Organic Chemical Technology

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Lecture - 29
Chemicals from Aromatic Compounds

Welcome to the MOOCs course organic chemical technology, the title of today's lecture is chemicals from aromatic compounds. In this particular chapter, we will be discussing production of aromatics as well as utilization of those aromatics as raw material for production of different types of intermediate and then end chemicals, okay? So aromatics by name, these components they have a good aroma kind of thing because of such characteristics, these compounds are known as the aromatics. Usually they have a benzene kind of structure and then with other functional groups and all that, okay?

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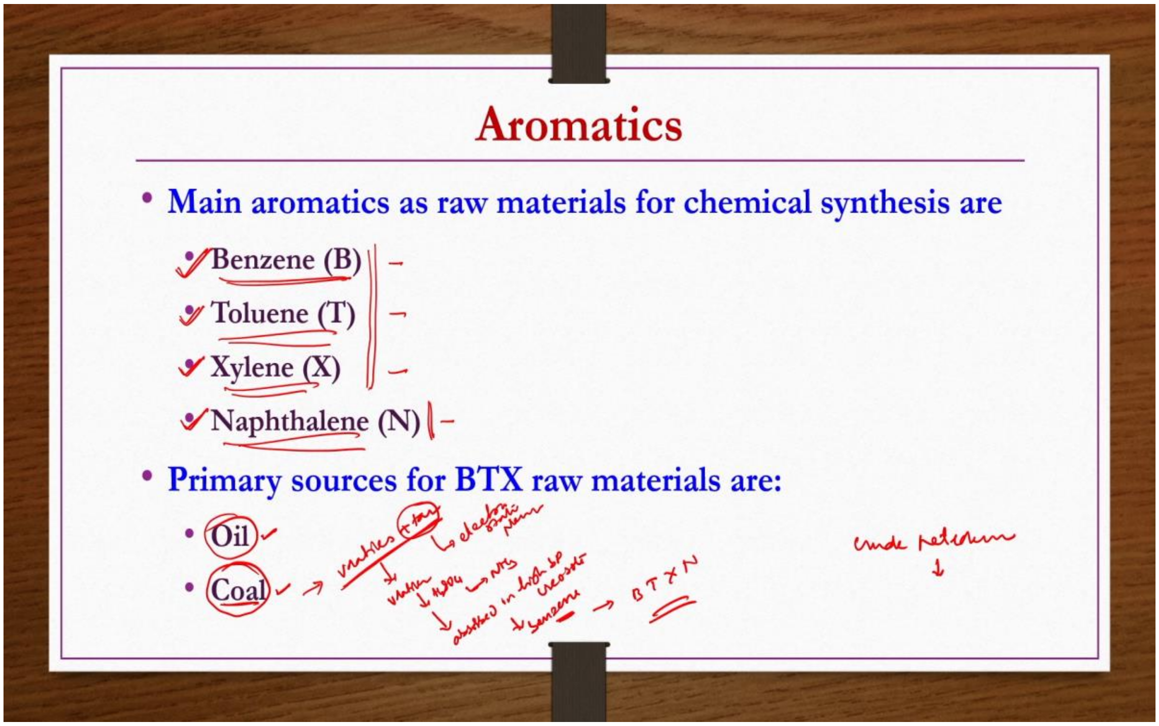

Aromatics

- Main aromatics as raw materials for chemical synthesis are
  - Benzene (B)
  - Toluene (T)
  - Xylene (X)
  - Naphthalene (N)
- Primary sources for BTX raw materials are:
  - Oil
  - Coal

volatiles (+ tar)
→ electrostatic precipitator
volatiles
H_2SO_4 → NH_3
absorbed in high bp creosote
benzene → BTXN
crude petroleum

So what are the main aromatics which can be used as raw materials for chemical synthesis if you list out primarily benzene, toluene, xylene and naphthalene. These are the important ones. There are so many types of aromatics, but these are the important aromatics out of which benzene is the most important one which can be used not only as a solvent, but also for the production of different types of other chemicals, okay? Then followed by the toluene which is also important, but from the applications point of view, it is having lesser application compared to the benzene.

That is the reason some of the toluene that is produced by the reforming processes that is also being converted into the benzene because the demand for the benzene is more, okay? Then next is the xylene and then followed by the naphthalene which are having applications in different types of resins manufacturing, etc. as we are going to see subsequently. So these are the raw materials for the production of different types of synthetic chemicals, but then how to produce them that is also important, right? If you have them, then only you can utilize them to produce different types of chemicals. For that purpose, two important sources are there which are natural sources.

Obviously, they are nothing but the oil and coal, okay? Let us say oil you are having or crude petroleum that you are having. So when we have studied the production of ethylene, acetylene, propylene, etc. by steam cracking of hydrocarbons, there we have seen different types of aromatics are also being produced, right? Then in the chapter of petroleum industry, generalized processes of reforming, isomerization, hydrodealkylation, etc. we have discussed. So some of the components can be hydrodealkylized to produce these aromatics, okay? But if you have let us say coal, right? Then let us say you need coal for different purpose. Let us say for metallurgical industries, you need coke like for production of metallurgical coke what you do? You do the carbonation of the coal. When you do the carbonation of the coal, what happens? Volatiles would also be produced. From these volatiles, you know when you produce actually, these volatiles when you produce or even you do the carbonation of coal, whatever the volatiles that you get, in those you also have some amount of the tar, right? So this tar you can remove by electrostatic precipitators, etc., right? Then only it is possible to remove such kind of tarry particles, then after this whatever the volatiles are there that may be still having some kind of impurities. So then what you do? You remove them by using HSO4, so that whatever the ammonia kind of components are there, they would be separated. So then after that whatever the volatiles are there, they would be absorbed in high boiling point oils like you know, creosote, etc., so that to get this benzene fractions, okay? So whatever these benzene fractions absorbed in this high boiling creosote kind of oils, they would be having all these benzene, toluene, xylene, naphthalene, etc., okay?

Such kind of processes are used to produce these aromatics from the coal. But however, whatever the aromatics that are being produced from the coal, they are less quantity only they are being produced. Majorly, these aromatics are produced from the crude petroleum, different types of naphtha, etc., as we have already discussed some of them and then some of them we are going to discuss now, right? So now before going into the details of production of different types of chemicals from such aromatics, we try to discuss some basic concepts of or some introduction and then applications of these aromatics as raw materials for production of different chemicals that is what we are going to see. We are also going to see how these are being produced by using oil and coal as sources, okay? We see only minimum introductory concepts about them because you know they are individually if you go into details they are you know huge organic chemistry subjects, okay? So what we have, we use them and then produce different types of chemicals like you know phenol, etc. So those things we study in detail, phthalic anhydride, phthalic acid, etc., these kind of chemicals we can produce from you know these aromatics. Those chemicals productions we do we study in detail, okay?

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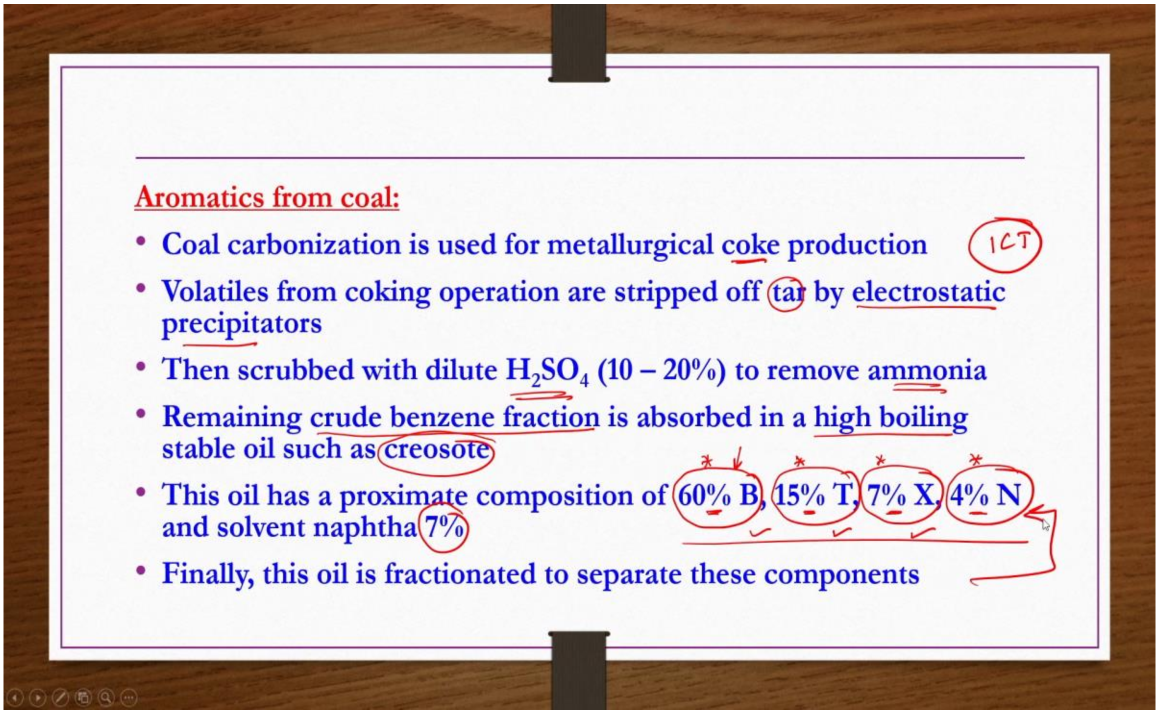

Aromatics from coal:

- Coal carbonization is used for metallurgical coke production
- Volatiles from coking operation are stripped off tar by electrostatic precipitators
- Then scrubbed with dilute H_2SO_4 (10 – 20%) to remove ammonia
- Remaining crude benzene fraction is absorbed in a high boiling stable oil such as creosote
- This oil has a proximate composition of 60% B, 15% T, 7% X, 4% N and solvent naphtha 7%
- Finally, this oil is fractionated to separate these components

Let us say aromatics from coal if you wanted to produce, coal carbonation you have to do. When you do the coal carbonation usually you get the coke and then such coke is very much useful in metallurgical industries as we have discussed in one of the previous course you know inorganic chemical technology which is also available in the NPTEL MOOCs portal, right? Volatiles from coking operations would also contain tar, so they would be separated out by the electrostatic precipitators. After separating the tarry particle whatever the volatiles are there, they will be scrubbed with dilute sulphuric acid to remove ammonia and then relevant components. Remaining crude benzene fraction whatever is there that would be absorbed in a high boiling stable oil such as creosote, right? So this oil has approximate composition of a 60% benzene, 15% toluene, 7% xylene and then 4% naphthalene, right? Some of these solvent, naphtha would also be there that would be approximately 7% and then there are other components would also be there, but these are the primary ones from the petroleum refinery applications point of view, these are the important ones, okay? Here you can see the aromatics that you are producing from coal you know different fractions are there, but subsequently when we study aromatics production from the hydrocarbons or petroleum crude, then you know you will realize that this B, benzene, T, toluene, xylene they are produced almost in equivalent quantities or their yield is almost equivalent if you are producing them from you know other oil sources not from the coal. From the coal you get less amount and out of that less amount also 60% is benzene. Finally this oil is fractionated to separate these components.

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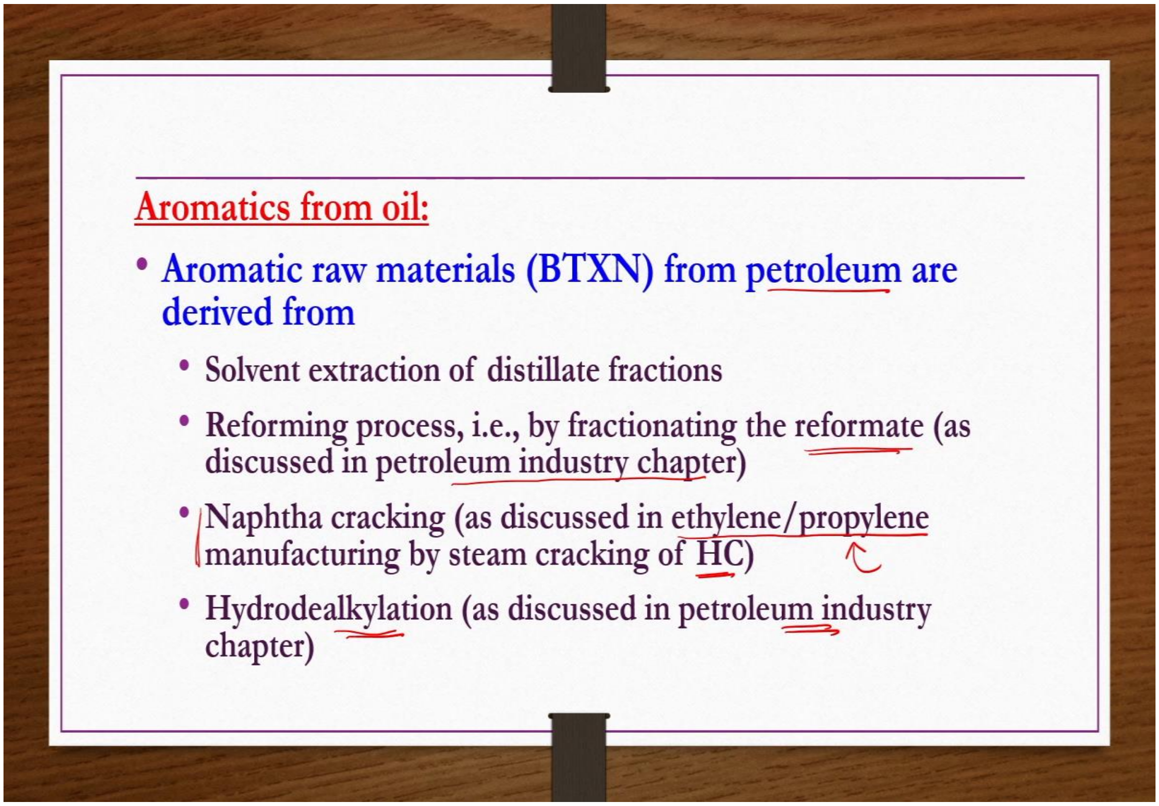

Aromatics from oil:

- Aromatic raw materials (BTXN) from petroleum are derived from
  - Solvent extraction of distillate fractions
  - Reforming process, i.e., by fractionating the reformate (as discussed in petroleum industry chapter)
  - Naphtha cracking (as discussed in ethylene/propylene manufacturing by steam cracking of HC)
  - Hydrodealkylation (as discussed in petroleum industry chapter)

Aromatics from oil, aromatic raw materials like benzene, toluene, xylene, naphthalene can also be produced from petroleum by different processes, something like solvent extraction of distillate fractions, reforming processes by fractionating the reformate. This we have already discussed in the petroleum industry chapter where we discussed about the catalytic reforming processes, you know by such processes also we get aromatics. Naphtha cracking, we have discussed this process when we were discussing production of ethylene, acetylene, propylene by steam cracking of hydrocarbons. In that process we have also seen that you know good amount of aromatics are also being produced. So, the process is same.

So, in this process when we discussed you know steam cracking of hydrocarbons, large number of products are being you know produced as co-products. So then operating conditions, catalyst, etc., you have to select such a way that you produce more of the desired component. Then other processes, hydrodealkylation which also we have discussed in the petroleum industry chapter. Let us say you know some kind of alkylates, you know benzene, naphthalene alkylates, you know alkylates in the sense you know having the alkyl functional group attached to the benzene rings or something like that. So if you do the hydrodealkylation, those alkyl groups would be removed and then you may be getting the aromatics. That process also we have discussed in petroleum industry chapter.

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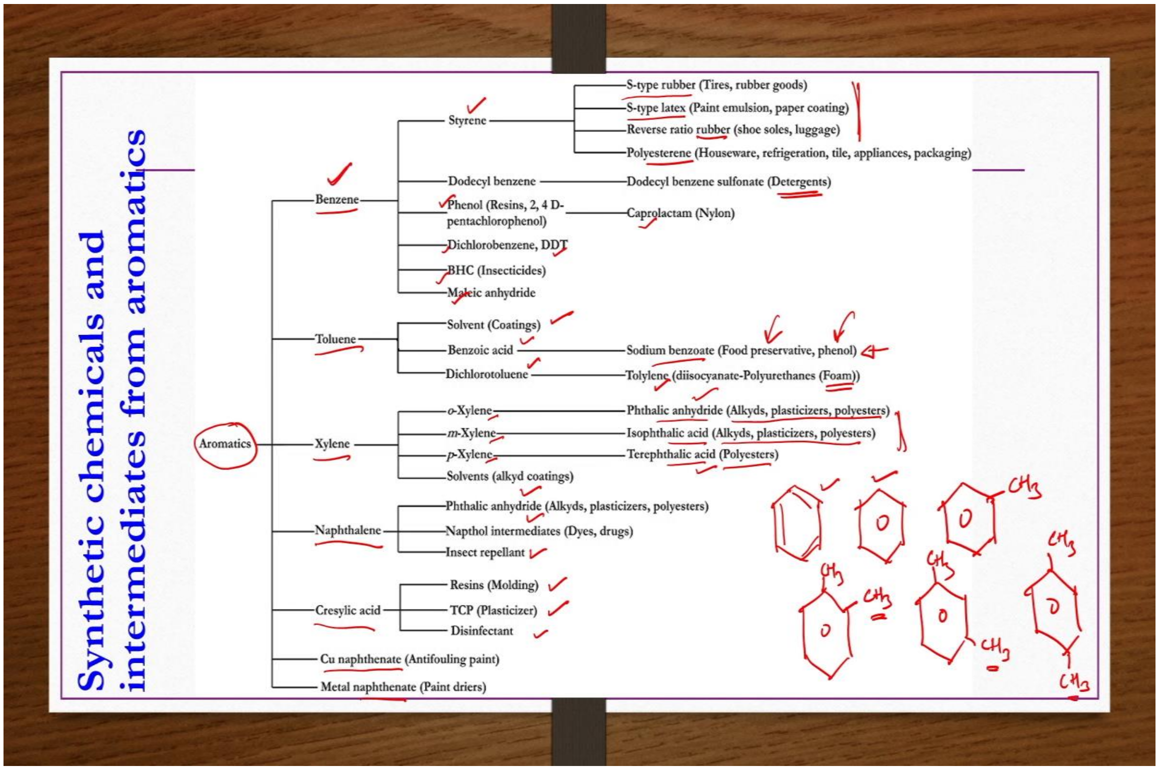

Synthetic chemicals and intermediates from aromatics

Aromatics
- Benzene
  - Styrene
    - S-type rubber (Tires, rubber goods)
    - S-type latex (Paint emulsion, paper coating)
    - Reverse ratio rubber (shoe soles, luggage)
    - Polyesterene (Houseware, refrigeration, tile, appliances, packaging)
  - Dodecyl benzene — Dodecyl benzene sulfonate (Detergents)
  - Phenol (Resins, 2, 4 D-pentachlorophenol) — Caprolactam (Nylon)
  - Dichlorobenzene, DDT
  - BHC (Insecticides)
  - Maleic anhydride
- Toluene
  - Solvent (Coatings)
  - Benzoic acid — Sodium benzoate (Food preservative, phenol)
  - Dichlorotoluene — Tolylene (diisocyanate-Polyurethanes (Foam))
- Xylene
  - *o*-Xylene — Phthalic anhydride (Alkyds, plasticizers, polyesters)
  - *m*-Xylene — Isophthalic acid (Alkyds, plasticizers, polyesters)
  - *p*-Xylene — Terephthalic acid (Polyesters)
  - Solvents (alkyd coatings)
- Naphthalene
  - Phthalic anhydride (Alkyds, plasticizers, polyesters)
  - Napthol intermediates (Dyes, drugs)
  - Insect repellant
- Cresylic acid
  - Resins (Molding)
  - TCP (Plasticizer)
  - Disinfectant
- Cu naphthenate (Antifouling paint)
- Metal naphthenate (Paint driers)

