PROCESS ENGINEERING AND DESIGN

1. Outline processes for manufacturing (a) HCl, (b) hydrogen, (c) acetic acid, (d) ammonia (e) sulfuric acid, (f) nitric acid, (g) HF, (h) NaOH, (i) chlorine, (j) methanol, (k) phosphoric acid, (l) EO, (m) PE, (n) HCN, (o) sulfur (p) formaldehyde, (q) ethanol, (r) acetone, (s) benzene, (t) phenol, (u) vinyl chloride (v) styrene, (w) urea.

2. Why is distillation done at high pressure?

3. If you have an HCl gas stream and an N_2 stream how do you dispose of them?

4. Which has larger diameter, the suction or discharge on a pump?

5. Sketch typical temperature and composition profiles in a distillation column.

6. How would you remove 1% phenol from water?

7. How would you control a distillation column?

8. How is syn gas made from coal?

9. How would you go about estimating the cost of a distillation column, pump or heat exchanger?

10. Suggest several methods for obtaining fresh water from sea water. Which would you use?

11. What is bleach? How is it made?

12. Outline a method for separating two organic compounds with similar boiling and melting points.

13. How would you obtain pure oxygen from air?

14. Living in Phoenix, Arizona where the temperature is 100F, how would you cool a room using 120F water?

15. Consider an exothermic, zeroth order reaction in a CSTR. What happens if there is a step change increase in the feed temperature?

16. Sketch and describe a multi-effect evaporator. How does the pressure vary through the system?

17. How would you separate ethanol and water?

18. How does an ice skate work?

19. Increasing the heat to the boiler of a steamboat caused the boat to slow down. Why?

20. Consider two pressurized vessels connected in series with recycle. If the recycle is cut off, how will the pressure in each vessel vary with time?

21. How would you remove water vapor from Ar gas to a level of 1ppb (volume%) if

the water is initially present at a level of 200ppb?

22. What is the lowest temperature water can be cooled to in a cooling tower?

23. Several years ago there was a report of a boiler explosion in a church. When interviewed the janitor explained that he lit the gas flame in the boiler. After a time he noticed the pressure gauge readings were too high. He immediately extinguished the burners. Five minutes later the boiler blew up. Why?

24. Given the pressure drop, L and D for a pipe, how would you find the velocity?

25. What is the reflux ratio and a pinch point?

26. Diagram an HCl or SO_2 absorber.

27. How do you make pure N_2 from air without cryogenic techniques?

28. Know how to establish a scheme to separate a multicomponent system of liquids.

29. Consider two pressurized vessels connected in series. If the downstream vessel suddenly develops a large leak what happens to the flowrate in the pipe connecting the two vessels? Sketch a flow vs. time curve.

30. How does a heat pump work in winter? How is it different in the summer?

31. What temperature and pressure are used in the synthesis of ammonia? Is the reaction reversible? exothermic? (why?). To carry it out economically what must you know about the reaction? How do you get K_{eq} without experimental data? How does K_{eq} depend on T?

32. Give expressions for:
a. reversible heat in an electrochemical cell
b. irreversible heat in an electrochemical cell
b. net work in an electrochemical cell

33. You have a continuous distillation set-up. What can you do to save energy (i.e. reduce heat duty at the reboiler).

34. You want to extract mechanical energy from geothermal steam which contains 1 % incondensible gases CO_2, H_2S, NH_3. What exit T, P would you choose? Would you get rid of the incondensibles? How?

35. Derive the Fenske equation.

36. What is the procedure for designing a multicomponent distillation column?

37. Outline the principles underlying pressure swing absorption. When would you use it?

38. Give a method for manufacturing acetylene, starting from inorganic compounds only.

39. How would you separate a single temperature sensitive component (e.g. a protein) from a stream containing a multicomponent mixture of similar sized molecules?

40. Where does bromine come from, e.g. that used in bromo-seltzer?

41. Why is there so much concern about high and low frequency outage to the electrical power of compressors feeding gas into tanks?

acetylene $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$

Process Design

1 a) D HCl Production

Pure HCl is gas @ STP. HCl in solution is muriatic acid.

- Mostly produced as byproduct of chlorination rxns

$$Benzene + Cl_2 \rightleftharpoons ClBz + HCl \quad (exothermic)$$

- Can use acid/base exchange: $2NaCl(s) + H_2SO_4(l) \rightleftharpoons 2HCl(g) + Na_2SO_4(s)$

- To make HCl soln (muriatic acid), absorb HCl gas in water (highly exotherm.

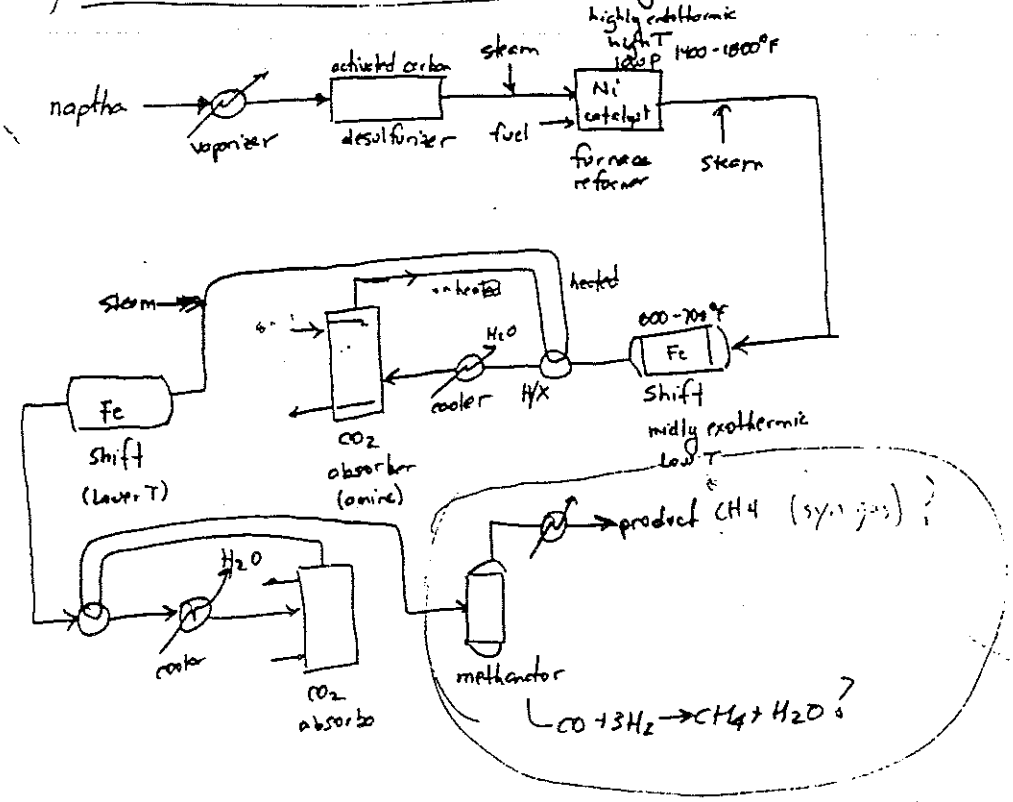
For sell. H_2SO_4 rxn, 1st absorb HCl in cooling tower, then strip out gas

b) 2) Hydrogen: Steam Reforming of Natural Gas

$$C_nH_m + H_2O \rightleftharpoons nCO + \left(\frac{m}{2} + n\right)H_2 \quad \text{endothermic} \quad \text{high T, low P (L'Chat)}$$

Water gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \text{ (Water-gas shift) exothermic}$$



$H_2S + O_2 \rightarrow SO_2 + H_2O$

$SO_2 + H_2O$

Alternative: electrolytic conversion of H_2O

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

Water/gas shift to convert CO to CO_2

CO_2/H_2S removed by absorption & stripping

1. Outline of Processes

a) HCl – majority as byproduct from chlorination of hydrocarbons

$$RH + Cl_2 \rightarrow RCl + HCl$$

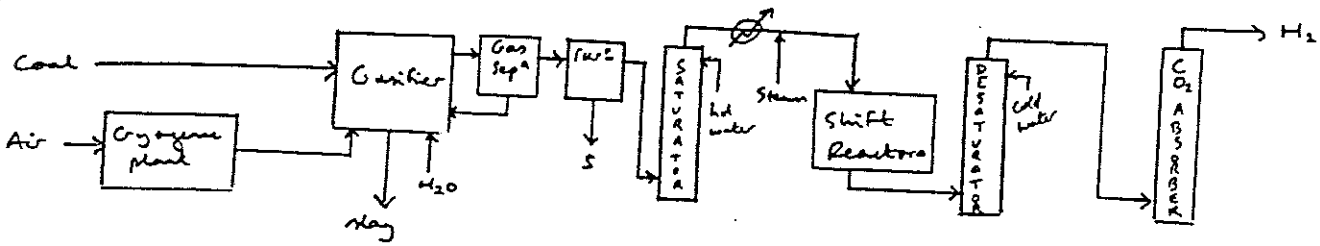
- highly exothermic
- must remove unchlorinated HC by absorbing HCl into H_2O @ chlorination T, P then drop P to lose H_2O

– add salt to H_2SO_4

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl\ (g)$$

– burn H_2 & Cl_2 – highly exothermic

b) H_2



- Alternatively can have steam reformer of CH_4 feeding into the network (burn CH_4 in H_2O/O_2)
- shift reactors convert $CO + H_2O \rightarrow CO_2 + H_2$ using chromium promoted iron oxide catalyst (2 stages of conversion)
- IF Coal gas^n is not used then H_2S removal is necessary before desaturator & CO_2 absorber. (H_2S removed using Fe_2O_3)
- CO_2 is removed using high temperature potassium carbonate wash with soln regeneration.
- Steam reformer converts about 70% of Nat Gas to Syn Gas using Ni: catalyst.
- EA or DEA can also be used for CO_2 scrubbing.

Alternatively:

Electrolytic decomposition

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta H = 136\ kCal$$

- gives 99.7% H_2
- Use a 15% NaOH soln @ Ni: plated Fe anode, Fe cathode
- T ~ 60 → 70 °C

) Acetic Acid

Methanol carbonylation $\frac{3}{4}CH_4 + \frac{1}{4}CO_2 + \frac{1}{2}H_2O = CO + 2H_2$

$CO + 2H_2 = CH_3OH$ (V)

$CH_3OH + CO = CH_3COOH$ ← Rh cat

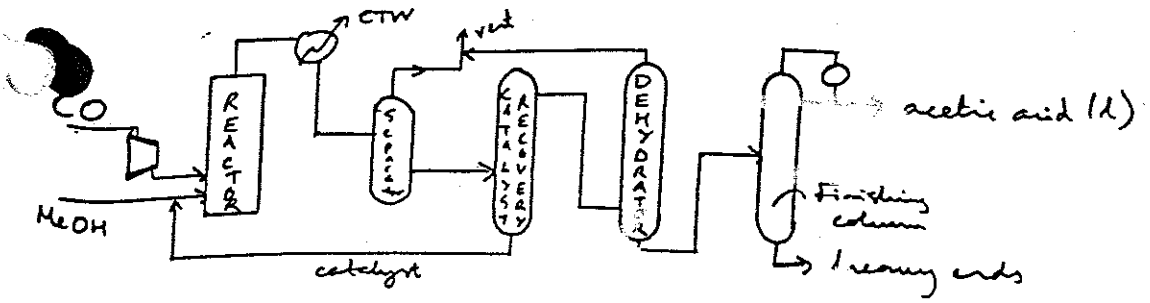
Acetaldehyde oxidn: $C_2H_6 = C_2H_4 + H_2$

$C_2H_4 + \frac{1}{2}O_2 = CH_3CHO$

$CH_3CHO + \frac{1}{2}O_2 = CH_3COOH$

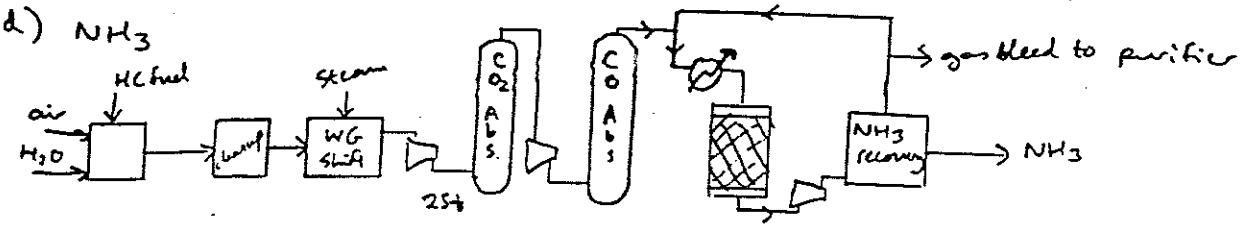
3) Butene oxidn

Main method is (1), Methanol Carbonylation



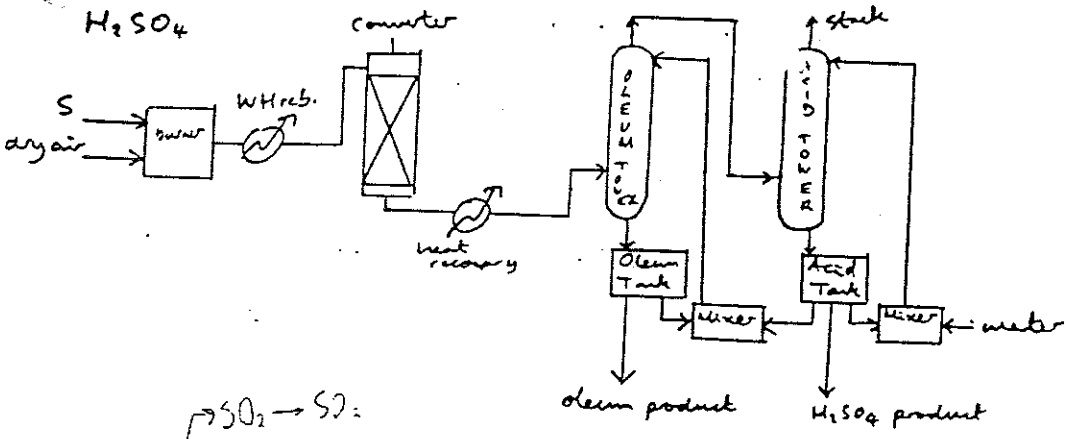
- Reactor runs @ 30 atm, Rh Co catalyst, 160°C (or Ir P Co cat).

d) NH_3



- Reactor is @ 450°C 200 atm ⇒600 using Fe ($+K_2O + Al_2O_3$) cat.
- NH_3 recovery either
  - absorb into H_2O then regenerate by distill.
  - refrigerate & condense out NH_3.

