

Maleic anhydride

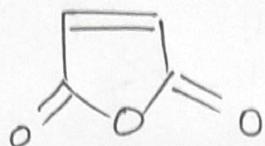
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formula - $C_4H_6O_3$

MP - $52.85^{\circ}C$

BP - $101 \cdot KP : - \underline{202^{\circ}C}$

Structure :-



Uses :-

- 1) Plastizer
- 2) copolymer - polyester
- 3) fibre reinforced plastic
- 4) coating material
- 5) Additives in Epoxy.

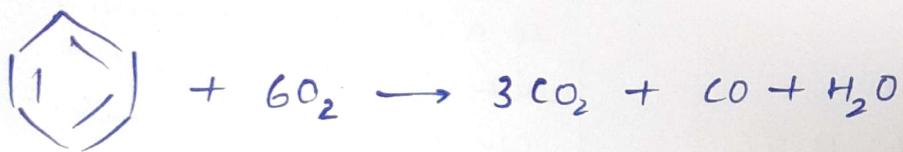
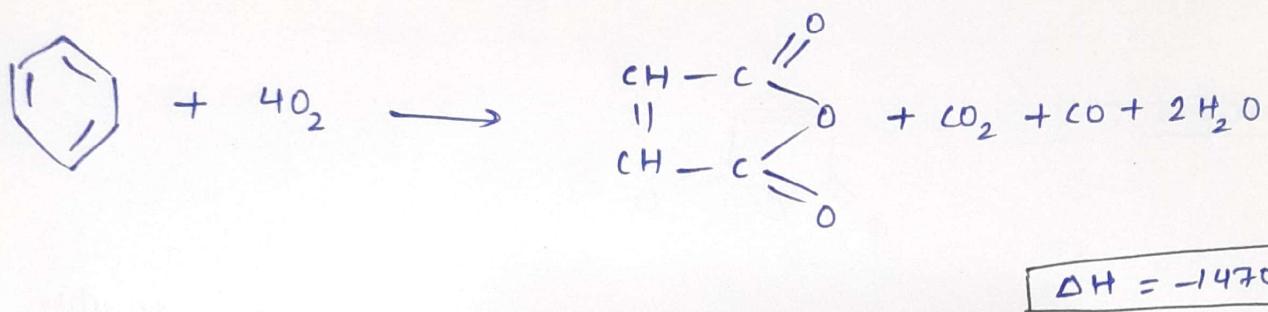
Because of its properties as a dicarboxylic anhydride with double bond, MA can be used for both polycondensation and polyaddition.

Methods :-

→ vapor phase oxidation
of Benzene
(Halon process)

→ n butane oxidation }

benzene feedstock currently accounts for less than 50% of world maleic Anhydride production capacity.



- * Highly exothermic reaction.

Halton process (design)

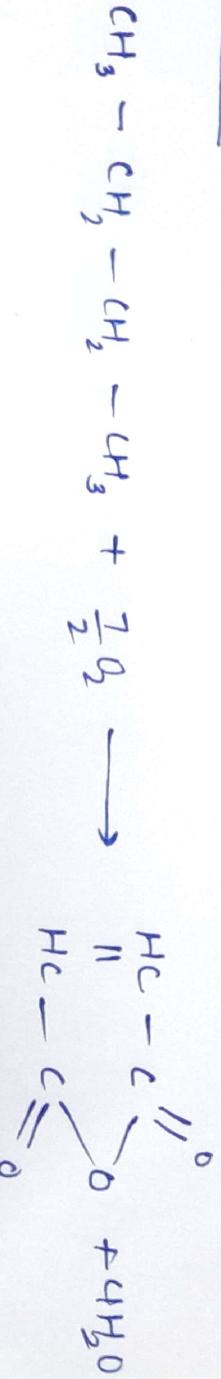
- ↳ Benzene concentration in the feed mixture
- ↳ Catalysts placed in the fixed bed, consists of vanadium pentoxide and molybdenum oxide (V_2O_5 & MnO_2)
- ↳ It also consists of phosphorous pentaoxide which stabilizes the catalyst.
- ↳ Temperature = $300 - 400^\circ\text{C}$

n-butane oxidation

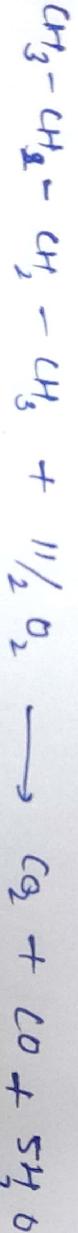
* First industrial plant using n-butane to manufacture maleic anhydride was started by Montanio in 1984.

n-butane is oxidised in vapor phase, in a multi-tube reactor on a fixed bed catalyst based on phosphorus vanadium ion, deposited on silica / alumina support.

