

100°C in crystallizer
 Prills ~ 1.5 mm, Nitration ~ 2-mm, Crystals ~ 4-5 mm,
 flakes ~ 2-2.5 mm.
 For crystals, in the top section for prills, replace Prilling Tower,
 screen and Dryer by a Crystallizer and Centrifugal separator

HNO_3 is preheated in 2 stages as HNO_3 is corrosive. 1st preheater
 is stainless steel, 2nd is of tantalum (rare earth element).
 Tantalum has good heat conductivity, and inert to acids.

2/4/19

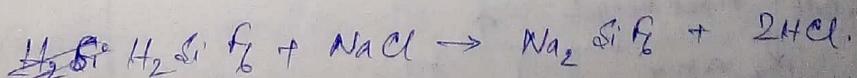
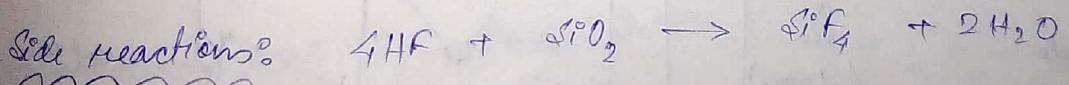
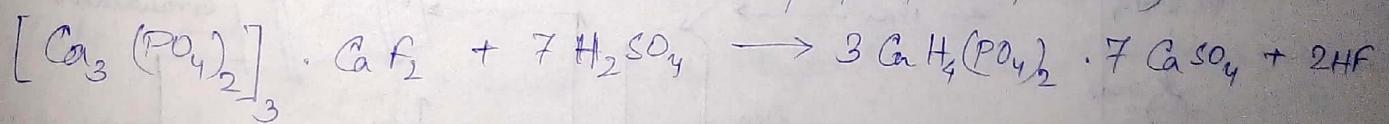
Phosphates

Production

Two types : i) Superphosphate ii) Triple superphosphate

Made from phosphate rocks.

Chemical reactions for superphosphate (15-20% phosphorous content in the superphosphate product).

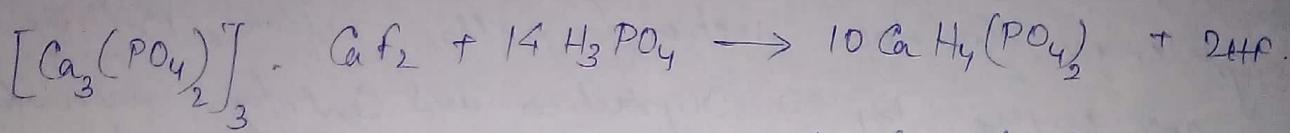


We want to remove the undesirable HF by the side reactions.
 SiO_2 is present as impurities in the phosphate rock. The plant
 also needs to have an inhouse H_2SO_4 production unit.



Hf is much more harmful than HCl.

Chemical reaction for triple superphosphate (Phosphorous content ~ 42-50%)