Now we see synthetic chemicals and then intermediates that can be produced from aromatics. So aromatics you know we can have out of aromatics, benzene fraction, toluene fraction, xylene fraction, naphthalene fraction and cresylic acids as well as some methyl naphthenates also being produced from these aromatics or the fractions of aromatics. So benzene can be utilized to produce styrene which is mostly used in the polymerization industry for the rubber, latex manufacturing, etc. So polystyrene manufacturing, etc., some of the applications are shown here like for the tires, rubber goods, paint emulsions, paper coating, shoes, soles, luggage, houseware, refrigeration tiles, appliance, packaging, for all these purposes styrene derived products are in general used. Dodecyl benzene can also be produced from the benzene which is sulfonated. After being sulfonated that is used for the detergents manufacturing. Benzene can also be used to produce phenol followed by the caprolactam like nylon purpose, then dichlorobenzene, DDT, BHC, maliec anhydride, etc.., all of them may be produced from the benzene. Coming to the toluene, primarily it is used as solvent but also used to produce benzoic acid. From benzoic acid you can produce sodium benzoate which is a very good food preservative and then it is also used for the production of phenol. So with flowchart this one we are going to discuss anyway. Dichlorotoluene also you can produce from the toluene and then tolylenes can be produced from there.

These tolylenes are used for the production of the foam materials, okay? Xylene you have a ortho xylene, meta xylene, para xylene. Actually basically this benzene is you know we have this structure, okay? And then toluene we have this structure. This circle inside this ring whatever is there that indicates the alternative double bonds. You can write this way or you can write this way also, right? So one double bond, then alternatively another one, alternatively other one. So either way you can write, okay? So this is benzene, this is toluene. Xylene you can have you know 2 CH3 functional groups attached. So if it is attached at ortho position it is called as ortho xylene. If it is attached at meta position then it is known as the meta xylene. If the second methyl functional is attached at the para position then it is known as the para xylene. Their properties would be different from each other though chemical formula is same, okay? Only the position of second CH3 group is changing from one to the other, okay? So this ortho xylene may be used for phthalic anhydride which we are going to discuss how to produce.

Similarly, meta xylene is used for the isophthalic acids and then para xylene used for the terephthalic acid which is also we are going to discuss in detail with flowchart how to produce them. These are primarily used for the alkyds, plasticizers, polyesters purpose in general as shown here. Naphthalene is used for phthalic anhydride, napthol intermediates and insect repellent manufacturing purpose these are used. Cresylic acid is used for the resins, plasticizers, disinfectant manufacturing purpose, etc.

These are used. Now, you can see so many applications are there. Only a few of them are shown. In fact, there are more number of applications possible from these chemicals also, right? So but we have seen most important one. So now what we do? We are going to discuss the production of benzene followed by the production of different types of chemicals from aromatics in this lecture and then coming couple of lectures.

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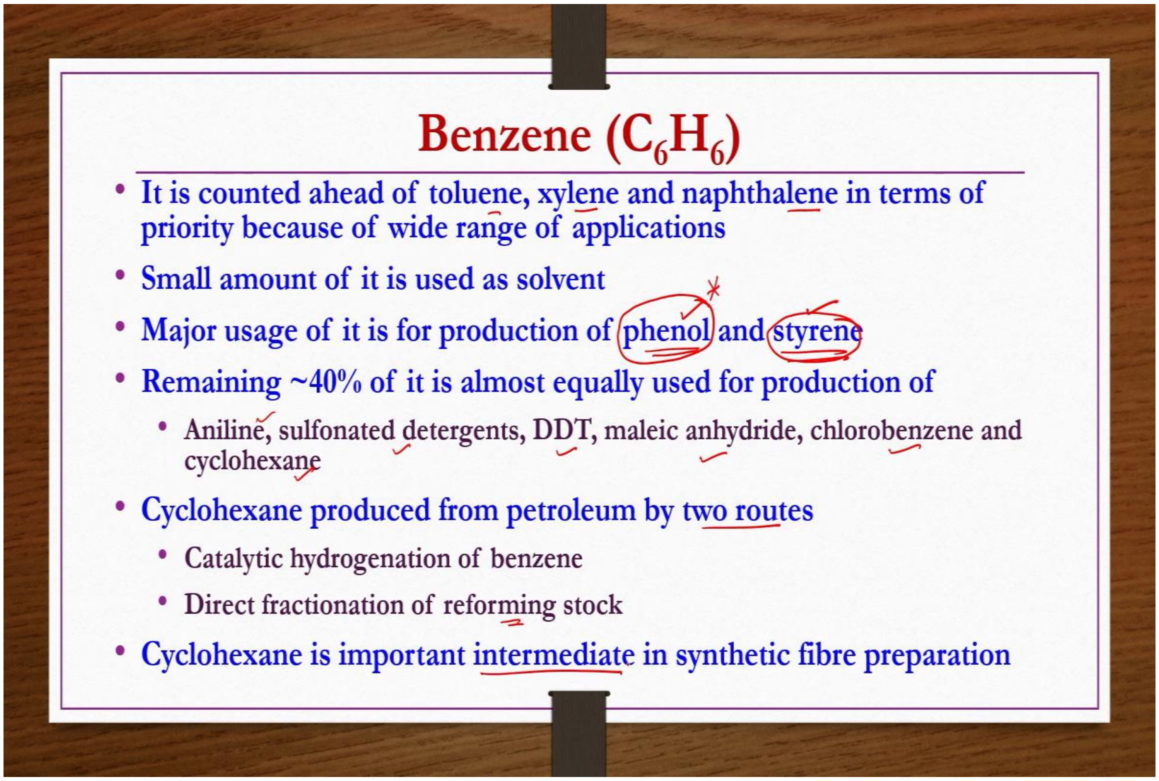

Benzene (C_6H_6)

- It is counted ahead of toluene, xylene and naphthalene in terms of priority because of wide range of applications
- Small amount of it is used as solvent
- Major usage of it is for production of phenol and styrene
- Remaining ~40% of it is almost equally used for production of
  - Aniline, sulfonated detergents, DDT, maleic anhydride, chlorobenzene and cyclohexane
- Cyclohexane produced from petroleum by two routes
  - Catalytic hydrogenation of benzene
  - Direct fractionation of reforming stock
- Cyclohexane is important intermediate in synthetic fibre preparation

However, before going into the details of production of these aromatics and then the derived intermediate and N chemicals, we will have a brief introduction about this aromatics, introduction in the sense, you know, some applications point of view, where are they being used, those kind of details we are going to see. So let us start with benzene which is nothing but C6H6 cyclic component. It is counted ahead of toluene, xylene, naphthalene in terms of priority because of wide range of applications. From the applications point of view, benzene is having the most applications as we have already seen in the previous slide also, right? Actually, you know, from the coal whatever the aromatics are produced, there 60% benzene is there, right? Whereas the toluene is 15% only, right? And then xylene is only 7%, right? Whereas if you produce these aromatics from the oil, so then approximately you know you get equal fractions, approximately 30%, 30 to 35% like that, okay? So they are producing equal fractions if you are producing from the oil, right? But however, from the applications point of view, benzene is having most applications compared to the toluene followed by the least applications by xylene. Small amount of benzene is used as solvent, whereas the major usage of it is for the production of phenol and styrene, both of these components we are going to see. Phenol is produced by so many number of methods, but 6 important processes are there.

So all those 6 processes we are going to discuss in detail with flowchart how the phenol is being produced industrially. Similarly, styrene production also we are going to see in the one of the lectures of this particular chapter. 40% of benzene is almost equally used for the production of different types of chemicals like aniline, sulfonated detergents, DDT, maleic anhydride, chlorobenzene and cyclohexane, okay? So cyclohexane is produced from petroleum by 2 routes, one is the catalytic hydrogenation of benzene and then direct fractionation of reforming stocks. This cyclohexane is one of the important intermediate in synthetic fiber preparation.