Reactions:-



It is accompanied by side reaction combustion of feed.



Advantage of this process:-

One of the advantage offered by n-butane conversion is that all the carbon atom it contains are theoretically found in anhydride.

whereas in case of Benzene, two of them are lost in form of CO_2 .

fixed
tubular
reactor

Difference :-

The essential difference lies in the recovery of maleic Anhydride by partial condensation of the transformation products.

- * In case of n-butane, the amount of water obtained per mole of anhydride formed is two times higher than in case of Benzene.

Soln

→ This higher water content in the effluent limits the temperature to which it can be cooled, so that only 30-50 % of anhydride can be condensed before it reached the water dew point.

↳ The fraction contained in gases is recovered by scrubbing or by adsorption in organic solvent (diethyl hexahydrophtalate).

In case of scrubbing the water is removed by thin layer of evaporators operating under vacuum.



Butane Based catalyst

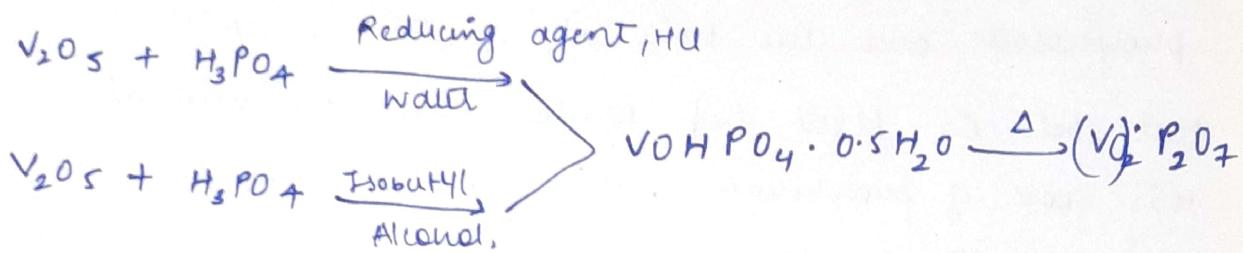
The predominant area of research concern the catalyst for butane to Maleic anhydride route is because of two Reasons :-

- (1) There is a complexity in Reaction :- for Maleic hydride to be produced from butane , eight hydrogen atoms be abstracted . three oxygen atoms to be inserted and a ring closure to be performed.
- (2) secondly all commercial process use same catalyst . This catalyst system is only commercially viable system that selectively produces Maleic Anhydride from Butane.

The catalyst used in the production of Maleic Anhydride (MA) from butane is vanadium - phosphorous oxide (VPO) Vanadium oxide (V_2O_5) and phosphoric acid are reacted to form Vanadyl hydrogen phosphate ($VOHPO_4 \cdot 0.5H_2O$)

This material is then heated to form Vanadylpyrophosphate ($VO_2P_2O_7$) . vanadyl pyrophosphate is believed to be catalytically active phase required for conversion of Butane to Maleic Anhydride.

The reaction of V_2O_5 & H_3PO_4 to form $VOHPO_4 \cdot 0.5H_2O$ can be carried out in either an aqueous or organic medium such as isobutyl alcohol.



The use of organic medium yield an increase in surface area of the $VOHPO_4 \cdot 0.5H_2O$. This increase in the surface area is carried over to vanadyl pyrophosphate and is desired because of concurrent increase in the activity towards butane is observed.

Additional effect of use of organic medium is the creation of more defects in the crystalline lattice in comparison to a aqueous solute.

[Promoters]:-

Promoters may be added during formation of catalyst precursor ($VOHPO_4 \cdot 0.5H_2O$) or impregnated onto the surface of the precursor before transforming into its activated phase ($(VO)_2P_2O_7$)

- ① Promoters facilitates the transformation of catalyst precursor into the desired vanadium phosphorous oxide active phase, while decreasing the amount of non selective VPO phase in the catalyst.
- ② second role of participation of promoter in formation of solid solⁿ which controls the activity of VO^{2+} .

