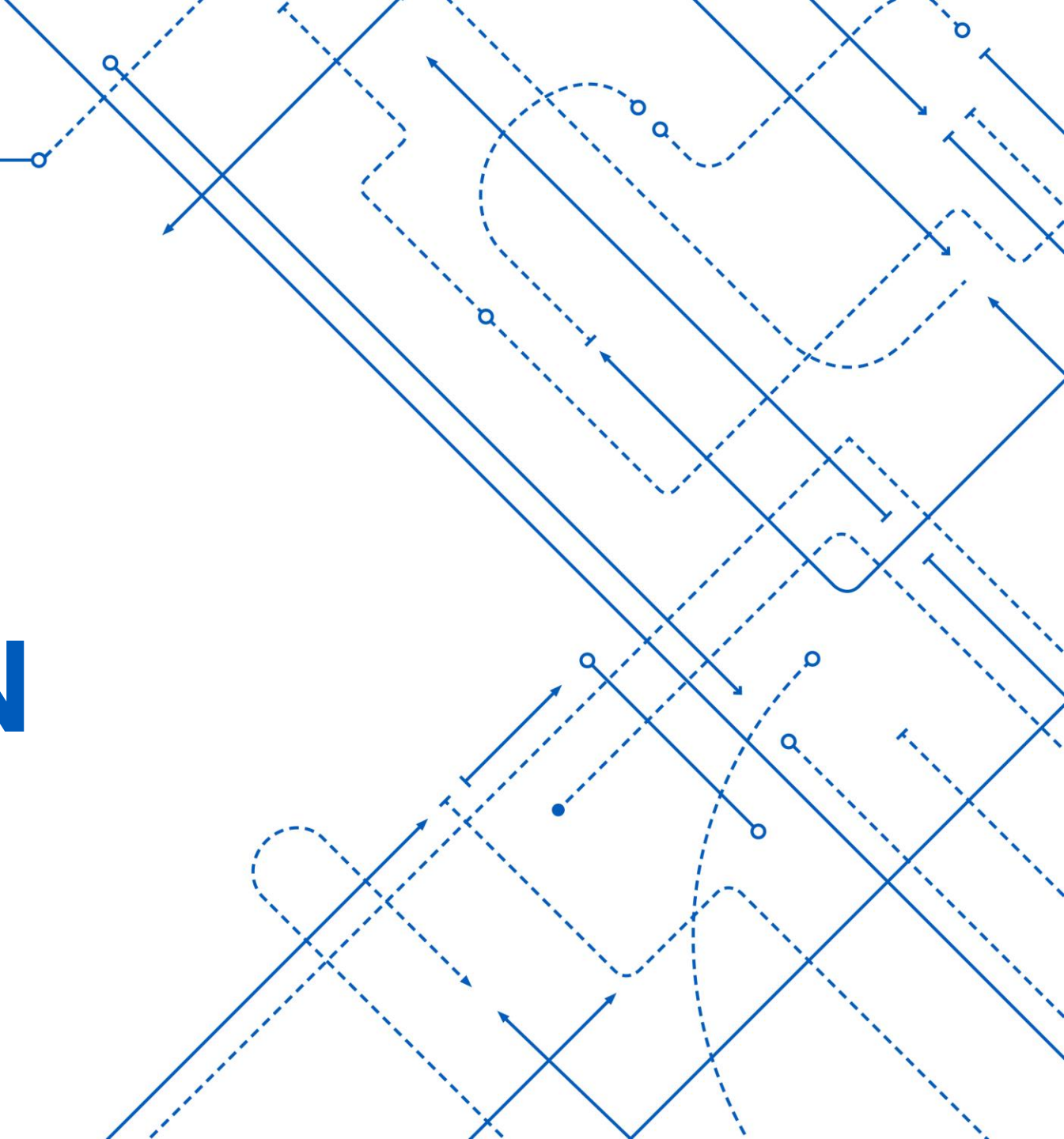
Includes material from the Linde Group



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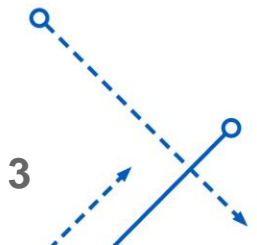
CRYOGENIC DISTILLATION



