1. Outline of Processes

a) HCl – majority as byproduct from chlorination of hydrocarbons

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

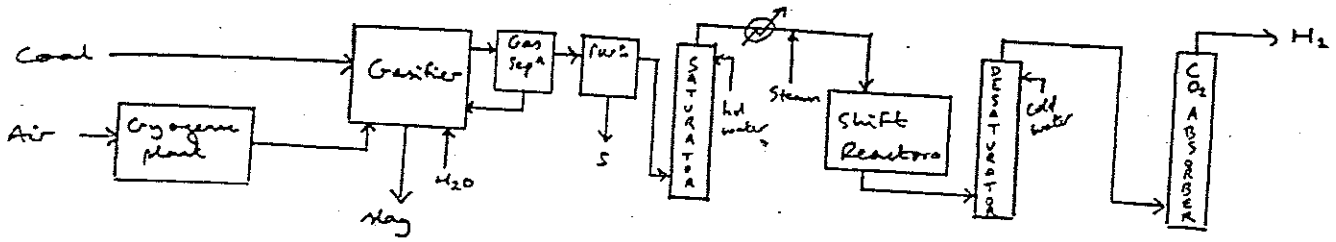
- highly exothermic
- must remove unchlorinated HC by absorbing HCl into H_2O @ chlorination T, P then drop P to lose H_2O

– 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 natural (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$^\Delta$ 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

ethanol carbonylation

$$\tfrac{3}{4}CH_4 + \tfrac{1}{4}CO_2 + \tfrac{1}{2}H_2O = CO + 2H_2$$

~~$CO + 2H_2 = CH_3OH$~~ (V)

$$CH_3OH + CO = CH_3COOH$$ ← Rh cat

aldehyde oxidn

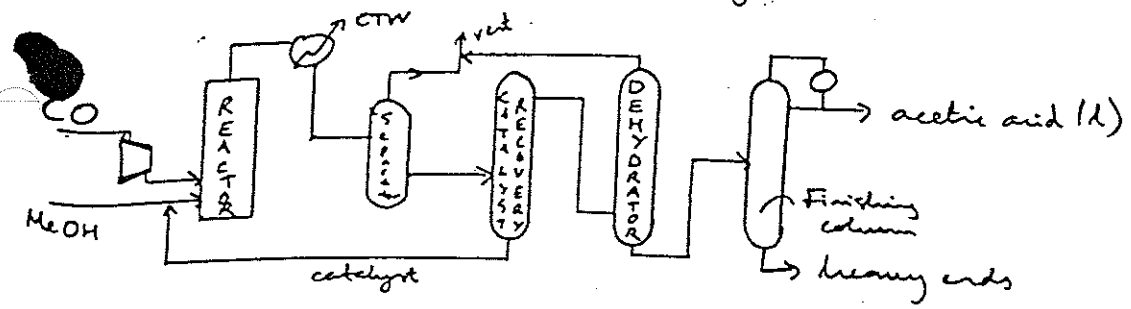
$$C_2H_6 = C_2H_4 + H_2$$

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

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

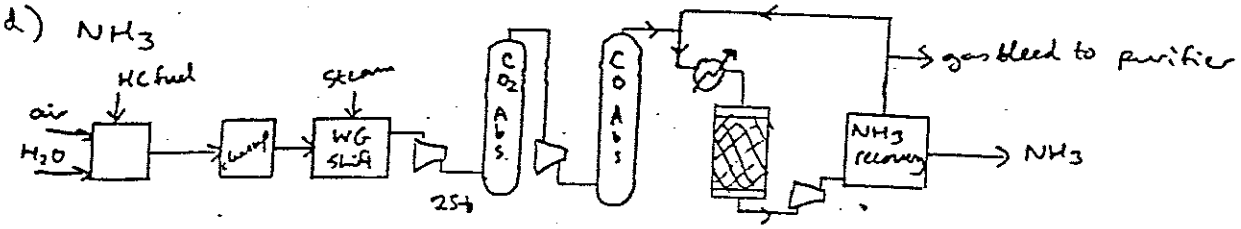
3). Butene Oxidn

. Main method is (1), Methanol Carbonylation



• Reactor runs @ 30 atm, Rh Catalalyst, 160°C (or hi P Co cat).

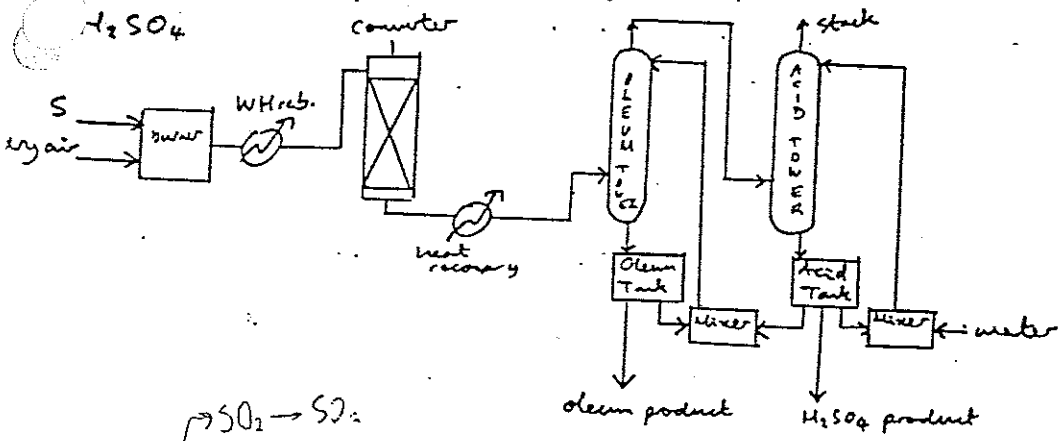
d) NH_3



• Reactor is @ 450°C 200 atm using Fe ($+K_2O + Al_2O_3$) cat.
→600

. NH_3 recovery either
- absorb into H_2O then regenerate by distill.
- refrigerate & condense out NH_3.

