Lec 31: Chemicals from Aromatic Compounds - 3.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from aromatic compounds part 3. In this particular lecture, we will be discussing production of styrene, phthalic anhydride and maleic anhydride. These compounds, production of these compounds we are going to discuss and then source of raw materials for the production of these compounds are nothing but the aromatics. Let us say styrene you can produced by ethyl benzene, but ethyl benzene you can produce by using you know benzene and ethylene.

Phthalic anhydride you can produce by using naphthalene or ortho xylene likewise maleic anhydride you can produce using you know benzene or butane.

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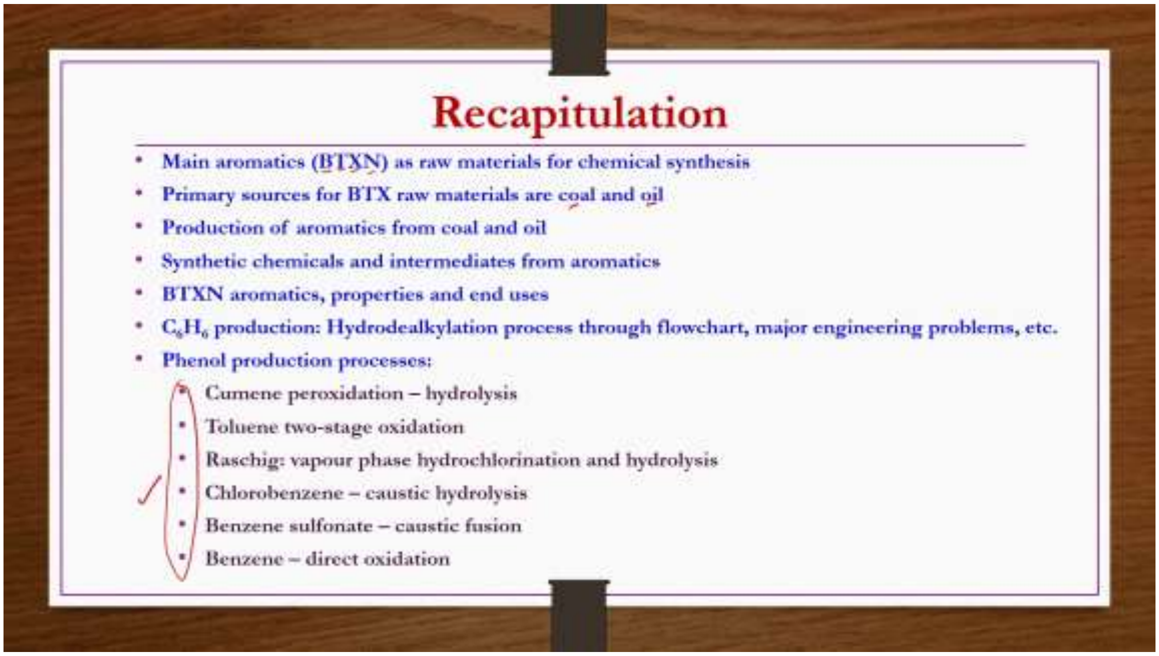

Recapitulation

- Main aromatics (BTXN) as raw materials for chemical synthesis
- Primary sources for BTX raw materials are coal and oil
- Production of aromatics from coal and oil
- Synthetic chemicals and intermediates from aromatics
- BTXN aromatics, properties and end uses
- C_6H_6 production: Hydrodealkylation process through flowchart, major engineering problems, etc.
- Phenol production processes:
  - Cumene peroxidation – hydrolysis
  - Toluene two-stage oxidation
  - Raschig: vapour phase hydrochlorination and hydrolysis
  - Chlorobenzene – caustic hydrolysis
  - Benzene sulfonate – caustic fusion
  - Benzene – direct oxidation

Before going to the details of production of these chemicals, we have a recapitulation of what we have discussed in last couple of lectures of this particular chapter. We started discussion on main aromatics which can be used as raw materials for synthesis of different types of chemicals which include benzene, toluene, xylene and then napthalelene. Then we also tried to find out the sources for such aromatic raw materials.

So, then we found that coal and oil are the better resources to produce such aromatics which can further be converted into different types of chemicals. Then we discussed production of these aromatics from coal and oil. Then we discussed different types of intermediates and n chemicals that can be produced from the aromatics, a list of such chemicals we have discussed. Then we discussed properties and end uses of these aromatics followed by the benzene production by hydrodealkylation process, then phenol production by 6 different processes as listed here we have discussed. We have discussed phenol production by all of these methods.

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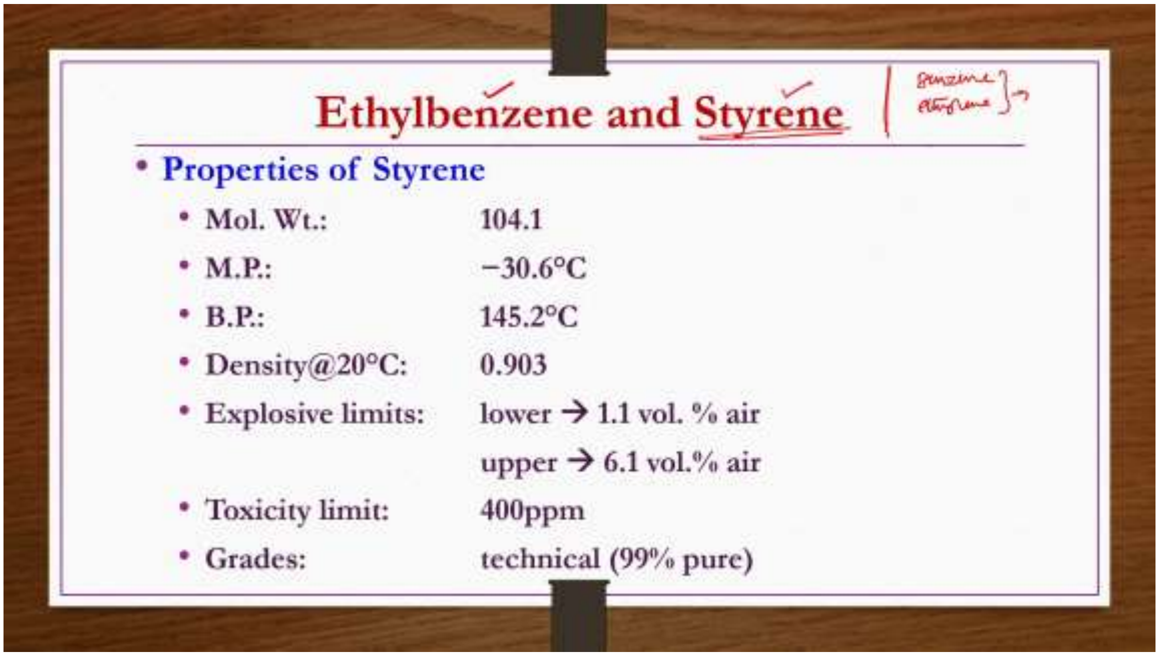

Ethylbenzene and Styrene

Benzene
ethylene

- **Properties of Styrene**

Mol. Wt.:	104.1
M.P.:	−30.6°C
B.P.:	145.2°C
Density@20°C:	0.903
Explosive limits:	lower → 1.1 vol. % air upper → 6.1 vol.% air
Toxicity limit:	400ppm
Grades:	technical (99% pure)

Now, in this lecture we discussed production of styrene. Styrene can be produced from the ethyl benzene actually, but ethyl benzene may not be available plentiful. So, what is the process is that you take a benzene and then ethylene as raw materials and then in the first step of the process you produce ethyl benzene and then you do the dehydrogenation of that ethyl benzene to get the styrene. So, that is the process actually so the styrene production from benzene raw material is a 2-step process. First, we see the pertinent properties of styrene, molecular weight is 104.1, melting point is minus 30.6 degrees centigrade, boiling point is 145.2 degrees centigrade, density at 20 degrees centigrade is 0.903 gram per cc, explosive limits lower and upper limits are 1.1 and then 6.1 volume percentage in air, respectively. Toxicity limit is 400 ppm, grades are technical grade with 99 percent purity.

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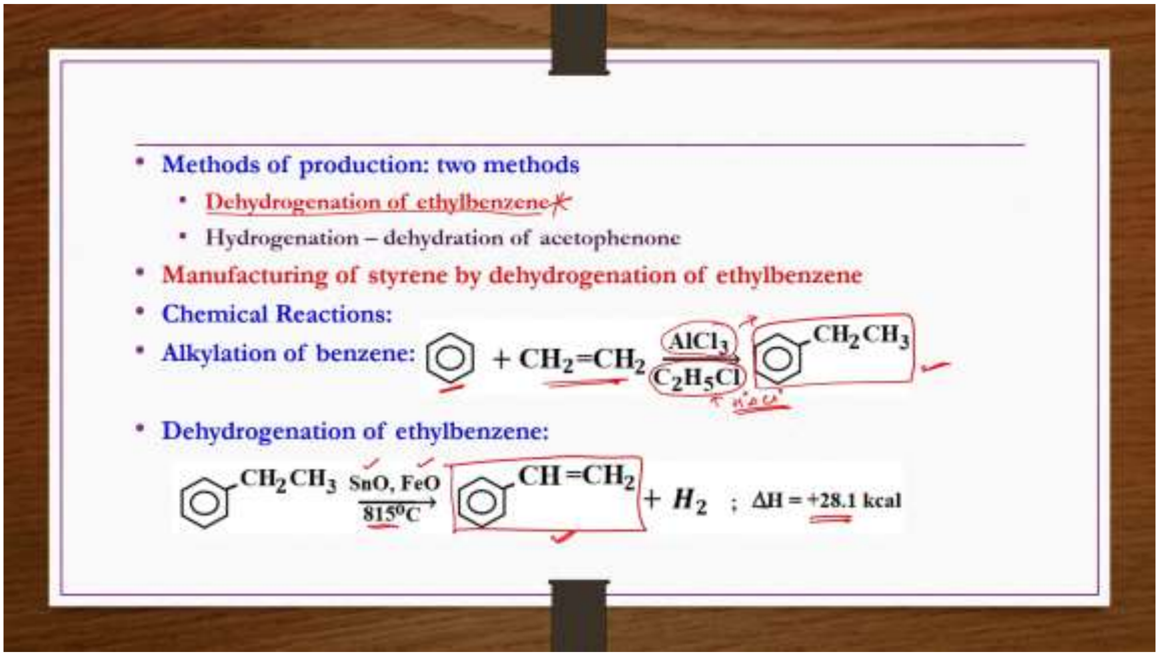

- Methods of production: two methods
  - Dehydrogenation of ethylbenzene
  - Hydrogenation – dehydration of acetophenone
- Manufacturing of styrene by dehydrogenation of ethylbenzene
- Chemical Reactions:
- Alkylation of benzene:
- Dehydrogenation of ethylbenzene:

Then methods of production, 2 methods are there, dehydrogenation of ethylene and then hydrogenation of dehydration of acetophenone. However, we discussed this particular method in detail. First, we produce the ethyl benzene in the first step and then in the second step we do the dehydrogenation of ethyl benzene to get the styrene.

Manufacturing of styrene by dehydrogenation of ethyl benzene, chemical reactions, first production of ethyl benzene is the reaction that is alkylation of benzene. How it is done? It is by the reaction between benzene and ethylene in the presence of aluminum chloride catalyst and then ethyl chloride as well because this ethyl chloride supplies the hydrogen and then chlorine free radicals. So, this will enhance the catalytic activity of aluminum chloride. So, this aluminum chloride is also added up with this ethyl chloride. Then this alkylation of this benzene with ethylene takes place, then you get the ethyl benzene component.

This reaction is also known as the Fredel-Craft reaction. This ethyl benzene will further undergo dehydrogenation of ethyl benzene in the presence of tin oxide or iron oxide at 815 degrees centigrade to produce styrene which is an endothermic reaction.

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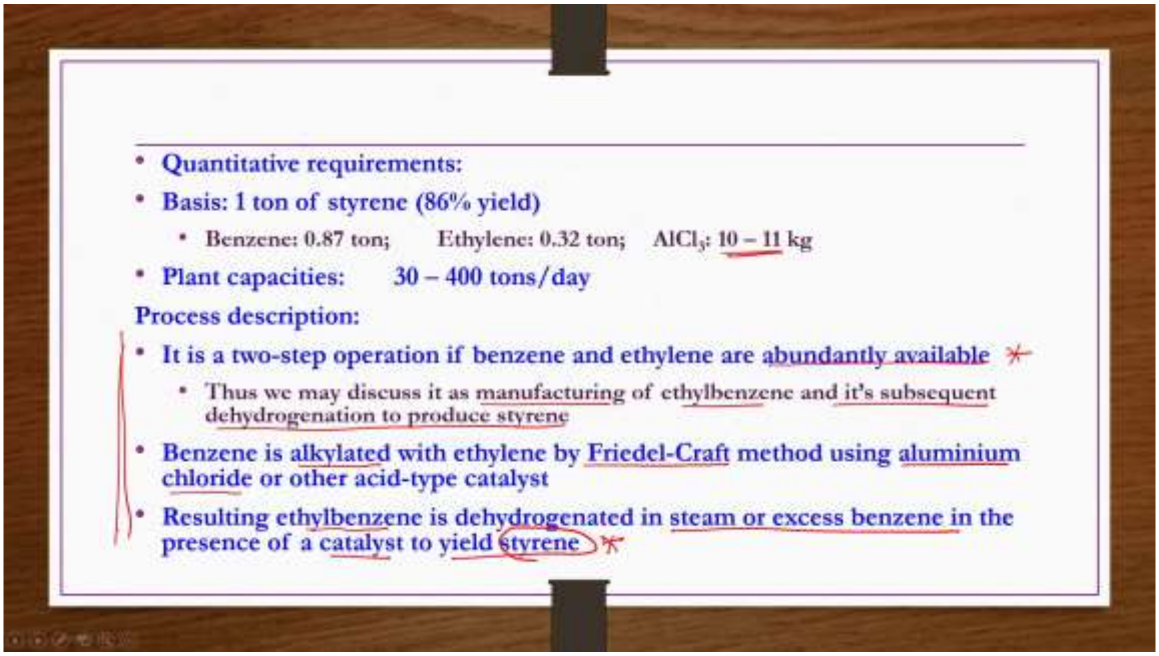

- **Quantitative requirements:**
- **Basis: 1 ton of styrene (86% yield)**
  - Benzene: 0.87 ton; Ethylene: 0.32 ton; $AlCl_3$: 10 – 11 kg
- **Plant capacities: 30 – 400 tons/day**

Process description:

- **It is a two-step operation if benzene and ethylene are abundantly available** *
  - Thus we may discuss it as manufacturing of ethylbenzene and it's subsequent dehydrogenation to produce styrene
- **Benzene is alkylated with ethylene by Friedel-Craft method using aluminium chloride or other acid-type catalyst**
- **Resulting ethylbenzene is dehydrogenated in steam or excess benzene in the presence of a catalyst to yield styrene** *

Quantitative requirements, if you want to produce 1 ton of styrene with 86 percent yield, benzene 0.87 tons required, ethylene 0.32 tons required, aluminum chloride 10 to 11 kgs.