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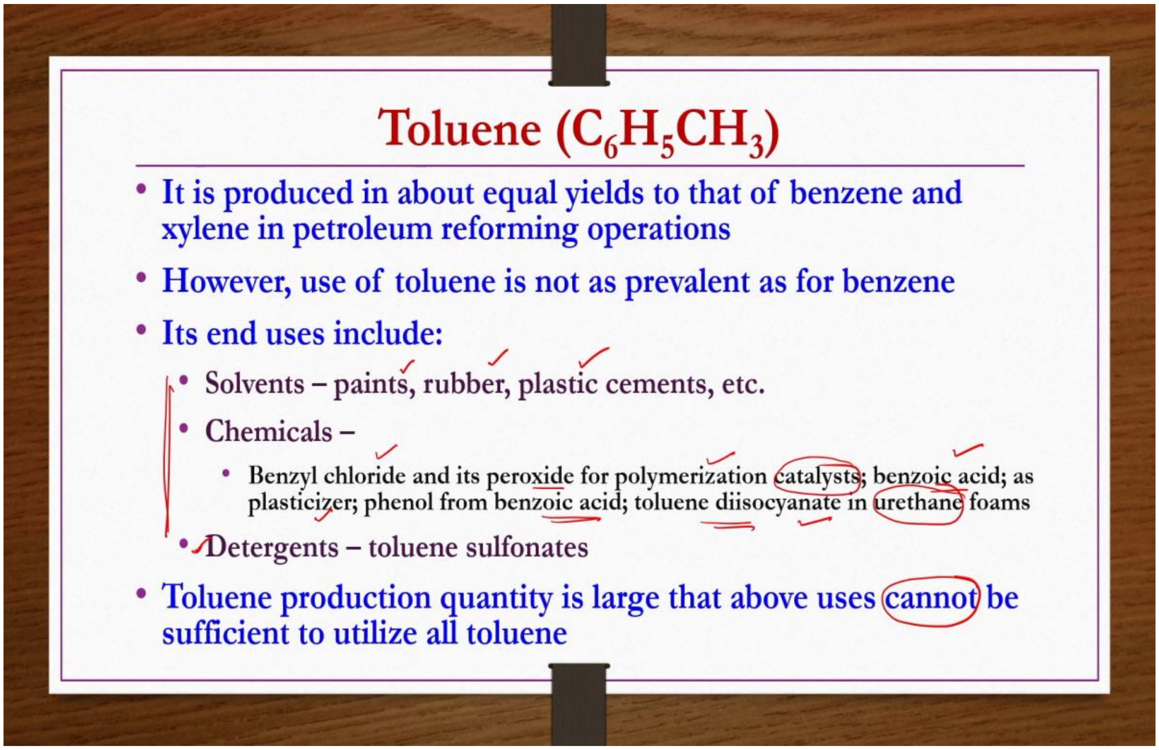

Toluene ($C_6H_5CH_3$)

- It is produced in about equal yields to that of benzene and xylene in petroleum reforming operations
- However, use of toluene is not as prevalent as for benzene
- Its end uses include:
  - Solvents – paints, rubber, plastic cements, etc.
  - Chemicals –
    - Benzyl chloride and its peroxide for polymerization catalysts; benzoic acid; as plasticizer; phenol from benzoic acid; toluene diisocyanate in urethane foams
  - Detergents – toluene sulfonates
- Toluene production quantity is large that above uses cannot be sufficient to utilize all toluene

Coming to the toluene, it is produced in about equal yields to that of benzene if it is produced from the petroleum oil sources and it is also equal in yields compared to the xylene, if it is produced in petroleum refining operations. If it is produced from the coal, then it is less compared to the benzene, much less in fact. However, use of toluene is not as prevalent as for benzene. So many applications benzene is having, but toluene is having less number of applications. In fact, toluene was initially produced to have it as a kind of blend in high octane motor fuels, motor petrol, etc. But later on that, you know, paradigm shift towards the production of different chemicals, nowadays it is not used much in the motor fuels as well, okay? So some of the applications of toluene include, it is used as solvents in paints industries, rubber, plastics, cements, etc.., also used for production of different types of chemicals like benzoyl chloride and its peroxide for polymerization catalyst. Benzoyl chloride and their peroxides in general used as catalyst for the so many polymerization processes as we are going to discuss it in the next chapter of the course. It is also used for the preparation of benzoic acid as plasticizer. It is also used to produce phenol from the benzoic acid, this process we are going to see from the toluene. First you prepare the benzoic acid, benzoic acid is again, you know, converted into the phenol.

So that process also we are going to see in detail. Toluene diisocyanate is also one of the chemical that can be produced by using toluene and then this chemical is used in the polyurethane foams production. It is also used, toluene is also used in the detergents manufacturing purpose, but once you do the sulfonation or the toluene sulfonates you take and then use them in the detergents manufacturing. Toluene production quantity is large that above uses cannot be sufficient to utilize all toluene. So, whatever that toluene so much it is produced, but applications point of view only fewer applications are there.

So, despite of having large quantities, you do not have a utility. So, then what you do in general you either use it as a, you know, additive in the high octane motor petrol or convert into the, you know, so called benzene and then that benzene you use for different types of applications because benzene is having much more applications compared to the toluene.

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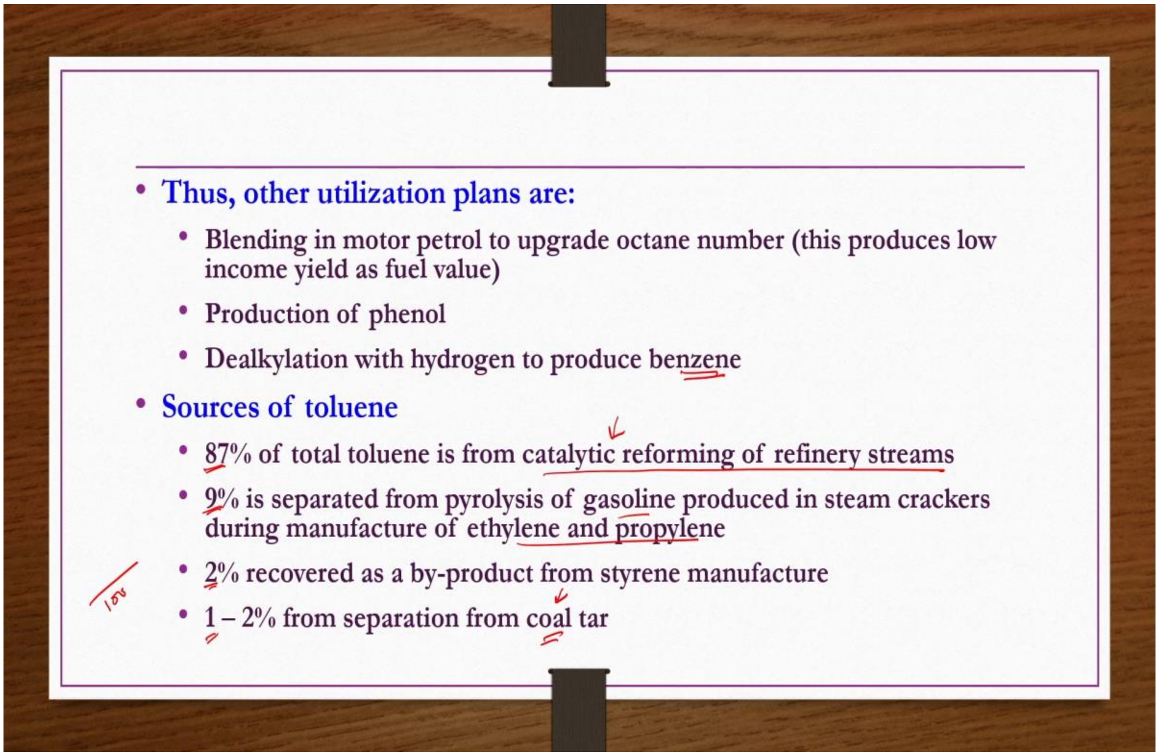

- Thus, other utilization plans are:
  - Blending in motor petrol to upgrade octane number (this produces low income yield as fuel value)
  - Production of phenol
  - Dealkylation with hydrogen to produce benzene
- Sources of toluene
  - 87% of total toluene is from catalytic reforming of refinery streams
  - 9% is separated from pyrolysis of gasoline produced in steam crackers during manufacture of ethylene and propylene
  - 2% recovered as a by-product from styrene manufacture
  - 1 – 2% from separation from coal tar

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So, some other utilization plans are blending in motor petrol to upgrade high octane number, this produces low income yield as a fuel value. It can also be used for the production of phenol which is also having so many applications especially in the resins manufacturing. So, phenol you produce so then you find the market. Dealkylation with hydrogen you do then you produce benzene. In fact, this process we are going to discuss now anyway with flowchart. So, this benzene when you are having so benzene is having so many applications so that way the toluene can also be utilized or excess of the toluene that is being produced from the oil fractions that can be converted into the benzene and then utilized. Sources of toluene, 87% of total toluene that is available in the world is from catalytic reforming of refinery streams.

Only 7% is coming from the coal. 9% is separated from pyrolysis of gasoline produced in steam crackers during manufacturing of ethylene and propylene. 2% recovered as a byproduct from styrene manufacture, 1 to 2% separation from coal tar. These numbers are not like you know from those you know respective processes. These are based on the total whatever the toluene that is available that is produced industrially either from the coal or oil. If you make that fractionation 87% of the total toluene that is available that is obtained by the catalytic reforming of refinery streams. Only 1 to 2% of toluene that is available is obtained by separation from coal tar while you know when you do the you know coal carbonation process.