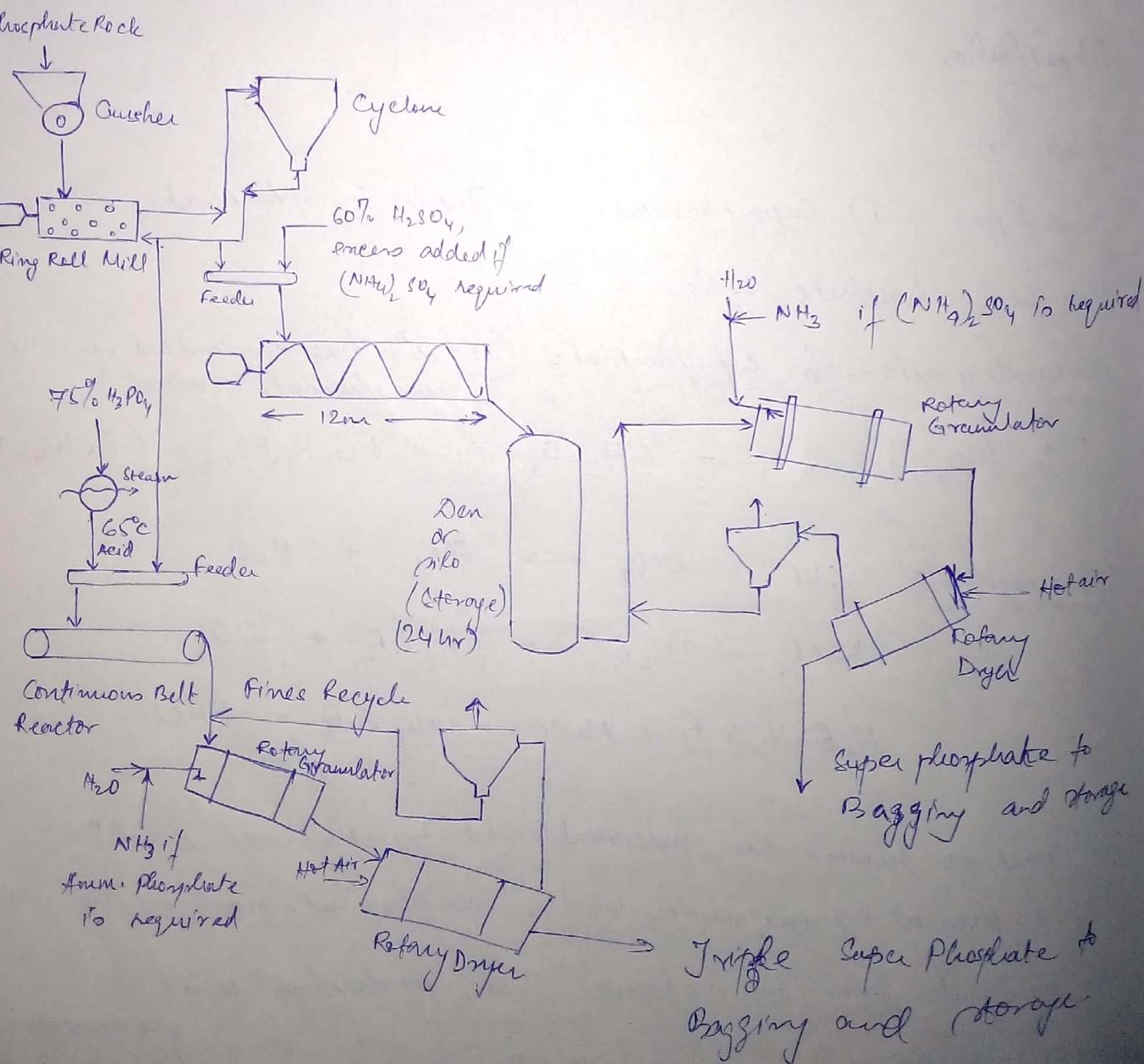


(higher phosphorous content)
as more from phosphoric acid

Side Reactions:

Same as for superphosphate

PFD



The Continuous Blender (screw blender) is used as steaming reaction, some H_2SiF_6 will be produced, which'll be spread out. It is a long blender, so the reactants are spread out as compacts to vessel.

⑥ The walls of the blender is lined with wood blocks as HF does not corrode wood as much as metal.

As it is a solid phase reaction, reaction is slow, so it is put in storage (vats) to complete the reaction.

for Triple Phosphate Production,

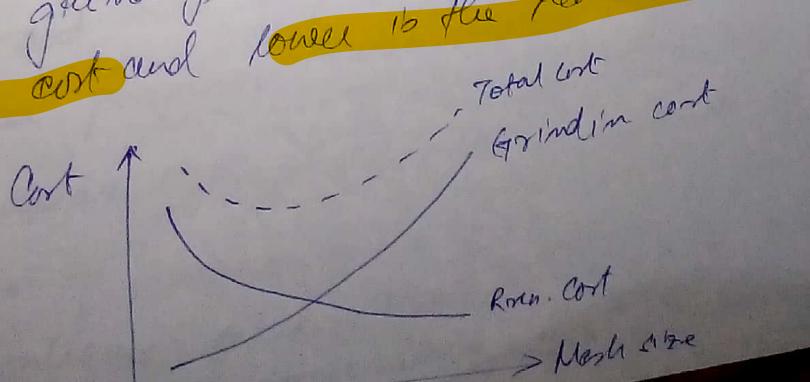
Phosphoric acid is produced in-house production now.

Phosphoric acid

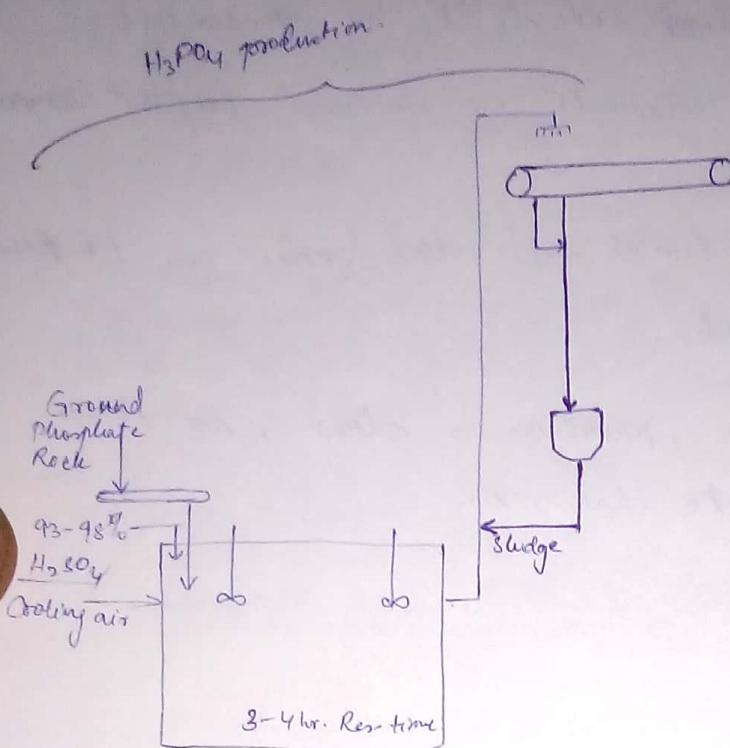


Triple Super Phosphate has 2.5 times more phosphorous than Normal Super Phosphate. But the cost of production of Triple Super Phosphate is > 2.5 times that of Normal Super Phosphate. So it is uneconomical to produce Triple Super Phosphate.