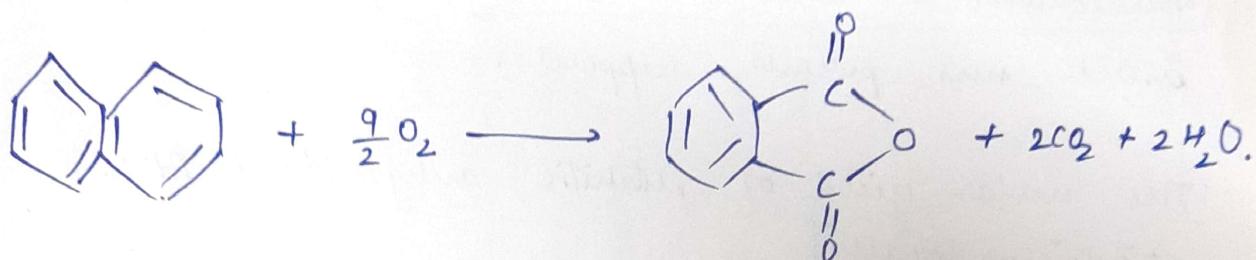
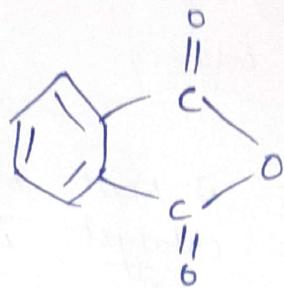
Phthalic Anhydride ($C_8H_4O_3$)

uses :- Plasticizers
Polyester Resins
Dyes.

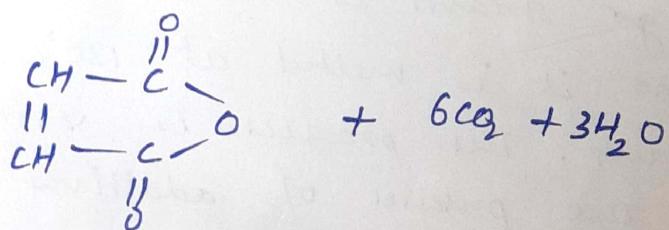
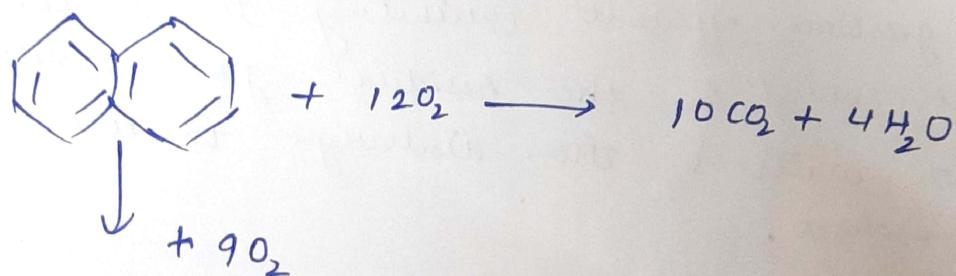
$$M.P = 131.6^\circ C$$