Cryogenic Fractional Distillation

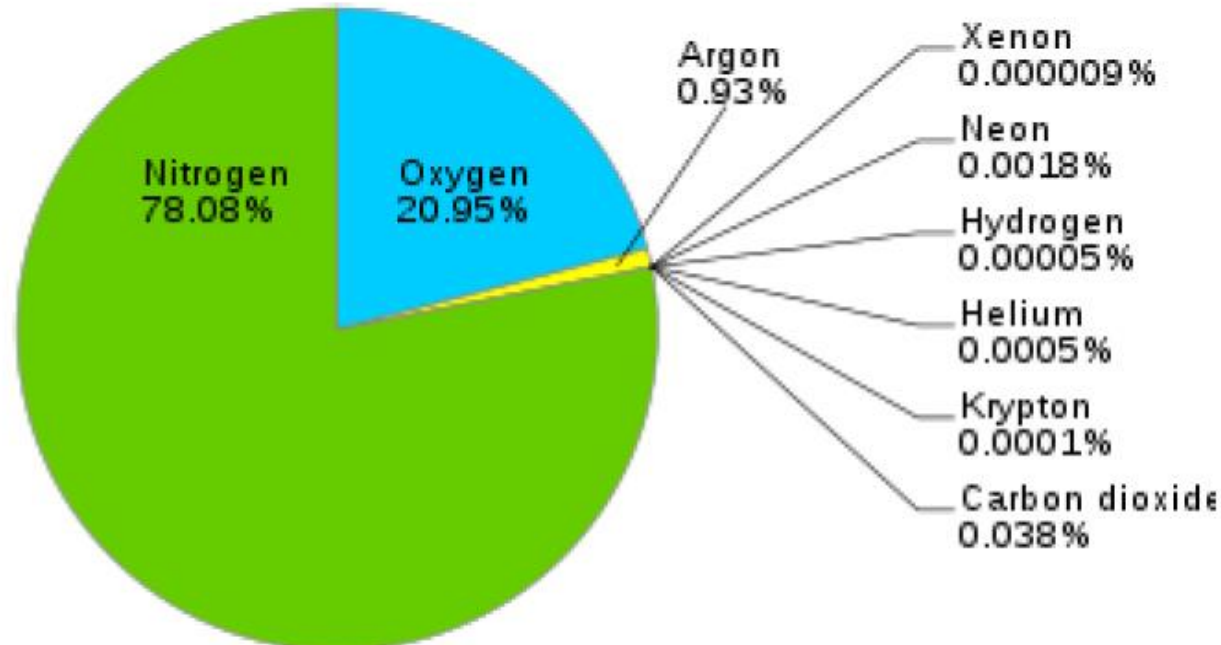
There are many process that require large amounts of relatively pure oxygen or nitrogen