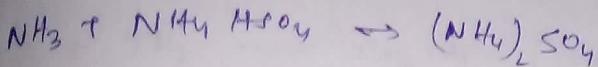
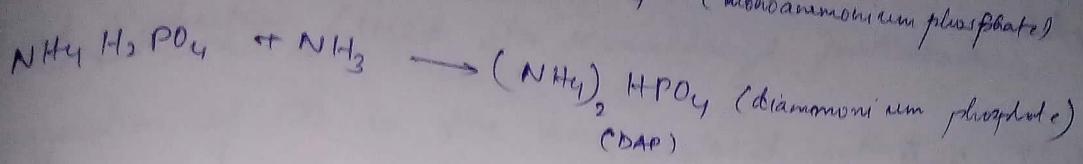
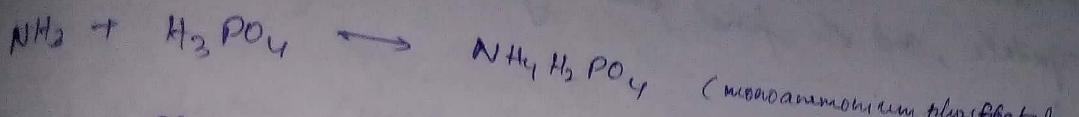
Small in grinding smaller the particle size, higher is the grinding cost and lower is the reaction cost.



$(\text{NH}_4)_3\text{PO}_4$
 ~~H_3PO_4~~ production



Ammonium phosphate



Ammonium phosphate has **both N, and P**. We need both NH_3 and H_3PO_4 . H_3PO_4 is produced in-house. In the Neutralising section, the **NH_3 is charged from bottom** in the CSTR so as to **control the rxn. rate** as, it is an exothermic reaction (reaction of NH_3 and H_2SO_4). In the neutralizing section, the pH is neutralized.

The **potash crystals** are added before granulating, so that the final product has all **3 (NPK)**. This produces mixed fertilizer.

Why do we add **H_2SO_4** along with H_3PO_4 in the reactors (neutralizing section)? Why do we need to form both phosphate and sulphate salts in the same reactor?

$(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ are **insoluble**, so the phosphate and ammonium sulphates are **precipitated** by the sulphates. So H_2SO_4 is added.

Phosphate salts are **partially soluble** in water, so the presence of the ammonium sulphate enhances the precipitation.

The ammonium sulphate as well as the ammonium phosphate precipitate, and the final product (granules) has both phosphates and sulphates.

Petrochemicals

Compounds based on C_1 - C_4 and aromatics.

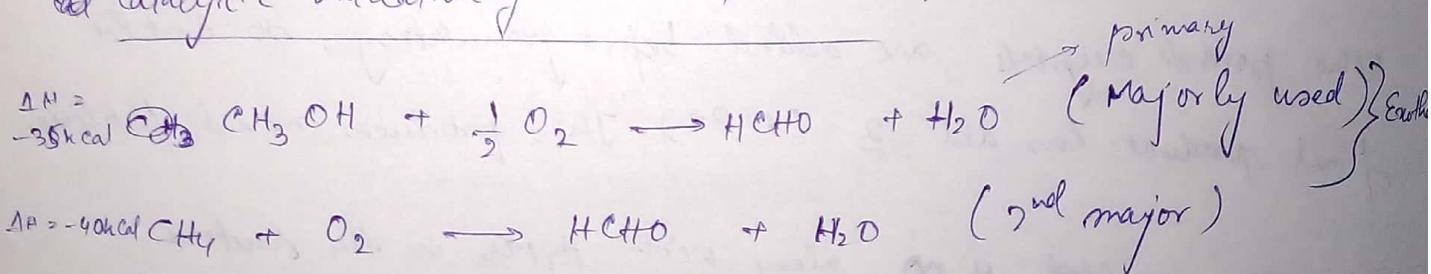
C_1

Important chemical produced from C_1 is formaldehyde. It's a precursor for production of resins (adhesives, class of polymers used to prepare adhesives).

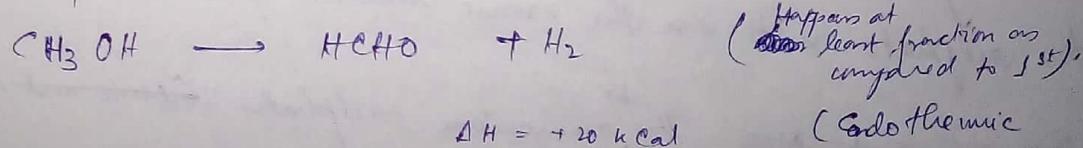
Production of Formaldehyde

One way is to do controlled oxidation of CH_4 in the presence of a catalyst.

Catalytic oxidation of Methanol/Methane



Pyrolysis of methanol

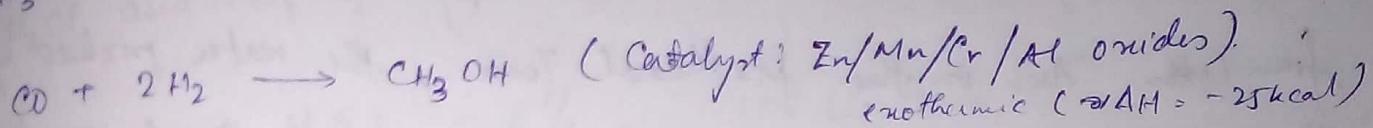


Formaldehyde is also called formalin. Used as antiseptic and preservation. Production of formaldehyde is primarily done by the 1st way. The CH_4 is not directly oxidized as the catalyst used for the 2nd way is very costly.