$$B.P = 295^\circ C$$

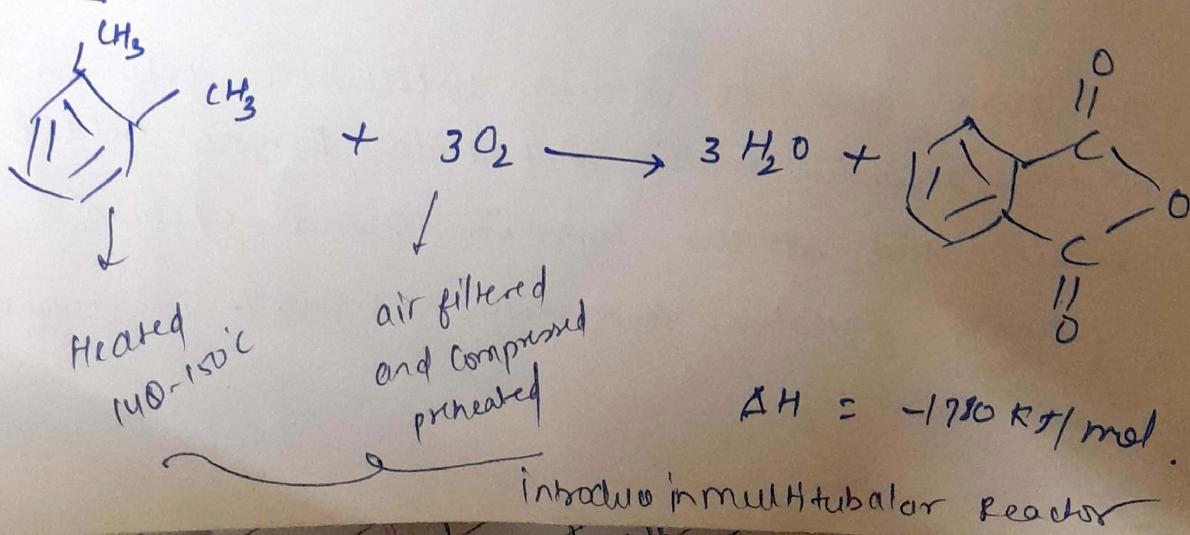
Structure :-



Air



Oxyacetylene



fixed bed or xylene process

O₂-oxyline heated to 140-150°C & air filtered compressed preheated is introduced in a multi-tubular reactor consisting of 1500 tubes 2.5 cm in diameter & 3.2 m high.

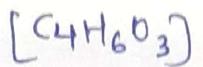
Temp. of about 380°C is kept by the circulation of molten salts. The catalysts in a mix of Nanadium & titanium oxide deposited on the inert non porous support.

[The molar yield of phthalic anhydride is 74%. stoichiometrically]

The gaseous effluent exiting the reactor is first cooled & the residual gases scrubbed with water & then discharge to the atmosphere.

The condensed gas stream is sent to the batch condenser where it is melted at 130°C & sent to storage tank. The product is vacuum preheated in the presence of additives to decompose non-volatile impurities.

It then goes to vacuum distillation column which separates maleic Anhydride, Benzoic Acid & folic Acid at the top in second vacuum column phthalic Anhydride 99.5 wt% is recovered at the top!

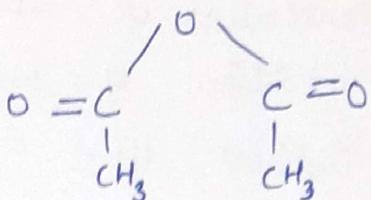


Acetic Anhydride

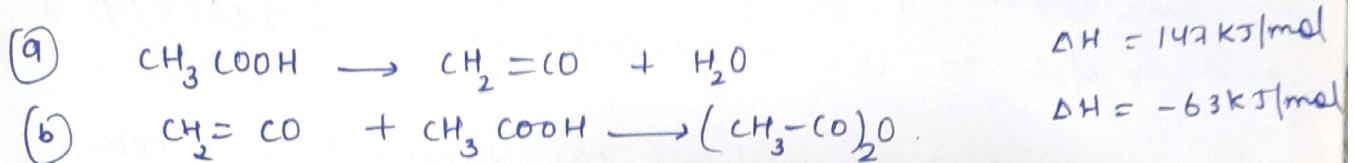
Acetic Anhydride

B.P = $138.6^{\circ}C$

MP = $73.1^{\circ}C$



1. Pyrolysis of Acetic Acid to Ketene
2. Action of Ketene obtained on Acetic Acid



The first conversion is highly exothermic takes place in vapor phase at high temperature ($700-800^{\circ}C$) pressure (10 to 20 kPa)

very short residence time of 1 sec, and the presence of catalyst. serve to limit the formation of the by-products notably in particular from the cracking of Acetic acid & Ketene: CO_2 , CO , CH_4 coke deposit H_2 ethylene etc.

The catalyst system employed for dehydration are usually organic phosphates (tri-ethyl, or bis-cresyl or dimethyl ammonium, pyridinium phosphate etc added continuously directly into the gas stream at a rate of 0.2 to 0.5 wt%.

The addition of water in small concentration (10% wt) to acetic acid offers similar advantages to those procured in steam cracking.

In particular it slows down the formation of coke.
The addition of small amount of ammonia exerts
an indirect effect on polymerization of ketene.
Once through conversion is 85-90%. & the molar
yield of 90-95%.