e) H_2SO_4

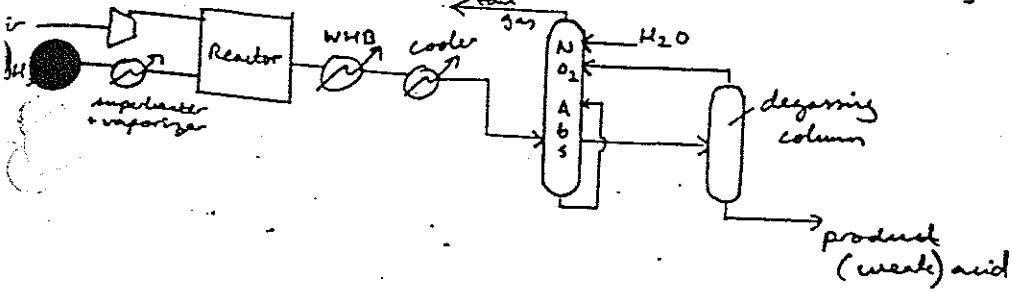


→ $SO_2 \rightarrow SO_3$

• Converter uses Vanadium catalyst, hi T.

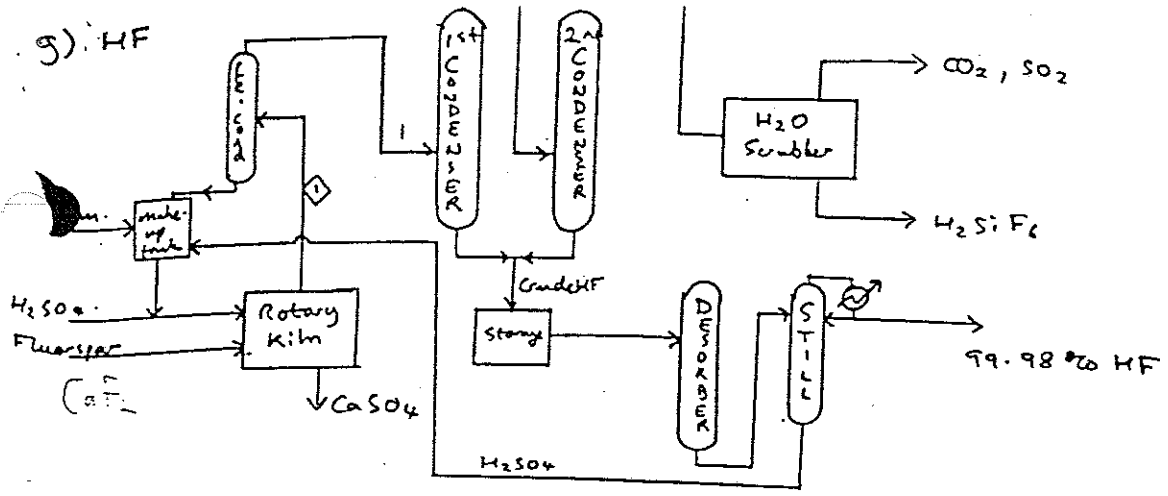
f) HNO_3

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



• Reactor ~900°C, Platinum Rhodium cat. hi P.

g) HF

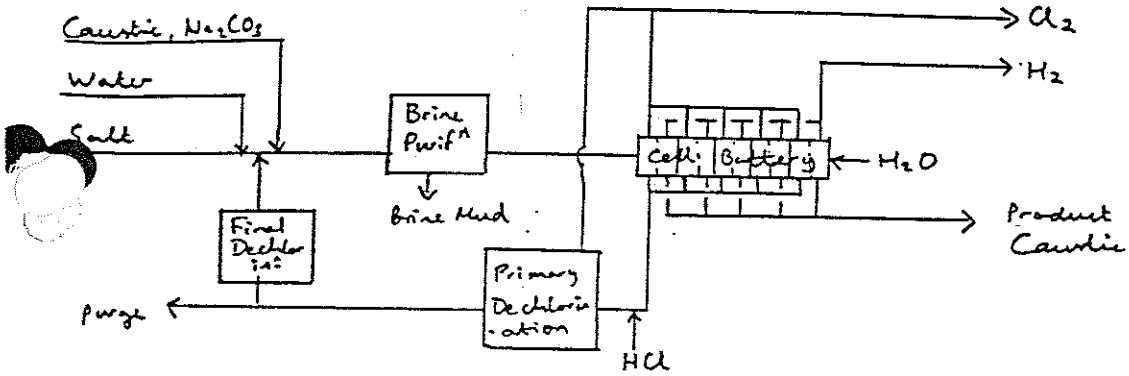


- Stream ① contains HF, H_2O, SO_2, SiF_4, CO_2, H_2SO_4.
- CaF_2 (Fluorspar) is finely ground feed product

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

- 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 Cathodyte $\quad H_2O \rightleftharpoons H^+ + OH^-$