H_2SO_4

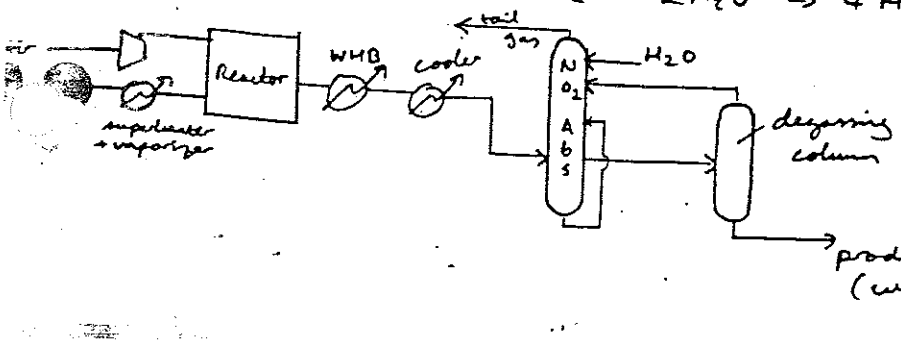


$SO_2 \rightarrow SO_3$

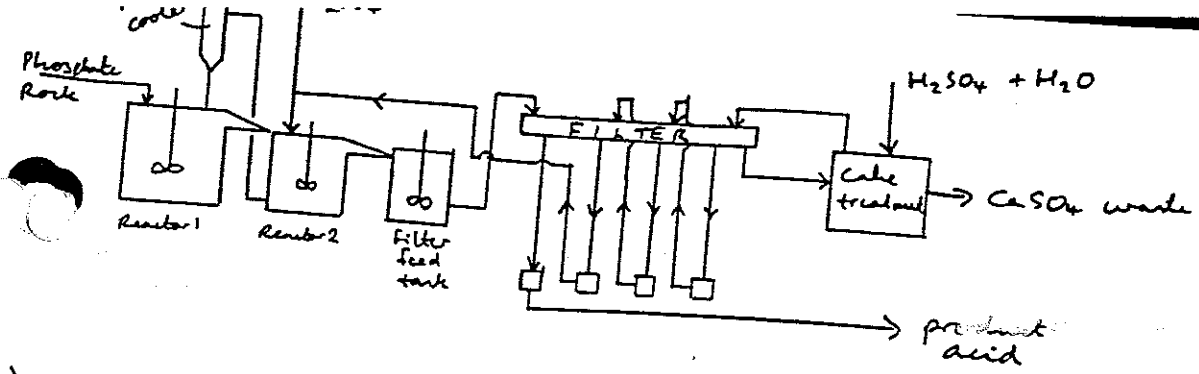
- Converter uses Vanadium catalyst, hiT.

e) HNO_3

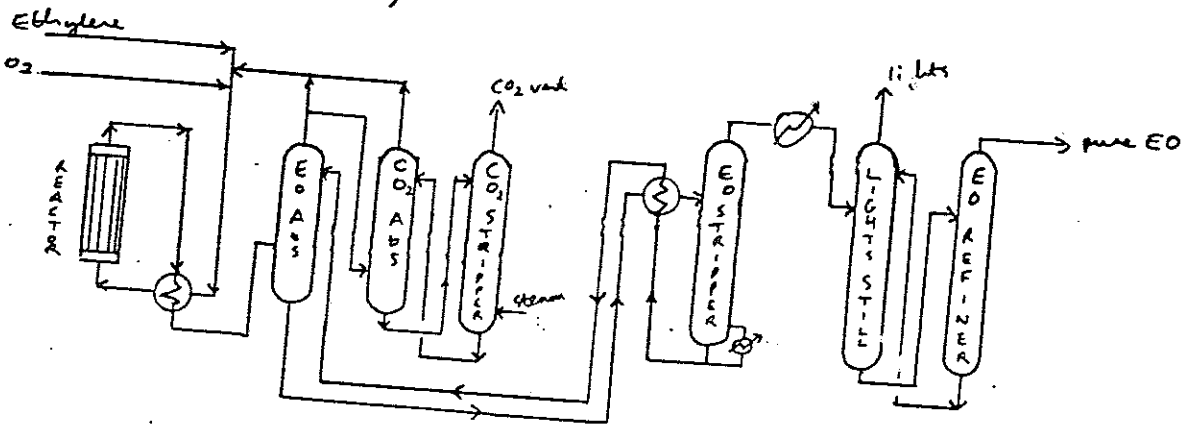
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + \text{heat} \quad (1)\ (\text{Reactor})$$
$$2NO + O_2 \rightarrow 2NO_2 + \text{heat} \quad (2)\ (\text{cooler})$$
$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 + \text{heat} \quad (3)\ (\text{Absorber})$$



- Reactor ~900°C, Platinum Rhodium cat. Hi P.



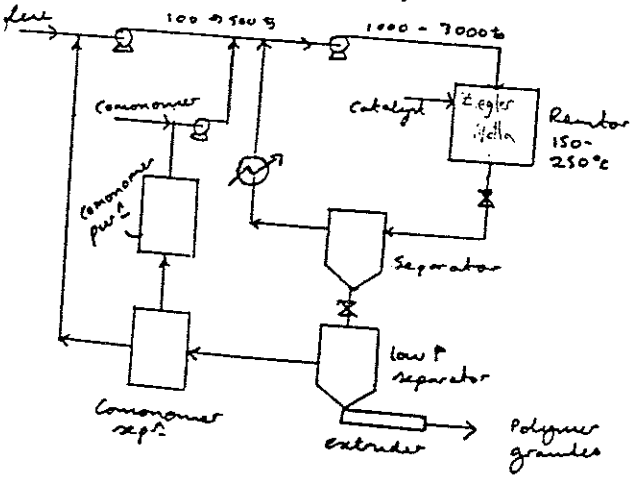
-) Ethylene Oxide (EO)



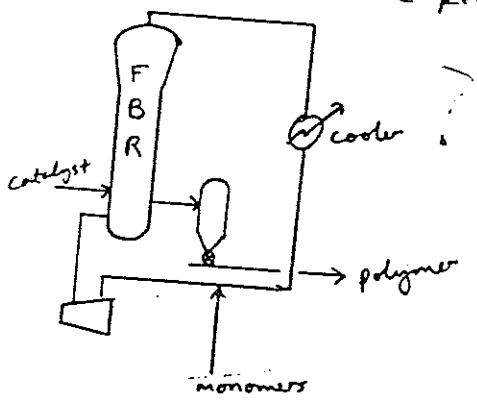
- EO is absorbed in water
- Silver based catalyst (usually proprietary) 200 → 300 °C, 10 → 30 bar

$$CH_2 = CH_2 + \tfrac{1}{2} O_2 \rightarrow CH_2 - CH_2 \quad (O) + \text{heat}$$

LDPE (high P process)



HDPE (BP Chimie process)



Use Ziegler Natta Catalysts for PE. - need to replace catalyst ∴ it remain attached to polymer.

HCN

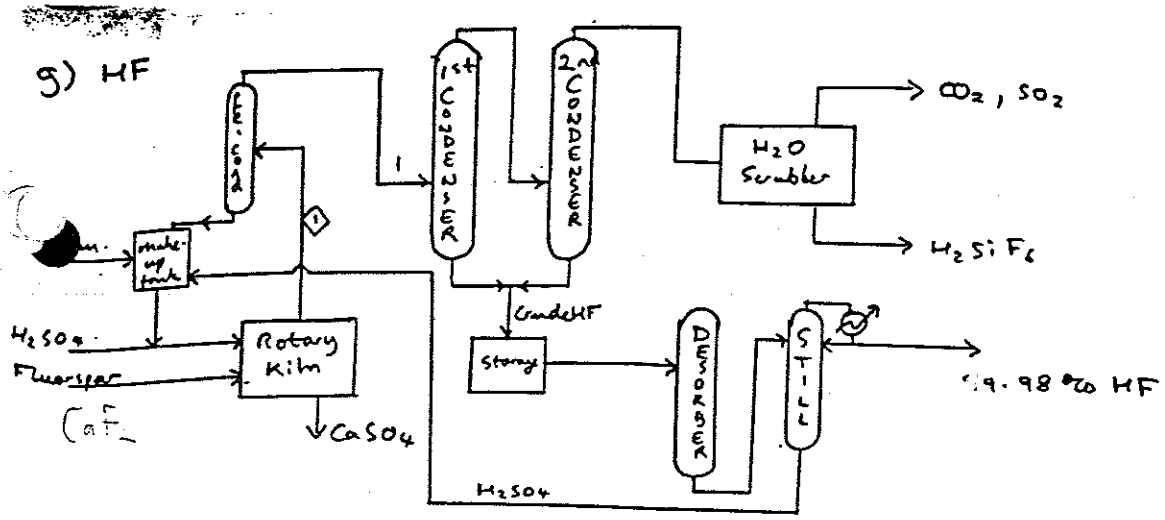
$$CH_4 + NH_3 + \tfrac{3}{2} O_2 \rightarrow HCN + 3H_2O$$

1000 - 1200 °C Platinum / Rhodium catalyst

HCN tends to polymerize in basic conditions ∴ add SO_2

NH_3 is absorbed in monoammonium phosphate

g) HF

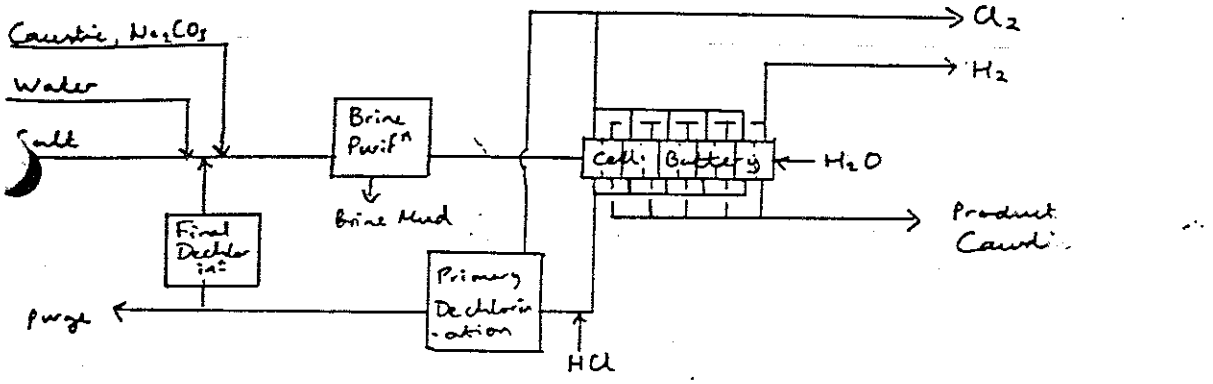


- Stream ① contains HF, H_2O, SO_2, SiF_4, CO_2, H_2SO_4.
- CaF_2 (Fluorspar) is finely ground feed product

$$CaF_2 + H_2SO_4 \Rightarrow CaSO_4 + 2HF \quad \text{endothermic} \quad @\ 200\text{-}250\,^\circ C$$

- mixing is important because of $CaSO_4$ product.
- + byproduct of Phos Acid Prodn

h) NaOH & (i) Cl_2



- Each cell contains a membrane acting as an ion exchange resin to provide resistance to the movement of anions. (Movement of Na^+ carries the electric current)
- In Anolyte $\quad 2Cl^- \rightleftharpoons Cl_2 + 2e^-$
- In Catholyte $\quad H_2O \rightleftharpoons H^+ + OH^-$

$$2H^+ + 2e^- \rightleftharpoons H_2$$

- Cell voltage ~ 3V moderate temperatures

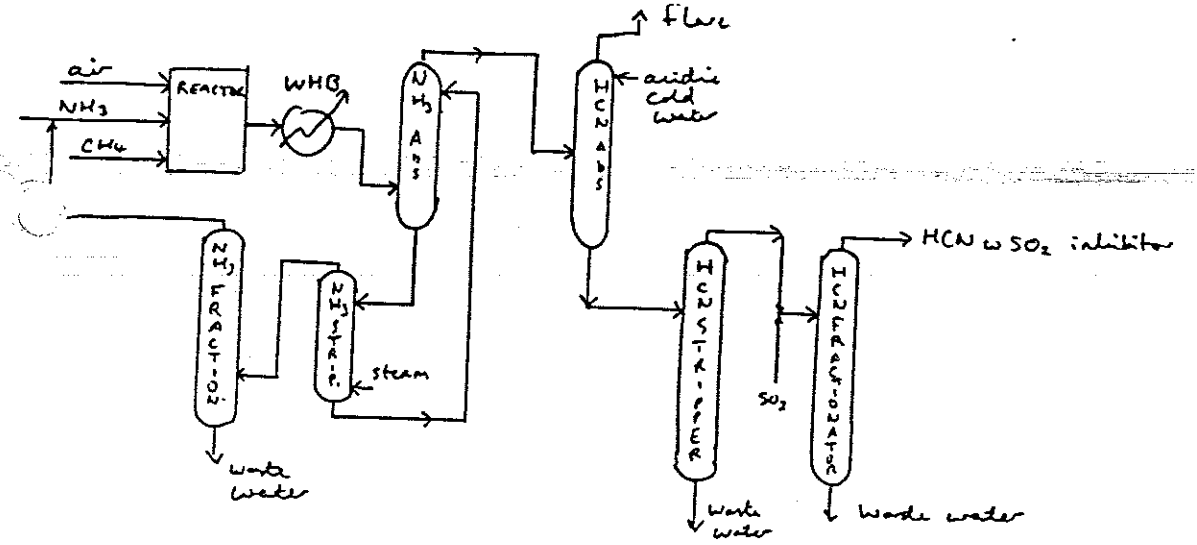
(j) CH_3OH - react products from synthesis gas generator in correct ratio ($CO + 2H_2$) over methanator catalyst (V).