- 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



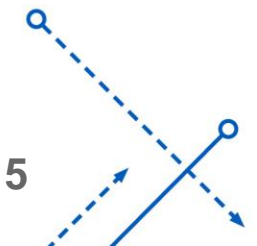
Cryogenic Fractional Distillation

- 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

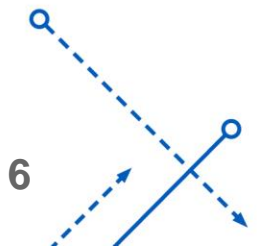
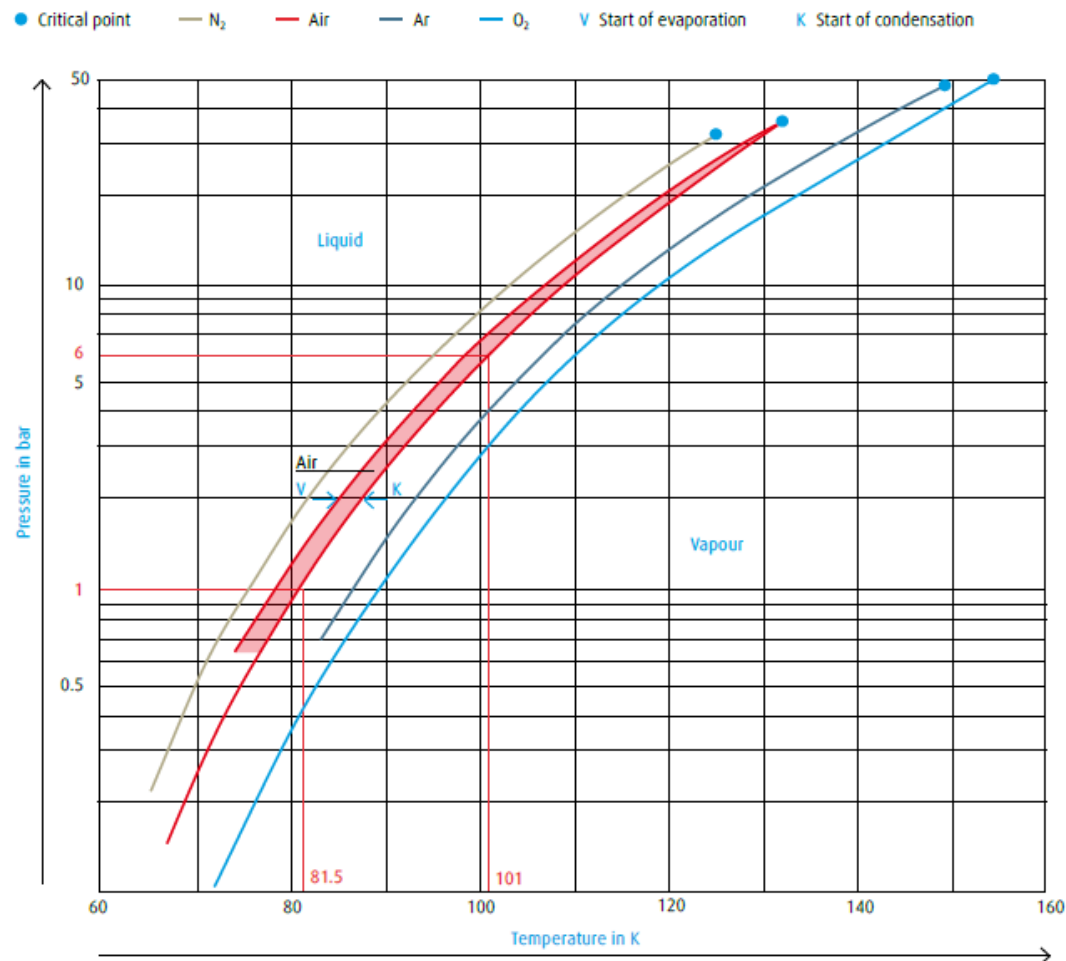
- First developed by Carl von Linde in 1895
- Industrial applications began in 1902
- Can produce high purity gases
- Very energy intensive!



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...

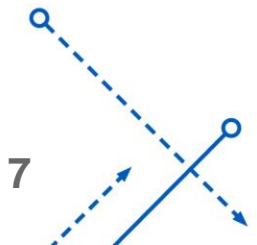
Vapour pressure curves of atmospheric gases