↳ The second conversion which is exothermic is carried
in the absence of catalyst by adsorption in acetic
acid, b/w 30-40°C at reduced pressure (7-1020 kpa)

High pressure & temp facilitate the dimerization of ketene
to diketene whose boiling point (127.4°C) fairly
close to that of anhydride (less than 2% wt%).
is usually formed so that yield of operation
with respect to both the acetic acid & Ketene
is higher than 95-98 molar%.

Production :-

Industrial facility has four sections :-

- Acetic Acid pyrolysis
- Ketene absorption
- Acetic Anhydride purification
- Recovery of unconverted acetic Acid.

The pyrolysis of about 53% of the feed acetic Acid
preheated to about 110°C & containing continuous
additions of trimethylphosphate is achieved by passing
through tubular furnace.

Uses & toxicological effects:

- ↳ dehydrating agent → (Acetic Acid)
 - ↳ Used to make fibre, plastic, dyes, explosives
 - ↳ eye irritation, with burning sensation
 - ↳ Prolonged exposure may lead to pulmonary edema
- Wetting process also be slowed down, by the addition of carbon disulfide to the feed.

The reactor effluents available at about 700°C . first receive an inline injection of ammonia to neutralise the catalyst.

They are then cooled rapidly to 0°C in a series of heat exchangers.

The liquid obtained by condensation and containing about 35% by wt% acetic acid is sent to recovery section.

Ketene adsorption takes place on the off gases with a counter current of acetic acid in two adsorptions in series, the first collecting 80% of available ketene. A series of two acetic anhydride & acid then serves to recover the acetic acid.

Pharmaceutical

phenol (C_6H_5OH) (Hydroxylbenzene)

Melting point = $40.9^\circ C$

Molar state = clear colourless liquid.

uses:-

- (a) bisphenol
- (b) Phenolic resins
- (c) aniline
- (d) alkylphenols.

Feedstock
chahiyé
cumene

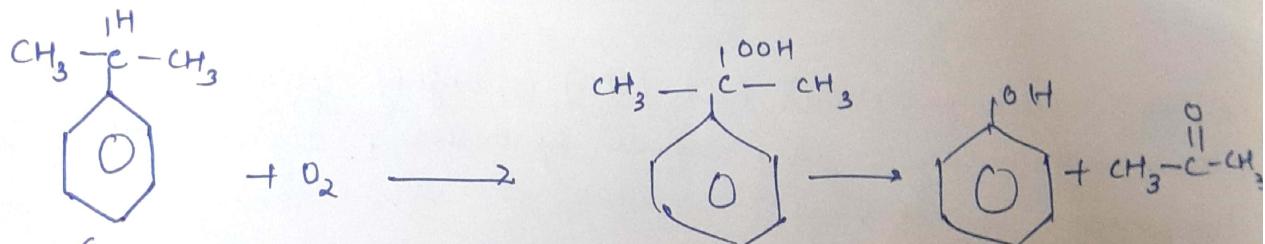
Manufacture: The cumene oxidation route is the leading commercial process of synthetic phenol production.

Accounting for more than 95% of phenol in the world.

* Several licenced process to produce phenol which was based on cumene

↓
All the processes consists of two fundamental chemical reaction

- Cumene is oxidized to form cumene hydroperoxide.
- Cumene hydroperoxide is cleaved to yield phenol & acetone.



Cumene formed by Alkylation of Benzene & propylene over an acid catalyst is oxidized to form cumene hydroperoxide (CHP)

The cumene hydroperoxide is concentrated & cleaved to produce phenol & acetone.

By product of oxidation Reaction is

ACP - Acetophenone

DMBA = dimethyl Benzyl Alcetal

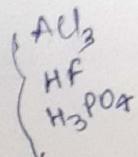
DMBA is dehydrated in the cleavage reaction to produce (AMS)

AMS = Alphamethyl styrene.

Production of cumene

↳ Cumene is produced commercially through the alkylation of benzene with propylene over an acid catalyst.

Catalyst :-
proposed : Aluminium chloride , phosphoric Acid ,
beron trifluoride , hydrogen fluoride .
phosphoric Acid .



80% of cumene of world produced by solid phosphoric Acid.

Although solid phosphoric Acid (SPA) is highly efficient & economical catalyst for cumene syntheses , it has two important limitations :-

- ① cumene yield is limited about 95% , because of oligomerization of propylene & formation of heavy alkylate by products.
- ② The catalyst is not regenerable & must be disposed at the end of catalyst cycle .