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

- Cell voltage ~ 3V moderate temperatures

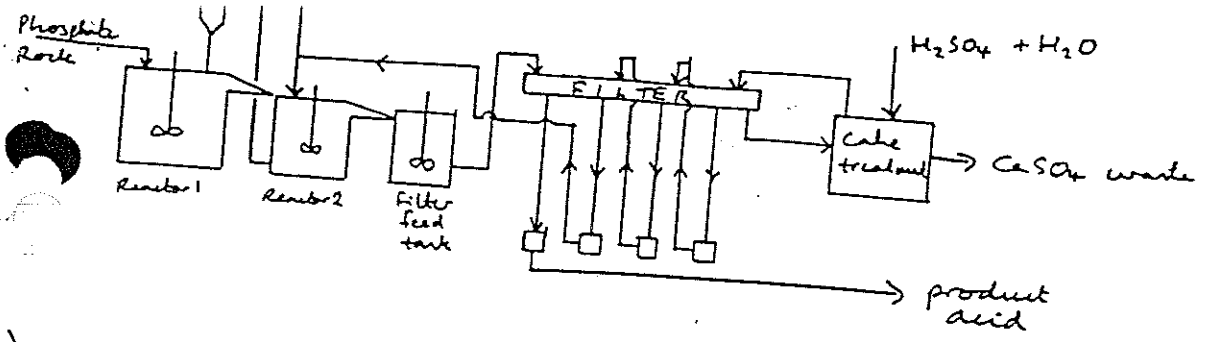
(j) CH_3OH - react products from synthesis gas generator in correct ratio $(CO + 2H_2)$ over methanator catalyst (V).

k) H_3PO_4 - 'Wet' process

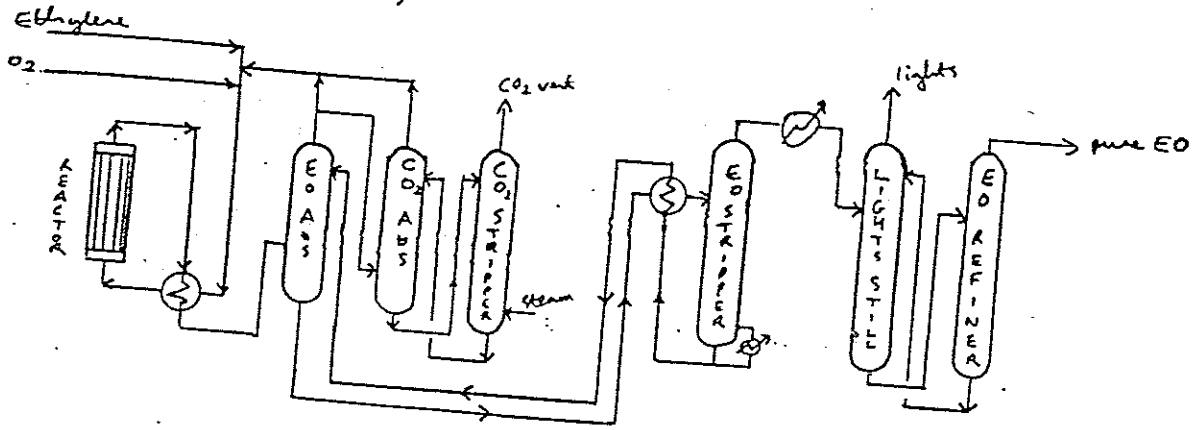
React phosphate rock with a mixture of H_3PO_4 & H_2SO_4

Simplistically

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



-) Ethylene Oxide (EO)

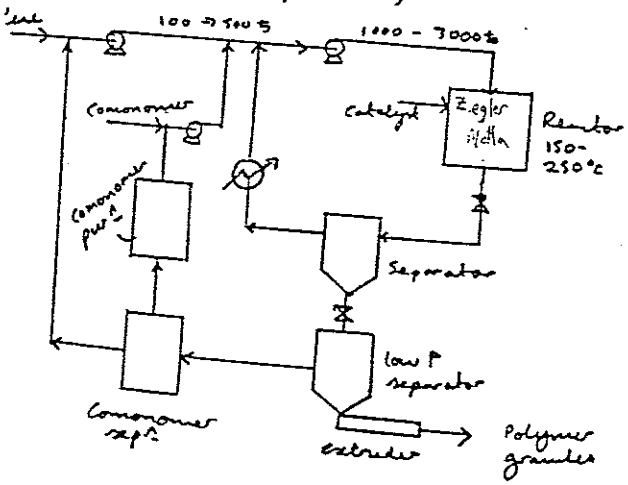


EO is absorbed in water

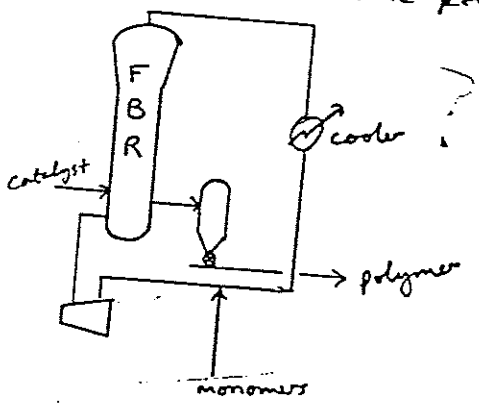
Silver based catalyst (usually proprietary) 200 → 300°C, 10 → 30 ŧ

$CH_2 = CH_2 + \frac{1}{2} O_2 \rightarrow CH_2 - CH_2$ (O bridge) + heat

PE (hi P process)



HDPE (BP Chimie process)



Use Ziegler Natta catalysts for PE. - need to replace catalyst ∴ it remains attached to polymer.