Cryogenic Fractional Distillation

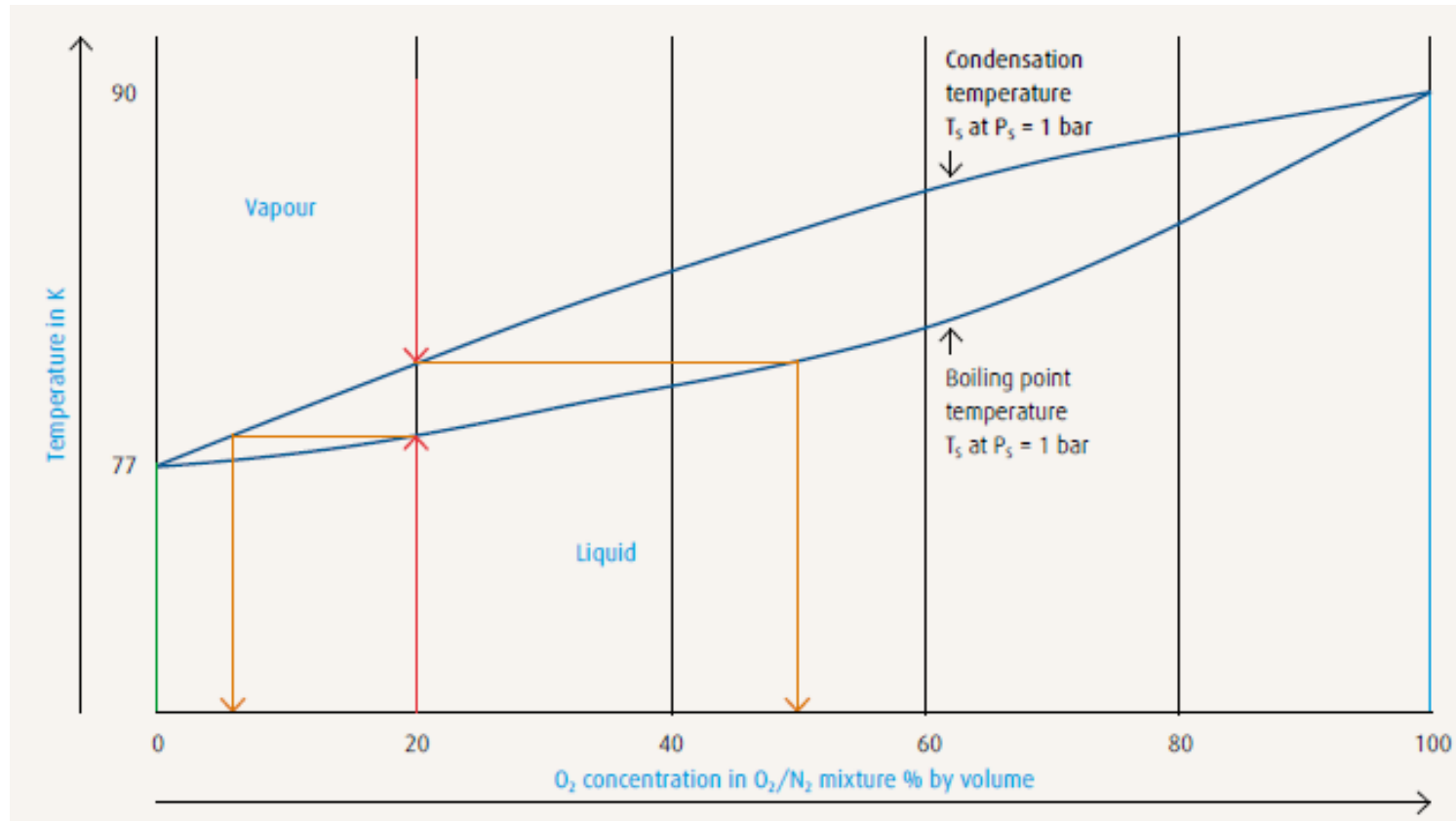
- **Joule-Thomson Effect**

- 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

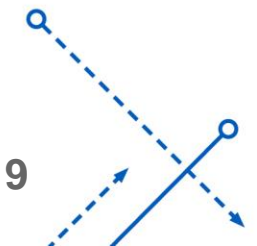
- Multi-stage turbo compressor raise air pressure to approximately 6 bar

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

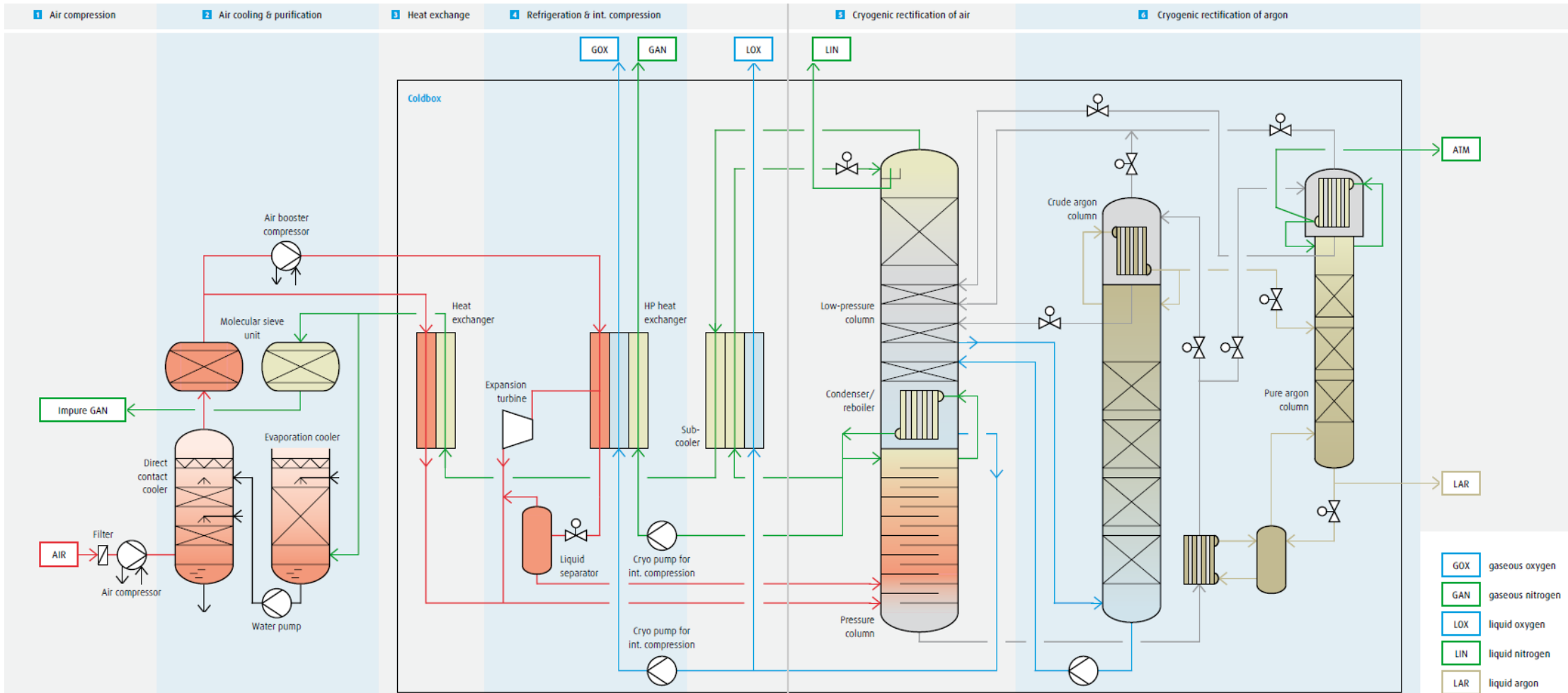
- Low pressure column produces Pure Oxygen (bottoms) and nitrogen waste gas (distillate)
- High pressure column produces pure nitrogen gas (distillate) and oxygen enriched liquid (bottoms)