Methanol's oxidation requires a regular metal/metal oxides like Cu/CuO as catalyst.

Methanol Production

Catalytic Hydrogenation of CO is the most preferred method for producing CH_3OH .



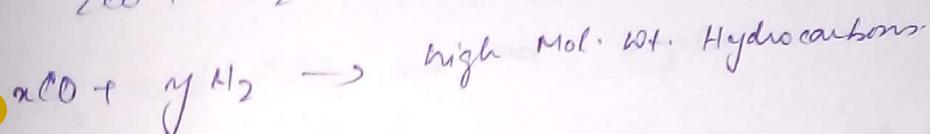
side rxn:



$(\Delta H = -50 \text{ kcal})$



$(\Delta H = -60 \text{ kcal})$



We can produce alkanol by catalytic oxidation of alkanes, but there H_2O is also produced, and separating the alkanol from H_2O requires distillation (more art).

$\text{Pr.} \sim 200 - 350 \text{ bar}$

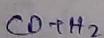
$T \sim 300 - 350^\circ\text{C}$

to get high rxn. rate, as it is a slow rxn. rate.

(We want high temp even though it's exothermic).

The high Pr. takes the rxn forward (Le Chatelier's Principle). This increases conversion

The high temp. increases the rate constant

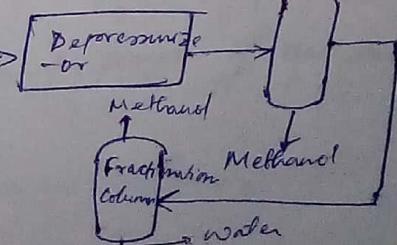


Compressor (Turbine)

Catalytic reactor

$\text{KMnO}_4 \text{ soln}$
(removal of the other HC)

Pg - 418



High space vel. so that side rxn. don't occur

The catalytic reactor exit is ~~at~~ under high pr., so it'll liquify. The liquid is passed through a KMnO_4 column to remove the ~~other~~ Hydrocarbons and we get only Methanol. Before that, the ~~hot~~ hot product exchanges heat with feed. After getting methanol from KMnO_4 column, it's depressurized. Then it's passed through Ether Tower, where ether comes out from top and methanol from bottom. Then in the Methanol Tower, the water picked up by the methanol in the KMnO_4 vessel is separated and methanol comes out from top. Methanol's bp is $\sim 75-80^\circ\text{C}$

Cloudy Challenge

- ④ The steel reactors are lined with copper as the methanol reacts with steel to produce ~~to~~ iron carbonyl which corrodes the steel and poisons the catalyst



9/4/19

Chloroformanes

As the no. of Cl atoms in CH_3Cl is 1, $\text{D/P} \uparrow$ as MW \uparrow .

As no. of Cl atoms \uparrow , solubility \downarrow in water as the H-bond b/w H of chloromethane and O of water \downarrow .

CH_3Cl and CH_2Cl_2 show explosive nature with air

$\text{CH}_3\text{Cl} \rightarrow \text{LEL} = 8\%$, $\text{UEL} = 20\%$

$\text{CH}_2\text{Cl}_2 \rightarrow \text{LEL} = 15\%$, $\text{UEL} = 30\%$

lower explosive limit upper explosive limit

CHCl_3 and CCl_4 are not explosive

The individual ΔH are not known as all ~~reaction~~ occur together, $\therefore \Delta H_{\text{rxn}} = -24 \text{ kJ/mol CH}_3\text{Cl}$

$\underbrace{\text{per mol CH}_3\text{Cl}}_{\text{constant}}$

The rxn. temp is optimum at $370 \text{--} 400^\circ\text{C}$

The HCl is removed by first water-washing, and then by Neutralization through caustic wash. After that, the Brine is passed through drying tower to remove ~~organic~~ water, using HgSO_4 (drying agent). Finally, in a multi-comp. fractionator, the different component CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 are separated.

(explosion)

If the $\text{CH}_3\text{Cl} : \text{CH}_2\text{Cl}_2 > 5$, then deterioration starts, and rxn. goes out of control. \Rightarrow There'll be significant amt. of unreacted CH_3Cl which are recycled.

We want more of CHCl_3 and CCl_4 (good solvents).

But we ~~want~~ see that more CH_3Cl and CH_2Cl_2 are formed in the run.

For a higher $\text{CH}_4 : \text{Cl}_2$ ratio, we'll get more CCl_4 than we got for lower $\text{CH}_4 : \text{Cl}_2$ ratio (although here also, more proportion of CH_3Cl and CH_2Cl_2).

A CH_3Cl and CH_2Cl_2 have high vap. pr. (lower bp.). This drives the run. forward (Le Chatelier). Also the Cl_2 will react more with CH_3Cl and CH_2Cl_2 to finally form more CCl_4 .

In the absorbers, HCl is removed by water wash. Inside the stripper, neutralization occurs.

The last column improves the purity of CCl_4 .