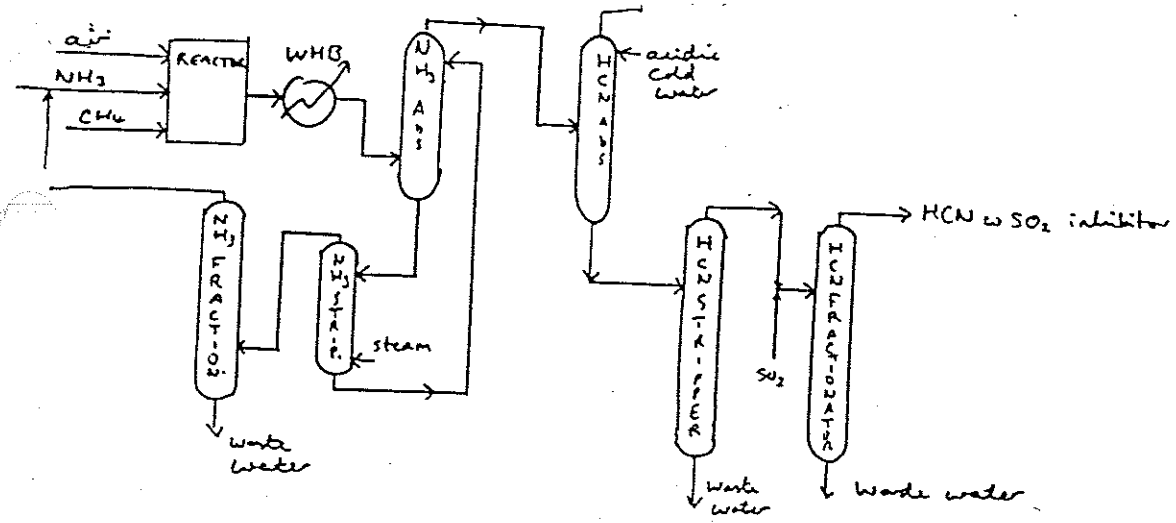
HCN

$CH_4 + NH_3 + 3/2\, O_2 \rightarrow HCN + 3H_2O$

~ 1000 - 1200°C Platinum / Rhodium catalyst

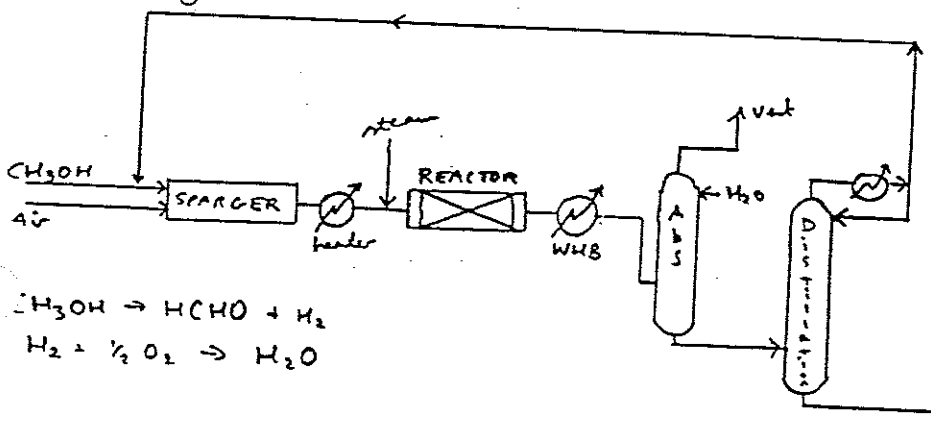
HCN tends to polymerize in basic conditions ∴ add SO_2

NH_3 is absorbed in monoammonium phosphate



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

p) Formaldehyde



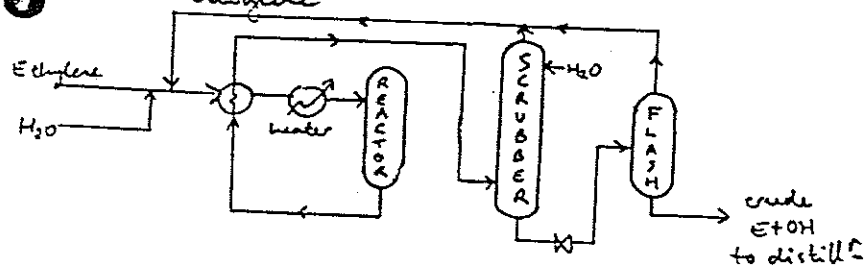
$CH_3OH \rightarrow HCHO + H_2$

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

or Fe/Mb =

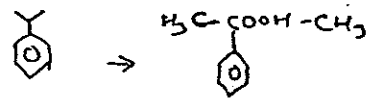
- Reactor uses Ag catalyst
600°C ~ 4b

.) CH_3CH_2OH
- fermentation
- From ethylene



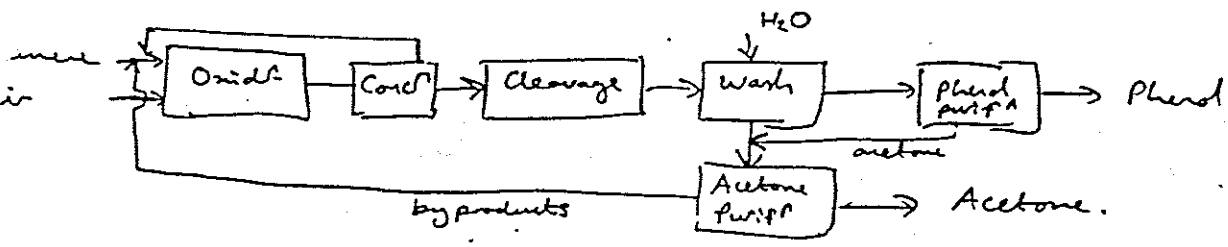
- Scrubber stream can also be put thru' purification to extract organic waste (bleed)
- Reactor 250°C, 70b? Phosphoric acid catalyst suspended on fixed bed