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

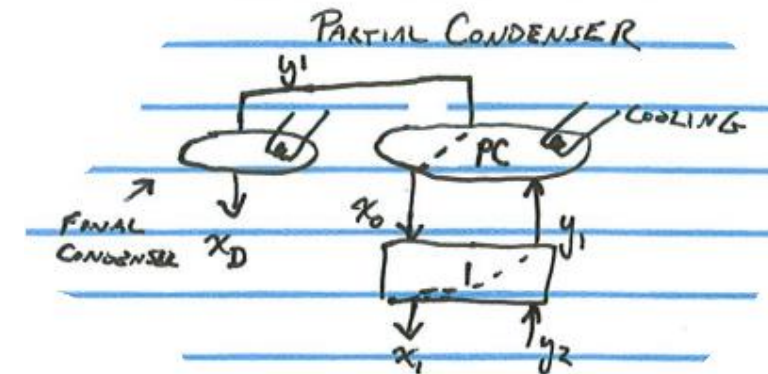
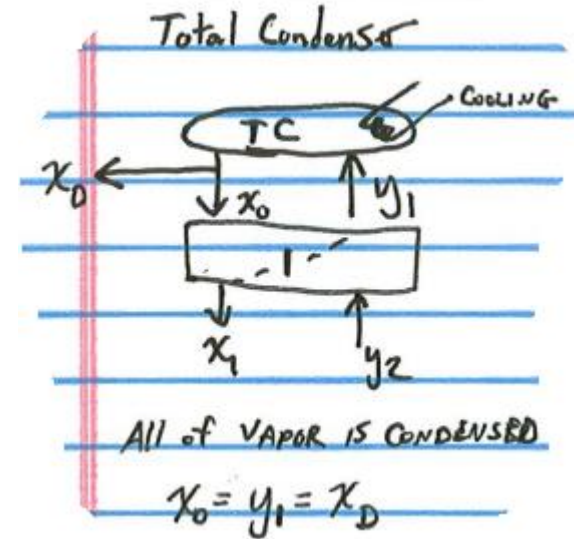
$$x_D = x_0 = y_1$$

- 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.