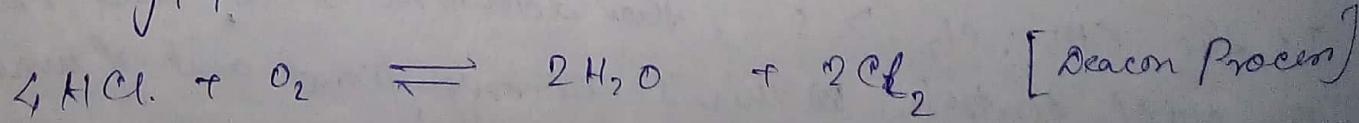
The compressor is used to increase the bp of the components, so that the ~~multicomp.~~ multi-comp. separation is ~~not~~ possible.

How to handle HCl ?

Deacon procn - Oxidation of HCl to give H_2O and Cl_2

The HCl that is produced is not sold as it is impure.

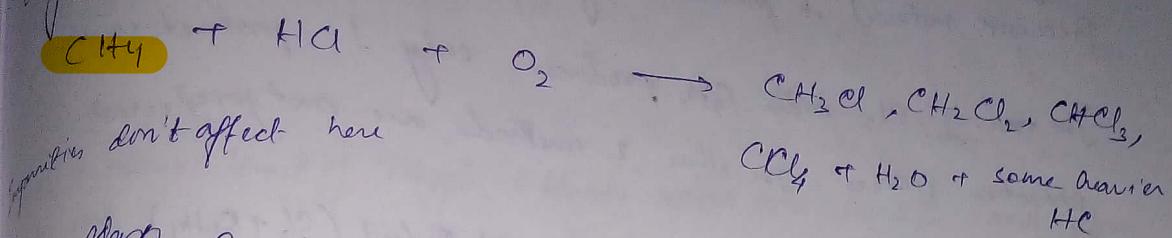
Not very popular as it is ~~reversible~~.



Occurs at high pr. (Le Chatelier).

Another way of disposing HCl is Oxychlorination

By chlorination:



~~Chloroethane~~ can be used as an intermediate step in the production of chloroethanes

C₂-Clans

Ethylenes ~~Acetylene~~

Production: Steam cracking / pyrolysis of LPG or Naphtha.

most preferred.

Dehydration of ethanol or thermal pyrolysis of ethane/propane are not very ~~not~~ preferred.

Temp. for pyrolysis of Naphtha is $700 - 800^\circ\text{C}$

There are 2 furnaces for 2 different grades of Naphtha.

After furnace, product is mixed with superheated steam for (HC)

Steam cracking

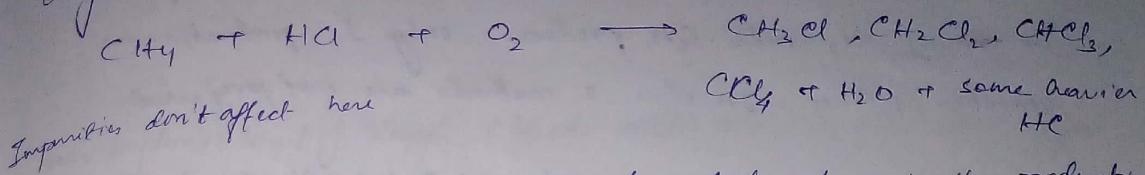
How to separate $\text{C}=\text{C}$ & $\text{C}\equiv\text{C}$?

Pass to compressor to obtain separation, then send to washer (caustic wash to remove acid compounds), then sent to Demethanizer, Deethanizer, & splitter (splits ethane and other HC comp.)

Why 2 heaters? Different conditions (typically 800°C). Then sent to Acetylene separation.

Another way of disposing HCl is Oxy chlorination

Oxy chlorination:



~~CH₂Cl₂~~ can be used as an intermediate step in the production of chloromethanes

C₂ - Clans

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Steam cracking:

Q) How to separate $\text{C}=\text{C}$ & $\text{C}\equiv\text{C}$?

A: Pour to compressor to obtain separating them send to washer (caustic wash to remove acid compounds), then sent to Demethanizer, Deethanizer,
C₂ splitter (splits ethane and other C₂ comp.)

Q) Why 2 heaters?

Ans: Different conditions (typically 800°C). Then sent to Acetylene
Separator.

Ethylene Dichloride (1,2-Dichloroethane)

Precursor material to produce vinyl chloride for producing PVC

The reac. of Cl_2 with C_2H_4 produces only 1 product, so no separation process. The other 2 methods are not preferred.

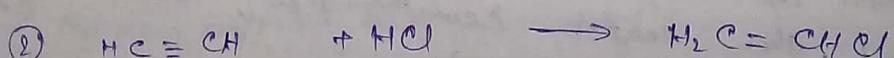
in liquid phase, and the feed ($\text{C}_2\text{H}_4 + \text{Cl}_2$) gas is

 The FeCl_3 or $\text{C}_2\text{H}_5\text{Br}_2$ catalyst is bubbled through the ~~feed~~ of liquid cat. in the reactor. There is an HCl scrubber that scrubs HCl from the off gas.

The catalyst $\text{C}_2\text{H}_5\text{Br}$ or FeCl_3 needs to be replenished as it can get poisoned by the impurities in the feed.