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



→ products

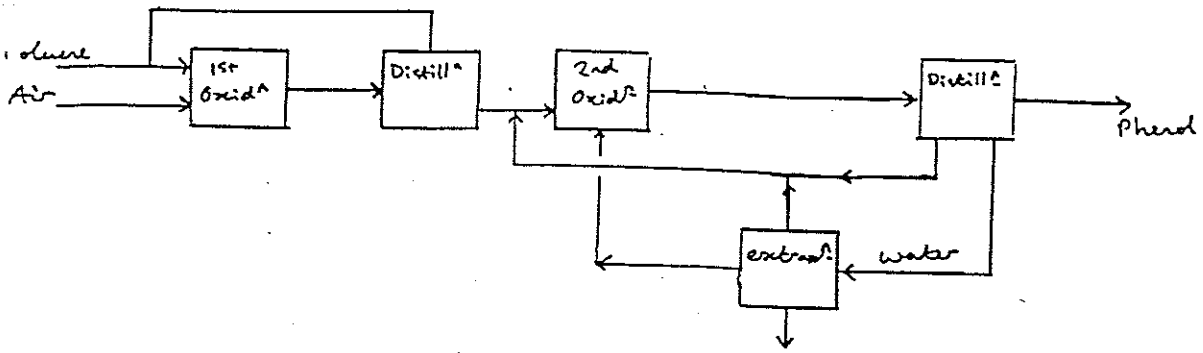
implistically:



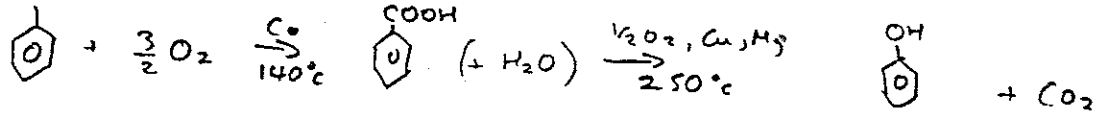
5) benzene • produced from fractionation of petroleum products or coal tar

6) Phenol • Oxidation of cumene (r)

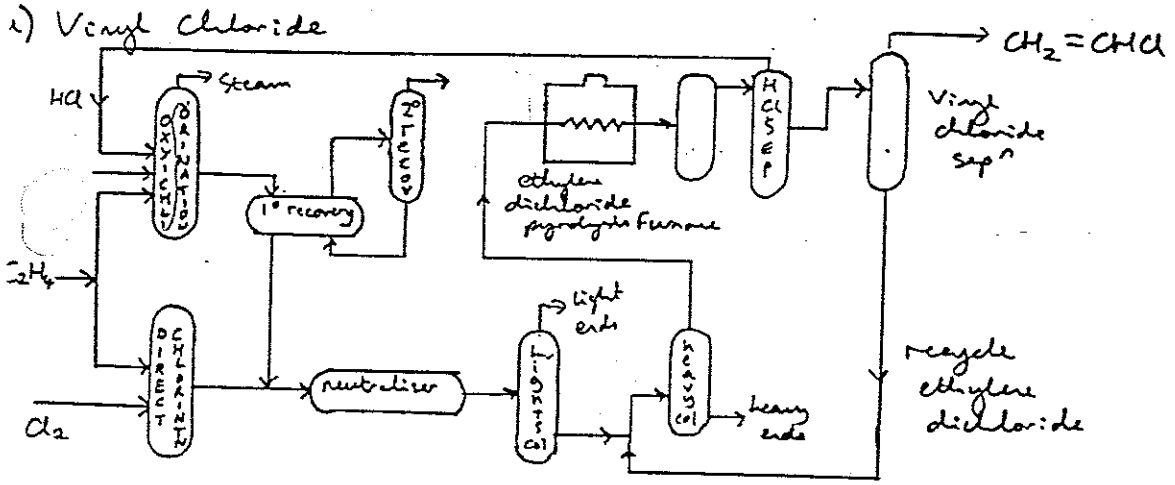
• Oxidation of toluene



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

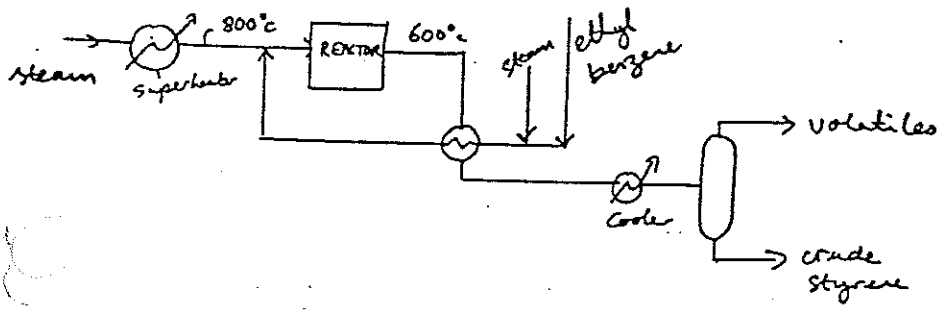


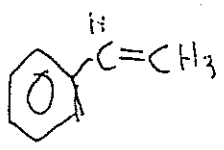
1) Vinyl Chloride



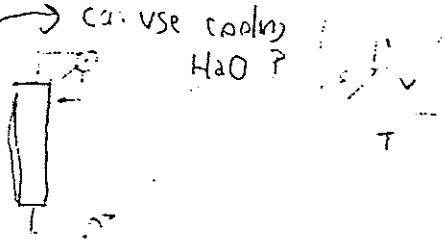
• Direct chlorination $FeCl_3$ cat. T ~ 60°C
• Oxychlorination $CuCl_2$ cat. T ~ 230°C, Fbr., 5 b
• Ethylene dichloride cracking is endothermic, 30 b, 550°C