Plant capacity 30 to 400 tons per day. Process description, it is a 2-step operation if benzene and ethylene are abundantly available, so which is very common in India. Thus, we may discuss it as manufacturing of ethyl benzene and its subsequent dehydrogenation to produce styrene. Benzene is alkylated with ethylene by Fredel-Craft method using aluminum chloride or other acid-type catalyst. Resulting ethyl benzene is dehydrogenated in steam or excess benzene in the presence of a catalyst to yield styrene, okay? This is the overall process in a summary.

In a nutshell this is what the process but however we see the entire process through flowchart with proper description, okay?

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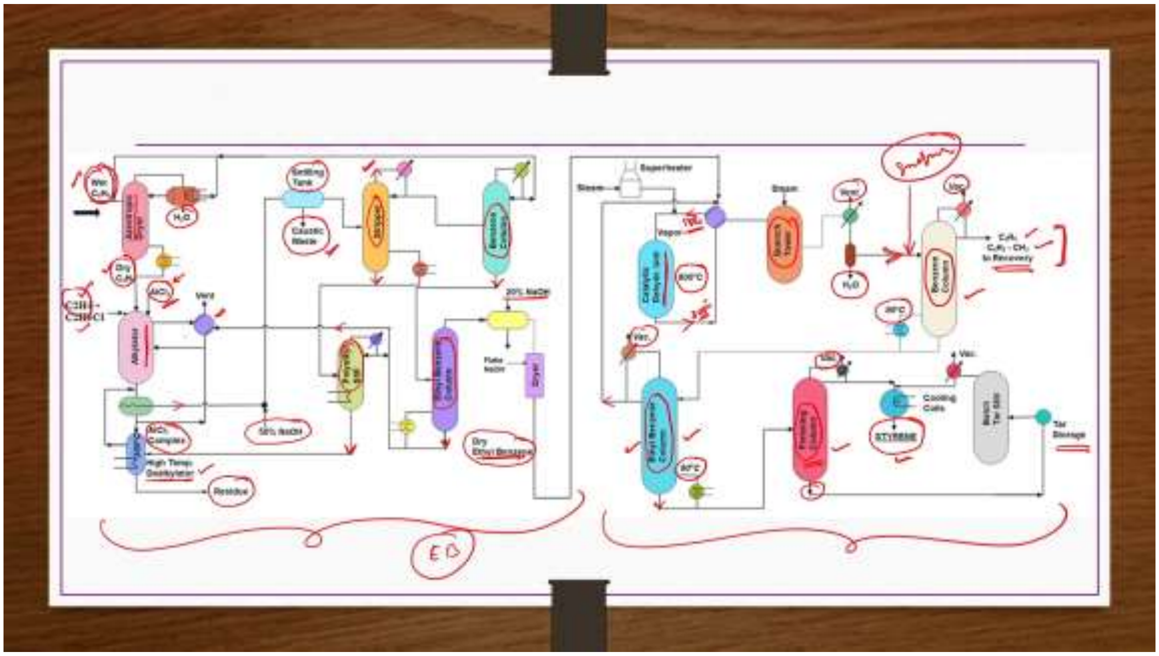

So, what we have? We have in general wet benzene but for this process we need completely dry benzene. Otherwise what happened? Whatever this aluminum chloride catalyst is there, its catalytic activity would be lost if the wetness is there in the raw materials. For that purpose, the benzene has to be dried and then for drying the benzene we have the azeotropic distillation column. When you take the wet benzene and do the azeotropic distillation, in the top you get water rich phase that you condense to separate out the water and then whatever the wet benzene little bit is there that you recycle back to the distillation column. Whereas from the bottom of the azeotropic distillation column you get the dry benzene.

This dry benzene along with the ethylene and ethyl chloride and then catalyst aluminum chloride is sent to the alkylator which is operating approximately at 95 degrees centigrade and then atmospheric pressure. So here alkylation reaction takes place and then you get ethyl benzene primarily. Theoretically that is the reaction but however there would be unreacted components like benzene and then poly alkyl benzene and other complicated alkylates may also be forming. So, for that purpose what you have to do? You have to take the product from the alkylator to a cooler to cool it to the 40 degrees centigrade where you can separate out the aluminum chloride complex and then recycle back to the alkylator. Whereas the higher molecular weight poly alkylates whatever are there they are taken to the high temperature dealkylator where this poly alkylates whatever are there something like polyethyl benzene, etc.

They would be undergoing dealkylation reaction to produce ethylene benzene and then ethyl benzene, etc. Those things are fed back to the system whereas the components which cannot be further you know undergo dealkylation reaction or reduction they would be taken as a residue. Whereas the ethyl benzene crude with ethyl benzene whatever is there that is in acidic in nature from the cooler you take it and then mix it with 50 percent NaOH to neutralize it that neutralized mixture you can take it to a settling tank where you can separate out the caustic as a waste. You can recover this caustic and reuse otherwise you can take off write off as a waste. Whereas the crude ethyl benzene and then product mixture is there that you take to a stripper.

This stripper would be separating the product mixture into 2 streams one is rich in poly alkyl benzene another one is rich in you know ethyl benzene and then benzene impurities. So, this poly alkyl benzene should be taken to the poly alkyl stills. These stills almost like you know distillation columns wherever it is not mentioned explicitly they are distillation columns. So here these poly alkyl benzenes undergo some kind of a fractionation to recover you know unreacted benzene or ethyl benzene, etc. they would be sent back to the alkylator through a preheater.

Whereas the heavier poly alkyl benzene which are not being fractionated here at the they will be collected as the bottom of this still and then sent back to the dealkylator. Whereas the top stream from the stripper which is rich in ethyl benzene and then with benzene impurities that would be taken to a benzene column where whatever the benzene impurities are there they would be separated as top product and then sent back to the azeotropic dryer for the drying of the benzene and then for reusing of dry benzene into the alkylation reactor. Whereas the bottom of this benzene column would be giving primarily ethyl benzene with some impurities if at all like you know some fraction of benzene, etc. would be there. So those benzene and then other impurities are separated out from the bottom and then fed back to the alkylator through preheater.

So, whereas the top product or top stream from the ethyl benzene column would be nothing but a pure ethyl benzene that would be stabilized by using or neutralized by using 20 percent NaOH and then pass it through a flaked caustic bed so that to dry it and then you get a dry ethyl benzene as a product. So, this is first step where we have got the dry ethyl benzene as product. Now this dry ethyl benzene would be used as a intermediate to get this styrene as per the subsequent part of the flow chart that is this part. So this ethyl benzene would be passed through a preheater then vaporized and then mixed with steam and then mixture of steam and then vaporized ethyl benzene would be taken to catalytic dehydrogenation unit which would be operating at approximately 800 to 815 degrees centigrade roughly and then product mixture whatever is there that is passed through a preheater again because this reactor product stream whatever is there that would also be at high temperature like 800 degrees centigrade something like that. So that heat would be passed through incoming reactants.

Incoming reactants are nothing but the ethyl benzene and then steam so they need to be preheated up to the temperature of 500 degrees centigrade. So, whatever the temperature carried by the product mixture that would be transferred to the reactants in the preheater so that the reactants would be preheated and then that preheated reactants would be sent to the catalytic dehydrogenation unit. These preheaters are important from the energy economic point of view. So once the temperature of the product mixture is reduced to certain low temperature after passing through feed preheater that is sent to the steam quench tower to reduce its temperature further and then mixture is sent to a condenser to separate out the vent gases like CO_2, etc. and then water is separated out from the condenser as the bottom.

After separating the water, the product mixture is primarily having the styrene along with benzene and toluene and then unreacted ethyl benzene impurities, etc. So that product mixture what you do you first take it to a benzene column then you take it through ethyl benzene column and then final finishing column. All of them are working under vacuum that means vacuum distillation is taking place or vacuum fractionation is taking place in these 3 columns. That is why it is because if you are doing the fractionation at high temperature there is a possibility of a polymerization of benzene, toluene and then styrene also. So, which is not good from the product point of view.

So, first this mixture is taken to a benzene column which is operating under approximately 160 mm of absolute pressure vacuum and then reboiler is operating at 90 degrees centigrade. So, here from the top of the column you get the benzene and then toluene for a recovery whereas from the bottom of the column you will be getting a product stream which is primarily having styrene along with the unreacted ethyl benzene. So, that mixture is taken to the ethyl benzene column which is also operating under vacuum but at approximately 35 to 60 mm absolute pressure and then boiler operating at 90 degrees centigrade. From this ethyl benzene column from the top you recover the unreacted ethyl benzene and then feed it back to the catalytic dehydrogenation unit by passing through a preheater. Whereas from the bottom of ethyl benzene primarily you get pure styrene and then the styrene is taken to the finishing column to further purify.

Purify by removing if at all some tar kind of materials are formed. This tar kind of materials are collected from the bottom of this finishing column and taken to the tar storage. Actually, to this product mixture that is you know coming out after the catalytic dehydration unit which has been quenched and you know temperature reduced to this one you usually add sulphur in order to make the styrene stabilized. Because you want styrene monomer you do not want it to be polymerized for that purpose if you add sulphur the styrene would be stabilized. So, such kind of you know sulphur also be removed along with the tar from the bottom of the finishing column whereas from the top of the column you get a pure styrene which you can refrigerate it to the 10 degrees centigrade or less and then store it as it is or directly you take it to the polymerization unit for the required polymerization to be done.

So, this is the styrene production via dry ethyl benzene intermediate. So, this ethyl benzene you are getting from the benzene and ethylene. So, basic raw material here is benzene which is aromatic.

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First step – ethylbenzene production

- Process for production of ethylbenzene is same as that of cumene manufacturing process
- In other words, ethylene alkylation of benzene in vapour phase over a catalyst produces ethylbenzene
- Separation of ethylbenzene from xylene fractions in petroleum reformate is difficult because ethyl benzene has only 2.1°C lower b.p than p-xylene
  - In order to separate them, recent refinery operations use several 250ft columns in series
  - Recovery of this high purity ethylbenzene overhead fraction avoids alkylation procedures
- However, bulk of plants use alkylation of benzene process because ethylene and benzene are more plentiful
- Alkylation operation must be done under very dry conditions with high purity feedstock to avoid activity loss of catalyst
- Thus all benzene feed must be dried by azeotropic distillation
- Ethyl chloride is added to ethylene which is fed continuously along with benzene to the alkylation tower operating at 95°C and 1 atm pressure

Now, we see process description for the first step that is ethyl benzene production. Process for production of ethyl benzene is same as that of cumene manufacturing process which we have already discussed in the previous chapter.

In other words, ethylene alkylation of benzene in vapor phase over a catalyst produces ethyl benzene. Separation of ethyl benzene from xylene fractions in petroleum reformate is difficult because of ethyl benzene has only 2.1 degrees centigrade slower boiling point than para xylene. Actually, this ethyl benzene also you get in petroleum reformates when you try to get the xylene fractions, etc. But this para xylene whatever is there that having only 2.1 degrees centigrade higher boiling point than the ethyl benzene. So, separation of ethyl benzene from the para xylene is not possible because of that reasons you know we choose the alkylation of benzene process to get ethyl benzene and then dehydrogenation of that ethyl benzene we do to get the styrene. However, in order to get the separation if at all you wanted to get ethyl benzene from the petroleum reformate in general what people do they use a very tall columns in series to get such kind of separation. Recovery of this high purity ethyl benzene overhead fraction avoids alkylation procedure but obviously such high towers you need to have. However, bulk of plants use alkylation of benzene process because ethylene and benzene are more plentiful than the ethyl benzene coming out from the petroleum reformate.

So, alkylation operation must be done under very dry conditions with high purity feedstock to avoid activity loss of catalyst, aluminum chloride catalyst we are using. Thus, all benzene feed must be dried by azeotropic distillation. Ethyl chloride is added to the ethylene which is fed continuously along with benzene to the alkylation tower operating at 95 degrees centigrade and 1 atmospheric pressure.