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

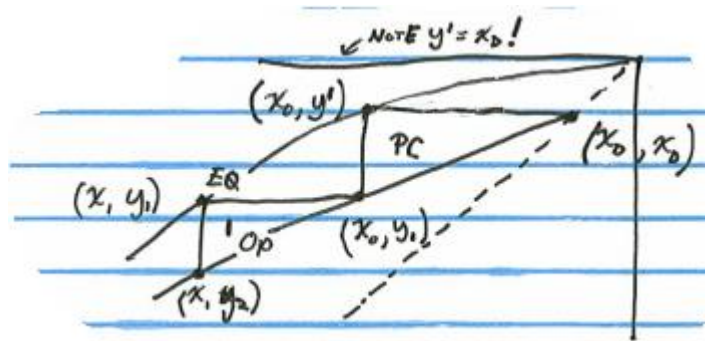
$$x_0 = x^*(y')$$

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



Partial Condensers and McCabe-Thiele

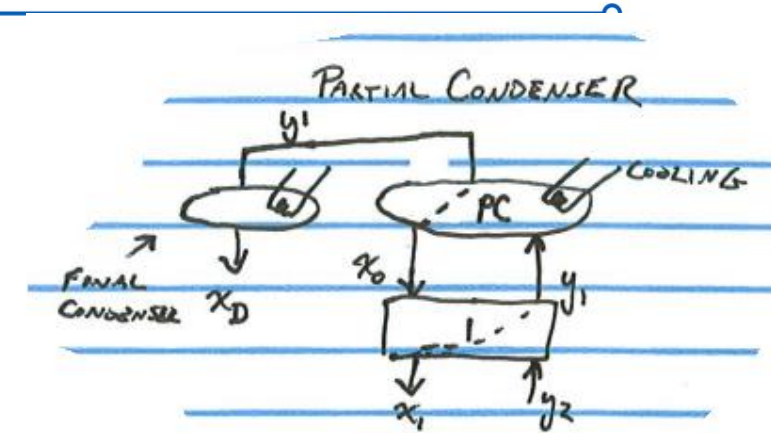
- Because of the equilibrium relationship between the vapor and liquid exiting the partial condenser there is separation being accomplished
- The first step on the McCabe-Thiele is the partial condenser
 - This step does NOT count as a stage
 - Stages are actual trays in the column



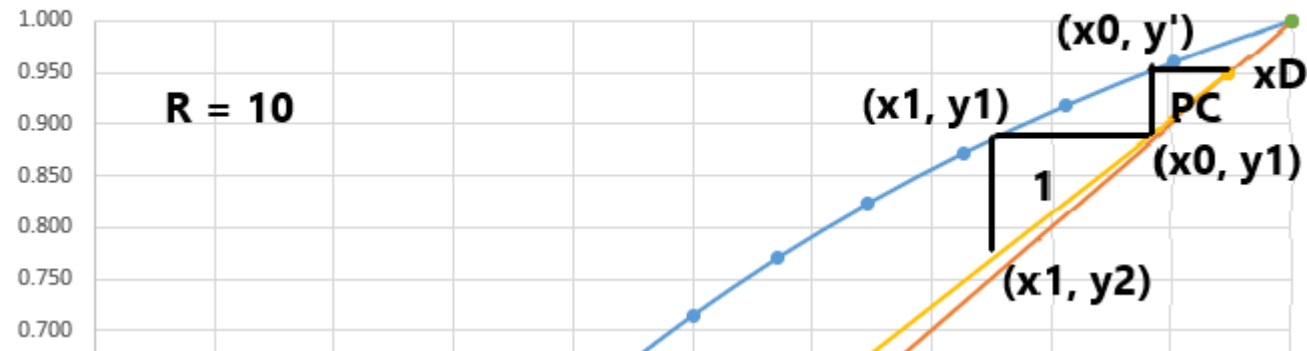
- Make sure you know whether the condenser is a Total Condenser or a Partial Condenser