Phenol production

- 1) Oxidation of Cumene as the first reaction step usually carried out in series of bubble column reactors.
- 2) Oxygen is used in each reactor as oxidant.
- 3) Bubble column operated at pressure - 600 KPA
Temperature - (120 °C)
- 4) Temperature is controlled by internal or external heat exchangers.
- 5) Phenol is a strong inhibitor, so any recycled cumene must be treated to remove even traces of phenol.

In early years:-

Cumene oxidation process carried out in three phase reaction.
so - called wet oxidation .

In addition of cumene & air an aqueous sodium carbonate solution was continuously added to reactor to extract & neutralize organic acids which are formed during oxidation.

Now IEOS Phenol, was first to operate the reactors without adding any caustic soda or sodium carbonate , process known as dry oxidation .

Phenol from Toluene

Two steps:

- 1) Oxidation of toluene to benzoic acid
- 2) Oxidation of benzoic acid to phenol.

Principle :- complete oxidation of methyl group.

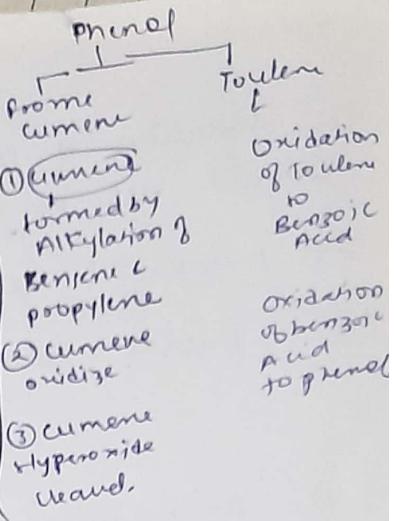
By product :- CO_2 & H_2O .

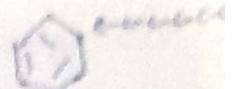
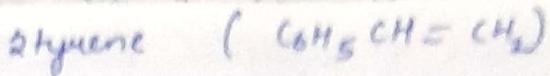
first step:

- Oxidation of toluene carried out in liquid phase
- Temperature = $100 - 150^\circ\text{C}$
- Gauge pressure = 2 bar.
- Catalyst - Cobalt Naphthenate used as soluble catalyst.
conⁿ b/w 0.1 - 0.3%.
- complex Radical main Mechanism
- Intermediates form \rightarrow Benzyl Alcohol & biphenyl
Benzaldehyde.
- By product = Benzyl benzoate
= Biphenyl
= Acetic Acid, small amount CO_2 , CO .

Second Step

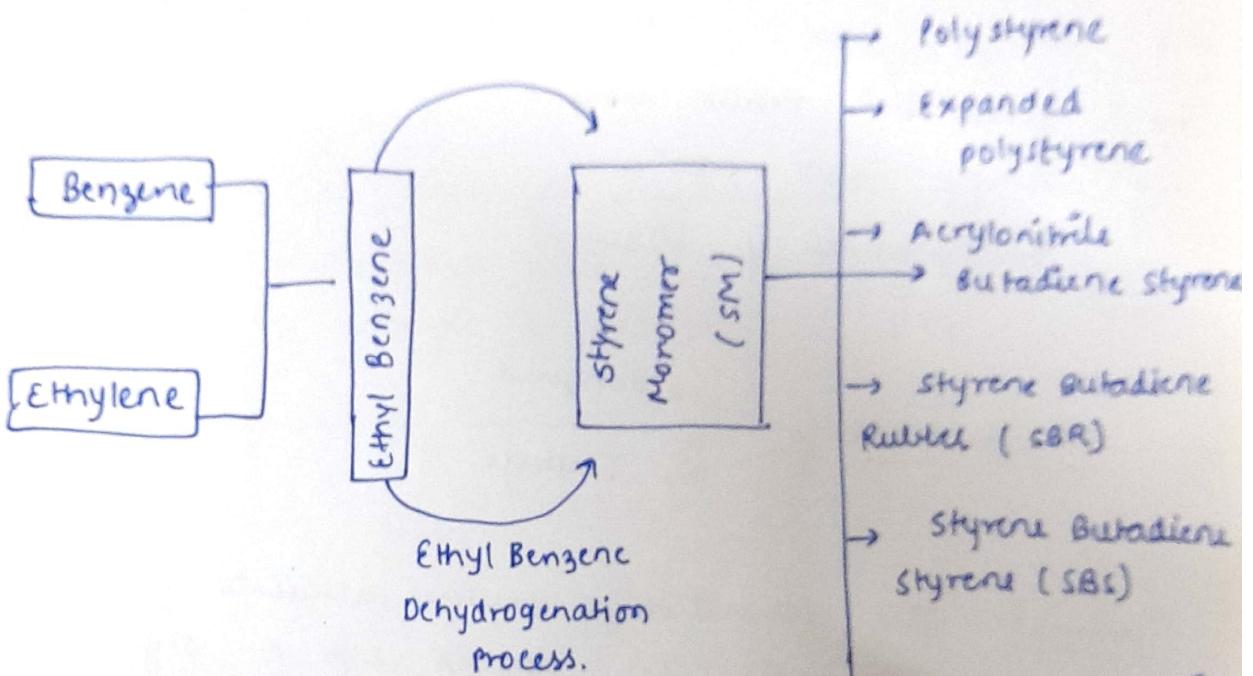
- ↳ Benzoic Acid as reactant (solvent medium)
- ↳ Temperature = $230 - 240^\circ\text{C}$ at atmospheric pressure.
- ↳ Catalyst = Soluble copper (II) benzoate
- ↳ Magnesium salts added to act as promoter.