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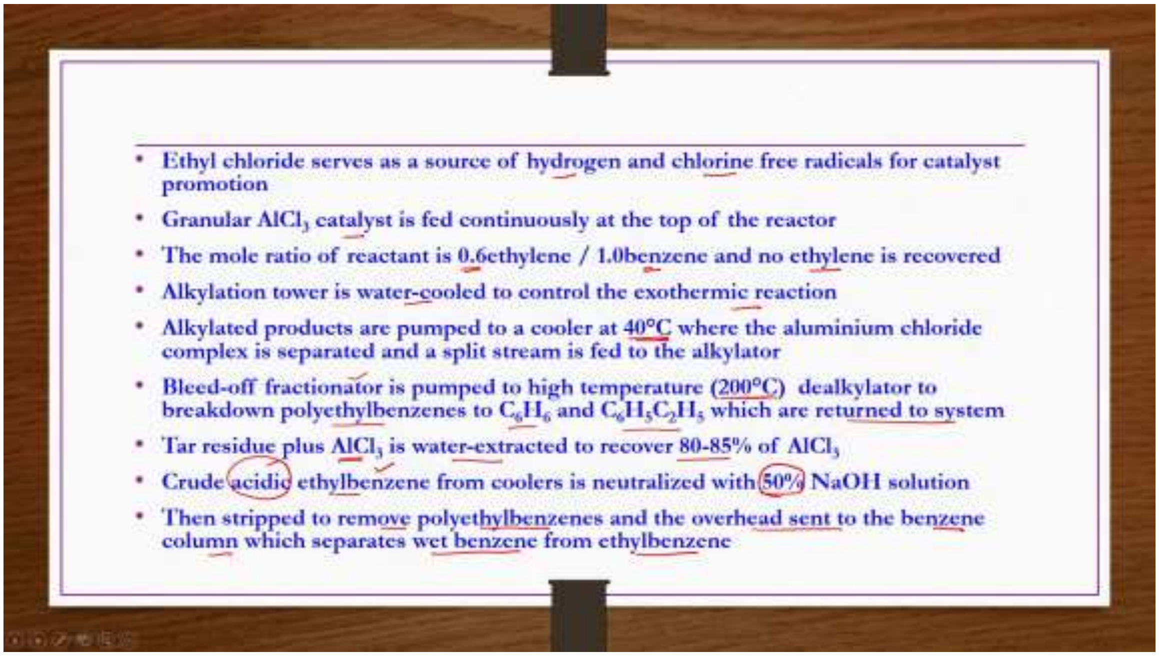

- Ethyl chloride serves as a source of hydrogen and chlorine free radicals for catalyst promotion
- Granular $AlCl_3$ catalyst is fed continuously at the top of the reactor
- The mole ratio of reactant is 0.6ethylene / 1.0benzene and no ethylene is recovered
- Alkylation tower is water-cooled to control the exothermic reaction
- Alkylated products are pumped to a cooler at 40°C where the aluminium chloride complex is separated and a split stream is fed to the alkylator
- Bleed-off fractionator is pumped to high temperature (200°C) dealkylator to breakdown polyethylbenzenes to C_6H_6 and $C_6H_5C_2H_5$ which are returned to system
- Tar residue plus $AlCl_3$ is water-extracted to recover 80-85% of $AlCl_3$
- Crude acidic ethylbenzene from coolers is neutralized with 50% NaOH solution
- Then stripped to remove polyethylbenzenes and the overhead sent to the benzene column which separates wet benzene from ethylbenzene

Ethyl chloride serves as a source of hydrogen and chlorine free radicals for catalyst promotion. Granular aluminum chloride catalyst is fed continuously at the top of the reactor.

The mole ratio of the reactant is 0.6 moles of ethylene per mole of benzene and no ethylene is recovered in this process almost all ethylene is being consumed to get ethyl benzene. However, there would be some unreacted benzene. Alkylation tower is water cooled to control the exothermic reaction. Alkylated products are pumped to a cooler at 40 degrees centigrade where the aluminum chloride complex is separated and a split stream is fed to the alkylator. Bleed off fractionator is pumped to high temperature dealkylator to break down polyethylbenzene to benzene and ethylbenzene which are returned back to the system that is to the alkylator.

Tar residues plus aluminum chloride is water extracted to recover the 80 to 85 percent of aluminum chloride. Crude acidic ethyl benzene from coolers is neutralized with 50 percent NaOH solution because this ethyl benzene is acidic in nature. Then stripped to remove polyethylbenzene and the overheads into the benzene column which separates wet benzene from the ethyl benzene.

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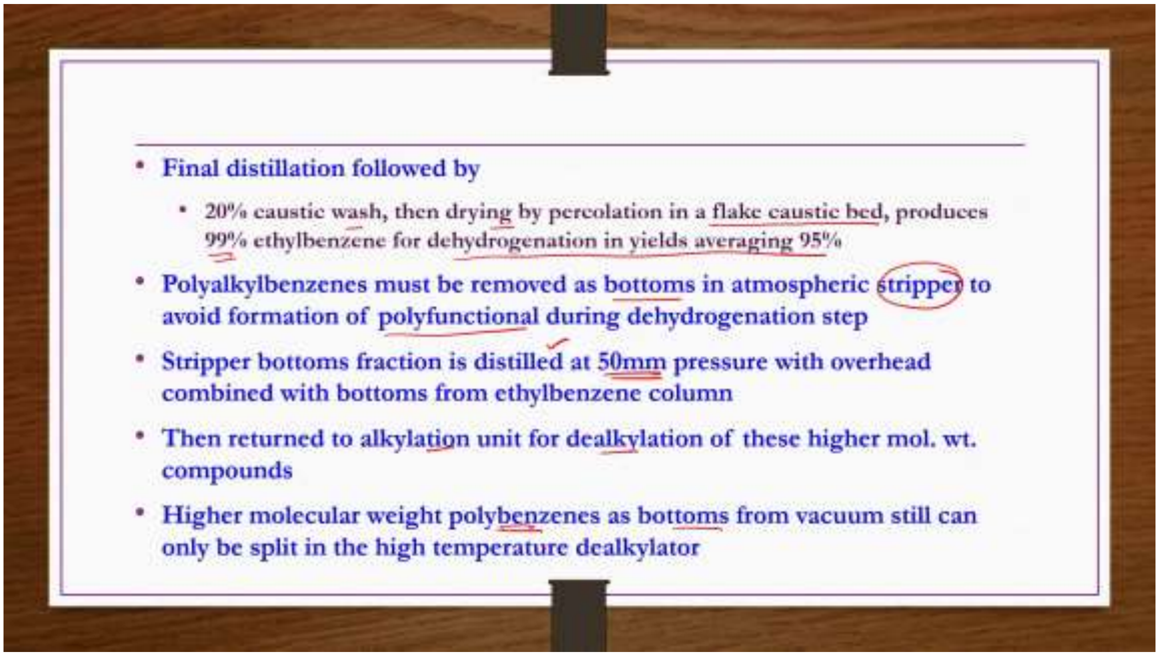

- Final distillation followed by
  - 20% caustic wash, then drying by percolation in a flake caustic bed, produces 99% ethylbenzene for dehydrogenation in yields averaging 95%
- Polyalkylbenzenes must be removed as bottoms in atmospheric stripper to avoid formation of polyfunctional during dehydrogenation step
- Stripper bottoms fraction is distilled at 50mm pressure with overhead combined with bottoms from ethylbenzene column
- Then returned to alkylation unit for dealkylation of these higher mol. wt. compounds
- Higher molecular weight polybenzenes as bottoms from vacuum still can only be split in the high temperature dealkylator

Final distillation followed by 20 percent caustic wash then drying by percolation in flake caustic bed produces 99 percent pure ethyl benzene for dehydrogenation step in yields averaging 95 percent. Polyalkylbenzene must be removed as bottoms in the atmospheric stripper to avoid formation of poly functional during dehydrogenation step.

Stripper bottoms fraction is distilled at 50 mm pressure with overhead combined with bottoms from ethyl benzene column as discussed in the flow chart. Then return to the alkylation unit for dealkylation of this higher molecular weight compounds. Higher molecular weight polybenzene or polyethylbenzene as bottoms from vacuum still can be split in the height temperature dealkylators.

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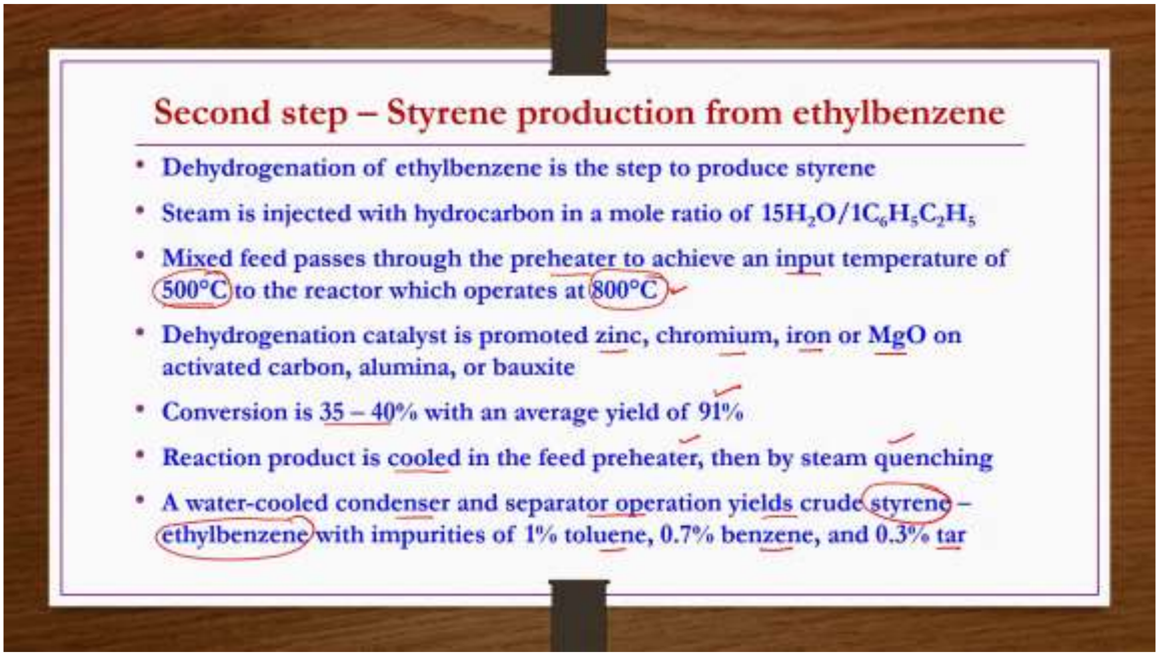

Second step – Styrene production from ethylbenzene

- Dehydrogenation of ethylbenzene is the step to produce styrene
- Steam is injected with hydrocarbon in a mole ratio of $15H_2O/1C_6H_5C_2H_5$
- Mixed feed passes through the preheater to achieve an input temperature of 500°C to the reactor which operates at 800°C
- Dehydrogenation catalyst is promoted zinc, chromium, iron or MgO on activated carbon, alumina, or bauxite
- Conversion is 35 – 40% with an average yield of 91%
- Reaction product is cooled in the feed preheater, then by steam quenching
- A water-cooled condenser and separator operation yields crude styrene – ethylbenzene with impurities of 1% toluene, 0.7% benzene, and 0.3% tar

So, that is the purification step of ethyl benzene. Once you have the pure ethyl benzene you can do the dehydrogenation of ethyl benzene to get the styrene that is the second step.

Dehydrogenation of ethyl benzene is the step to produce the styrene. Steam is injected with hydrocarbon in a mole ratio of 15 moles of steam per 1 mole of ethyl benzene. Mixed feed passes through the preheater to achieve an input temperature of 500 degrees centigrade to the reactor which operates at 800 degrees centigrade. So, reactor operates at 800 degrees centigrade trying to achieve such high temperature within the reactor by fuels or electric furnace, etc. may not be give may not give the you know energy or heat economies for that purpose the feed is preheated to 500 degrees centigrade then send it to the reactor so that the reactor duty would be less.

Dehydrogenation catalyst is promoted zinc, chromium, iron or magnesium oxide on activated carbon, alumina or bauxite. Conversion is 35 to 40 percent with an average yield of 91 percent. Reaction product is cooled in the feed preheater then by steam quenching. A water-cooled condenser and a separator operation yields crude styrene, ethyl benzene mixture with impurities of toluene, benzene and thaw in minor quantities.

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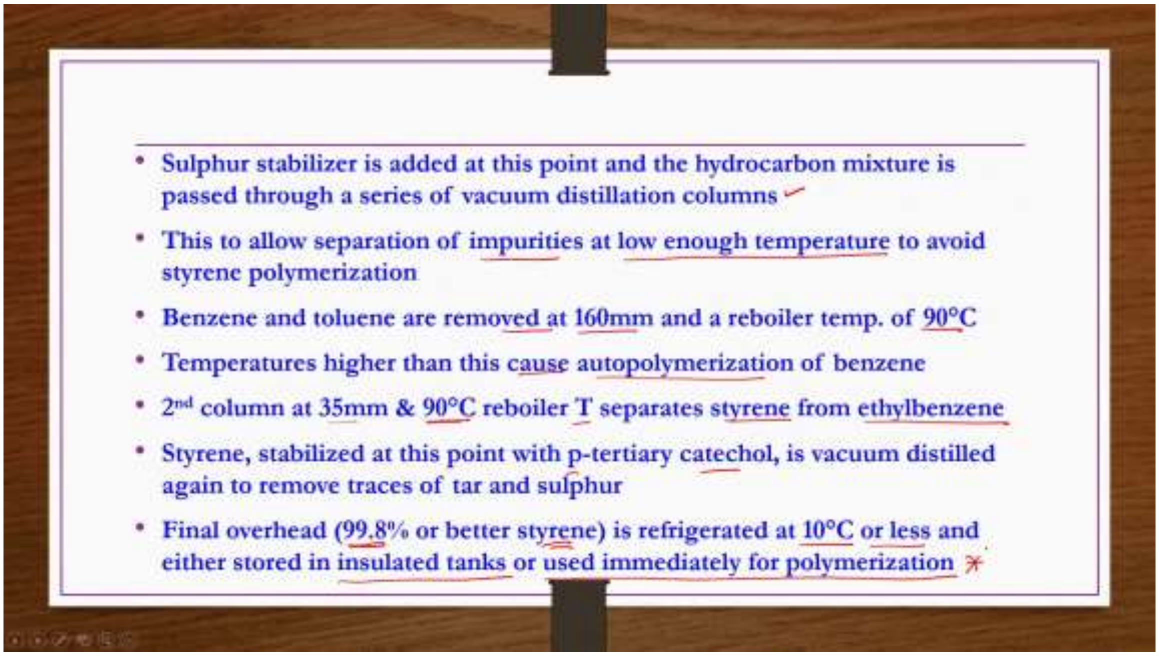

- Sulphur stabilizer is added at this point and the hydrocarbon mixture is passed through a series of vacuum distillation columns
- This to allow separation of impurities at low enough temperature to avoid styrene polymerization
- Benzene and toluene are removed at 160mm and a reboiler temp. of 90°C
- Temperatures higher than this cause autopolymerization of benzene
- 2nd column at 35mm & 90°C reboiler T separates styrene from ethylbenzene
- Styrene, stabilized at this point with p-tertiary catechol, is vacuum distilled again to remove traces of tar and sulphur
- Final overhead (99.8% or better styrene) is refrigerated at 10°C or less and either stored in insulated tanks or used immediately for polymerization

Sulphur stabilizer is added at this point and the hydrocarbon mixture is passed through a series of vacuum distillation columns.