An alternative reaction method is to send the feed at a higher temp. $\sim 75-80^\circ\text{C}$ and then a solid catalyst like FeCl_3 or Alumina can be used to have a gas-solid reac., where the gas flow can be regulated, and replenishment of cat. not required.

Vinyl Dichloride



The $\textcircled{2}^{\text{nd}}$ reac. consumed the HCl produced in 1st reac., so that it is not released into the atm. The acetylene is taken from the Propylene plant.

The 2 step process reduces the HCl handling and disposal costs.
But cost increases.

lower explosive limit of Vinyl Chloride ⁱⁿ Air is 5% and upper limit is 23%.

Reaction ①
the dichloroethane is first preheated by steam and passed through a dryer to remove any water. The water is removed as, if water is present, then in the quencher, the water will be condensed and absorb the HCl gas, and HCl can't be vented off.

In the Vinyl still, the bottom product is ~~Dichloro Ethane~~ ^{unreacted} Ethylene Dichloride (Or Dichloroethane) along with some polychlorides. The Ethylene Dichloride is recycle. To prevent uncontrolled ^{at high temp} polymerization of Vinyl Chloride as stabilizer is added.

The catalyst in the reactor is charcoal or pumice. As ΔT is at high temp, coking might take place at very high temp.

Reaction ②

Here, no drying step, as HCl is consumed, not produced.

The catalyst used in the reactor is charcoal, and some excess HCl is used than stoichiometry. The HCl reduces the efficiency of the catalyst. At the end, some Ethylene Dichloride is produced that is recycled to the 1st reaction plant.

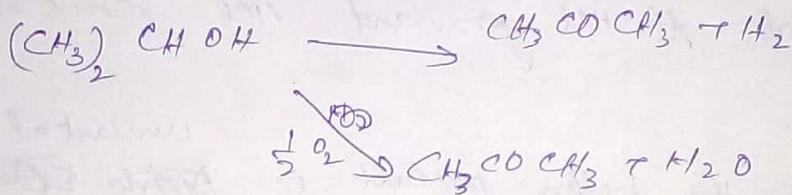
C₃ Compounds

The base material is Propylene, produced by
Heave Cracking of Naphtha.

Acetone

Used as an organic solvent. Highly volatile ^{some} explosive
nature

Catalytic Dehydrogenation of Isopropanol



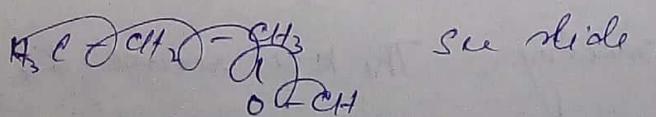
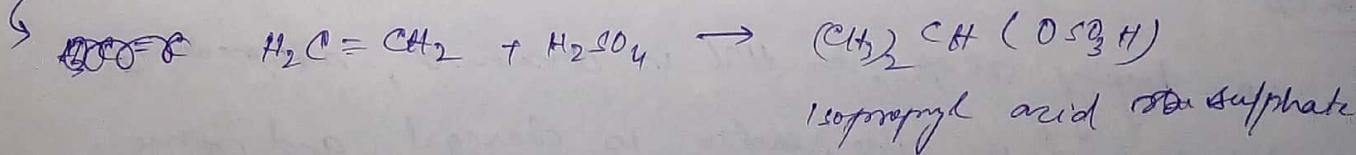
Direct ~~oxy~~ oxidation of propylene is another method, but not preferred as cat. is very expensive.

How is Isopropanol produced?

Used to produce Acetone.

→ Direct catalytic hydration of propylene (more economical as above).

→ Hydration of propylene via isopropylation \rightarrow Hydrolysis



Side on is a drawback.

the sulphuric acid used is ~60-70%. Pr. is around 20-25 atm. at temp. is ~60-70%. At atmospheric temp ~30-35°C. The temp. is maintained by a coolant (refrigerated brine)..

the H_2SO_4 is scrubbed off, concentrated and reused. Here, the residence time of the H_2SO_4 a water wash occurs and here only, Hydrolysis take place. We need to have a high residence time here.

In Hydrolysis section, a higher temp. is maintained ~50-60°C, so there is a partial condense. The caustic wash is to neutralize remaining H_2SO_4 .

In the ether column, the top product Isopropyl Ether is sold in the market. Some amt. of Isopropanol is also there that is fed back to the sulphonation reaction.

The bottom product of ether column is Di-isopropyl ether and isopropanol, which are fed to the IPA column. The top product is Isopropanol and bottom product is H_2O & Heavy HC.

In the Azeotropic distillation, the Isopropyl Ether is used as an entrainer. Bottom product, and top product is water.

Isopropyl Ether.

In Dehydration of Isopropanol, the cat. used in the reactor is Brans or Copper.

In Acetone column, top product is Acetone and bottom is Isopropanol & water.

In Isopropanol Column, top is Isopropanol, bottom is water.

The H_2 from Water Scrubber is used as fuel.

But the $H_2 + Acetone$ has explosive nature, so safety issues.

Cumene (Isopropyl Benzene)

Propylation Cumene was primarily produced to improve the Octane no. of fuels (Only benzene if used is 73 times the amt. of cumene needed to improve the octane no. by same amt.)

Cumene is also used as starting material to produce phenol.

A staged Packed Bed Reactor is used to maintain uniform temp. The cat is charcoal with some fluosilicate.