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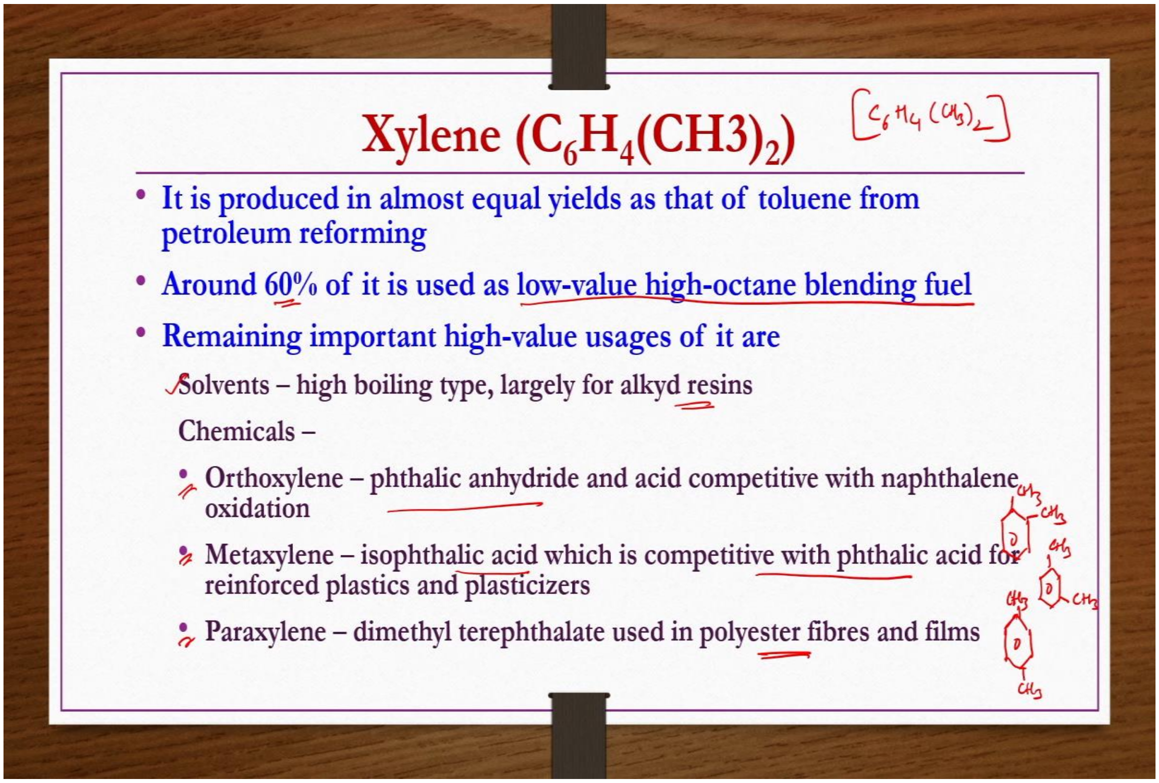

Xylene ($C_6H_4(CH3)_2$)

$[C_6H_4(CH_3)_2]$

- It is produced in almost equal yields as that of toluene from petroleum reforming
- Around 60% of it is used as low-value high-octane blending fuel
- Remaining important high-value usages of it are

  ✓ Solvents – high boiling type, largely for alkyd resins

  Chemicals –

  - Orthoxylene – phthalic anhydride and acid competitive with naphthalene oxidation
  - Metaxylene – isophthalic acid which is competitive with phthalic acid for reinforced plastics and plasticizers
  - Paraxylene – dimethyl terephthalate used in polyester fibres and films

Next aromatic is xylene which is C6H4(CH3)2. So it is produced in almost equal yields as that of toluene from petroleum reforming. So all B, T, X are produced in almost equal yields if these are being produced from the petroleum reforming processes. Around 60% of it is used as low value high octane blending fuel like toluene.

Remaining important high value usages of xylene include as solvents especially in high boiling type largely for alkyd resins purpose you know largely in production of alkyd resins these are used as solvents. Xylene is also used for the production of different types of chemicals. Let us say if you have ortho xylene which is nothing but second CH3 group attached to the ortho position of the ring. So that can be used for the production of phthalic anhydride and acid competitive with naphthalene oxidation. Let us say if you have a metaxylene that is second methyl functional is attached at the meta position of the ring then that can be used for the iso-phthalic acid production which is competitive with phthalic acid for reinforced plastics and plasticizers.

Let us say if you have a para xylene that is second methyl functional is attached at the para position of the ring like this then it is used for dimethyl terephthalate used in polyester fibers and films. See they are slightly different, but applications also slightly different, but overall finally they are being used for the polyesters, fibers, films, etc. for those purpose these are being used for the plasticizers, plastics manufacturing purpose these are used.

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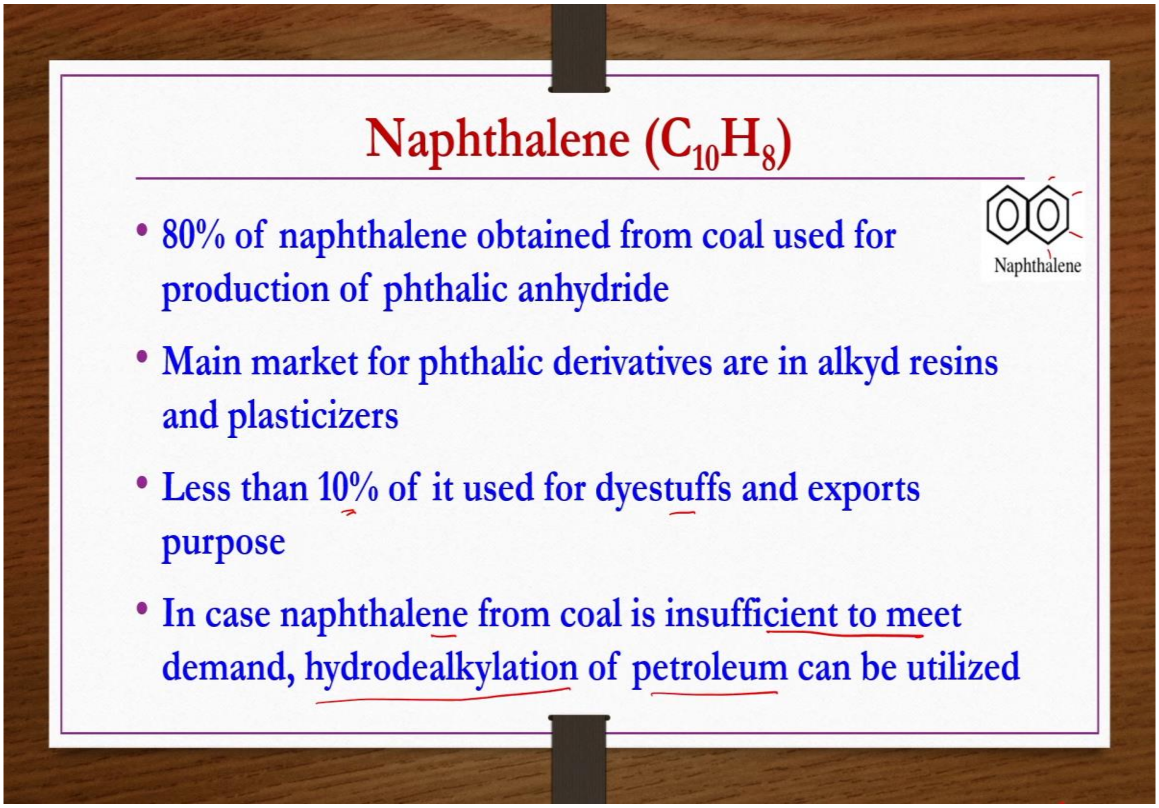

Naphthalene ($C_{10}H_8$)

- 80% of naphthalene obtained from coal used for production of phthalic anhydride
- Main market for phthalic derivatives are in alkyd resins and plasticizers
- Less than 10% of it used for dyestuffs and exports purpose
- In case naphthalene from coal is insufficient to meet demand, hydrodealkylation of petroleum can be utilized

Fourth one is the naphthalene which is having the structure like two benzene rings attached like this. So, here what you have you have only 8 H atoms and then 10 carbon atoms. So these are the C6H6, C7, C8, C9, C10 and then only 2 more hydrogen atoms can be accommodated here because of the alternative double bonds. That is the reason it is C10H8. 80 percent of naphthalene obtained from coal used for production of phthalic anhydride. Main market for phthalic derivatives are in alkyd resins and plasticizers. Less than 10 percent of it used for dyestuff and exports purpose.

In case naphthalene from coal is insufficient to meet demand, hydrodealkylation of petroleum can also be done to obtain naphthalene and then that can be utilized.

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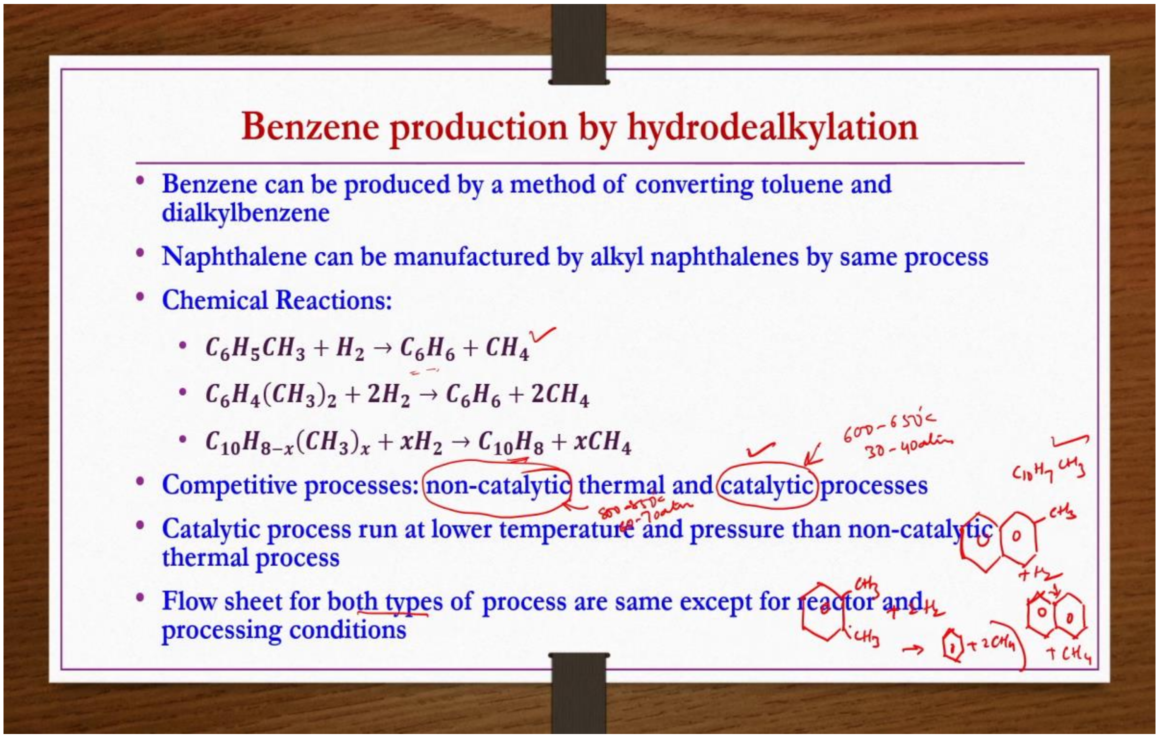