7) Styrene - adiabatic dehydrogenation of ethyl benzene





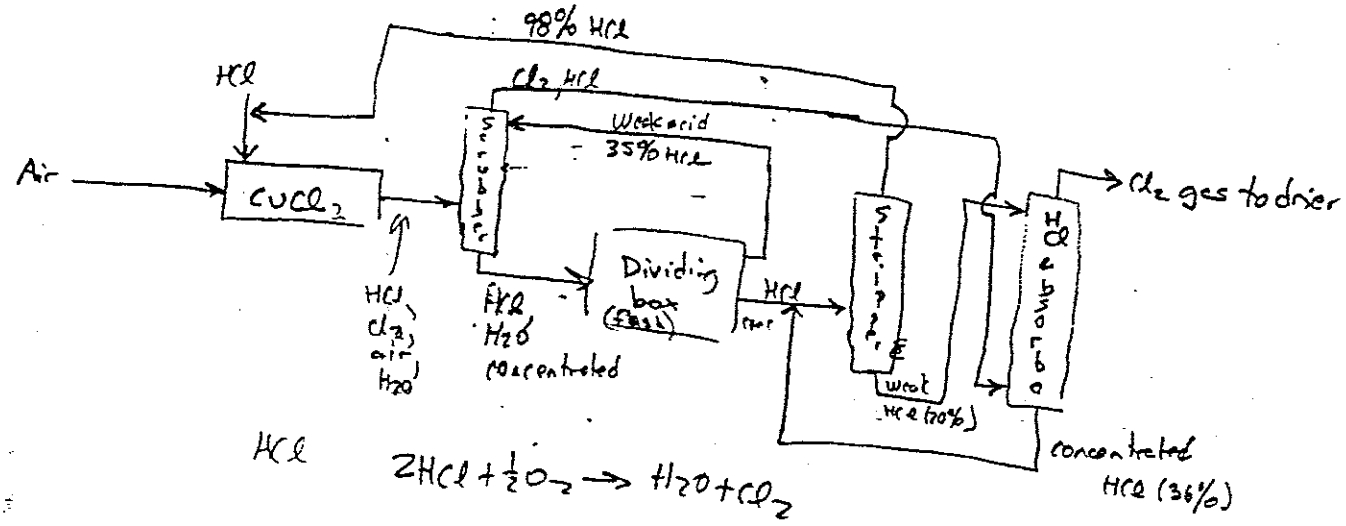
Distillation is done @ high P to make the condenser load smaller (avoid using refrigeration at condenser)
- increases vapor density and makes column volume required smaller.



) 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~~ recovery Cl_2 gas - mix HCl w/ Air and Oxidize over $CuCl_2$ catalyst.



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

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?

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

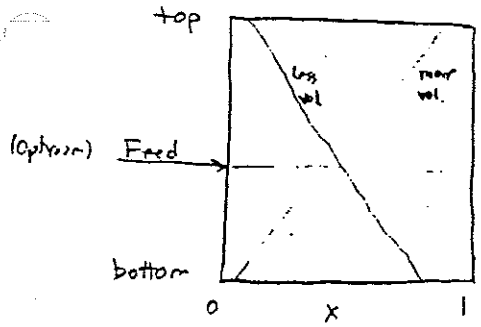
$$\underbrace{\frac{P_2 - P_1}{\rho}}_{+} = \frac{V_1^2 - V_2^2}{2} \underbrace{- W_s}_{+}$$

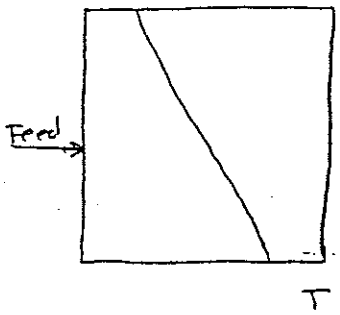
don't want P_1 to be too low or liq will vap. if $P_1 < P_{bubble}$