This is to allow separation of impurities at low enough temperatures to avoid styrene polymerization if you apply high temperature by styrene polymerization may take place that is the reason low temperature vacuum distillation columns are used for the purification of styrene. Benzene and toluene are removed at 160 mm and a reboiler temperature of 90 degrees centigrade. Temperatures higher than this cause auto polymerization of benzene which is also not good. Second column operating at 35 mm and 90 degrees centigrade reboiler temperature separates styrene from ethyl benzene unreacted ethyl benzene. Styrene stabilized at this point with para-tertiary catechol is vacuum distilled again to remove traces of tar and sulphur.

Final overhead having 99.8 percent or higher purity styrene is refrigerated at 10 degrees centigrade or low temperature than that and either stored in insulated tanks or used immediately for polymerization as per the requirement. All these we have already discussed in the flow chart as well.

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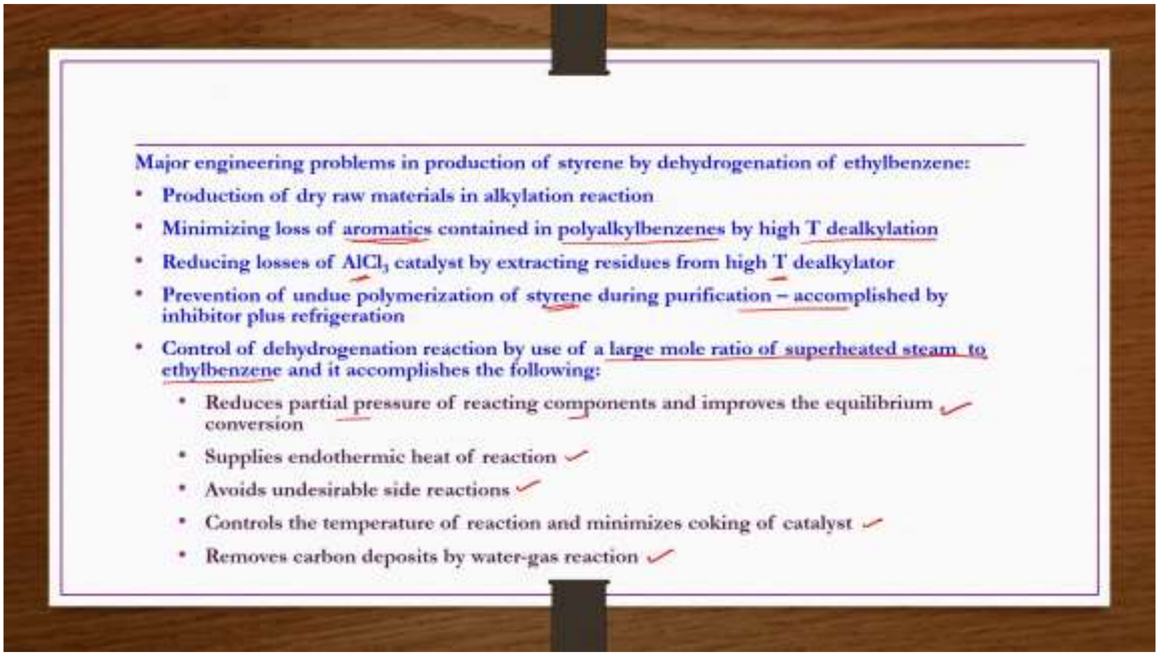

Major engineering problems in production of styrene by dehydrogenation of ethylbenzene:

- Production of dry raw materials in alkylation reaction
- Minimizing loss of aromatics contained in polyalkylbenzenes by high T dealkylation
- Reducing losses of $AlCl_3$ catalyst by extracting residues from high T dealkylator
- Prevention of undue polymerization of styrene during purification – accomplished by inhibitor plus refrigeration
- Control of dehydrogenation reaction by use of a large mole ratio of superheated steam to ethylbenzene and it accomplishes the following:
  - Reduces partial pressure of reacting components and improves the equilibrium conversion
  - Supplies endothermic heat of reaction
  - Avoids undesirable side reactions
  - Controls the temperature of reaction and minimizes coking of catalyst
  - Removes carbon deposits by water-gas reaction

Now coming to the major engineering problems in the production of styrene by dehydrogenation of ethyl benzene. Benzene is the primary basic raw material to get ethyl benzene that must be very dry enough. So, getting dry raw materials in alkylation reaction is one step to be taken care.

Then minimization of loss of aromatic compounds in polyalkylbenzene by high temperature dealkylation. When you do the high temperature dealkylation of polyalkylbenzene, so some of the aromatics may be lost. So, that loss should be minimized. Then reducing losses of aluminum chloride catalyst by extracting residues from high temperature dealkylator is also essential. Prevention of undue polymerization of styrene if you do not control the temperature, styrene polymerization may take place at high temperature.

So, prevention of undue polymerization of styrene during purification is accomplished by inhibitor plus refrigeration that is the reason we are storing at 10 degrees centigrade or less temperature. Control of dehydrogenation reaction by use of a large mole ratio superheated steam to ethyl benzene is essential and it accomplishes the following reduces partial pressure of reacting components which is good and improves the equilibrium conversion. Supplies endothermic heat of the reaction then avoids undesirable side reactions, controls the temperature of reaction and minimizes coking of catalyst and then finally removes carbon deposits by water gas reaction. So, this is all about the production of styrene from ethyl benzene and then ethyl benzene is used and intermediate whereas the primary raw material were benzene and then ethylene.

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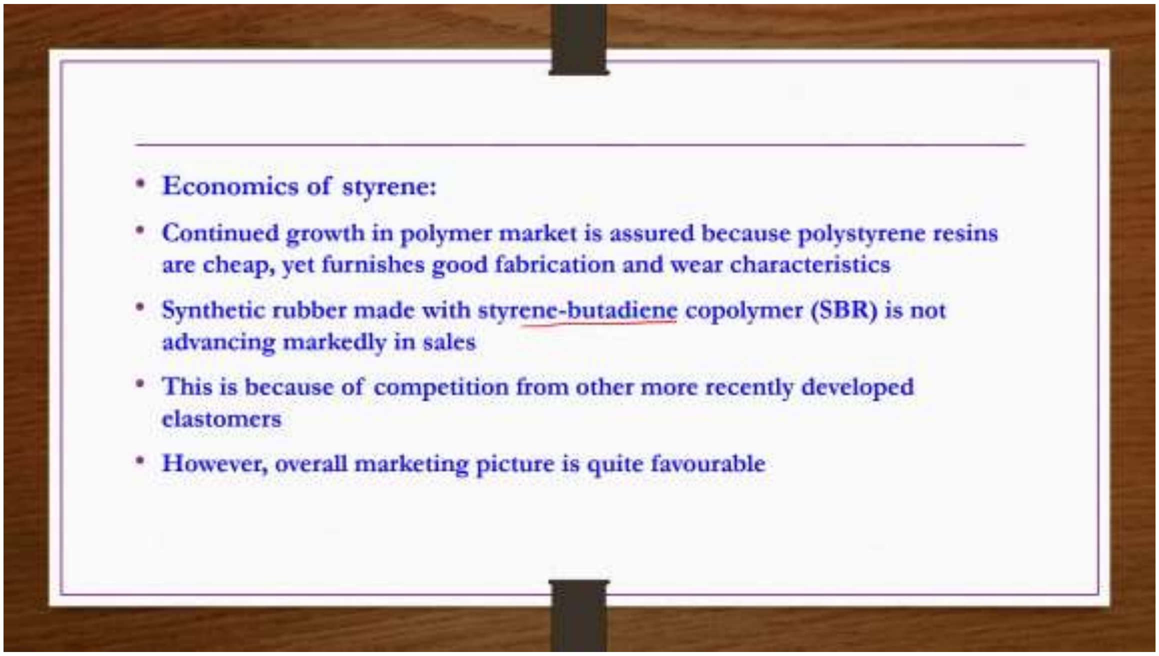

- Economics of styrene:
- Continued growth in polymer market is assured because polystyrene resins are cheap, yet furnishes good fabrication and wear characteristics
- Synthetic rubber made with styrene-butadiene copolymer (SBR) is not advancing markedly in sales
- This is because of competition from other more recently developed elastomers
- However, overall marketing picture is quite favourable

Economics of styrene continued growth in polymer market is assured because polystyrene resins are economic, cheap, it furnishes good fabrication and wear characteristics.

Synthetic rubber made with styrene butadiene copolymer that is SVR is not advancing markedly in sales. This is because of competition from other recently developed elastomers. However, overall marketing picture for the styrene is quite favorable.

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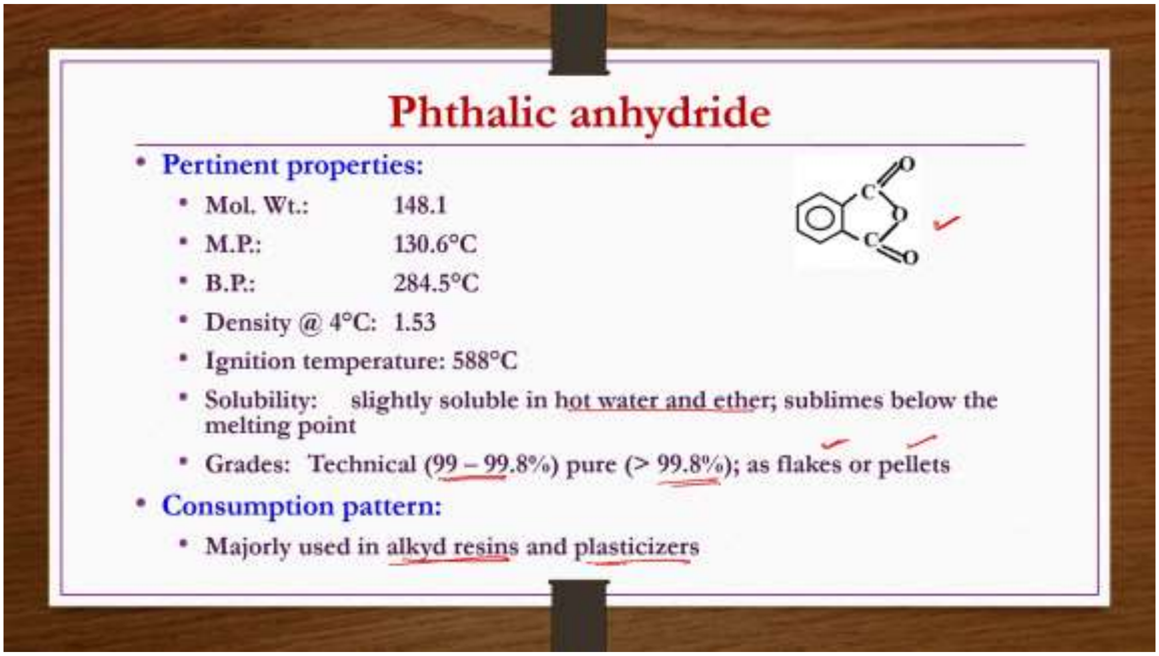

Phthalic anhydride

- **Pertinent properties:**
  - Mol. Wt.: 148.1
  - M.P.: 130.6°C
  - B.P.: 284.5°C
  - Density @ 4°C: 1.53
  - Ignition temperature: 588°C
  - Solubility: slightly soluble in hot water and ether; sublimes below the melting point
  - Grades: Technical (99 – 99.8%) pure (> 99.8%); as flakes or pellets
- **Consumption pattern:**
  - Majorly used in alkyd resins and plasticizers

Now, we discussed about pphthalic anhydride which is having the chemical structure as shown here. Pertinent properties of this compound provided here, molecular weight 148.1, melting point 130.6 degrees centigrade, boiling point 284.5 degrees centigrade, density at 4 degrees centigrade is 1.53 gram per cc, it is a very dense material, ignition temperature is 588 degrees centigrade. Solubility, it is slightly soluble in hot water and ether, sublimes below the melting point. Grades, technical grades having 99 to 99.8 percent whereas the pure more than 99.8 percent is also one of the grade. It can be produced in flakes or pellet forms as well. Consumption pattern primarily used in alkyd resins and plasticizers productions only.