Benzene production by hydrodealkylation

- Benzene can be produced by a method of converting toluene and dialkylbenzene
- Naphthalene can be manufactured by alkyl naphthalenes by same process
- Chemical Reactions:
  - $C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$
  - $C_6H_4(CH_3)_2 + 2H_2 \rightarrow C_6H_6 + 2CH_4$
  - $C_{10}H_{8-x}(CH_3)_x + xH_2 \rightarrow C_{10}H_8 + xCH_4$
- Competitive processes: non-catalytic thermal and catalytic processes
- Catalytic process run at lower temperature and pressure than non-catalytic thermal process
- Flow sheet for both types of process are same except for reactor and processing conditions

Now we start our discussion on benzene production by hydrodealkylation. Benzene can be produced by a method of converting toluene and dialkyl benzene. Let us say toluene is nothing but this particular function you have CH3 here. Now if you react with hydrogen, dealkylation would be taking place.

Dealkylation in the sense removing the alkyl group and then you will be having the benzene like this. So sometimes you may be having more than one, let us say two functional or their methyl functional. So then hydrodealkylation should be done. So then here again this alkyl groups whatever the methyl functional groups are there, they would be removed by the hydrogenation reaction. So that is the reason it is known as hydrodealkylation and then you get the benzene as well.

We have already seen at the beginning of petroleum industry chapter that breaking of the bonds, the CH3 functional groups etcetera easy compared to breaking of any of the bonds that are in the making the formation of rings like this. So this is very difficult, this is very easy that is the reason dealkylation can be done easily to get the benzene. From the benzene getting cyclohexane is a bit tough. Naphthene can be manufactured by alkyl naphthalene by same process. Let us say naphthene what structure we have? We have this structure, 2 benzene rings are attached like this and they will be having C10H8 form.

Let us say if it is having CH3 then C10H7 CH3 would be there. This also if you do the hydrogenation, so dealkylation will take place and then you can get the naphthalene like this. The process is same. Chemical reactions let us say C6H5CH3 reacts with hydrogen then you get benzene and then methane as just now I have written a reaction. Likewise let us say if you have xylene also or dialkyl benzene also if you are having like this 2 functional groups, 2 methyl functional groups are there then you react with 2 hydrogen atoms.

So, what you get? You get the benzene ring plus 2 moles of methane. So this is also possible. Let us say if you have alkyl naphthene like this, let us say now C10H8 minus x CH3 x if x is 1, so then C10H7 CH3 as I have written like this and then you react with 1 mole of hydrogen to get so called 1 mole of naphthalene plus 1 mole of methane. If you have 2, if x is 2, then this is C10H6CH3 twice plus 2 moles of H2 giving rise to C10H8 and then 2 moles of methane. Competitive processes both catalytic and non-catalytic processes are existing.

In fact, initially catalytic processes were developed, but however, in order to overcome the royalty payment issues with the patented processes, people subsequently developed non-catalytic processes also. Yield is approximately same by either of the process, whether catalytic or non-catalytic. Only thing that in the catalytic process temperature you may be using 600 to 650 degrees centigrade and then 30 to 40 atmosphere whereas in the catalytic process you may be using you know 800 to 850 degrees centigrades and then pressure 60 to 70 atmosphere like that. Obviously, the purpose of having catalyst is to reduce the severity of the conditions required for the reaction to undergo. Catalytic processes run at lower temperature and pressure than non-catalytic thermal processes.

Flow sheets for both types of processes are same except for the reactor and processing condition that we are going to see with flowchart here.

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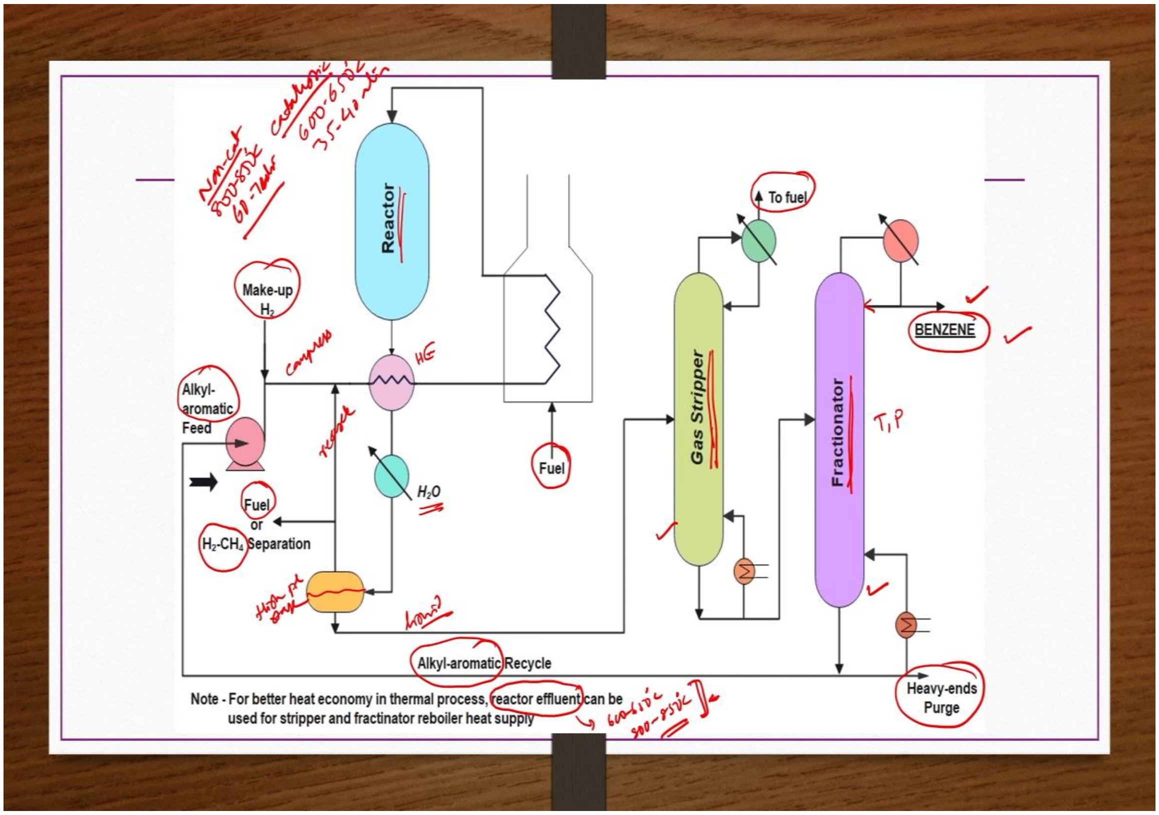

Note - For better heat economy in thermal process, reactor effluent can be used for stripper and fractinator reboiler heat supply

Now, here we have a process to production of a benzene by hydrodealkylation. So what you do here, you take make up H2 or the fresh H2 you take and then you mix with the recycled gas, compress them, then you mix with the liquid alkyl aromatic feed. So this mixture whatever is there compressed gases and liquid mixture whatever are there they would be preheated using the heat exchanger or preheated using the heat exchanger then further preheating would be done by using the fired preheater like that. Fired preheater in the sense for the preheating purpose whatever the energy is there that would be obtained by the firing the fuel.

So once preheating this mixture, the reactant mixture is going to the reactor. So here this reactor if it is a catalytic process, then you may be having tubular reactor within the shell of the reactor as a bundle as we have already discussed different types of tubular packed bed reactors and then temperature you may be using you know so called lower temperature or moderate temperature of 600 to 650 degrees centigrade and then pressures of 35 to 40 atmospheres. If you are having a non-catalytic process, then you will be having simply tubular reactor operating at 800 to 850 degrees centigrade and then 60 to 70 atmospheres of pressures. Then after the reaction whatever the product mixture is there that would be preheated again using the heat exchanger then again cooled using the condenser after that it will be passed through a high pressure stage where liquids and gases are being separated.

These gases most of the gases are used for the recycle purpose. Some fraction are also taken to separate H2 from the methane or H2 methane separation so that that H2 can be reused for the hydrodealkylation reaction or it can also be used as a fuel. Whatever the liquid fractions are there, they would be taken to a gas stripper so that if any lighter gases fractions are there, they would also be removed from the liquid by the gas stripping and then those gases would be collected as a fuel. So after separation of the traces of gases from the liquid sample, whatever the liquid is there that would be primarily you know benzene and crude benzene. So that would be taken to a fractionator where the temperature pressure you maintain such a way that more volatile benzene you can get it as a top product. Some of the benzene may also be recycling until they required a purification of benzene is being done.

Whereas the bottom should be heavy ends collected as a heavy ends which are primarily alkyl aromatics, either they can be collected as a purge or they would be recycled back to the reactor so that further dealkylation can be taken place to produce more benzene. So here whether you take the catalytic process or non-catalytic process, whatever the reactor effluents would be there, they would be at such high temperatures of corresponding processes. If you are doing catalytic process, then 600 to 650 degrees centigrade and they would be carrying. If you are doing non-catalytic process, so those reactor effluents would be at 800 to 850 degrees centigrade. So these energy may be recovered and then may be used for the stripper and then reboiler of a fractionating column. That is important from the heat economy point of view and then in fact that is done in the most of the processes wherever there is a reactor effluent is having lot of energy.