k) H_3PO_4 - 'Wet' process

React phosphate rock with a mixture of H_3PO_4 & H_2SO_4

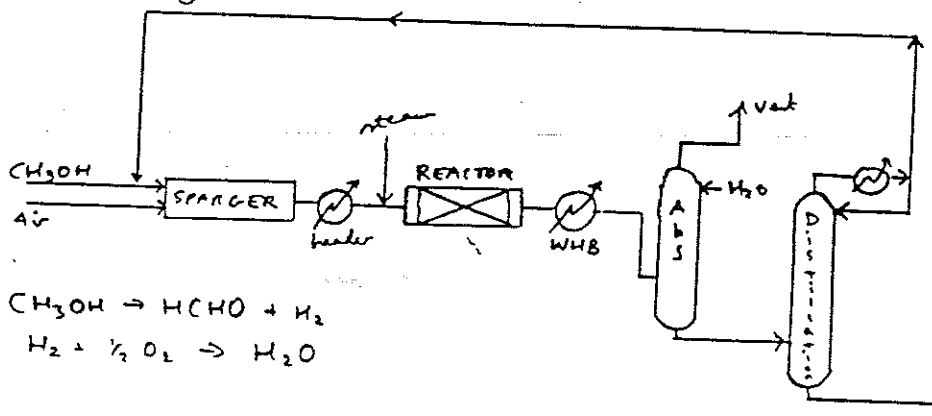
Simplistically

(Phosphate Rock) + H_3PO_4 + H_2SO_4 + H_2O $\Rightarrow$ $CaSO_4$ + HF + H_3PO_4 + $(SiF_4 + H_2SiF_6 + CO_2)$ + H^+



O) Sulphur
- extract naturally from eg. Java
- use recovery from coal eg UCBSRP
- Use recovery from refinery streams eg CLAUS

P) Formaldehyde



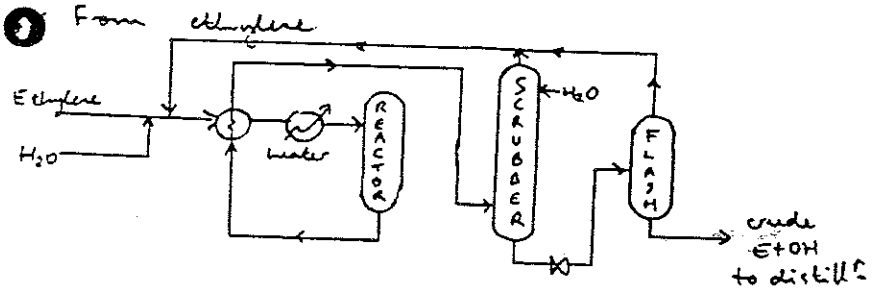
$CH_3OH \rightarrow HCHO + H_2$

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

or Fe/Mb =

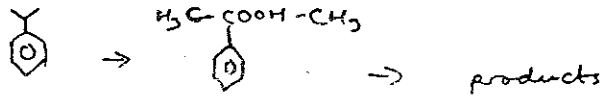
- Reactor uses Ag catalyst
600°C ~ 4 b

) CH_3CH_2OH
- fermentation
- From ethylene



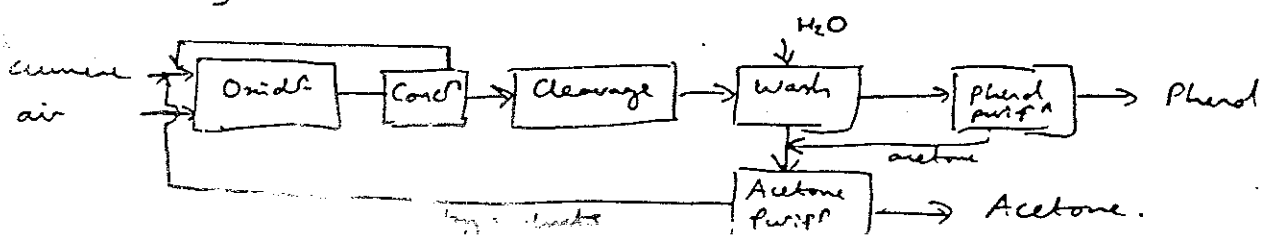
- Scrubber stream can also be put thru' purification to extract organic waste (bleed)
- Reactor 250°C, 70 b ?
Phosphoric acid catalyst suspended on fixed bed

$CH_3\overset{O}{\overset{\|}{C}}CH_3$ +  produced from oxidn of cumene  , hiT, hi P



→ products

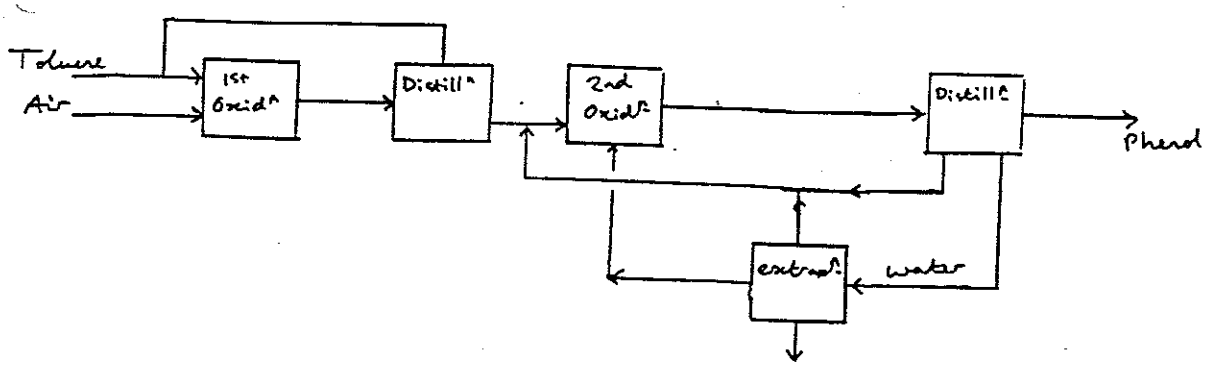
Simplistically:



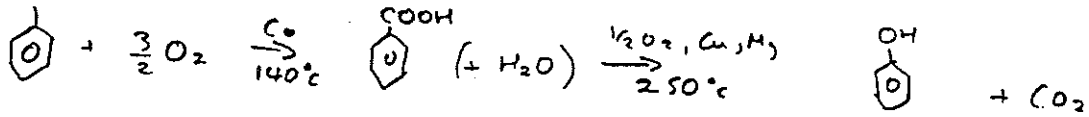
5) benzene · produced from fractionation of petroleum products or coal tar

6) Phenol · Oxidation of cumene (P)

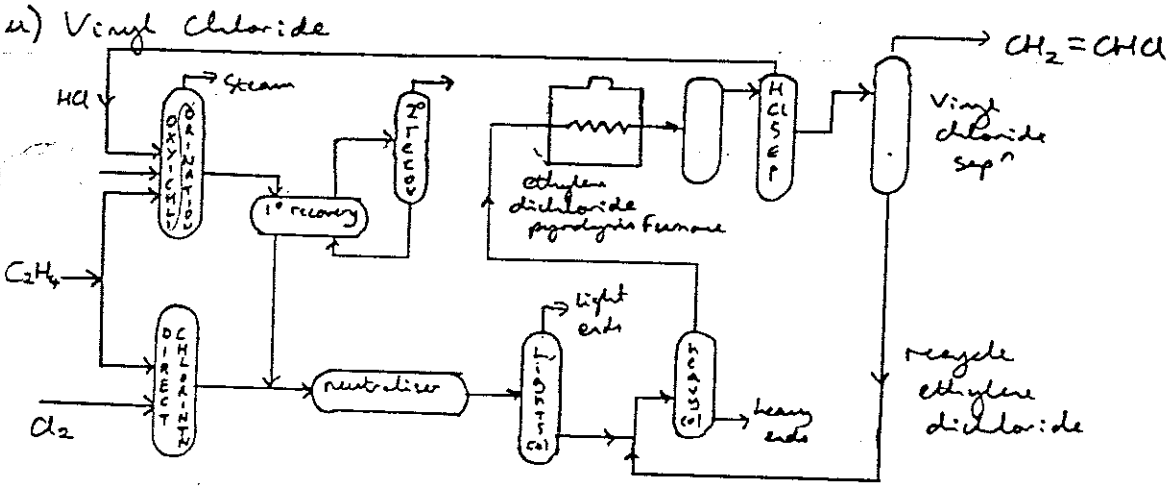
· Oxidation of toluene



· 1st Oxidn liq phase free radical
2nd Oxidn oxydecarboxylation @ 250°C ⊃ Cu Salt as catalyst

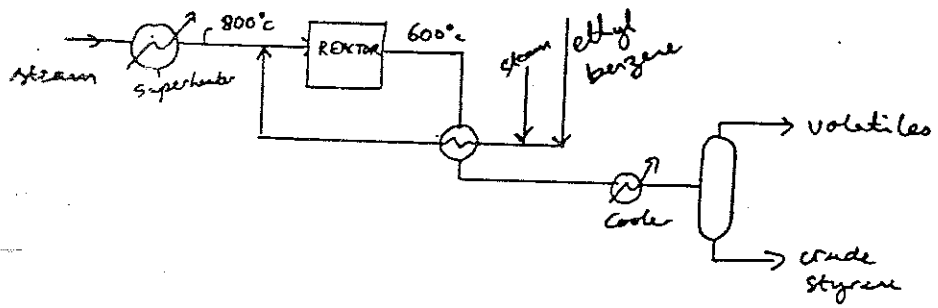


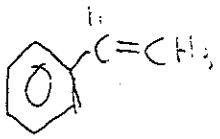
u) Vinyl Chloride



· Direct chlorination $FeCl_3$ cat $T \sim 60°C$
· Oxychlorination $CuCl_2$ cat. $T \sim 230°C$, Fbr., 5 b
· Ethylene dichloride cracking is endothermic, 30 b, 550°C

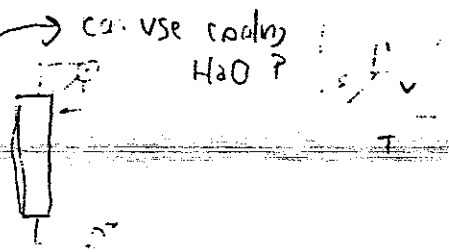
✓) Styrene - adiabatic dehydrogenation of ethyl benzene





② Why is distillation done @ high P?

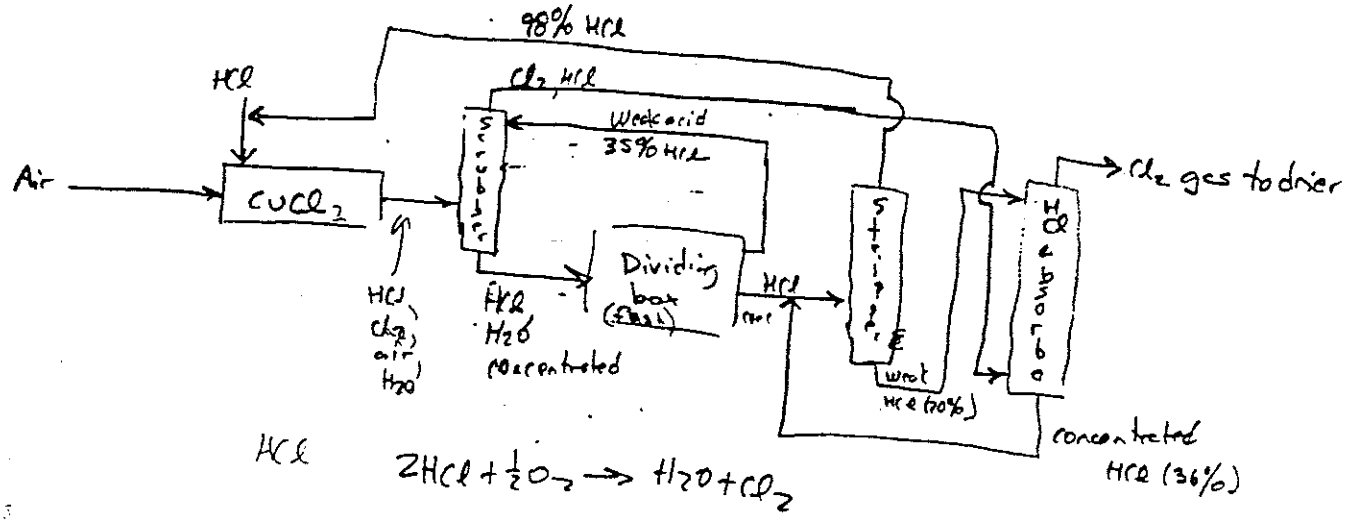
Distillation is done high P to make the condenser load smaller (avoid using refrigeration at condenser) also increases ~~gf~~ vapor density and makes column volume required smaller.



③ How do you dispose of a HCl gas stream and N_2 stream?

To dispose of HCl gas stream, either

- Make use of ~~process for recovery~~ Cl_2 gas - Mix HCl ~~w/~~ Air and Oxidize over $CuCl_2$ catalyst.



HCl $\quad 2HCl + \frac{1}{2}O_2 \rightarrow H_2O + Cl_2$

To dispose of N_2 stream either

- Use cryogenics to purify and sell
- React w/ H_2 to form NH_3
- Vent it

Suction on a pump has larger diameter than outlet. Why?

$$\frac{P_1}{\rho} + \frac{V_1^2}{2} - W_s = \frac{P_2}{\rho} + \frac{V_2^2}{2} + \text{loss}$$

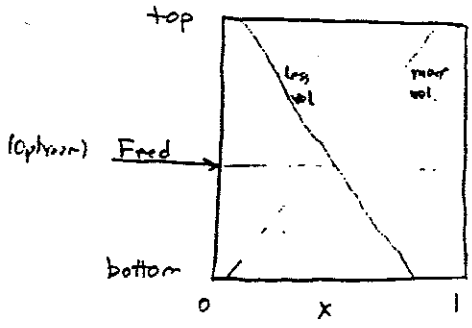
$$\underbrace{\frac{P_2 - P_1}{\rho}}_{+} = \frac{V_1^2 - V_2^2}{2} \underbrace{- W_s}_{+}$$

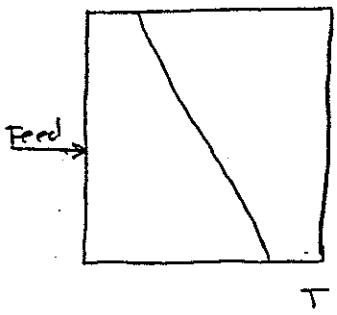
don't want P_1 to be too low or liq will vap if $P_1 < P_{bubble}$

$\therefore V_1^2 - V_2^2 < 0 \quad V \propto \frac{1}{A}$

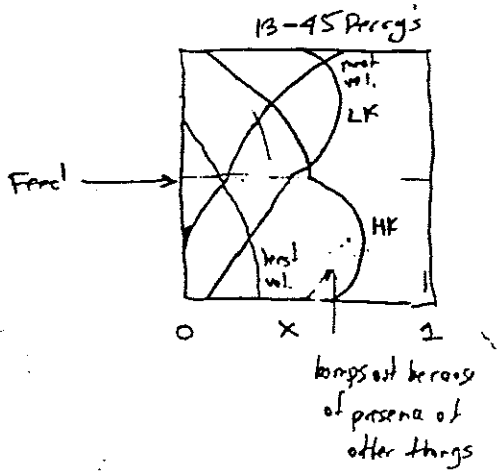
⑤ Typical temp & conc'n profiles in distillation column.