- ↳ also known as Styrene monomer (SM)
- ↳ Styrene is produced in large quantities for polymerization
- ↳ versatile Monomer

uses - manufacture of plastics
including crystalline polystyrene
Rubber modified impact polystyrene
Acrylonitrile.



Styrene produced from dehydrogenation of Ethylbenzene is used nearly 90% of the worldwide styrene production.

The rest is obtained from coproduction of propylene oxide (PO) & styrene (SM)

This method is → complex
→ capital intensive

The global demand of propylene oxide is only $\frac{2}{10}$
of that of styrene by $\sqrt{7}\%$.

The ratio of propylene oxide to styrene from $P_0 - S^M$
route is more than 4:10.

Dehydrogenation

- ↳ dehydrogenation of ethylbenzene to styrene.
- ↳ catalyst used: iron oxide - potassium oxide catalyst
- ↳ fixed bed reactor used
- ↳ Temp - $550 - 680^\circ C$
- ↳ in presence of steam.



Toluene: the formation of toluene accounts for the
biggest yield loss. i.e approx 2% of styrene produced
when selectively catalyst is used.

Benzene: formation of benzene accounts for yield
loss of up to 1% of styrene produced,

mostly the result of thermal decomposition of ethylene
allylbenzene, vinytoluene, cumene, butylbenzene
ethytoluene & heavy aromatics.

These compounds can effect the cost of purification
& the quality of styrene produced product.

steam co-fed with styrene



its purposes are:-

(one way steam is added with styrene during formation of styrene.)

- ① as energy carrier (supplies the endothermic heat of reaction)
- ② as a diluent (it shifts the equilibrium towards the formation of styrene).
- ③ as a reactant in water gas reaction: It retards and limits carbon deposition on the catalyst.

It is important as steam in dehydrogenation reaction.
SHR (Steam Hydrocarbon ratio) is imp consideration in the selection of catalyst & process.

catalysts :- 40-90% Fe_2O_3

5-30% K_2O_3

Role:

↳ steam stability : which refers to the ability of the catalyst to sustain the desired styrene conversion under a given set of operating conditions (Press. Temp.)

Steam instability is characterized by accelerated decrease in the styrene conversion as a result of rapid carbon deposition on the catalyst.

The quantity of catalyst used for a given plant capacity is related to Liquid hourly space velocity * (LHSV)

LHSV - Liquid Hourly space velocity

The volume of liquid hydrocarbon feed per hour per volume of catalyst.

To determine the optimal LHSV for a given design several factors are considered

- styrene conversion
- styrene selectivity
- Temperature
- pressure, pressure drop.

Adiabatic Dehydrogenation

- ↳ Styrene plants carry out the dehydrogenation reaction adiabatically in multiple reactor.
- ↳ The necessary heat of reaction is applied at inlet to each stage, either by injection of superheated steam or by indirect heat transfer.
- ↳ fresh ^{catalyst} benzene feed is mixed with recycled ethyl benzene & vaporized.
- ↳ dilution steam must be added to prevent the ethyl benzene from forming coke.