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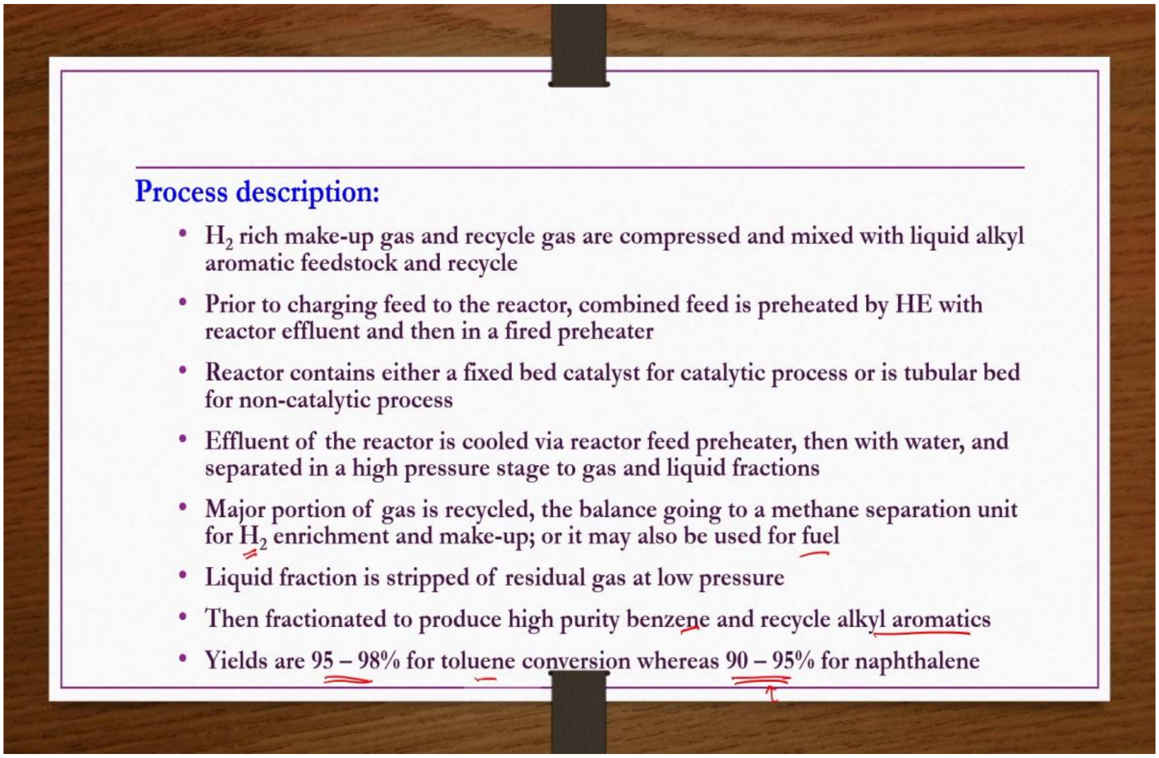

Process description:

- H_2 rich make-up gas and recycle gas are compressed and mixed with liquid alkyl aromatic feedstock and recycle
- Prior to charging feed to the reactor, combined feed is preheated by HE with reactor effluent and then in a fired preheater
- Reactor contains either a fixed bed catalyst for catalytic process or is tubular bed for non-catalytic process
- Effluent of the reactor is cooled via reactor feed preheater, then with water, and separated in a high pressure stage to gas and liquid fractions
- Major portion of gas is recycled, the balance going to a methane separation unit for H_2 enrichment and make-up; or it may also be used for fuel
- Liquid fraction is stripped of residual gas at low pressure
- Then fractionated to produce high purity benzene and recycle alkyl aromatics
- Yields are 95 – 98% for toluene conversion whereas 90 – 95% for naphthalene

Process description, hydrogen rich makeup gas and recycle gas are compressed and mixed with liquid alkyl aromatic feedstock and recycle. Prior to charging feed to the reactor, combined feed is preheated by heat exchange with reactor effluent and then in a fired preheater. Reactor contains either a fixed bed catalyst for catalytic processes or is tubular bed for non-catalytic process. Effluent of the reactor is cooled via reactor feed preheater then with water and separated in a high pressure stage to gas liquid fractions.

Major portion of gas is recycled, the balance going to the methane separation unit for H2 enrichment and makeup or it may also be used for a fuel purpose. So, liquid fraction is stripped off residual gas at low pressures, then fractionated to produce high purity benzene and then recycle alkyl aromatics. Yield is usually 95 to 98 percent for toluene conversion whereas 90 to 95 percent for naphthalene conversion. The process is same, if you are taking alkyl naphthene to produce naphthalenes then process is same, but the yield would be slightly less let us say if you are comparing with the benzene production from the toluene.

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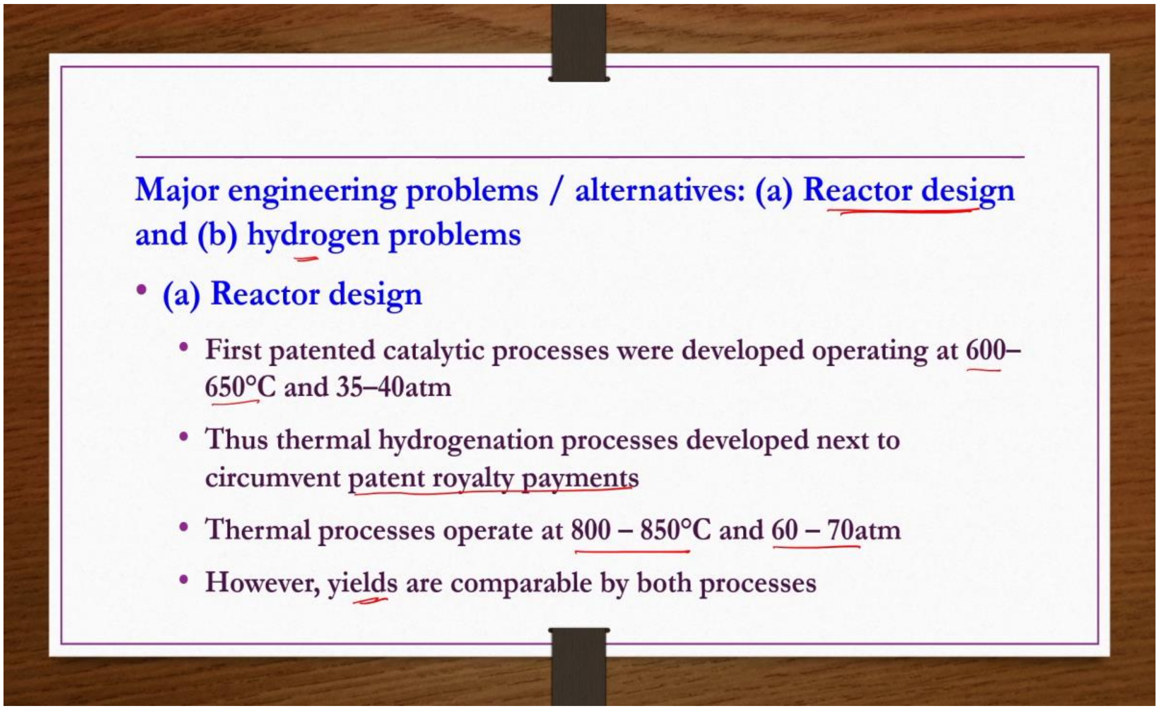

Major engineering problems / alternatives: (a) Reactor design and (b) hydrogen problems

- (a) Reactor design
  - First patented catalytic processes were developed operating at 600–650°C and 35–40atm
  - Thus thermal hydrogenation processes developed next to circumvent patent royalty payments
  - Thermal processes operate at 800 – 850°C and 60 – 70atm
  - However, yields are comparable by both processes

Major engineering problems obviously reactor design because of different types of processes that is non-catalytic and catalytic process and then wherever there is a hydrogen, so the problem associated with the hydrogen especially explosion proof reactors or MOC of the reactor such a way that that should not undergo embrittlement etc.., such kind of problems would always be there. Reactor design, first patented catalytic processes were developed for production of benzene from alkyl benzene or alkyl aromatics which were operating at 600 to 650 degrees centigrade and 35 to 40 atmosphere.

However, to circumvent the patent royalty payment issues, thermal hydrogenation processes were developed which were operating at 800 to 850 degrees centigrade and 60 to 70 atmospheres. However, yields whether you do the catalytic process or non-catalytic process they are comparable by both processes.