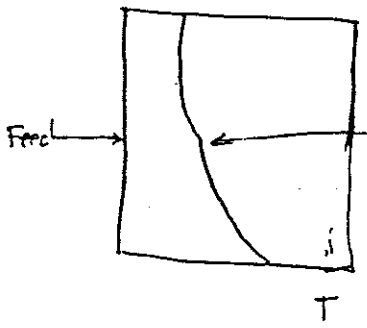
Binary Distillation

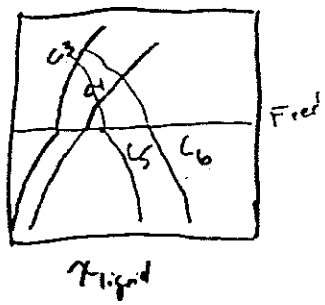




multicomponent





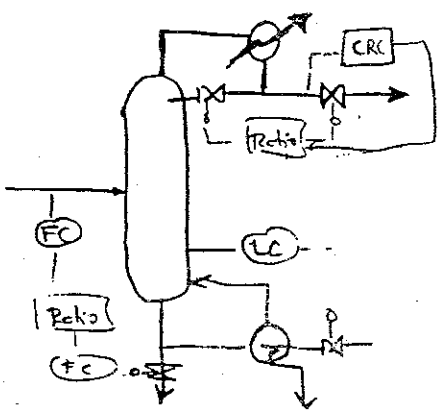


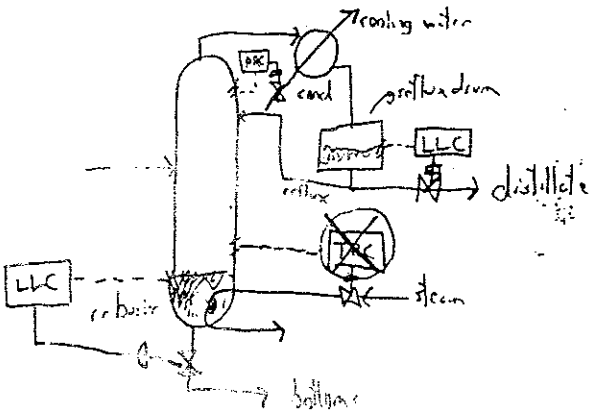
⑥ How to remove 1% phenol from water?

- Adsorb w/ activated carbon
- LLE w/ some solvent such as Benzene or Isoamyl Acetate ?
  - liq/liq extraction

⑦ Distillation control

- Composition by reflux and boilup
- Flow of product must equal feed - i.e. little surge capacity





Process

- Hydrogen Gas Production. $C_3H_8 + 3H_2O = 3CO + 7H_2$

  propane + water $C_3H_8 + 6H_2O = 3CO_2 + 10H_2$

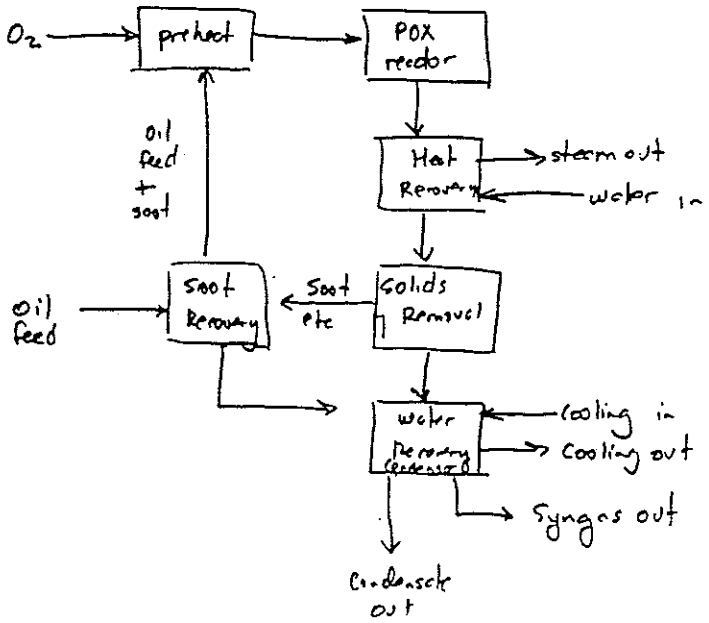
(8) Synthesis Gas Production

$O_2 + fuel \rightarrow CO + H_2$

Equilibrium rxn is water/gas shift

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Temperature of rxn determines distribution of products



(11) What is bleach. How made.

Bleech is super-oxidizing mixture of ~~sodium~~ and calcium hypochlorites mfg: $NaOH + Cl_2 \rightarrow NaOCl + HCl$

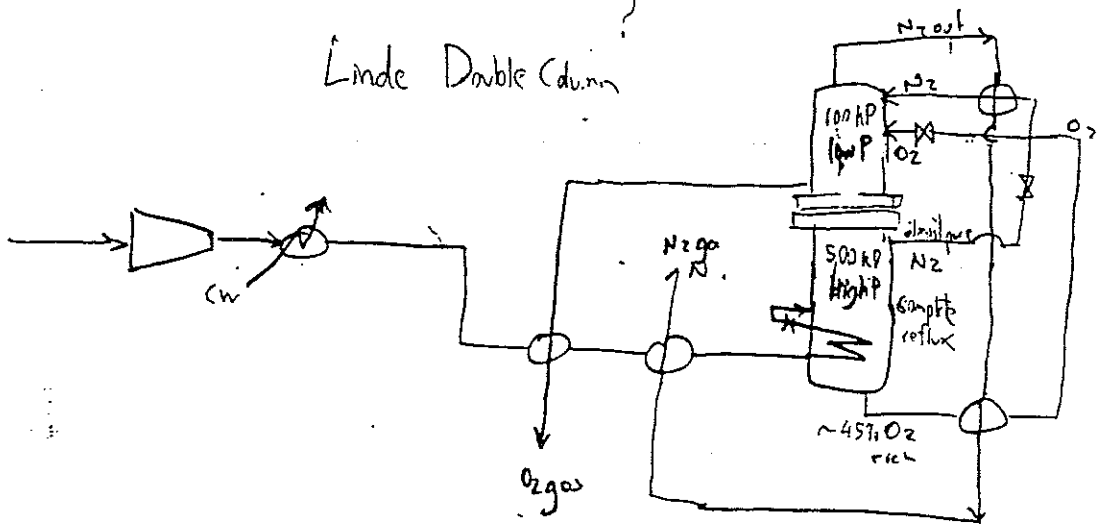
$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 \cdot H_2O$ ↓T

Pass Cl_2 over solid NaOH & $Ca(OH)_2$ in a solid gas reactor (rotating cylinder w/ lifting blades) @ 50°C

(12) Two organics w/ similar melting & boiling pts.

- LL Extraction. using solvent which preferentially absorbs one.
- Extractive distillation using a (MSA) which forms azeotrope.

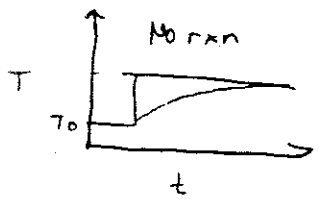
(13) Linde Double Column



(14) How cool room using 120°F water w/ $T_{amb} = 100°F$.

Want to use a refrigerator extracting heat from room and rejecting it to the hotter H_2O. Could reduce pressure of H_2O which would allow it to vaporize @ less than 100°F, or could use a cooling tower to reach $T_w < T$ for $H_R < 100\%$ and then use it to cool

(15) Exothermic 0th order rxn in CSTR. Step change increase in feed T.



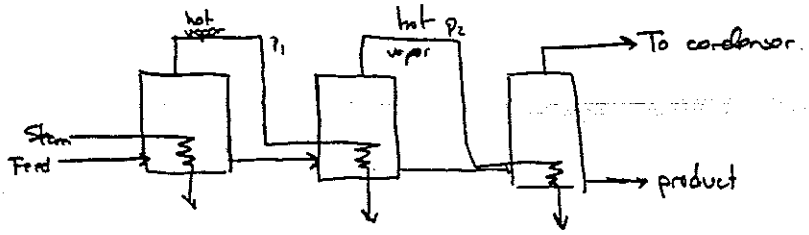
For rxn $QC_p T_0 = QC_p T + r(-\Delta H)V$

Exothermic ⇒ $T > T_0$ due to R term.

If To increases to T, R will also increase due to Arrhenius, so will get higher temp rise

multiple Effect Evaporation

(16)



Used for economizing energy consumption.
steam economy gain @ expense of capital cost.

Used for desalination

should produce almost 2 lb vapor for each lb steam consumed in 1st stage if feed is preheated.

$P_1 > P_2 > ?$
$T_1 > T_2 > ?$

(2nd evaporator should be operated at lower Pressure than the 1st so that a positive value of $(-\Delta T)$ is achieved across the steam-chest surface of the 2nd evaporator.

Latent heat will increase w/ decreasing pressure, so efficiency drops in later stages.

Air Conditioning – controls temperature, humidity, cleanliness, distribution.

Consists of a fan unit which forces fresh outdoor air and room air through devices which clean, change temperature, and change humidity of the air. Heating coil and humidifier may be used to provide winter humidification.

Cooling: Either water or direct expansion refrigerant coils,
Heating: Steam or hot water coils
Humidification: target type water nozzles, pan humidifiers, steam humidifiers, air washers, or sprayed coils.
Cleaning: disposable filters.

See pg 12-25 Perry's. Cycle?

Drying Agents

Capacity & Efficiency

Mechanisms

1. Chemical Rxn
   a. Formation of new compd. eg $CaO + H_2O \rightarrow Ca(OH)_2$, $P_2O_5 + H_2O \rightarrow 2HPO_3$
   b. Formation of hydrate $CaCl_2 + H_2O \rightarrow CaCl_2 \cdot 2H_2O$
2. Physical absorption, constant relative humidity
   (solid + water = saturated soln)
3. Physical absorption, variable rel. humidity
   (a solution or liquid = dilute d soln)
4. Adsorption

Regeneration - Temp. is raised and system is adjusted by vacuum or by a purge until the vapor pressure of the water in equilibrium w/ the drying agent is greater than that of the surrounding atmosphere.

Pressure Vessels – Safety key consideration

1) Decide size and shape as required by function
2) Decide materials of construction to resist chemical attack
3) Provisions for heat transfer & temp. control should be worked at.
4) Safe thickness of vessel wall and other parts and attachments should be calculated based on stresses in vessel wall and tensile strength of materials of construction.
5) Method of fabrication
6) Types of closures

Materials of Construction – High strength weldable steel.

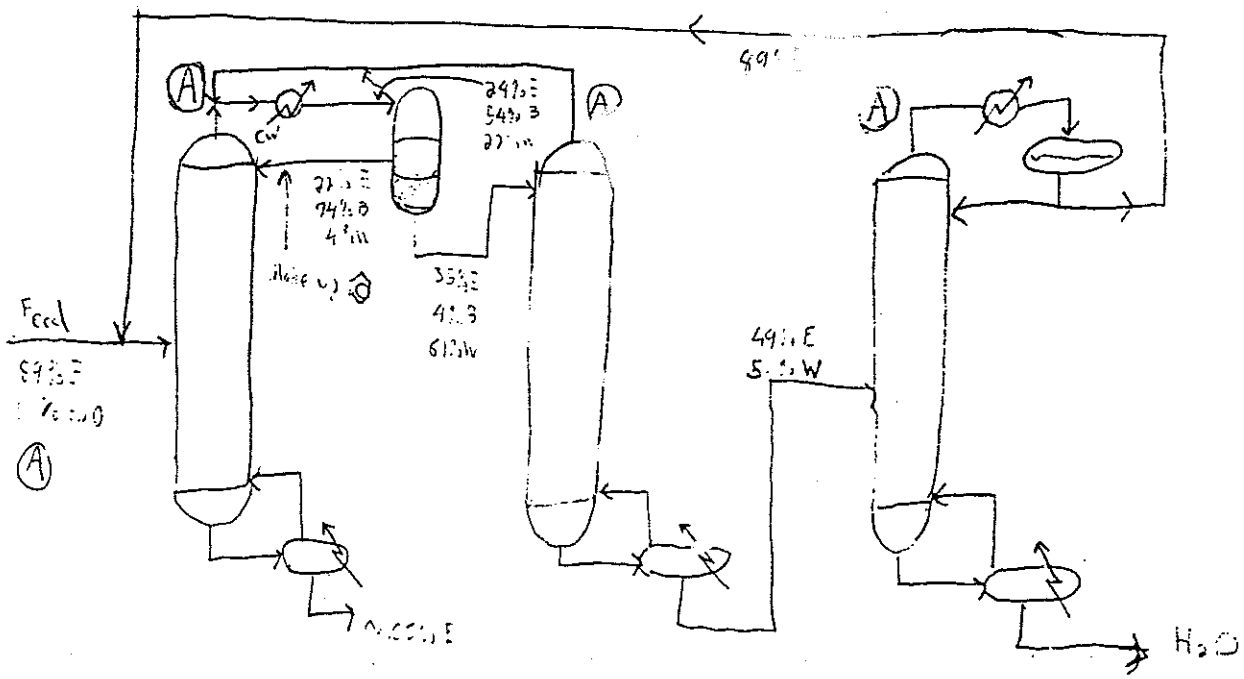
Multilayers often used w/ only inner & outer shell made of high most corrosion-resisting material.