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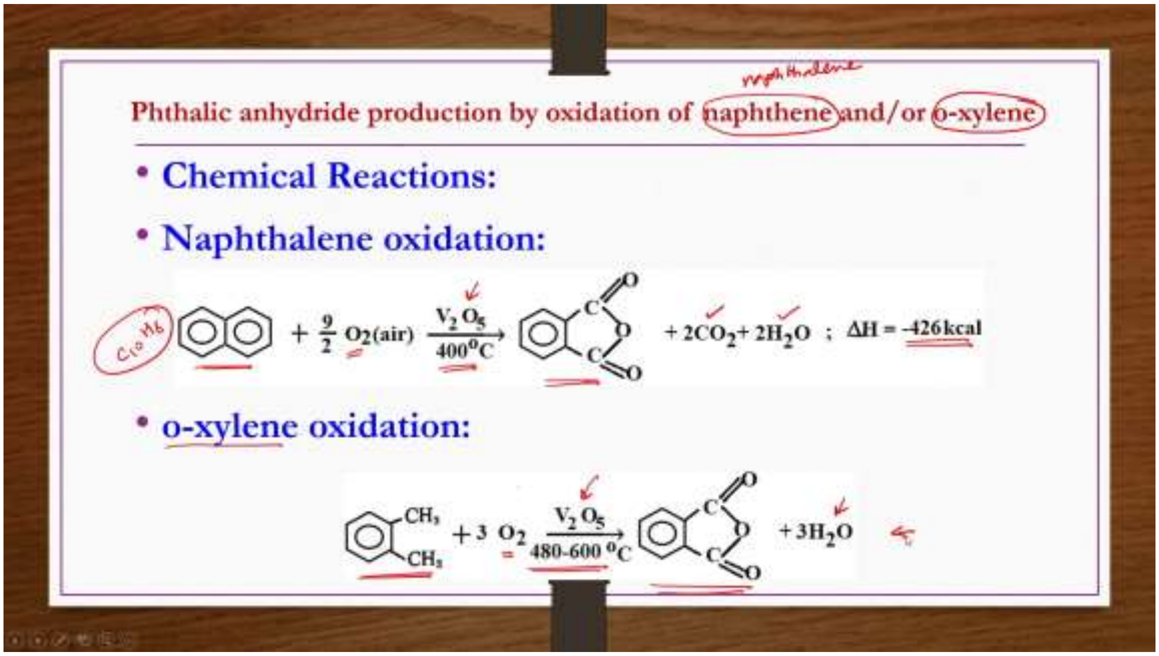

Phthalic anhydride production by oxidation of naphthene and/or o-xylene

naphthalene

- **Chemical Reactions:**
- **Naphthalene oxidation:**

$C_{10}H_8$

$$+ \frac{9}{2} O_2(\text{air}) \xrightarrow[400^{o}C]{V_2O_5} \quad + 2CO_2 + 2H_2O \ ; \ \Delta H = -426\text{kcal}$$

- **o-xylene oxidation:**

$$+ 3\ O_2 \xrightarrow[480\text{-}600\ ^{o}C]{V_2O_5} \quad + 3H_2O$$

Now, we discussed the production of pphthalic anhydride using the naphthalene raw material that is if you do the oxidation of naphthalene, then you can get the pphthalic anhydride or if you do the oxidation of ortho xylene, then also you can get the pphthalic anhydride or you take the mixture of these 2 and do the oxidation of the mixture, then also you get the pphthalic anhydride.

So, accordingly reactions separately we take. Chemical reactions, naphthalene oxidation. So, here this naphthalene that is $C_{10}H_8$ reacts with oxygen or air in the presence of V_2O_5 catalyst at 400 degrees centigrade to produce pphthalic anhydride along with that one you also get carbon dioxide and then water vapors and then reaction is highly exothermic reaction. If you use ortho xylene as reactant and do the oxidation, then xylene, ortho xylene reacting with oxygen in the presence of same V_2O_5 catalyst but slightly higher temperature 480 to 600 degrees centigrade will also give you pphthalic anhydride and water vapor. In this case, there is no CO_2 formation at all.

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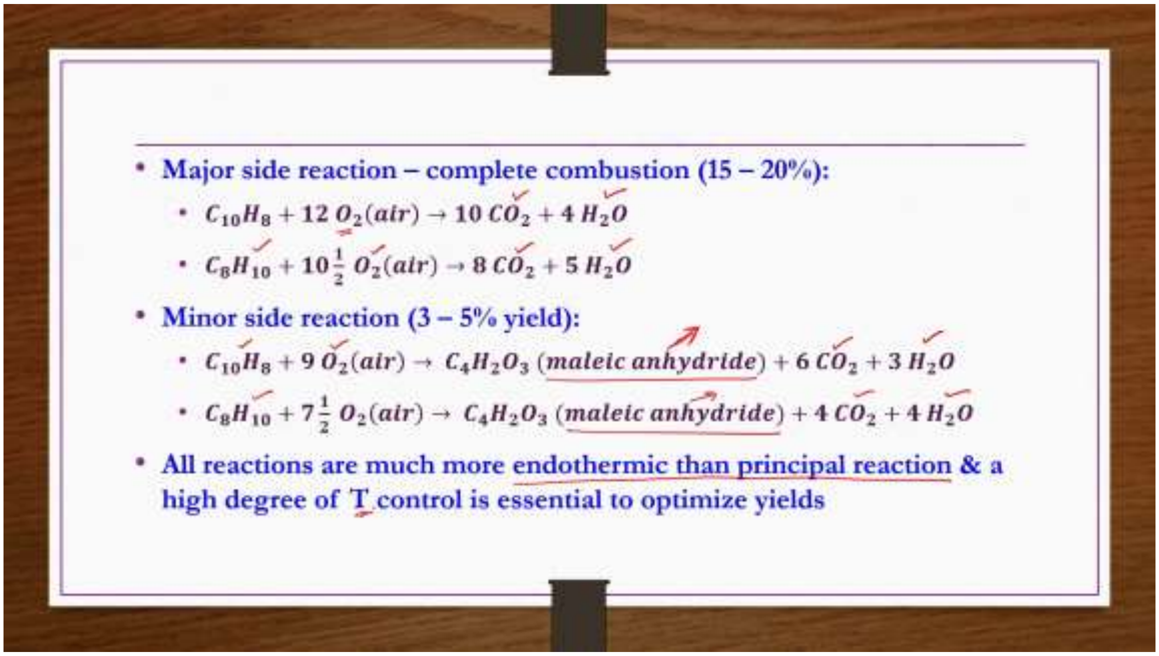

- **Major side reaction – complete combustion (15 – 20%):**
  - $C_{10}H_8 + 12\ O_2(air) \rightarrow 10\ CO_2 + 4\ H_2O$
  - $C_8H_{10} + 10\frac{1}{2}\ O_2(air) \rightarrow 8\ CO_2 + 5\ H_2O$
- **Minor side reaction (3 – 5% yield):**
  - $C_{10}H_8 + 9\ O_2(air) \rightarrow\ C_4H_2O_3\ (maleic\ anhydride) + 6\ CO_2 + 3\ H_2O$
  - $C_8H_{10} + 7\frac{1}{2}\ O_2(air) \rightarrow\ C_4H_2O_3\ (maleic\ anhydride) + 4\ CO_2 + 4\ H_2O$
- **All reactions are much more endothermic than principal reaction & a high degree of T control is essential to optimize yields**

There are some side reactions also there. If you do not control the temperature, complete combustion takes place that is major side reaction where $C_{10}H_8$ that is naphthalene reacting with 12 O_2 giving rise to 10 CO_2 and 4 H_2O. Otherwise you know ortho xylene reacting with 10 1 by 2 oxygen to give 8 CO_2 and then 5 H_2O. Minor side reactions are possible where this naphthalene reacts with oxygen to give maleic anhydride which we are going to discuss its production in the subsequent section of the particular lecture. This reaction also produces CO_2 and H_2O. If you have ortho xylene, it also undergoes oxidation and then produces maleic anhydride along with CO_2 and H_2O.

See now, you cannot control the exactly theoretical requirement of naphthalene and air or xylene and air mixture so that you get only pphthalic anhydride. You also get the impurities like maleic anhydride, CO_2, H_2O, etc. would also be formed in the reactor and then subsequent separation of impurities is becoming essential from the product purity point of view. All reactions are much more endothermic than principal reaction and a high degree temperature control is essential to optimize yields.

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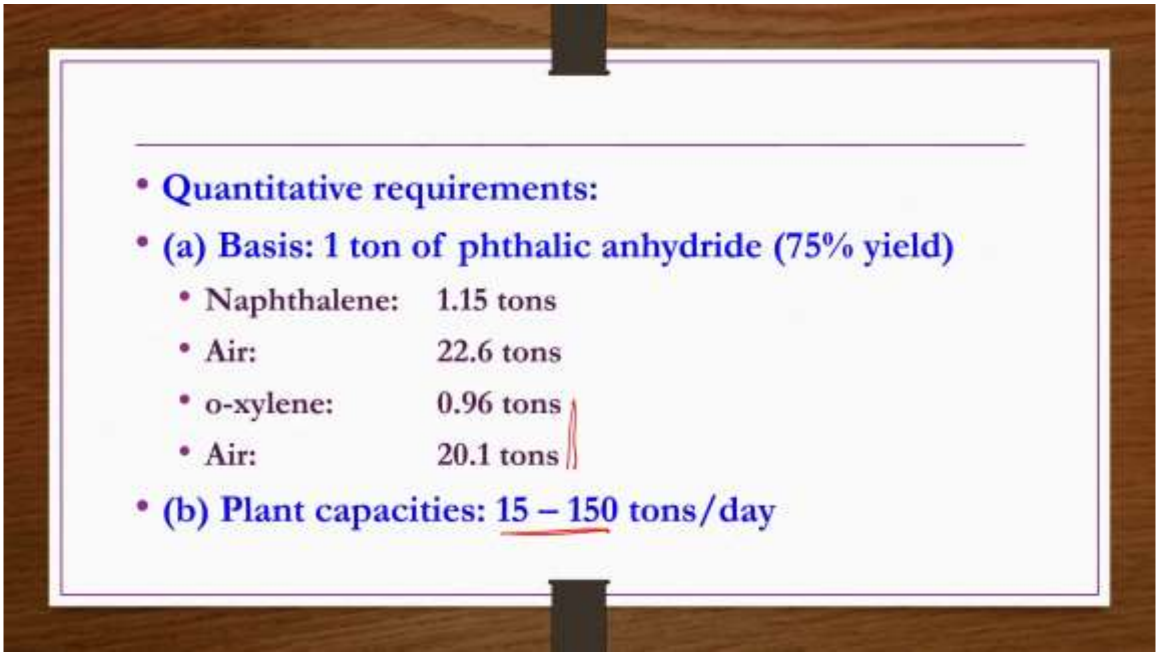

- **Quantitative requirements:**
- **(a) Basis: 1 ton of phthalic anhydride (75% yield)**
  - Naphthalene: 1.15 tons
  - Air: 22.6 tons
  - o-xylene: 0.96 tons
  - Air: 20.1 tons
- **(b) Plant capacities: 15 – 150 tons/day**

Quantitative requirements, 1 ton of ppphthalic anhydride 75 percent yield. If you are using naphthalene then 1.15 tons and then air, 22.6 tons required. If you are using ortho xylene then 0.96 tons required, air 20.1 tons required. So, requirement of the raw materials is slightly less if you are using xylene in comparison with naphthalene and air. Plant capacities 15 to 150 tons per day.

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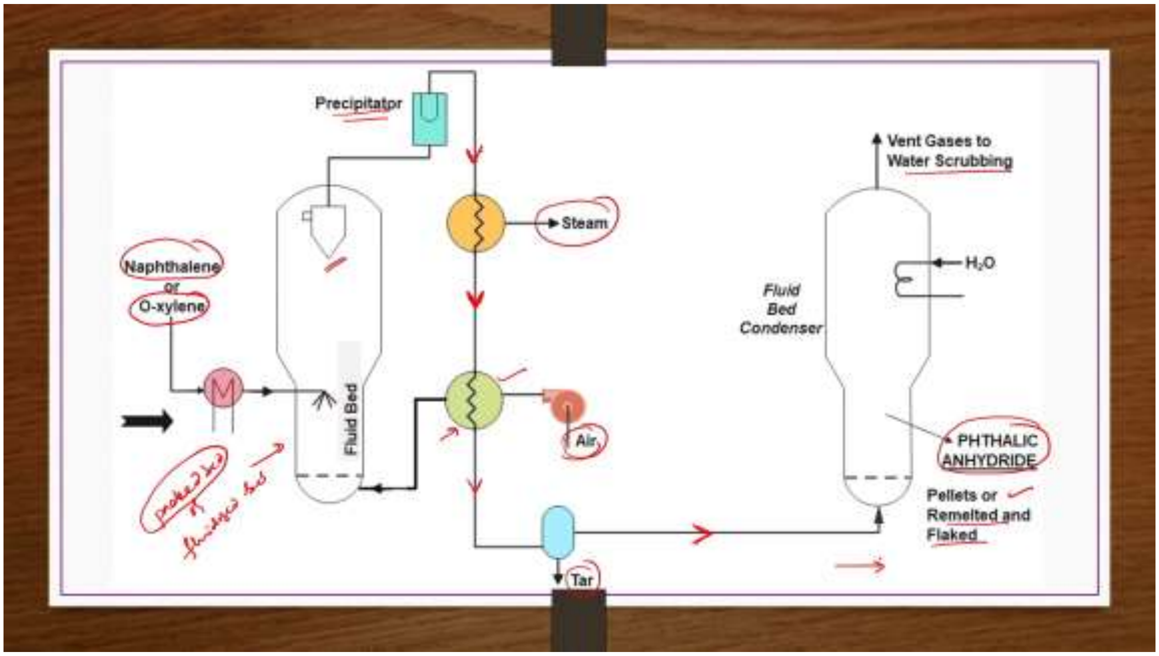

This is the flowchart provided here. So, whether you take naphthalene or ortho xylene or mixture of it, what you have to do? You have to preheat it and then melt it and then that melted mixture of the reactants or individual reactants are fed to a reactor.