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

⑤ Typical temp & conc'n profiles in distillation column

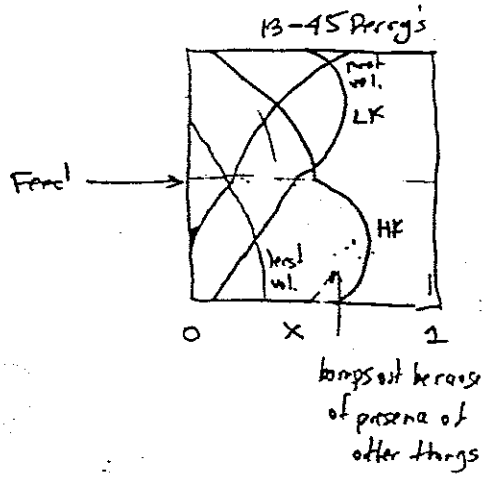
Binary Distillation



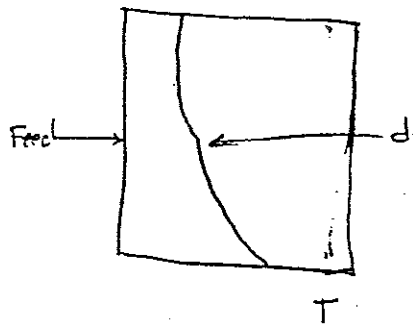


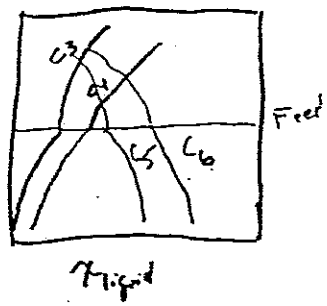
multicomponent

13-45 Perry's



bumps at breaks of presence of other things





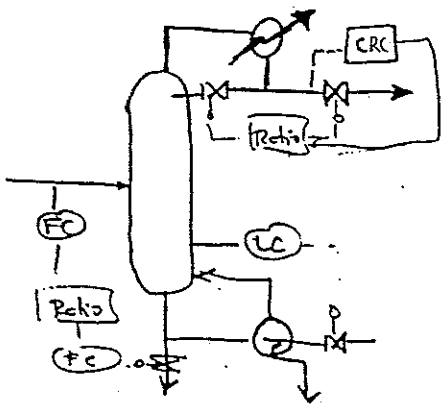
Rigid

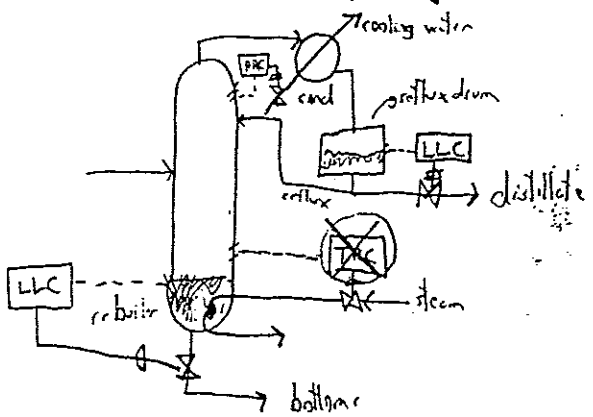
⑥ How to remove 1% phenol from water?

- 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 products must equal feed - i.e. little surge capacity





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

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

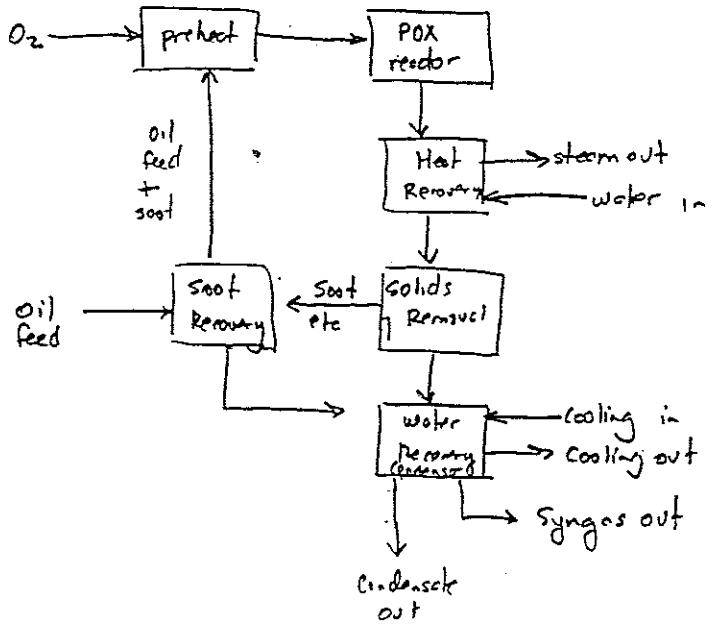
(8) Synthesis Gas Production

$O_2 + \text{fuel} \rightarrow CO + H_2$

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

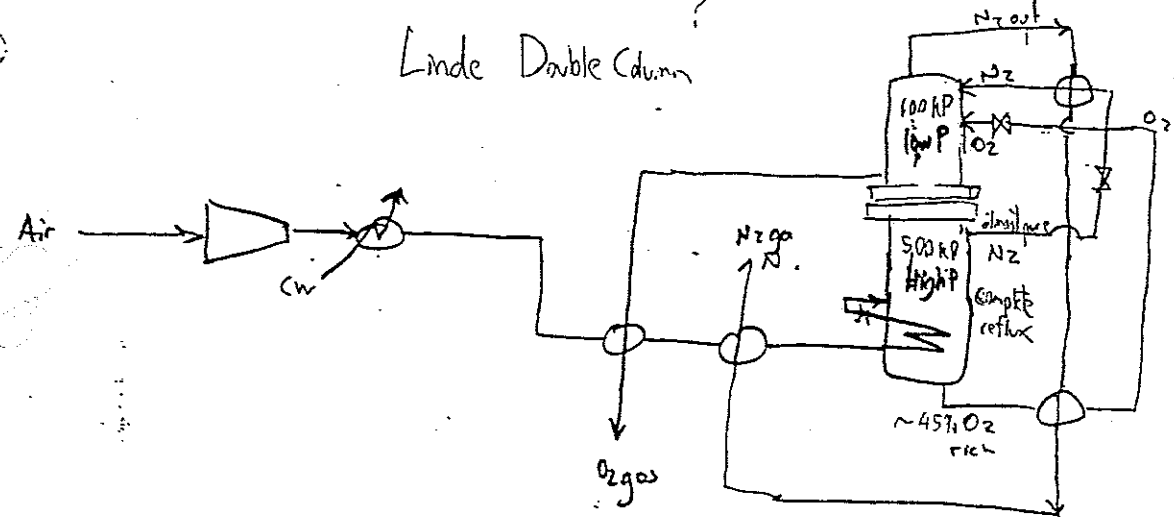
Pass Cl_2 over solid NaOH & $Ca(OH)_2$ in a solid gas reactor (rotating cylinder w/ lifting blades) @ 50°C

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

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

?

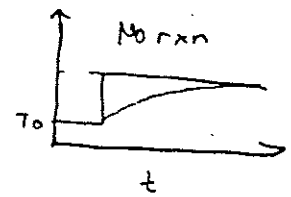
(13)



(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.



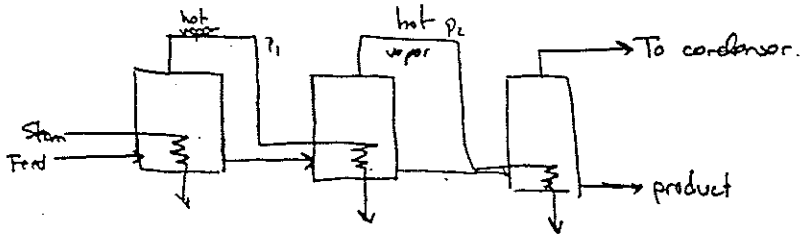
For rxn $\dot{Q}\rho C_p T_0 = \dot{Q}\rho C_p T + r(-\Delta H)V$

Exothermic ⇒ $T > T_0$ due to R term.