Must be coded and meet all ASME standards

Safety factor of 3 -3.5 based on ultimate strength.

$$t = \frac{(\text{Pressure})(\text{inside radius})}{(\text{Stress allowed})(\text{Welding efficiency}) - 0.6P}$$

17) Separate ethanol & water (King p 346)



A → azeotrope

Benzene Entrainer

(30)

Heat Pump

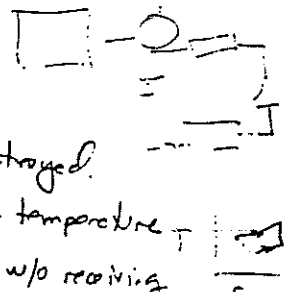
Year-round heating and cooling

Summer — Cooling season: Evaporator of standard refrigeration system removes heat from supply air to conditioned space and dispels it through the condenser to outside air or water.

Winter — Heating season: Cycle is reversed. Evaporator removes heat from outdoor air, water, or preferably from a higher temperature source such as process exhaust air stream. The heat is then 'pumped' to the condenser which provides the heat to the air supply to the conditioned space.

E/E

Refrigeration



Rooted in 1st & 2nd laws of Thermo.

1) Energy may be neither created nor destroyed.
2) No system can receive heat at a given temperature and reject it at higher temperature w/o receiving work from the surroundings.

Ideal refrigeration cycle is reverse Carnot Cycle.

$$\text{coefficient of performance} = \frac{T_1}{T_2 - T_1}$$

where T_1 = evaporator temperature
T_2 = condensing temperature

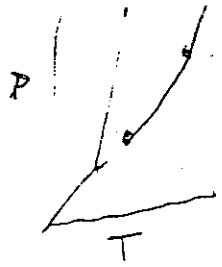
Refrigerants – Liquids w/ low boiling points are used in mechanical refrigeration.

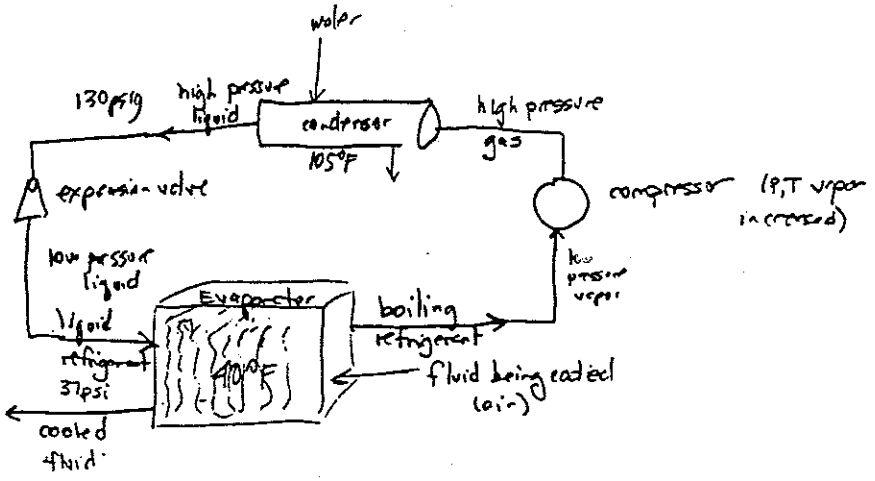
Primary refrigerants – liquids that change from liquid to gas after absorbing heat.

Secondary refrigerants – Only act as heat carriers (brine, air, water

Refrigeration – (Cont'd)

Single-stage vapor compression refrigeration cycle





Flow Meters – Application of Conservation of Energy

Usually based on relating measured pressure drop to flow.

Pressure drop brought about by changes in kinetic energy, by skin friction, or by form friction.

General meter equation

Cons. Energy. – Constant Density, w/ $\Delta z = 0$, $W_f = 0$, $Q = 0$

$$V(P_2 - P_1) + \frac{\bar{V}_2^2 - \bar{V}_1^2}{2g_c\alpha} + \Sigma F = 0$$

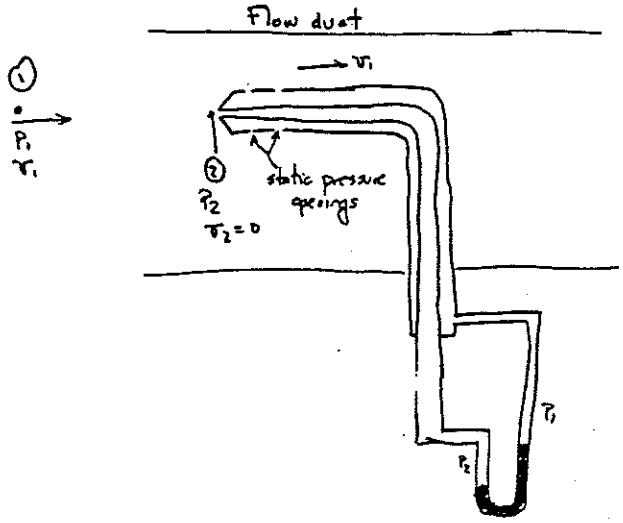
Continuity $\rho_1 \bar{V}_1 A_1 = \rho_2 \bar{V}_2 A_2$

$$\rho_1 = \rho_2$$

$$V_2 = \frac{\bar{V}_1 A_1}{A_2}$$

$$\Rightarrow \bar{V}_1 = \sqrt{\frac{2g_c\left[\left(\frac{-\Delta P}{\rho}\right) - \Sigma F\right]}{\left(\frac{A_1^2}{A_2^2} - 1\right)}}$$

Pitot Tube - Measures Point Velocity



$v_2 = 0$, so $(V_1)^2 = 2g_c\left[\left(-\frac{\Delta P}{\rho} - \Sigma F\right)\right]$

$$-\frac{\Delta P}{\rho} - \Sigma F = c_1^2\left(-\frac{\Delta P}{\rho}\right)$$

$$\Rightarrow V_1 = c_p\sqrt{2g_c\left(-\frac{\Delta P}{\rho}\right)}$$

usually $c_p \sim 1$

$\Rightarrow$ Frictional losses between ① & ② are very small and the pressure drop measured by the pitot tube is attributable only to the kinetic energy change

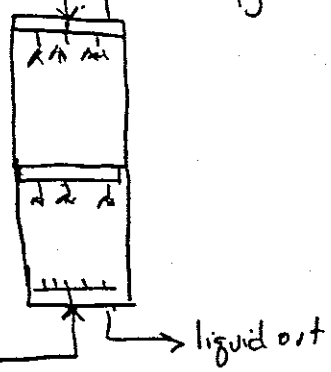
$\Rightarrow \Delta P \propto \frac{1}{2} m v^2 \propto \frac{1}{2}\rho V v^2$

$\Rightarrow v^2 \propto \frac{2\Delta P}{\rho}$

$$v \propto \sqrt{\frac{2\Delta P}{\rho}}$$

$$v = c_p\sqrt{2g_c\left(-\frac{\Delta P}{\rho}\right)}$$

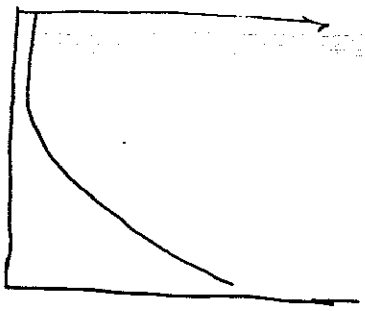
(26) SO_2 absorber absorbent → cleanses



what's the absorbent?

gas in (SO_2)

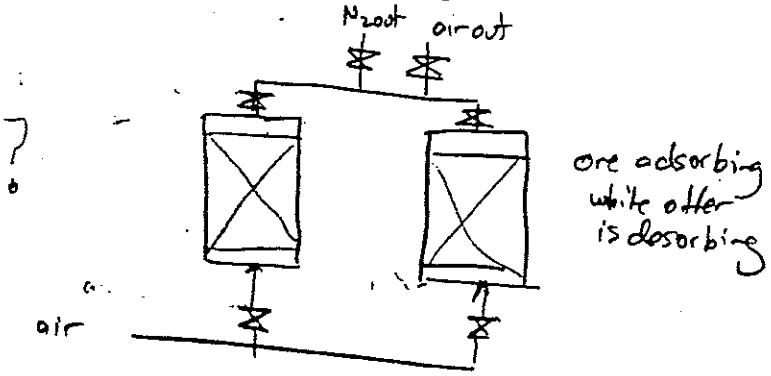
→ liquid out



conc. SO_2 in liquid or gas

(27) Pure N_2 from air w/o cryogenics

Pressure-swing adsorption



- zeolites preferentially adsorb N_2

- Could burn H_2 in air and condense out H_2O
- Burn CH_4 in air, absorb CO_2 w/ (MEA), and condense out H_2O
- Can't get pure N_2 w/ air w/o cryogenics 'cause you can't get Ar out.

(28) Separation of multicmpt liquids

M Choose methods
- favor distillation
- if MSA used, remove it in next sep
- Avoid vacuum and refrigerated distillation
- Avoid excursions in T, P if possible

D Choose design — separations sequence
- Identify forbidden splits
- Simplify

S Species dependent
- Remove corrosive & hazardous cmpts 1st.
- Perform hardest sep's last
- (w/o presence of nonkeys).

C Composition dependent
- Remove most plentiful cmpts 1st to reduce volume
- Favor 50/50 splits where possible

Treatment of wastes

1) Gases: Solids removal - cyclone
- electrostatic precipitation
— Activated carbon for removal of solvent vapors.

2) Liquids - Solids removal - filtration
- centrifugation
- gravity settling
- Liquid phase activated carbon - phenol removed from H_2O by passing thru activated carbon bed.
- Ion exchange for removal of inorganic salts
Sodium zeolite, exchanges sodium ion for calcium or magnesium ion in water.
Used for removal of metal ions in plating wastes.

Disposal of wastes

1) Gases - High temp. incineration - hydrogen cyanide
hydrogen sulfide
CO, H_2
Hydrogen sulfide incineration produces SO_2, which must be scrubbed (eg, w/ MEA) before release.
Thermal incineration - for waste gases containing small (~~<25%~~) amounts of organic materials at $\leq 25\%$ of the lower combustible limit.
Auxiliary fuel is burned to heat organic above autoignition temp
1000 - 1500°F.

Absorption Methods SO_2 from burning fossil fuels

2) Liquid Wastes - Combustion - benzene, toluene, alcohol, acetone, still bottoms
Organic compds containing chlorine can't be incinerated, must be scrubbed (eg, w/ caustic).

(32) Give expression for { reversible heat / irreversible heat / net work } in electrochemical cell.

- net electrical work by cell emf: When charge q moves spontaneously through ΔP of $\mathcal{E}$ volts, the external electrical work which can be done on the surroundings is $w_{ext} = q\mathcal{E}$

$\therefore \Delta H = q - w_{ext}$

$\Delta G = q - T\Delta S - w_{ext} = -w_{ext}$

$\Delta S = \frac{q}{T}$ or $T\Delta S = q$

$\Rightarrow \Delta G = -w_{ext} = -q\mathcal{E}$

For one electron rolling through a potential inverse of $\mathcal{E}$,

$$\Delta G = -e\mathcal{E}$$

For a mole of electrons, $\Delta G = -Ne\mathcal{E} = -\mathcal{F}\mathcal{E}$

In a reaction w/ n electrons per molecule of reaction.

$$\Delta G = -n\mathcal{F}\mathcal{E}$$

Reversible heat

$$\Delta H = \Delta G + T\Delta S = \Delta G - T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

$$= nF\left[T\frac{\partial \mathcal{E}}{\partial T} - \mathcal{E}\right]$$

Non reversible heat:

$$\Delta G = \Delta G^\circ + RT\ln K_a$$

$$-nF\mathcal{E} = -nF\mathcal{E}^\circ + RT\ln K_a$$

Process Design

Peters & Timmerhaus

$Q_r = -211{,}500$ BTU/h heat of reaction to be removed

Calculate mass of cooling water $Q_r = mC_p\Delta T$, Assume 10°F temp. difference

$$m = \frac{Q_r}{C_p \Delta T}$$

Heat Transfer area required to cool reactor

$$Q = UA\Delta T_{lm}$$

$$A = \frac{Q}{U\Delta T_{lm}} \qquad U = 45 \frac{BTU}{h\text{-}ft^2\text{-}°F}$$

(22)

Cooling Tower - Evaporative cooling

Water usually cooled by exposing it's surface to air.

Heat transfer process - 1) Latent heat transfer owing to vaporization of small portion of the water. (80%)

2) Sensible heat transfer owing to temperature difference of water and air. (20%)

- Theoretical possible heat removal depends on moisture content and temperature of the air. Indication of air moisture content is the wet bulb temperature. Ideally, the wet-bulb temperature is the lowest theoretical temperature to which the water can be cooled.

Psychrometry

Absolute humidity, $H = \frac{\text{lbs water vapor}}{\text{lb dry air}} = \frac{M_w P_w}{M_a (P - P_w)}$ P = total pressure, P_w = partial pressure of water vapor

Saturation humidity, H_s = when partial pressure of water vapor in the air (p) equals the vapor pressure of water (p_s) @ the same temperature, the air is saturated.

$$\% \text{ relative humidity} = \frac{p_i}{p_s}(100) = \frac{\text{partial pressure of water in air}}{\text{vapor pressure of water}} \text{ @ given } T$$

Dew Point or Saturation Temp = temperature at which a given mixture of water vapor and air is saturated, ie, temp. at which water exerts a vapor pressure equal to its partial pressure in air.

wet bulb temperature - Dynamic equilibrium temperature attained by a water surface when the rate of heat transfer to the surface by convection equals the rate of mass transfer away from the surface

Heat balance at surface @ equilibrium $k_g\lambda(p_s - p) = h_c(t - t_{wb})$

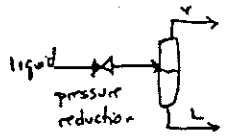
λ = latent heat of vaporization
P_s = vapor pressure of water at the wet bulb temperature
p = partial pressure of water in environment
h_c = heat transfer coefficient
t = temperature of air/water vapor mixture
t_{wb} = wet bulb temperature.

Can be written $H_s - H = \dfrac{h_c(t - t_{wb})}{k'\lambda}$ when P_s, p small relative to P

where $k' = \left(\dfrac{M_a}{m_w}\right) k_g$

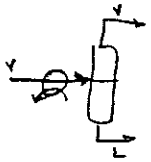
Interphase Mass Transfer Operations

1) Flash vaporization – used when species to be separated differ widely in their tendency to vaporize. Liquid feed is partially vaporized by reducing the pressure (eg, with a valve)



Recovery of water from seawater

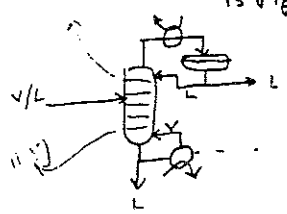
2) Partial condensation – used when species to be separated differ widely in tendency to condense. Vapor feed partially condensed by removing heat.