This reactor can be fluid bed or packed bed, anything it can be. So, if it is a packed bed actually you have a tubular columns as we have already discussed in some of the other production methods, tubular packed columns. So, those tubular columns are packed with the catalyst of V_2O_5 and then through those tubes the air and naphthalene mixture is being passed so that the oxidation takes place to get the product mixture. Now, here in this case if you are using fluid as bed, so this melted reactants are further vaporized by bubbling with preheated air. So, this air is preheated and then supplied to the bottom of the fluid bed and then that preheated air makes the vaporization of the melted raw materials. And then this air quantity is supplied such a way that required 22 kg of air per kg of the naphthalene whatever requirement is there that accordingly such flow rates are provided here and in this fluid as bed reactor the reaction takes place and then you get the pphthalic anhydride along with the maleic anhydride and other impurities.

So, then reaction mixture is passed through cyclone and then precipitated to collect the dust, etcetera if at all present in the mixture and then this product mixture is passed through a waste heat boiler to recover some of the energy from the product streams in the form of steam. And then still the product streams are hot enough they would be passed through a preheater used for preheating the air so that the some of the heat of the product stream is passed to the air so that that air can be preheated and sent to the fluid bed reactors so that the heat economy can be managed. Then the temperature of the product stream reduces further and then that is passed through a separator to separate out the tar and then product stream is taken to subsequent steps of vacuum distillation and then condensation in fluid bed condenser etcetera to separate out the impurities and then get the pphthalic anhydride as a products in the form of pellets or they would be remelted and flaked as well as per the requirement form. The separation different types of separations are there all those things we discussed in the process description anyway.

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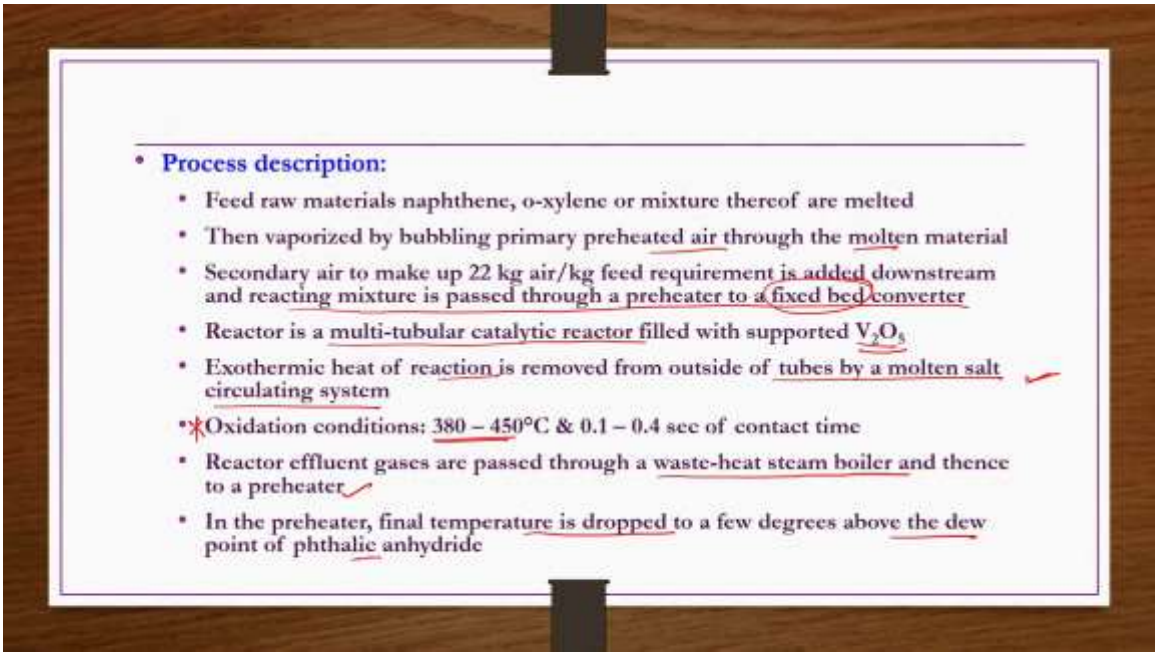

- **Process description:**
  - Feed raw materials naphthene, o-xylene or mixture thereof are melted
  - Then vaporized by bubbling primary preheated air through the molten material
  - Secondary air to make up 22 kg air/kg feed requirement is added downstream and reacting mixture is passed through a preheater to a fixed bed converter
  - Reactor is a multi-tubular catalytic reactor filled with supported V_2O_5
  - Exothermic heat of reaction is removed from outside of tubes by a molten salt circulating system
  - Oxidation conditions: 380 – 450°C & 0.1 – 0.4 sec of contact time
  - Reactor effluent gases are passed through a waste-heat steam boiler and thence to a preheater
  - In the preheater, final temperature is dropped to a few degrees above the dew point of phthalic anhydride

Process description feed raw materials naphthalene, ortho xylene or mixture thereof are melted then vaporized by bubbling primary preheated air through the molten material.

Secondary aid to make up 22 kg of air per kg of feed requirement is added downstream and reacting mixture is passed through a preheater to a fixed bed converter you can also have the fluid bed converter. This fixed bed reactor if you are using it is a multi-tubular catalytic reactor filled with supported V_2O_5 catalyst. Exothermic heat of reaction is removed from outside of the tubes by a molten salt circulating system that is not shown in the flowchart but such kind of a tubular packed bed reactors with provision to cooling the tubes or reactants you know or the product mixture such kind of provisions we have already seen in the production of some other chemicals several times in fact we have seen in last couple of chapters. Oxidation conditions in the reactor is approximately 380 to 450 degrees centigrade and 0.1 to 0.4 seconds of contact time. Remember all these conditions are for the you know packed bed reactor if you are using packed or fixed bed reactor. Reactor effluent gases are passed through a waste heat steam boiler and tends to a preheater. In the preheater final temperature is dropped to a few degrees above the dew point of phthalic anhydride.

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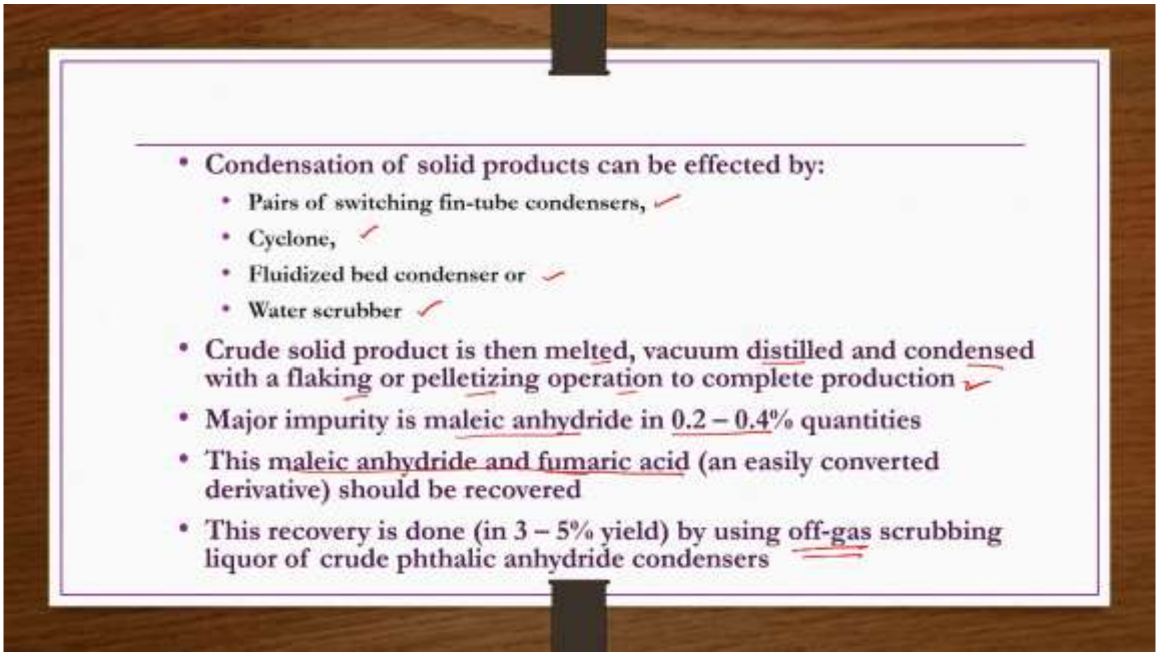

- Condensation of solid products can be effected by:
    - Pairs of switching fin-tube condensers,
    - Cyclone,
    - Fluidized bed condenser or
    - Water scrubber
- Crude solid product is then melted, vacuum distilled and condensed with a flaking or pelletizing operation to complete production
- Major impurity is maleic anhydride in 0.2 – 0.4% quantities
- This maleic anhydride and fumaric acid (an easily converted derivative) should be recovered
- This recovery is done (in 3 – 5% yield) by using off-gas scrubbing liquor of crude phthalic anhydride condensers

Condensation of solid products can be affected by pairs of switching fin-tube condensers or cyclones or fluidized bed condensers or water scrubbers any of them can be used or all of them may be used in general. Crude solid product is then melted vacuum distilled and condensed with a flaking or pelletizing operation to complete the production of a dry pellets of phthalic anhydride or flakes of phthalic anhydride.

Major impurity is maleic anhydride in 0.2 to 0.4 percent quantities only this maleic anhydride and fumaric acid should be recovered the production of these two we are discussing after completion of this particular phthalic anhydride topic. This recovery is done by using off gas scrubbing liquor of crude phthalic anhydride condensers.

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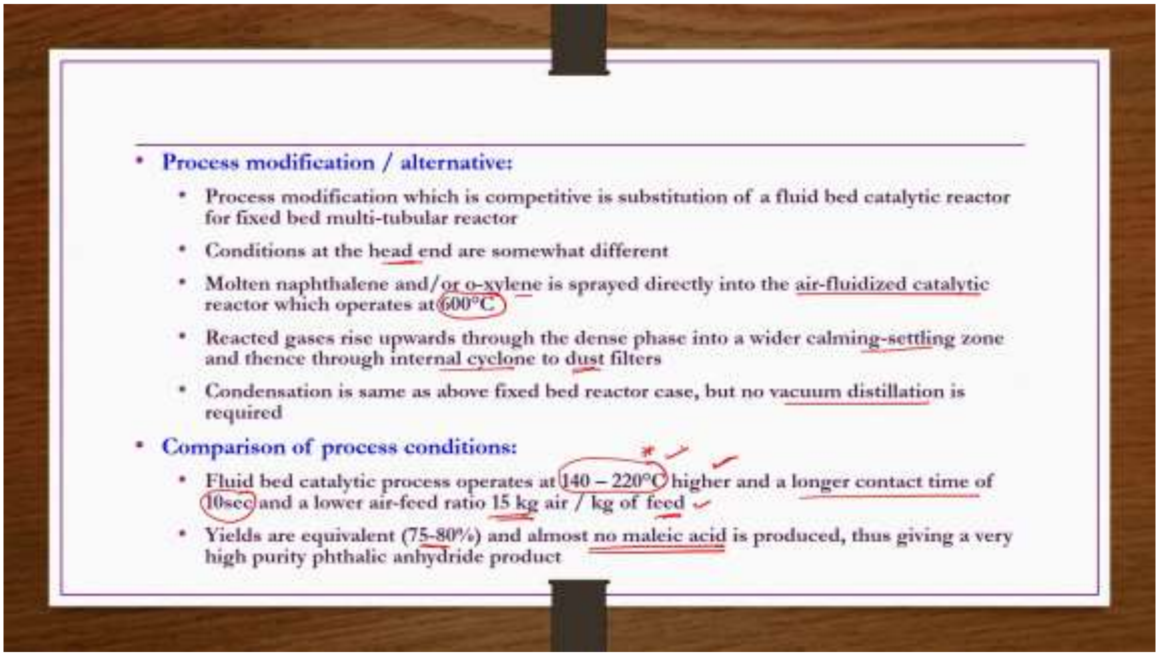

- **Process modification / alternative:**
  - Process modification which is competitive is substitution of a fluid bed catalytic reactor for fixed bed multi-tubular reactor
  - Conditions at the head end are somewhat different
  - Molten naphthalene and/or o-xylene is sprayed directly into the air-fluidized catalytic reactor which operates at 600°C
  - Reacted gases rise upwards through the dense phase into a wider calming-settling zone and thence through internal cyclone to dust filters
  - Condensation is same as above fixed bed reactor case, but no vacuum distillation is required
- **Comparison of process conditions:**
  - Fluid bed catalytic process operates at 140 – 220°C higher and a longer contact time of 10sec and a lower air-feed ratio 15 kg air / kg of feed
  - Yields are equivalent (75-80%) and almost no maleic acid is produced, thus giving a very high purity phthalic anhydride product

Process modifications and alternatives as already mentioned in place of fixed bed reactors we can also have fluid bed reactors as well. So, let us say if you use the fluid bed reactors then conditions at the head end are somewhat different. Molten naphthalene or ortho xylene is spread directly into the air fluidized catalytic reactor which operates at 600 degrees centigrade slightly higher temperature than the case of packed bed reactors.

Reacted gases arise upwards through the dense phase into a wider calming settling zone and thence through internal cyclone to dust filters by precipitators. Condensation is same as above fixed bed reactor case but no vacuum distillation is required to get the pellets of phthalic anhydride. Comparison of process conditions fluid bed catalytic process operates at 140 to 220 degrees centigrade higher than the packed bed reactor and a longer contact time of 10 seconds. However, it requires lower air that is 15 kg of air per kg of the field.