Partial Condensers and McCabe-Thiele

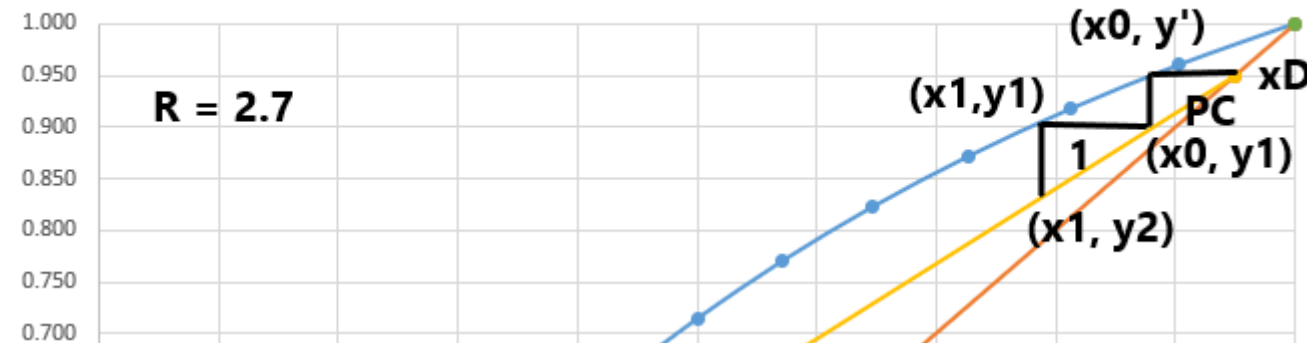
- Note that the same y' is equal to x_D no matter what Reflux ratio is used
- Note that the required x_0 is NOT dependent on the Reflux Ratio
 - It is the liquid mole fraction in equilibrium with vapor x_D
- Note that the required y_1 is dependent on the Reflux Ratio



Benzene and Toluene at Atmospheric Pressure



Benzene and Toluene at Atmospheric Pressure



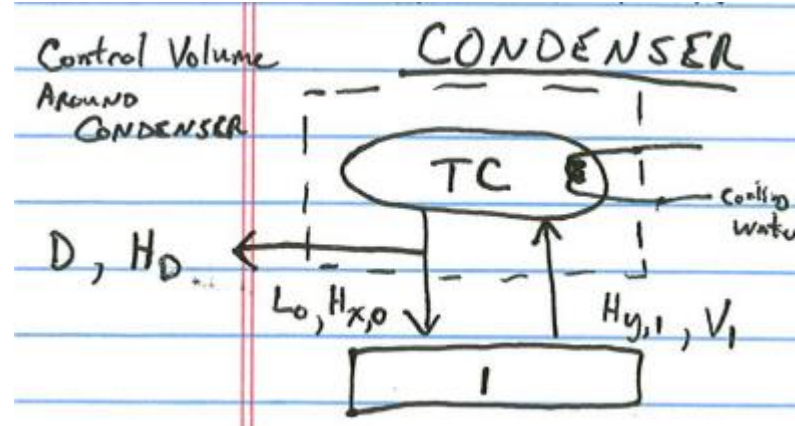
Continuous Distillation – Enthalpy Balances with Total Condenser

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

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

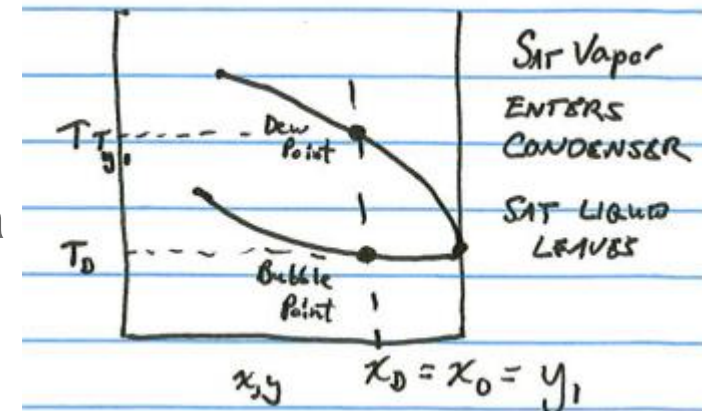
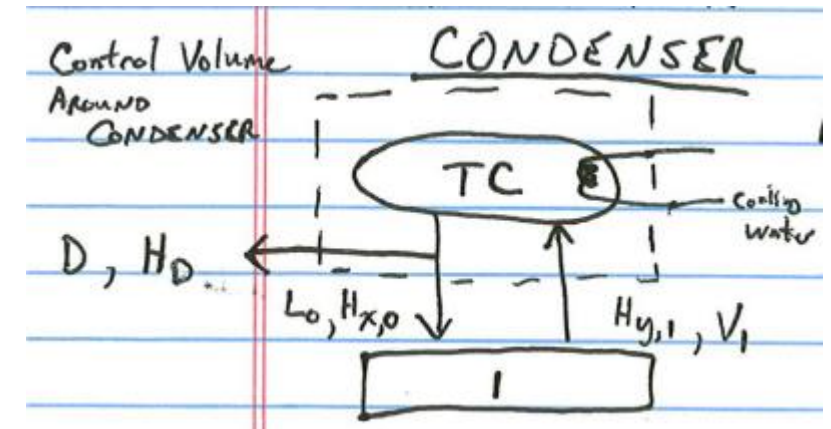
$$= (D + L_0)H_{x,0} - V_1H_{y,1}$$
- Note: q_c is defined as the amount of heat **REMOVED** via the condenser and is a positive number. The enthalpy balance is the amount of heat added, therefore the term appears as $-q_c$ in the equation. The fact that $-q_c$ is therefore a negative term is consistent 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