Recovery of H_2 and N_2 from NH_3 by partial condensation and high pressure phase separation. ?

(Often used distillation to refine products of 1, 2)

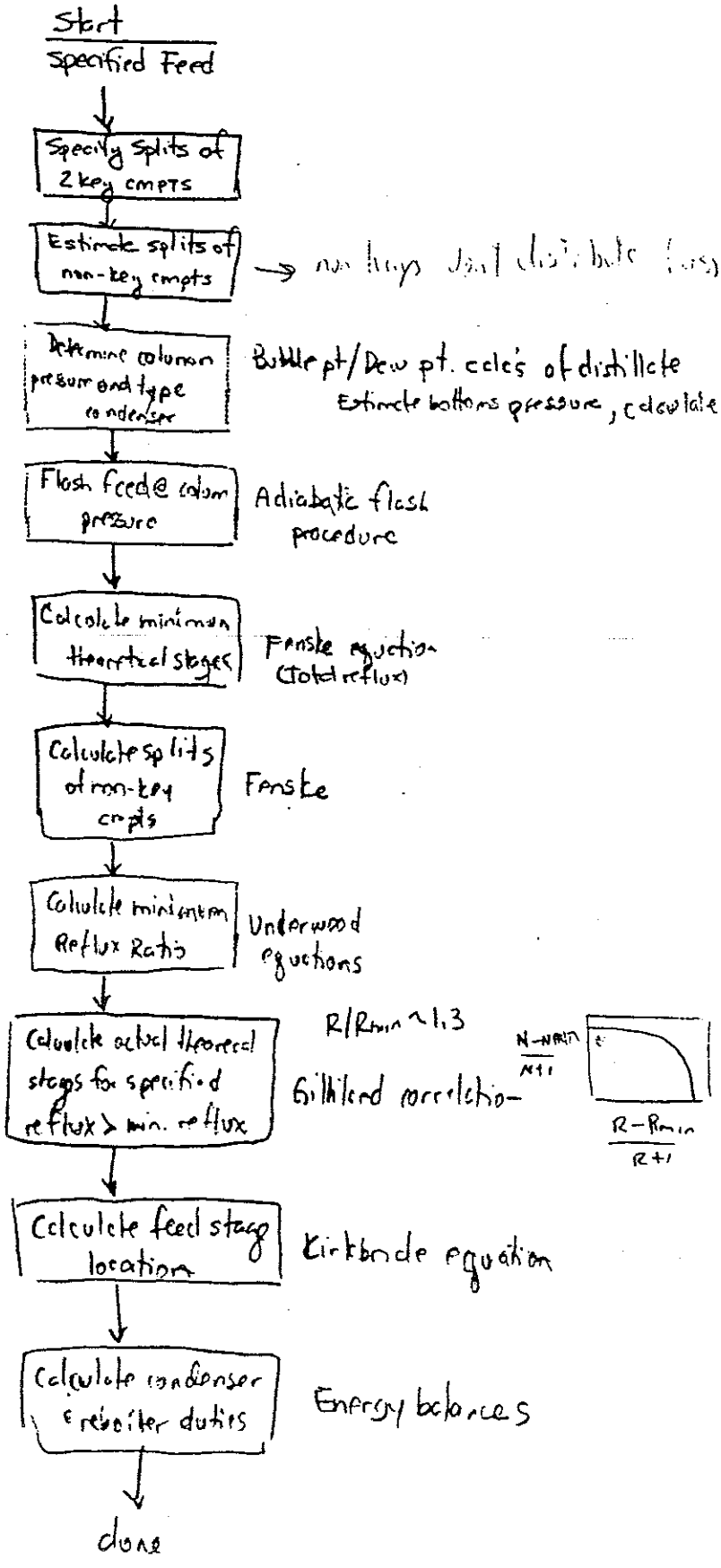
3) Distillation – multiple contacts between L and V phases. Each contact involves mixing the 2 phases for partitioning and phase separation
Vapor is continuously enriched w/ respect to more volatile species as it travels up, and vice versa for liquid as it travels down.
Above feed is enriching section and below feed is stripping section.
– Liquid is required for making contact w/ vapor above feed tray – vapor from top of column is condensed to provide contacting liquid called reflux similar liquid @ bottom is vaporized to provide boilup



Distill gasoline to remove isobutane and low MW hydrocarbons

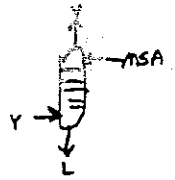
Multicomponent Distillation

Empirical (Fenske-Underwood-Gilliland)



4) Absorption – If feed is vapor and stripping section is not needed, a MSA is added to the top. Frequently done @ ambient temp and high pressure. Constituents of vapor feed dissolve in the absorbant to varying extents depending on their solubility

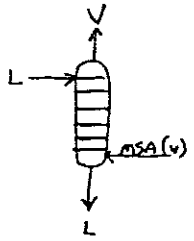
Gas feed



Separation of CO_2 from combustion products by absorption with aqueous ethanolamine.

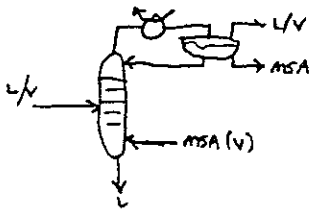
5) Stripping – A liquid mixture is separated (generally at ambient pressure and elevated temperature) by contacting liquid feed with an MSA called a stripping vapor. The MSA eliminates the need to reboil the liquid at the bottom of the column

L.q feed



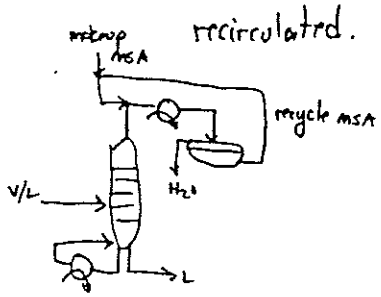
Steam stripping of naptha, kerosene, and gas oil side cuts from a crude distillation unit to remove light ends

If contacting trays above the feed tray are needed, use reflux stripping (steam distillation)



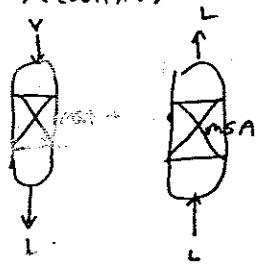
6) Azeotropic Distillation – when fractional distillation not feasible

Eg, want to separate acetic acid from water. n-butyl acetate, which forms a heterogeneous minimum boiling azeotrope w/ water, is used to facilitate the separation of acetic acid from water. The azeotrope is taken overhead, the acetate and water layers are decanted, and the MSA is recirculated.



7) Adsorption - Remove cmpts. present in low concentrations.

Adsorbents activated carbon, aluminum oxide, silica gel, molecular sieves (zeolites)



regenerated by passing hot gas,

pressure cycle (desorption by decompression)

purge gas cycle (desorption by partial pressure lowering)

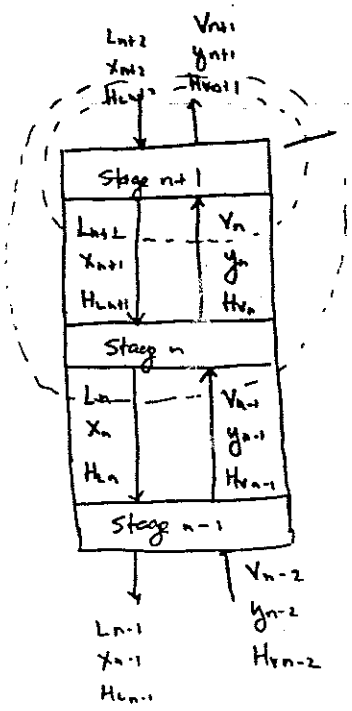
Removal of water from air by adsorption on activated alumina

8) Drying - Removal of liquid from solid by evaporation of the liquid.

Vapor pressure of liquid must be greater than its partial pressure in the gas stream

9) Ion-exchange - Eg, water softening, an organic or inorganic polymer in its sodium form removes calcium ions by exchange calcium for sodium

McCabe-Thiele Method



Mass balance about stage n+1

$$L_{n+2}x_{n+2} + V_n y_n = L_{n+1}x_{n+1} + V_{n+1}y_{n+1}$$

$$(1) \quad \text{or} \quad y_n = \frac{L_{n+1}}{V_n}x_{n+1} + \frac{V_{n+1}y_{n+1} - L_{n+2}x_{n+1}}{V_n}$$

Mass balance about stage n & n+1

$$L_{n+2}x_{n+2} + V_{n-1}y_{n-1} = V_{n+1}y_{n+1} + L_n x_n$$

$$(2) \Rightarrow y_{n-1} = \frac{L_n}{V_{n-1}}x_n + \frac{V_{n+1}y_{n+1} - L_{n+2}x_{n+1}}{V_{n-1}}$$

(1) and (2) can be used to locate points (y_n, x_{n+1}) and (y_{n-1}, x_n) and others on the x-y diagram. The line passing through these points is the operating line, which relates all passing streams.

If the ratio of phase flows is constant throughout the section of stages, then $L/V = L_{n+1}/V_n = L_n/V_{n-1}$ etc, and the slopes of all lines defined by (1) and (2) are identical. Further, if V & L are constant, all passing streams in the column lie on the same straight operating line of slope L/V, which may be drawn if we know either

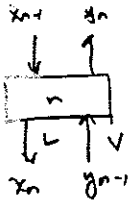
1) The concentration for only one set of passing streams and L/V (Given L/V and inlet & outlet compositions at one end, calculate the inlet and outlet compositions at the other end and the # of stages.)

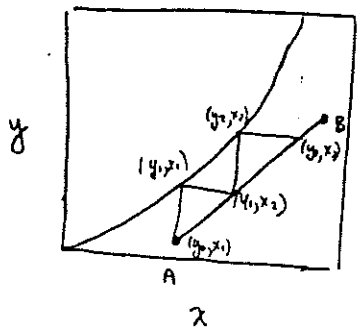
2) The concentration of any two pairs of passing streams (Given inlet & outlet concentrations, calculate L/V and the # of stages)

If we assume L-d V are constant, then eqtn 1 & 2 gives

$$y_n - y_{n-1} = \frac{L}{V}(x_{n+1} - x_n) + 0$$

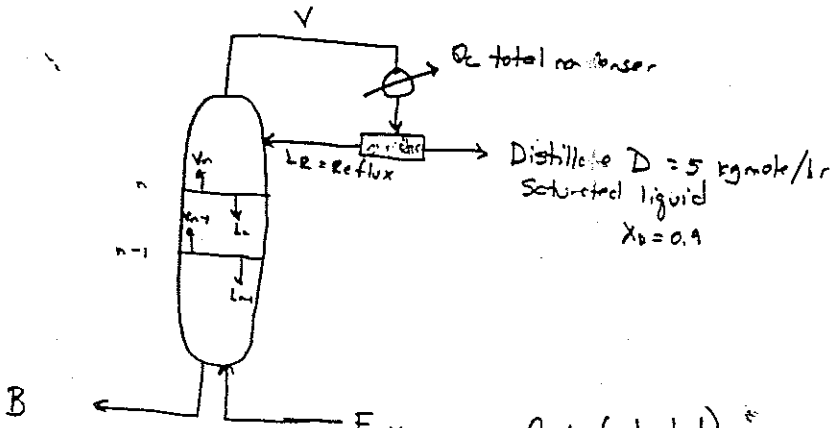
or $$\boxed{\frac{y_n - y_{n-1}}{x_{n+1} - x_n} = \frac{L}{V}}$$





stages = # points on equilibrium curve

Application to Binary Rectification



Internal Reflux Ratio $= \frac{L_n}{V_n}$

External Reflux Ratio $= \frac{L_R}{D}$

Overall Mass Balance $F = D + B$

$40 = 5 + B$, $B = 35$ kgmole/hr

Hexane Material Balance $x_D D + x_B B = y_F F$

$(0.9)(5) + x_B(35) = (0.2)(40)$

$\Rightarrow x_B = 0.1$

Overall Enthalpy Balance

Q_c = heat removed in condenser J
H = enthalpy J/kgmole

$\Rightarrow F H_F = B H_B + D H_D + Q_c$

Dew & Bubble Pt calculations are necessary to determine stream temp's before determining enthalpies $\Rightarrow Q_c$ can be calculated.

Enthalpy Balance around condenser & divider

$$V_n H_n = L_R H_R + D H_D + Q_c \quad (3)$$

$$\text{w/ } V_n = L_R + D \quad (4)$$

Total condenser $\Rightarrow y_n = x_B$, Reflux is saturated $\Rightarrow T_D$ can be calculated by a bubble pt. on D, and $H_R = H_D$ are fixed.

Then T_n is obtained by a dew pt. on V_n, which establishes H_{V_n}.

Then (3) and (4) can be solved for L_R and V_n

Stage to Stage Calculations

a) Total material balance
b) Benzene material balance
c) Phase equilibrium relationship
d) Enthalpy balance

Major simplification: if $L_R = L_n = L$ = constant

$V_n = V_{n-1} = V$ = constant, then it is possible to dispense w/ one equation per stage, namely the enthalpy balance.