Major challenge is prevention of formation of polyalkyl benzenes (side rxn.) by maintaining temp. uniform in the bed

$250 \pm 5^\circ C$. Low heat steam is sometimes used to maintain the temp. Also, benzene: propylene = 50:1 (5-6): 1 feed composition prevents side rxn (of polyalkyl benzene).

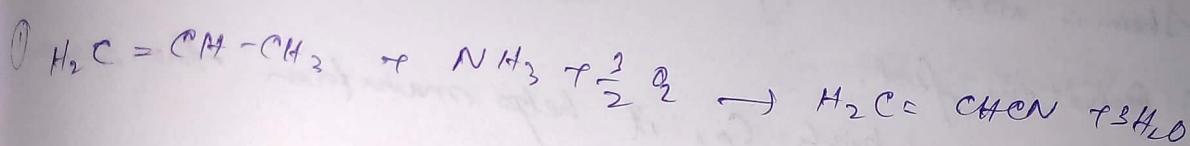
There is lot of unreacted benzene in recycle.

PAN - Poly Acrylonitrile

PAN - Poly Acrylonitrile.

Methods

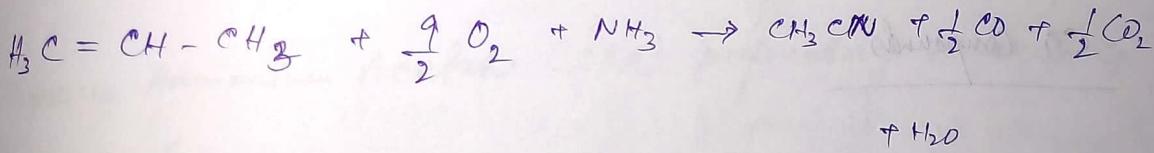
- ① Oxidation of Propylene by Ammonia + Air
- ② Acetylene + HCN rxn
- ③ Acetaldehyde + HCN rxn } Not preferred as HCN is very toxic.



$$\Delta H \approx -136 \text{ kcal}$$

(highly exothermic).

Side rxn: Acrylonitrile to Acetonitrile.



The feed is compressed to $\sim 20\text{ atm}$ and fed to a fluidized catalytic bed reactor. Catalyst is Molybdenum - Bismuth alloy.

In the water scrubber, the Acrylonitrile, Acetonitrile and non-condensables.

Acrylonitrile $\text{BP} \sim 78^\circ\text{C}$
(atm) } to split in product splitter

Acetonitrile $\text{BP} \sim 85^\circ\text{C}$
(atm)

Azeotropic column \rightarrow has azeotrope of Acrylonitrile + water and some cyanide compound. Oxalic Acid is the entrainer. The azeotropic distillation occurs in the Purifying Column.

In case of Acetonitrile, the entrainer is glycerol.

Steam is added in the feed to :

- ① Reheat the feed.
- ② As steam has high C_p , it helps maintain the reactor temp.

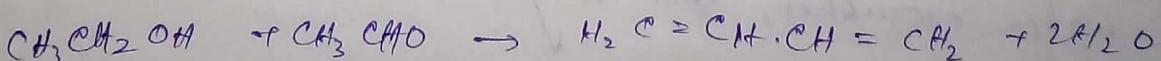
Acrylonitrile and Acetonitrile both are valuable.

C4 Compounds

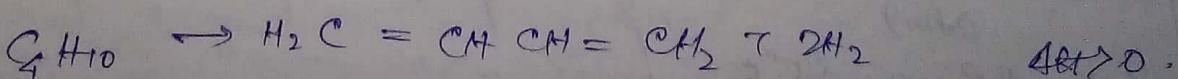
Butadiene

for making Synthetic Rubbers.

Dehydrogenation - Dehydration of ethanol :

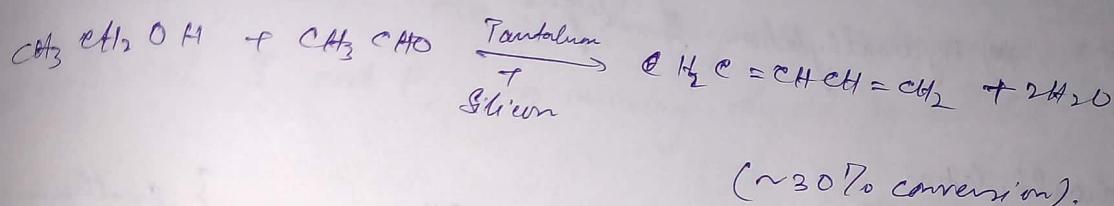
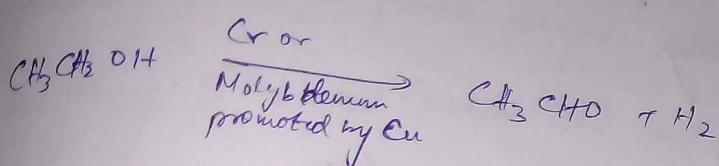


Dehydrogenation of C_4 butane



water and
air.
Column.

The 1st reactor is prepared in India in less content as consumption
of ethanol is less in India than western countries.
Also, in India, butane is used in LPG.