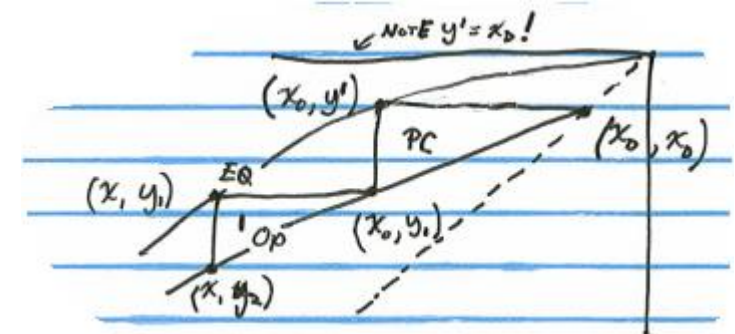
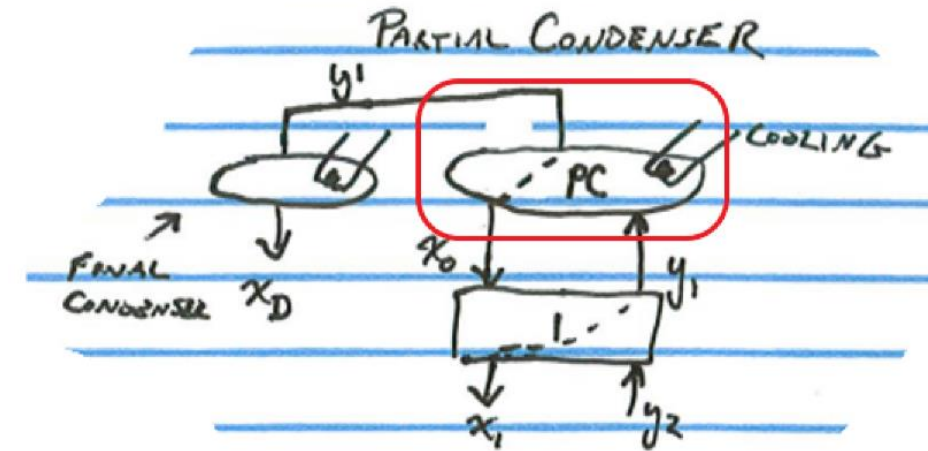


Continuous Distillation – Enthalpy Balances with Partial Condenser

- 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!



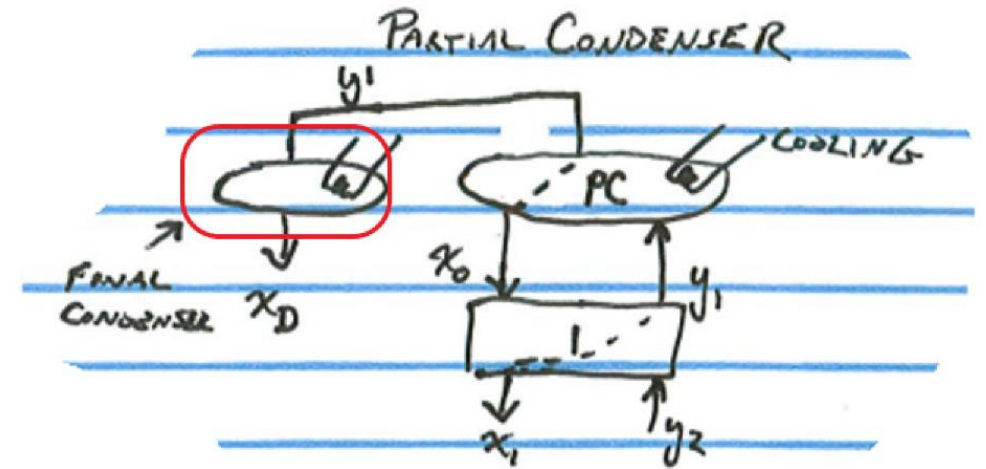
Partial Condensers Revisited

- 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