This is called the constant molal overflow assumption

This is valid if 1) The heats of vaporization of both species of the binary system are equal

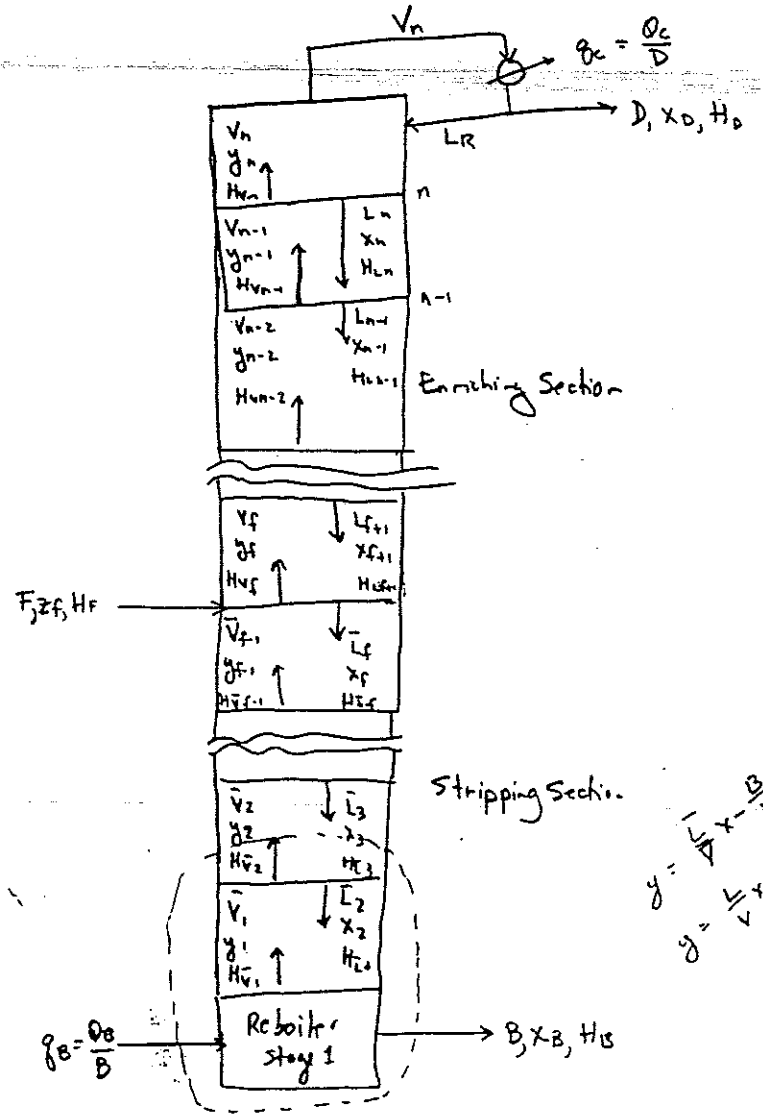
2) Heats of mixing, stage heat losses, and sensible heat changes of both vapor and liquid are negligible.

The result is that every mole of condensing vapor vaporizes exactly 1 mole of liquid. Since it is the molar latent heats which are assumed equal, the flows must be specified in terms of moles and concentrations in terms of mole fractions.

Enriching (rectifying): $L < V$

Stripping $(L > V)$

Binary Distillation - More complicated case



Reboiler Total: $\bar{L}_3 = \bar{V}_2 + B$ Stripping operating line from reboiler cmpt. balance.

Cmpt: $\bar{L}_3 x_3 = \bar{V}_2 y_2 + B x_B$

$$\Rightarrow y_2 = \frac{\bar{L}_3 x_3 - B x_B}{\bar{V}_2} = \frac{\bar{L}}{\bar{V}} x_3 - \frac{B}{\bar{V}} x_B$$ ← Stripping operating line

Enthalpy: $\bar{L}_3 H_{\bar{L}3} = \bar{V}_2 H_{\bar{V}2} + B H_B - B q_B$

Generalized Stripping operating line

$$y = \frac{\bar{L}}{\bar{V}} x - \frac{B}{\bar{V}} x_B \quad (A)$$

Similarly for Enriching section

$$y = \frac{L}{V} x + \frac{D}{V} x_D \quad (B)$$

Subtracting B from A

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

Overall compt balance: $F z_F = D x_D + B x_B$

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

Total material balance around feed

$$\bar{L} = L + \bar{V} - V - \bar{L}$$

$$\text{or } (V-\bar{V}) = F - (\bar{L}-L)$$

$$\Rightarrow y(F-(\bar{L}-L)) = x(L-\bar{L}) + F z_F$$

Define $\boxed{q = \frac{\bar{L}-L}{F}}$

$$\Rightarrow y(F-qF) = xqF + z_F$$

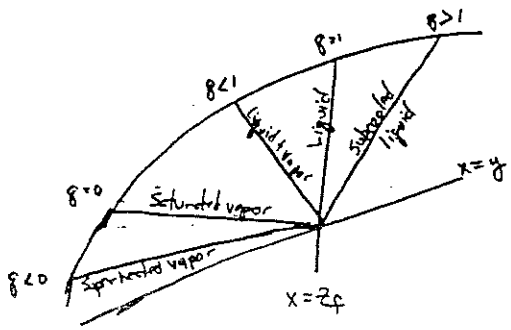
$$\text{or } y = -\frac{x\,q}{1-q} + \frac{z_F}{1-q}$$

$$\text{or } \boxed{y = \left(\frac{q}{q-1}\right)x - \left(\frac{z_f}{q-1}\right)}$$ q-line equation

Slope of q line marks intersection of enriching and stripping operating lines. The q-line intersects the $y=x$ line @ $x = z_f$

q is related to the thermal condition of the feed.

$$q = \frac{H_{Vf} - H_F}{H_{Vf} - H_{If}} = \frac{\text{enthalpy required to bring feed to sat'd vapor}}{\text{Latent heat of vaporization of feed}}$$



Limited Operating Conditions

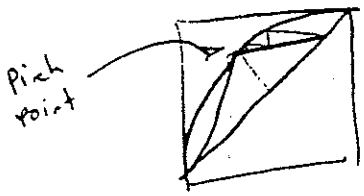
a) Minimum # stages $\frac{L}{V} = 1$, Total Reflux, no product withdrawn

$\frac{\bar{L}}{\bar{V}} = 1$, Total Reboil, no bottoms withdrawn

b) Minimum reflux ratio. (L_R/D or L/V)

$$L_R/D = \frac{L/V}{1 - L/V}$$

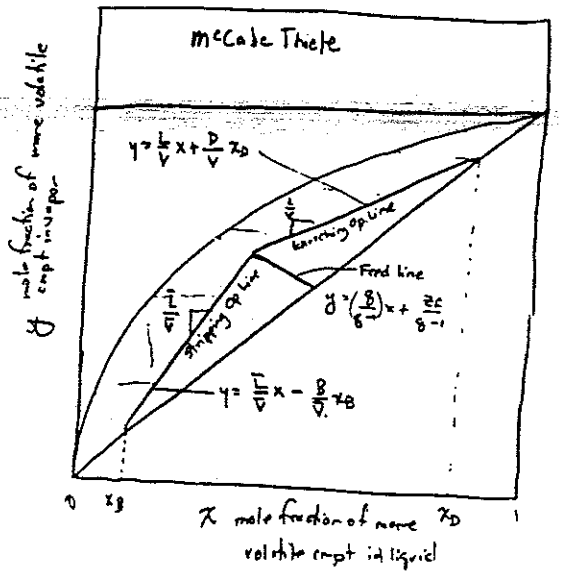
Minimum slope of operating line corresponds to intersection w/ equilibrium curve.



Infinite # stages required to achieve separation @ minimum reflux.

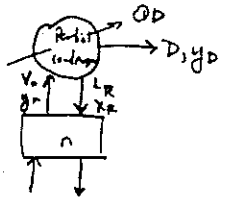
Pinch Point - often encountered in extraction - When an operating line coincides with a tie line, and successive extract and raffinate streams remain constant.

For binary distillation at minimum reflux, most of the stages are crowded into a constant composition zone that bridges the feed stage. In this zone, all vapor and liquid streams have essentially the same composition as the flashed feed. This zone is a pinch point.



Partial Reboiler – Equivalent to single theoretical stage

Partial Condenser – Equivalent to single theoretical stage, L_R, D leaving condenser are in equilibrium



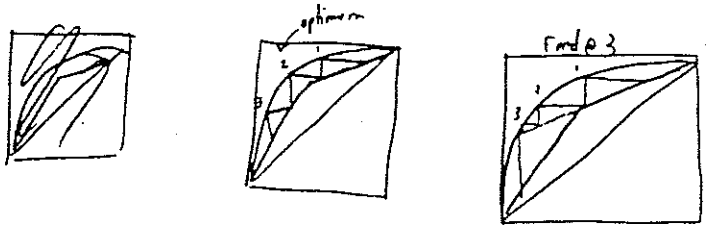
Material balance about n on top of column

$$V_n y_n = L_R x_R + D y_D$$

$$\text{or } y_n = \frac{L}{V} x_R + \frac{D}{V} y_D \text{ is enriching operating line}$$

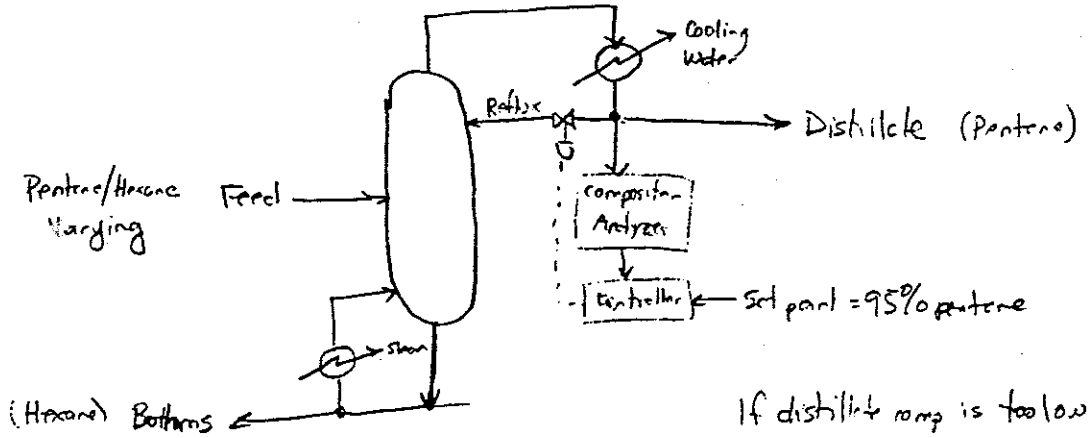
It intersects the x-y line @ $x = y_D$

Location of Feed Feed is at changeover point from stepping off stages on two operating lines.



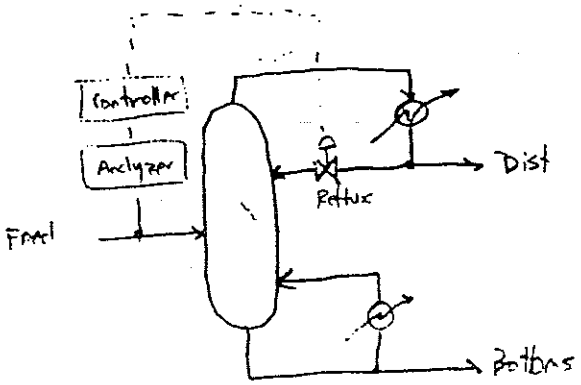
Process Control of a Distillation Column

a) Simple Feed back

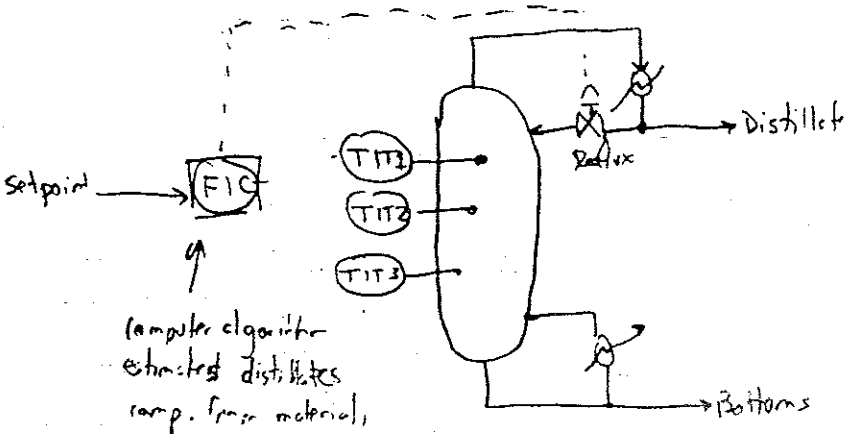


If distillate comp is too low, open reflux valve

b) Feed forward



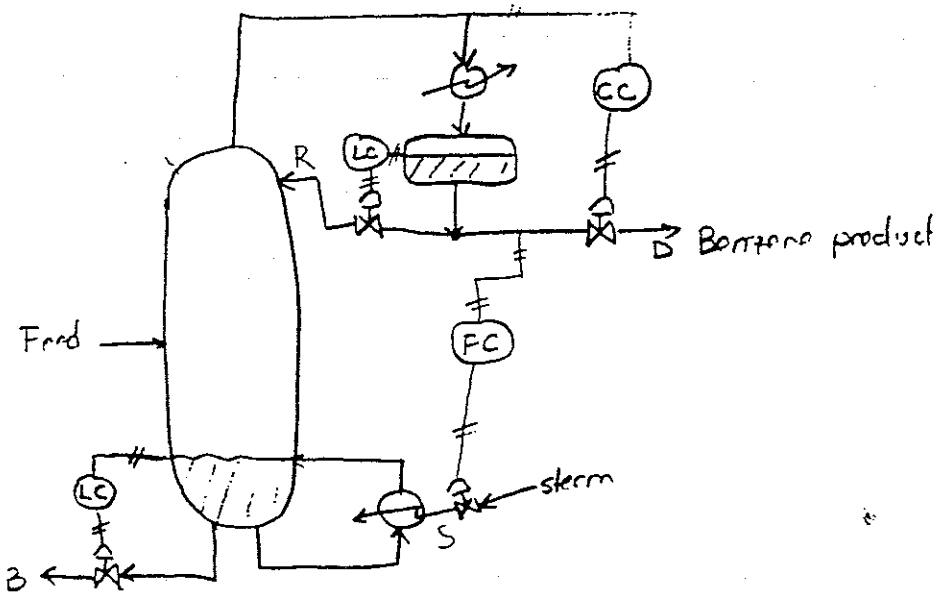
c) Inferential



Benzene Column control

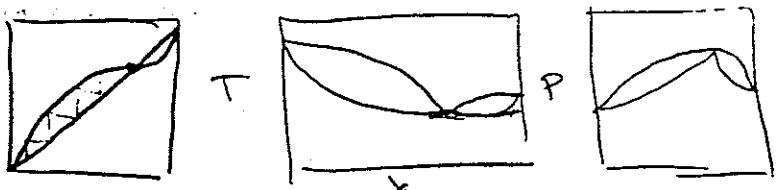
Control variables: 1) Benzene product purity
2) Fractional recovery of benzene in overhead product (distillate rate)
3) Liquid level in overhead accumulator
4) Liquid level @ bottom of column.