This is one advantage this is some disadvantage. So, but however, though the yields are equivalent in either of the processes but if you use the fluid bed catalytic process no maleic acid is produced thus giving a very high purity phthalic anhydride product. If you wanted to have high purity phthalic anhydride it is better to go for the fluid bed catalytic converter. Though the temperature is slightly higher and then contact time is also slightly higher. This is about phthalic anhydride production.

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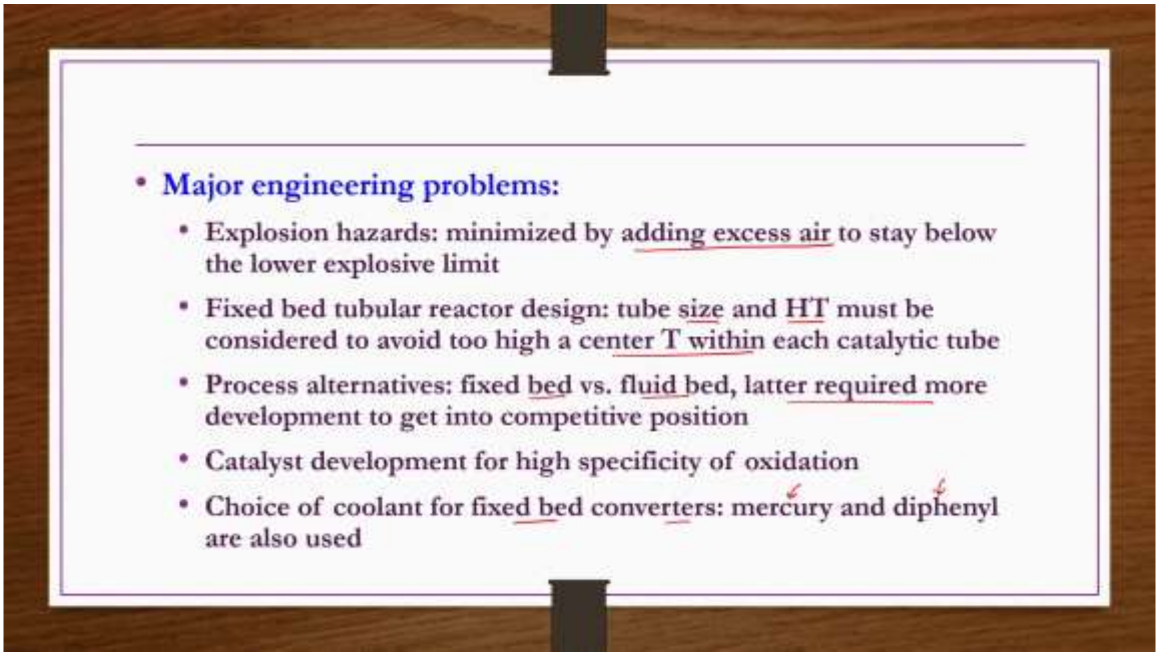

- **Major engineering problems:**
  - Explosion hazards: minimized by adding excess air to stay below the lower explosive limit
  - Fixed bed tubular reactor design: tube size and HT must be considered to avoid too high a center T within each catalytic tube
  - Process alternatives: fixed bed vs. fluid bed, latter required more development to get into competitive position
  - Catalyst development for high specificity of oxidation
  - Choice of coolant for fixed bed converters: mercury and diphenyl are also used

Now, we discuss major engineering problems associated with this process. Explosion hazards are important ones to be taken care. They can be minimized by adding excess air to stay below the lower explosive limits and then fixed bed tubular reactor design. Tube design and heat transfer must be considered to avoid too high a center temperature within each catalytic tube if you are using fixed bed tubular reactor. Process alternatives fixed bed versus fluid bed are the options. However, fluid bed required some more development to get into more competitive position though it is stands very good now itself.

Catalyst development for high specificity of oxidations are required. Choice of coolant for fixed bed converters are also essential to discuss where mercury and diphenyls are also used as a coolant for fixed bed.

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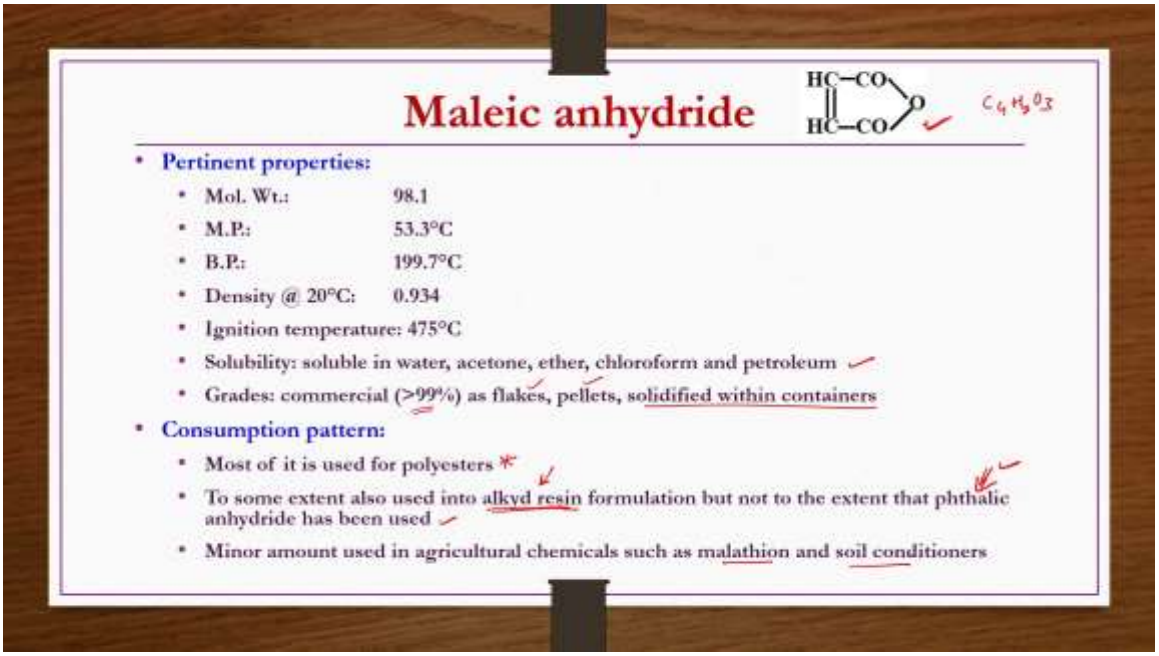

Maleic anhydride

$C_4H_2O_3$

- **Pertinent properties:**
  - Mol. Wt.: 98.1
  - M.P.: 53.3°C
  - B.P.: 199.7°C
  - Density @ 20°C: 0.934
  - Ignition temperature: 475°C
  - Solubility: soluble in water, acetone, ether, chloroform and petroleum
  - Grades: commercial (>99%) as flakes, pellets, solidified within containers
- **Consumption pattern:**
  - Most of it is used for polyesters *
  - To some extent also used into alkyd resin formulation but not to the extent that phthalic anhydride has been used
  - Minor amount used in agricultural chemicals such as malathion and soil conditioners

Now, we discuss production of maleic anhydride. Its structure is given by this one that is $C_4H_2O_3$. Pertinent properties molecular weight 98.1, melting point 53.3 degrees centigrade, boiling point 199.7 degrees centigrade, density at 20 degrees centigrade is 0.934, ignition temperature is 475 degrees centigrade. Solubility, it is soluble in water, acetone, ether, chloroform and petroleum.

Grades, commercial grades having more than 99 percent purity are there. They would be in flakes forms, pellets forms or solidified within the containers as well. Consumption pattern, primarily it is used for the polyester's production to some extent also used into the alkyd resin formulation but not to the larger extent that the phthalic anhydride has been used or that means it is used lesser extent because phthalic anhydride is primarily used only for the alkyd resins whereas maleic anhydride is used only to lesser extent to produce alkyd resins. Minor amount of it is also used in agricultural chemicals such as malathion and soil conditioners.

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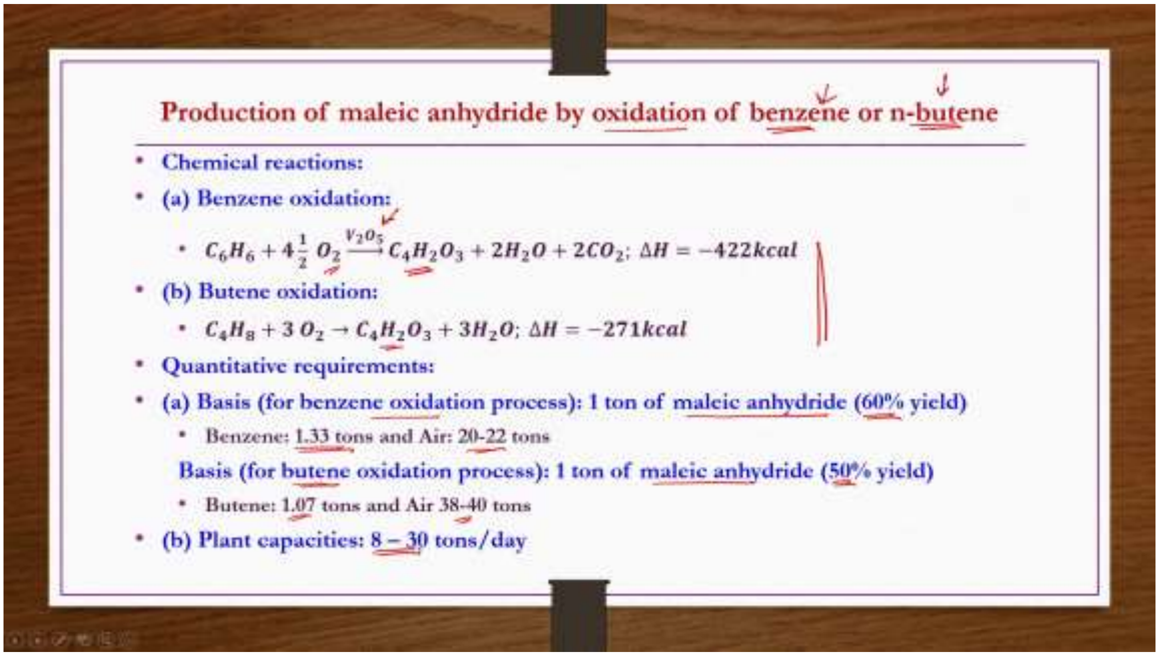

Production of maleic anhydride by oxidation of benzene or n-butene

- Chemical reactions:
- (a) Benzene oxidation:
  - $C_6H_6 + 4\frac{1}{2}\,O_2 \xrightarrow{V_2O_5} C_4H_2O_3 + 2H_2O + 2CO_2;\ \Delta H = -422kcal$
- (b) Butene oxidation:
  - $C_4H_8 + 3\,O_2 \rightarrow C_4H_2O_3 + 3H_2O;\ \Delta H = -271kcal$
- Quantitative requirements:
- (a) Basis (for benzene oxidation process): 1 ton of maleic anhydride (60% yield)
  - Benzene: 1.33 tons and Air: 20-22 tons

  Basis (for butene oxidation process): 1 ton of maleic anhydride (50% yield)
  - Butene: 1.07 tons and Air 38-40 tons
- (b) Plant capacities: 8 – 30 tons/day

Now, we discuss production of maleic anhydride by oxidation of benzene or n-butene. Either of them you can take, do the oxidation to get the maleic anhydride. So, we see chemical reactions. If you take the benzene and do the oxidation, benzene reacts with oxygen in the presence of V_2O_5 catalyst to get the maleic anhydride and water vapor and then carbon dioxide. Butene if you take and do the oxidation, then also you get the maleic anhydride and water vapor. Both of these reactions are highly exothermic.

Quantitative requirements, basis for benzene oxidation process. If you are taking benzene as raw material and then to produce 1 ton of maleic anhydride at 60 percent yield, you required 1.33 tons of benzene and 20-22 tons of air. Whereas if you use butene and do the oxidation to get maleic anhydride, to get 1 ton of maleic anhydride at 50 percent yield, you require 1.07 tons of butene and then 38 to 40 tons of air. Plant capacity is very low, 8 to 30 tons per day in general.

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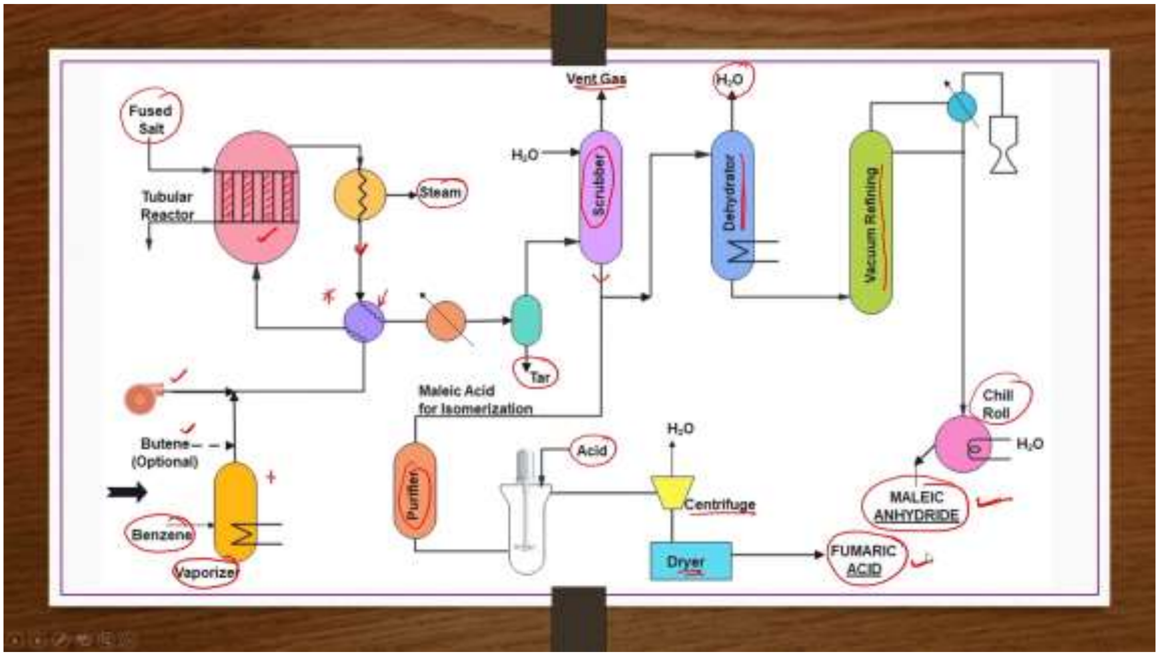

This is the flowchart here. So, what we have, the benzene whatever is there that you pass through a vaporizer and then vaporize it and then you can mix with butene which is optional if you wanted to use both of them. Otherwise, the vaporized benzene is mixed with the air. If you are using benzene only, then it is mixed with air. If you are using butene only, then vaporizer is not required and then you can mix this butene with the air and then preheat them and then send it to the tubular catalytic reactor.