If T_0 increases to T_1, 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.

$P_1 > P_2 > P_3$
$T_1 > T_2 > T_3$

(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.

∴ P decrease through system

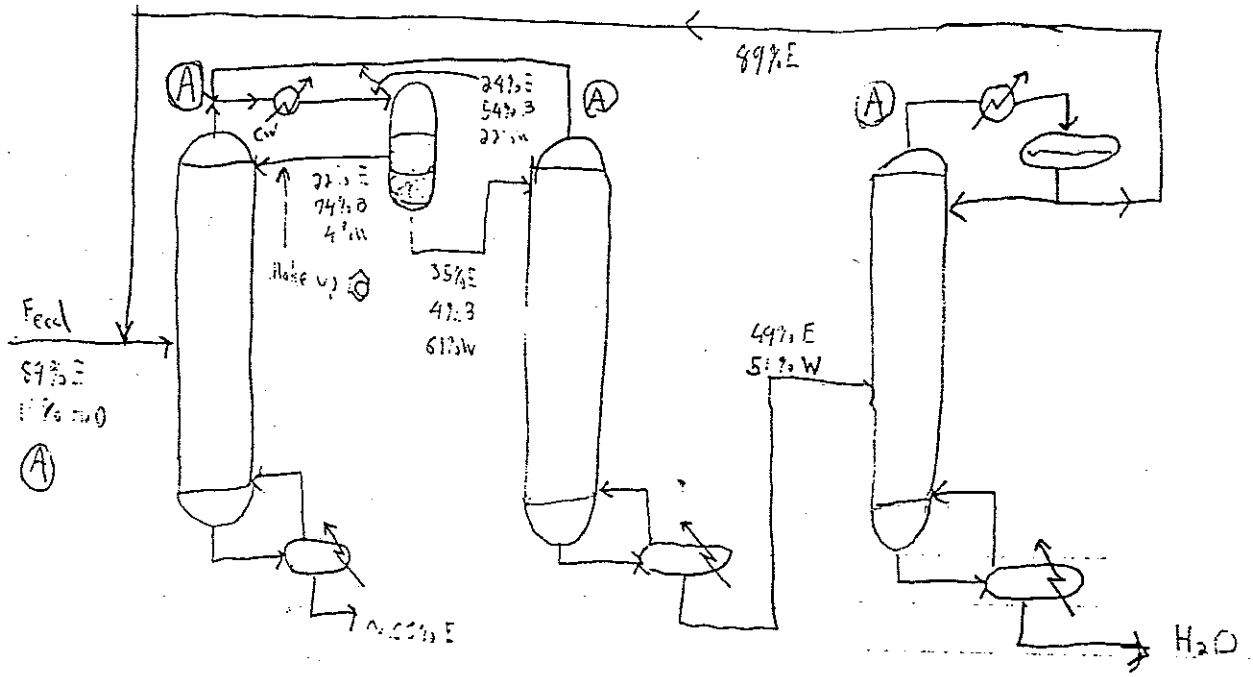
Air Conditioning – controls temperature, humidity, cleanliness, distribution.

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?

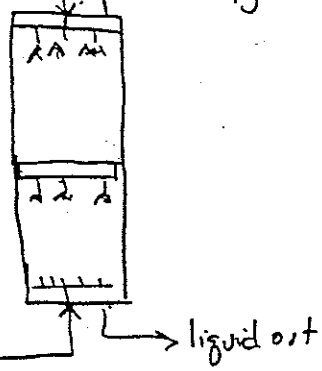
17) Separate ethanol & water (King p 346)



(A) → azeotrope

Benzene Entrainer

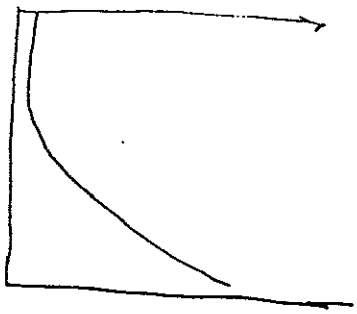
(26) SO_2 absorber absorbent → cleaned gas



what's the absorbant?

gas in (SO_2)

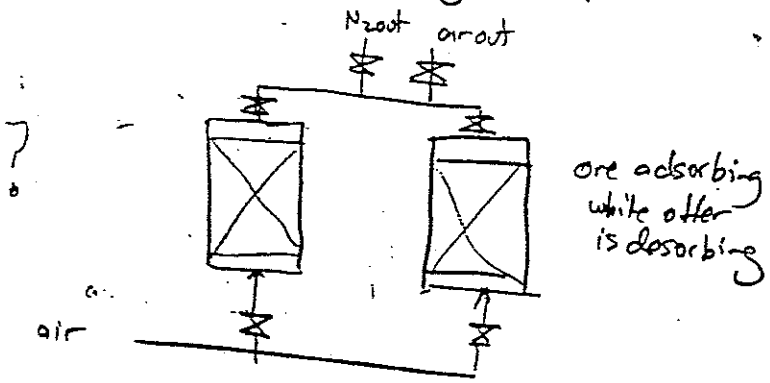
liquid out



conc. SO_2 in liquid 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 segregate
- 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

O Observe

(30)

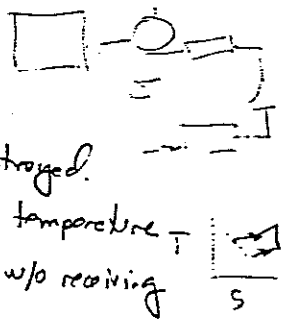
Heat Pump — Year-round heating and cooling

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

5c) Give expression for reversible heat, irreversible heat, not 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:

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

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