Manipulated variables: 1) Distillate rate, D
2) Reflux rate, R
3) steam flow rate, S
4) Bottoms flow rate, B



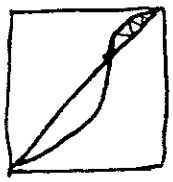
Azeotropes

For minimum boiling azeotrope, total pressure is greater than vapor pressure of either cmpt. Thus, in distillation, the azeotropic mixture would be the overhead product



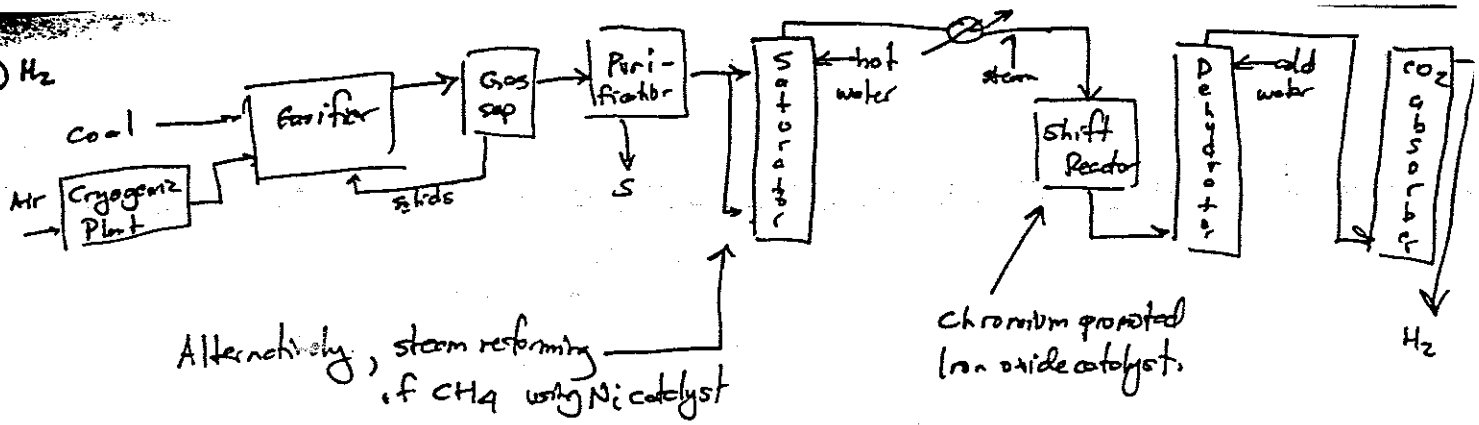
For maximum boiling azeotrope, the azeotropic mixture is bottoms product. because the minimum total pressure is below the vapor pressures of the pure cmpts.

Here



Azeotropes limit the separation that can be achieved by ordinary distillation techniques. It is possible in some cases to shift the equilibrium by changing the pressure sufficiently to 'break' the azeotrope, or move it away from the region where the required separation must be made.

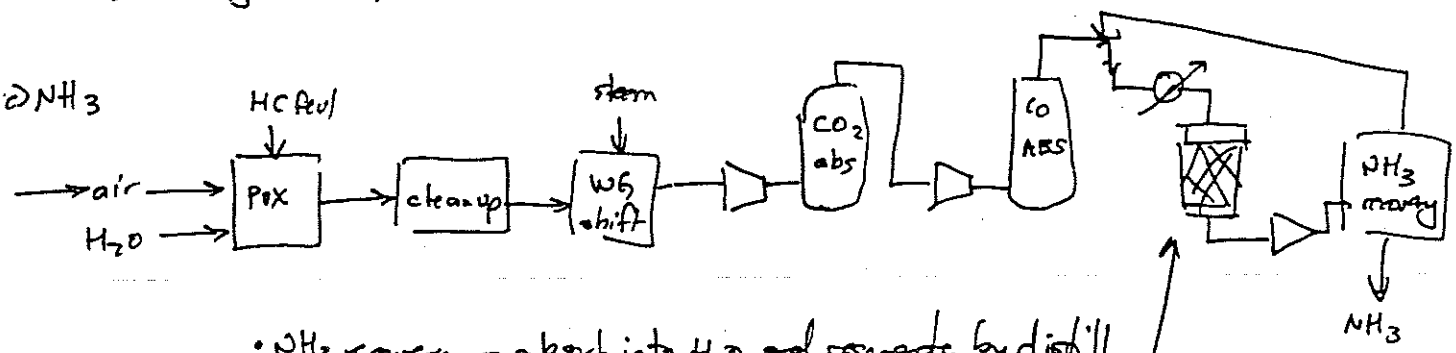
b) H_2



- H_2S removed using Fe_2O_3 (adsorption)
- CO_2 removed using high T Potassium Carbonate wash

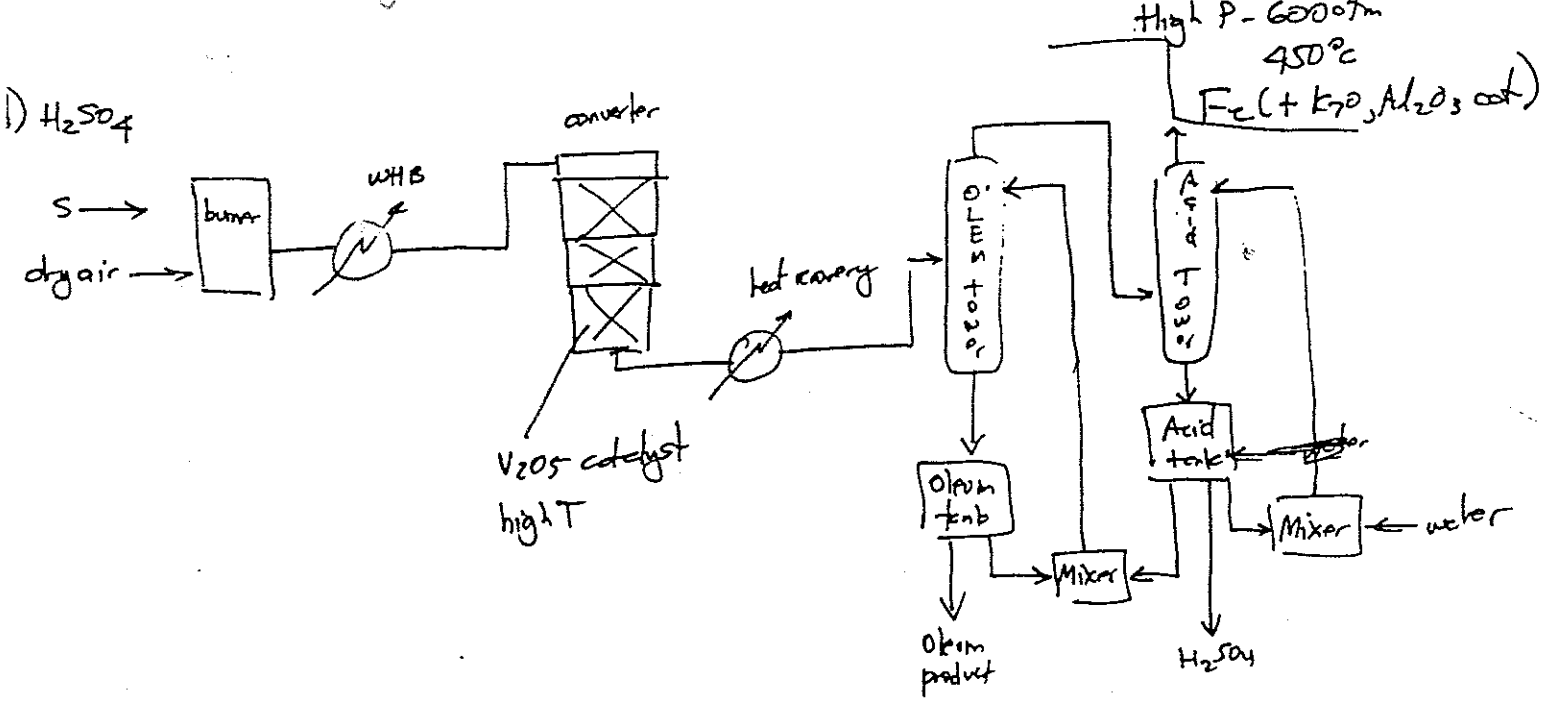
Also, Electrolytic decomposition.

c) NH_3



- NH_3 recovery - absorb into H_2O and regenerate by distill.
- refrigerate and release out NH_3

d) H_2SO_4



h) CH_3OH – React products of synthesis gas ($CO + H_2$) in correct ratio

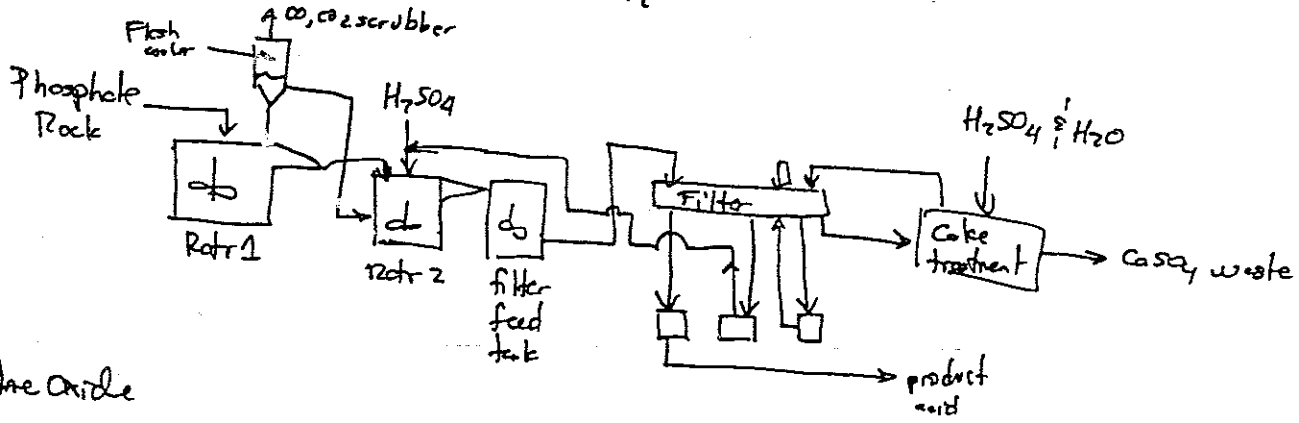
j) $CO + 2H_2 \rightarrow CH_3OH$ over methanation catalyst (V_2O_5).

i) H_3PO_4 – 'Wet Process'

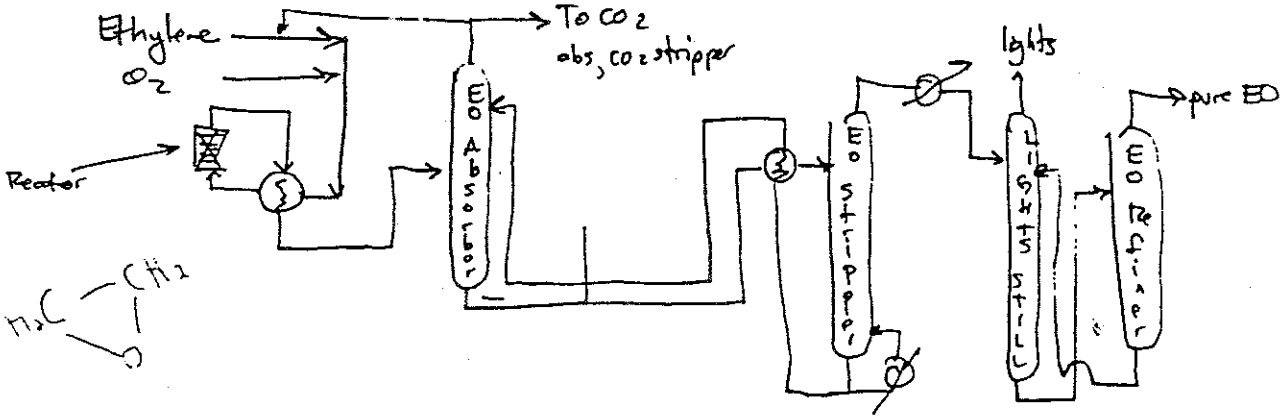
k • React Phosphate rock with a mixture of H_3PO_4 and H_2SO_4

Simplistically:

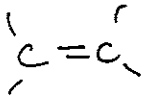
$$(\text{Phosphate Rock}) + H_3PO_4 + H_2SO_4 + H_2O \rightarrow CaSO_4 + HF + H_3PO_4 + (SiF_4 + H_2SiF_6 + CO_2) + H_2O$$



l) Ethylene oxide

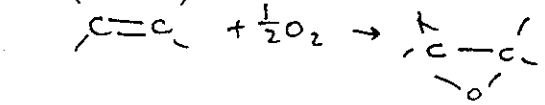


$+ O_2$



- EO is absorbed in water
- Silver based catalyst 200–300°C

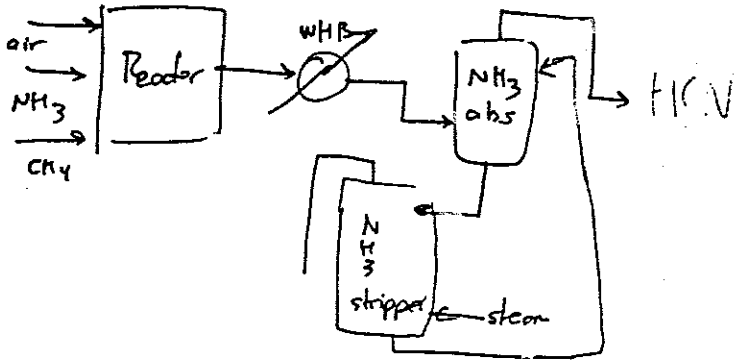
$$CH_2=CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_2-CH_2 + \text{heat}$$



HCN

- $CH_4 + NH_3 + 3/2 O_2 \rightarrow HCN + 3H_2O$
- $T = 1000 - 1200°C$ Pt/Rh catalyst
- HCN tends to polymerize under basic conditions, ∴ add SO_2
- NH_3 absorbed in monoammonium phosphate

h)



i) Formaldehyde $CH_3OH \rightarrow HCHO + H_2$ $\quad HCH(=O)$

$H_2 + 1/2 O_2 \rightarrow H_2O$ exothermic