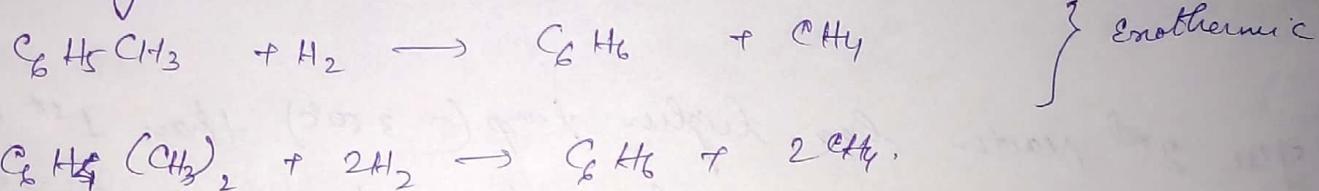


The 2nd reactor has higher temp (~350°C) than 1st reactor.
So, the H₂ produced in 1st reactor is burned or oxidized
in 2nd reactor.

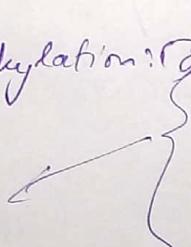
Cuprous Ammonium Acetate (CAA) preferentially removes G
compounds.

Benzene

- Production: i) Solvent Extraction of Benzene from some cuts of crude.
ii) Catalytic Reforming.
iii) Naphtha Cracking.
iv) Hydroalkylation of higher aromatics

Hydroalkylation

Major use: Produce any aromatic derivatives - aniline, chlorobenzene, nitrobenzene, cyclohexane, PTA (phthalic anhydrides)

2 ways of hydroalkylation: 

- i) Thermal route \rightarrow $800-850^\circ\text{C}$
(No catalyst) 70 atm
High energy cost
+
No cat. cost
- ii) Catalytic route \rightarrow $500-550^\circ\text{C}$
 $30-35\text{ atm}$
Low energy cost
+
catalyst cost

After reaction, the pr. is reduced, so that the non-condensable ($\text{H}_2, \text{C}_2\text{H}_4$ etc) are removed in a reflux drum. Then, Gas stripping is done to remove other non-condensables and pr. is brought to atm. conditions

... then fed to a fractionator, from top, lightest ^{comp.} benzene is removed.

Challenges

- i) Handling of H_2 at such severe condition is an issue.
- ii) Recycling of H_2 and (unreacted) and makeup need to be in stoichiometric ratio. Also feed/makeup H_2 and recycle are at different T and P, so mixing should be handled.

Source of H_2 : Steam reforming of Naphtha.

Phenol



After benzene, phenol is most demanded.

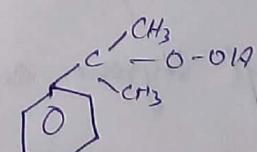
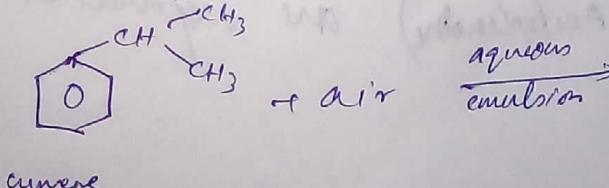
Biggest use of phenol: ① Produce resins with formaldehyde.

↓
long chain molecule (used as adhesives), soft material used for lamination, mould making etc.

② Another use is disinfectant

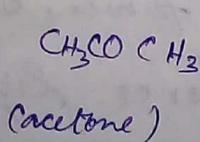
Most preferred method of production is Cumene peroxidation - hydrolysis
Here Acetone is also produced, so both products can be sold.

Peroxidation:
step

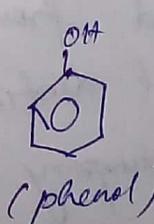


cumene hydroperoxide

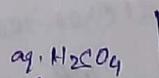
Hydrolysis:
step



(acetone)



(phenol)



aq. H_2SO_4

The aq. emulsion is an emulsion of weak alkali (Na_2CO_3) and cumene. Air is passed through this to get peroxidation step. Cumene : air = 1:3. Atm T and P.

Then, product sent to an agitator vessel for hydrolysis by aq. H_2SO_4 at $60-65^\circ\text{C}$. It is called a cleavage reaction.

Conversion is not 100%, so amt. of phenol is 15-16%. Rest is unreacted Cumene, Acetone (8-10%), α -Methyl Styrene

and Acetophenone

So, essentially, there are 5 products, so we need 4 distillation columns.

The product from the cleavage reactor goes to a separator, where Phenol and heavier HC are separated by settling. The Phenol sent to wash tower (acidified wash water from bottom).

Then this Phenol and other products (unreacted Cumene, Acetone, Methyl Styrene and Acetophenone) are separated in 4 distillation columns.

The pr. is decreased from Acetone one to Cumene to Methyl Styrene to Phenol distillation tower. Due to this, we don't need ~~the~~ any pumping to force liquid from one to another.

BP : Acetophenone > Phenol > ~~②~~ Methyl Styrene > Cumene > Acetone
(~200°C)

The Cumene is recycled back along with Methyl Styrene.
Some H₂ is added to convert some part of the Methyl Styrene
to Cumene. If H₂ is not added right after the separator
or wash tower, as the other compounds (like acetone)
may react with the H₂.

If pH is increased beyond 9, production of Methyl Styrene
is significantly reduced.