You can use both of them as well which is optional anyway. So, the reactant mixture whatever is there that is passed through a preheater then to the bottom of a tubular reactor in which you have n number of tubes. So, these tubes are filled with V_2O_5 catalyst and through these catalytic tubes or tubes filled with catalyst, when this reactant mixture passes through, oxidation of a benzene or butene will take place and then you get the phthalic anydride along with the impurities like CO_2 and H_2, etc. In order to control the temperature of the reaction, fused salt is circulated to the shell side of the reactor to control the temperature. The product stream coming out of the tubular bed reactor would be having higher temperature. So, that would be passed through waste steam boiler in order to recover the energy in the form of steam and then still if the product mixture is at higher temperatures, that would be passed through a feed preheater so that to transfer some of the energy of the product streams to the feed so that the required preheating of the feed can also be taken place.

This is very essential from the heat economy point of view. Then the material is passed through a condenser cooled to separate out the tar. After separating out the tar, whatever the product mixture is there that is sent to a scrubber to scrub out the vent gases and then from here whatever the product that you get, you get 40% maleic acid solution. This solution you can take to the dehydrator where you remove water and then after the dehydration the product mixture subsequently is taken to the vacuum refining to further purify the product and then product is chilled low temperature to collect maleic anhydride products. Whereas the portion of a product mixture from the scrubber is taken for the isomerization to produce the maleic acid. So that product is purified and then isomerized using the acid followed by the centrifugation and drying leads to the production of fumaric acid as well. This is taken as a co-product.

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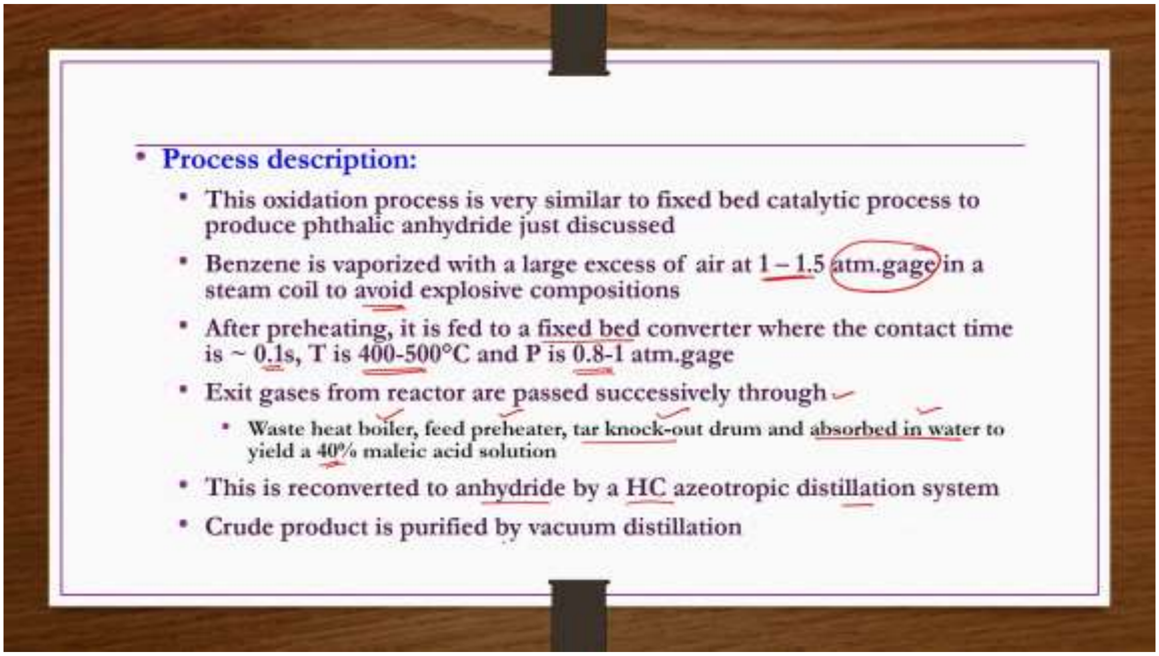

- **Process description:**
  - This oxidation process is very similar to fixed bed catalytic process to produce phthalic anhydride just discussed
  - Benzene is vaporized with a large excess of air at 1 – 1.5 atm.gage in a steam coil to avoid explosive compositions
  - After preheating, it is fed to a fixed bed converter where the contact time is ~ 0.1s, T is 400-500°C and P is 0.8-1 atm.gage
  - Exit gases from reactor are passed successively through
    - Waste heat boiler, feed preheater, tar knock-out drum and absorbed in water to yield a 40% maleic acid solution
  - This is reconverted to anhydride by a HC azeotropic distillation system
  - Crude product is purified by vacuum distillation

Coming to the process description, this oxidation process is very similar to fixed bed catalytic process to produce phthalic anhydride which we just discussed. Benzene is vaporized with a large excess of air at 1 to 1.5 atmospheric gauge pressure. So, if you want to have the atmospheric pressure one should be added to this one that is 2 to 2.5 atmospheric pressure in a steam coil to avoid explosive composition. After preheating it is fed to a fixed bed converter where the contact time is approximately 0.1 seconds, temperature is 400 to 500 degrees centigrade and pressure is 0.8 to 1 atmospheric gauge or 1.8 to 2 atmospheric pressure. Exit gases from reactor are passed successively through waste heat boiler, feed preheater, tar knock out drum and absorbed in water to yield a 40 percent maleic acid solution. This is reconverted to anhydride by a hydrocarbon azeotropic distillation system. Crude product is purified by vacuum distillation.

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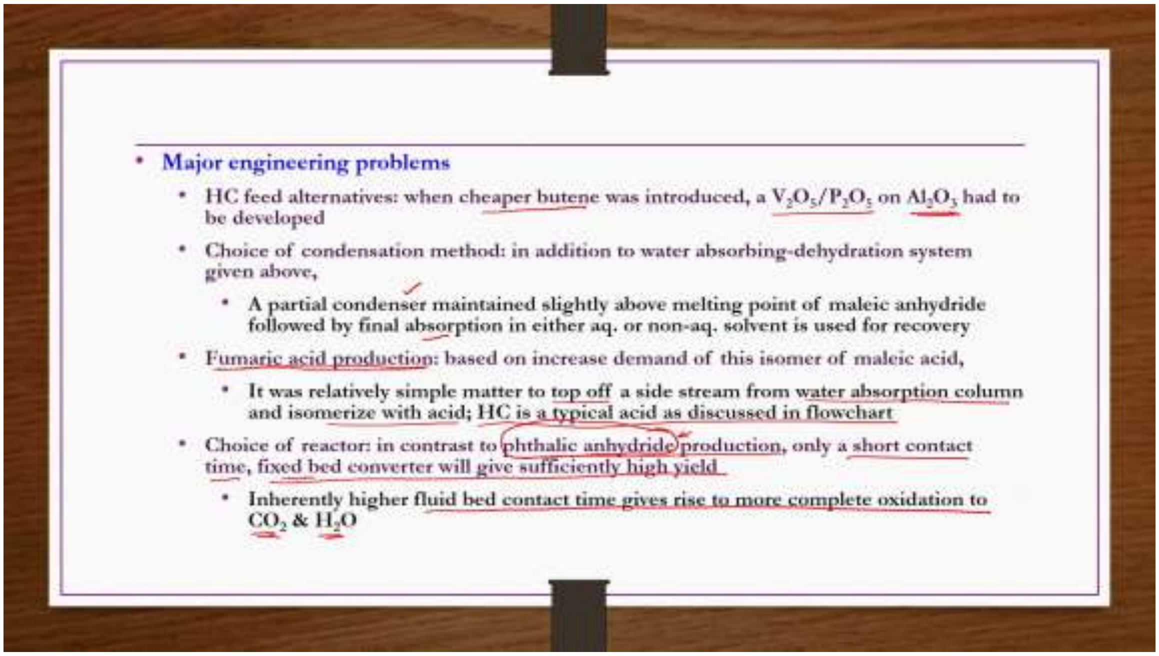

- **Major engineering problems**
  - HC feed alternatives: when cheaper butene was introduced, a V_2O_5/P_2O_5 on Al_2O_3 had to be developed
  - Choice of condensation method: in addition to water absorbing-dehydration system given above,
    - A partial condenser maintained slightly above melting point of maleic anhydride followed by final absorption in either aq. or non-aq. solvent is used for recovery
  - Fumaric acid production: based on increase demand of this isomer of maleic acid,
    - It was relatively simple matter to top off a side stream from water absorption column and isomerize with acid; HC is a typical acid as discussed in flowchart
  - Choice of reactor: in contrast to phthalic anhydride production, only a short contact time, fixed bed converter will give sufficiently high yield
    - Inherently higher fluid bed contact time gives rise to more complete oxidation to CO_2 & H_2O

Coming to the major engineering problems of the process, hydrocarbon feed alternative when cheaper butene was introduced a V_2O_5 or P_2O_5 on alumina supported catalyst had to be developed. Choice of condensation method is also one issue in addition to water scrubbing or water absorption dehydration system given in the flowchart. A partial condenser maintained slightly above melting point of maleic anhydride followed by final absorption in either aqueous or non-aqueous solvent is used for the recovery. Fumaric acid production is also important as it is gaining the market based on increased demand of this isomer of maleic acid.

It was relatively simple matter to top of a side stream from water absorption column and isomerize with acid. Hydrocarbon is a typical acid as discussed in the flowchart. Choice of reactor in contrast to phthalic anhydride production only a short contact time fixed bed converter will give satisfactory high yield. In the case of phthalic anhydride production we have seen that either you use the fixed bed or fluid bed yields are equivalent. Only the temperature and then contact times are higher in the fluid bed though the less oxygen requirement is there and high purity of phthalic anhydride you are producing. So, those are the things associated with the comparison of a fixed bed versus fluid bed reactors for the phthalic anhydride.

But however, in the case of maleic anhydride, it has been found that fixed bed converter with short contact times are providing higher yield. This is because inherently higher fluid bed contact time gives rise more complete oxidation to CO_2 and H_2O rather forming maleic anhydride. So, that is the reason in the case of maleic anhydride production, it is better to go for the fixed bed tubular catalytic reactors rather fluid bed catalytic converters. So, this is all about the production of maleic anhydride.

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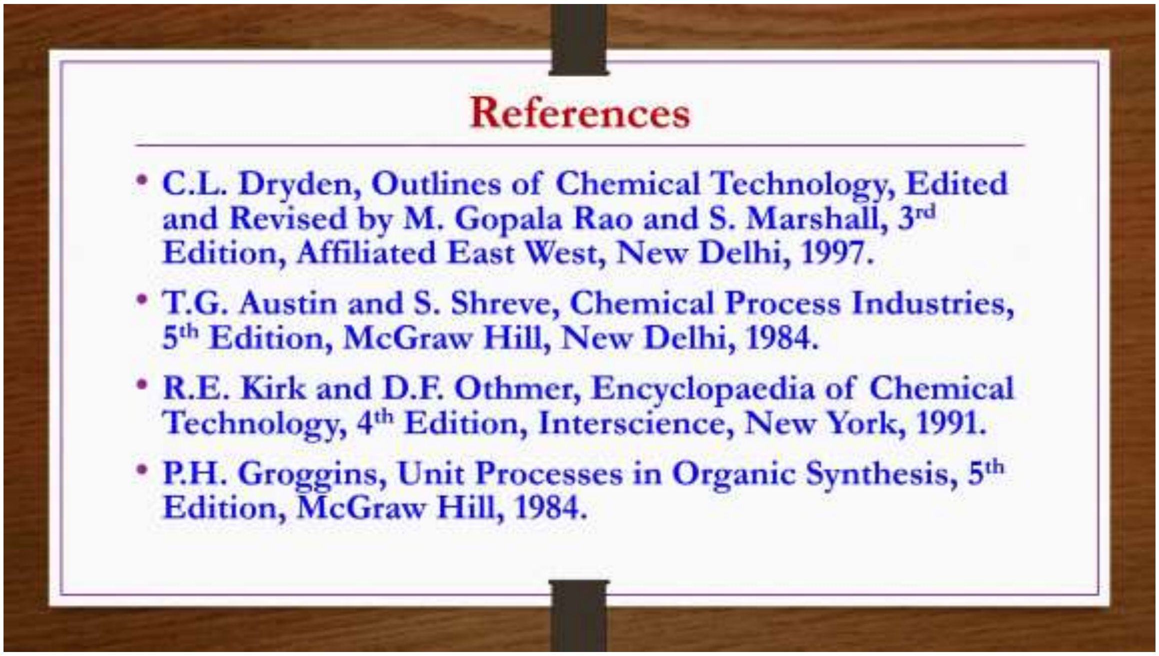

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The references for today's lecture are provided here. Thank you.