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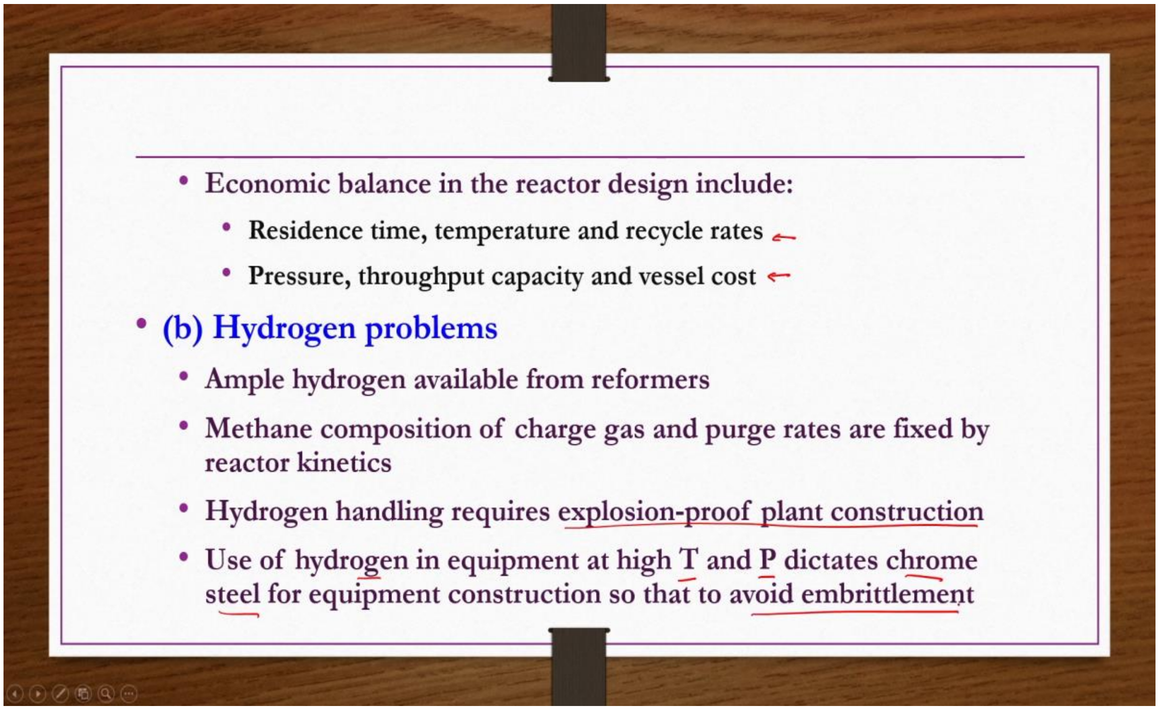

- Economic balance in the reactor design include:
  - Residence time, temperature and recycle rates
  - Pressure, throughput capacity and vessel cost
- **(b) Hydrogen problems**
  - Ample hydrogen available from reformers
  - Methane composition of charge gas and purge rates are fixed by reactor kinetics
  - Hydrogen handling requires explosion-proof plant construction
  - Use of hydrogen in equipment at high T and P dictates chrome steel for equipment construction so that to avoid embrittlement

Economic balance in the reactor design include residence time, temperature and recycle rates one has to consider as well as pressure, throughput capacity and vessel cost are the other categories. So, within these 2 categories one has to see the economic balance accordingly one has to select the residence time, temperature and then recycle rates or pressure, throughput and vessel cost.

Coming to the hydrogen problems ample hydrogen available from reformers, methane composition of charged gas and purge rates are fixed by the reactor kinetics. Hydrogen handling requires explosion proof plant construction as it is very explosive. Use of hydrogen in equipment at high temperature, high pressure dictates chrome steel for equipment construction so that to avoid embrittlement. So that is about the production of benzene by hydrodealkylation of alkyl aromatics. So we have seen the flowchart as well as the engineering problems.

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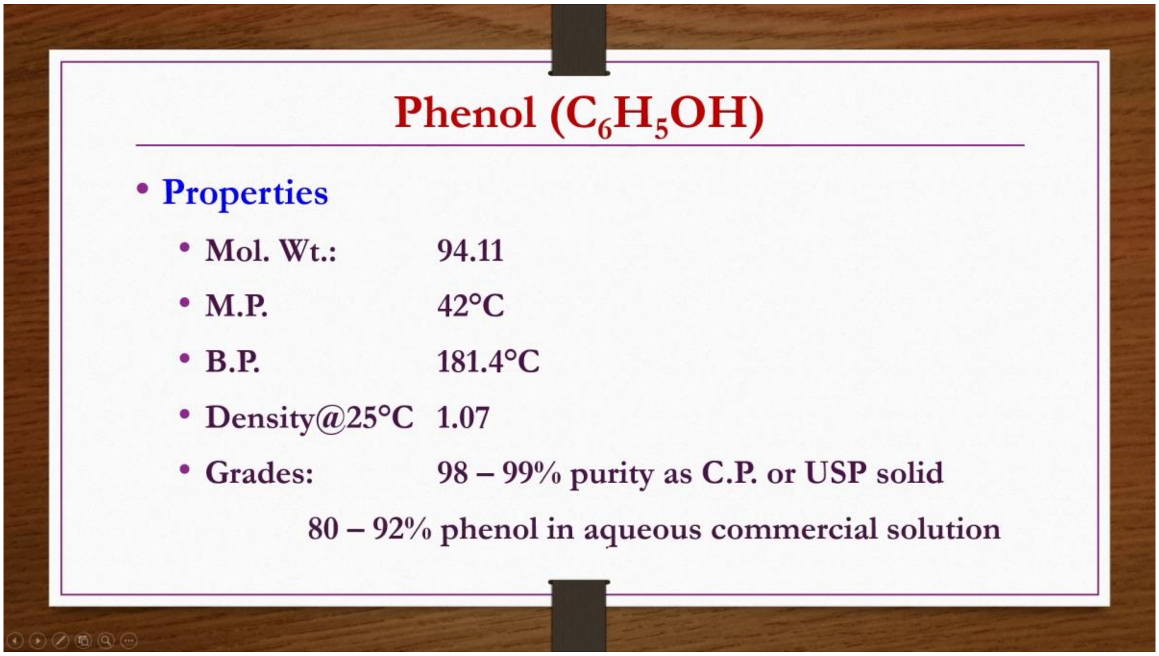

Phenol (C_6H_5OH)

- **Properties**
  - Mol. Wt.: 94.11
  - M.P. 42°C
  - B.P. 181.4°C
  - Density@25°C 1.07
  - Grades: 98 – 99% purity as C.P. or USP solid

    80 – 92% phenol in aqueous commercial solution

Now we discussed the production of phenol C6H5OH. First we see pertinent properties, molecular weight is 94.11, melting point is 42 degree centigrade, boiling point is 181.4 degree centigrade, density at 25 degree centigrade is 1.07 gram per cc, grades 98 to 99 percent purity as CP or USP solid or 80 to 92 percent phenol in aqueous commercial solutions are 2 different grades are available.

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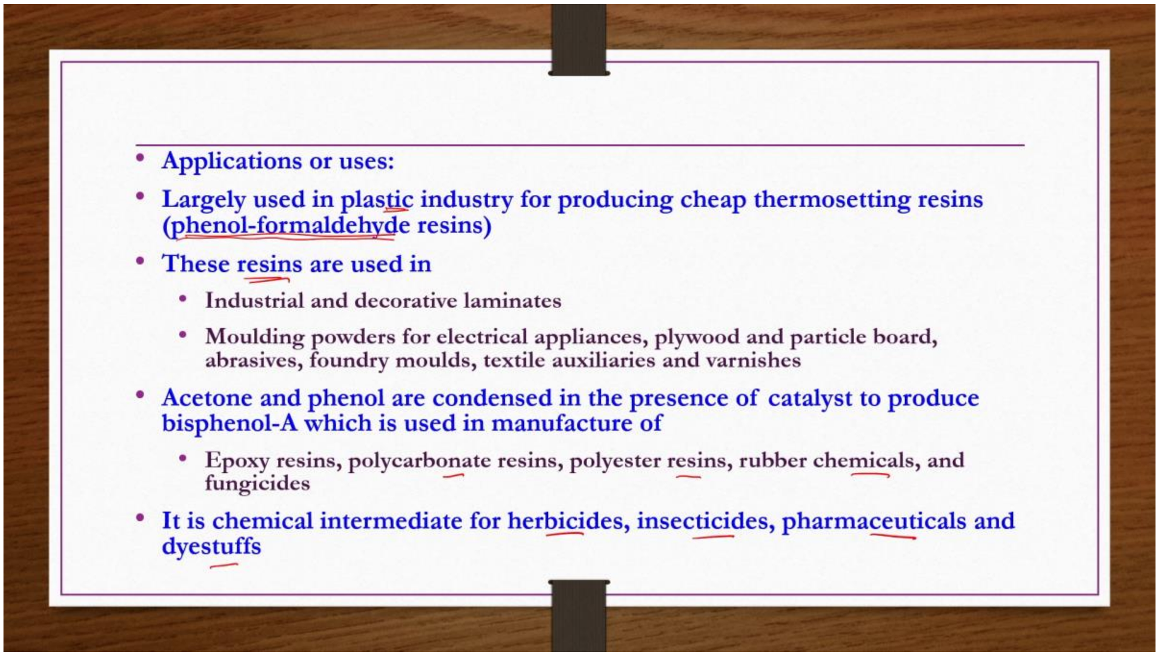

- Applications or uses:
- Largely used in plastic industry for producing cheap thermosetting resins (phenol-formaldehyde resins)
- These resins are used in
  - Industrial and decorative laminates
  - Moulding powders for electrical appliances, plywood and particle board, abrasives, foundry moulds, textile auxiliaries and varnishes
- Acetone and phenol are condensed in the presence of catalyst to produce bisphenol-A which is used in manufacture of
  - Epoxy resins, polycarbonate resins, polyester resins, rubber chemicals, and fungicides
- It is chemical intermediate for herbicides, insecticides, pharmaceuticals and dyestuffs

Applications of phenol if you see, largely it is used in plastic industry for production of thermosetting resins like phenol formaldehyde resins. These are very much used in several of the applications where phenol and then formaldehyde react to give different types of resin, thermoplastics or thermosetting both are possible. These resins are used in industrial and decorative laminates, moulding powders for electrical appliance, plywood and particle board, abrasive, foundry moulds, textile acceleration for varnishes also these phenol formaldehyde resins are used. Acetone and phenol are condensed in the presence of catalyst to produce bisphenol A which is used in the manufacture of epoxy resins, polycarbonate resins, polyester resins, rubber chemicals and fungicides. It is chemical intermediate for herbicides, insecticides, pharmaceuticals and dyestuffs as well.

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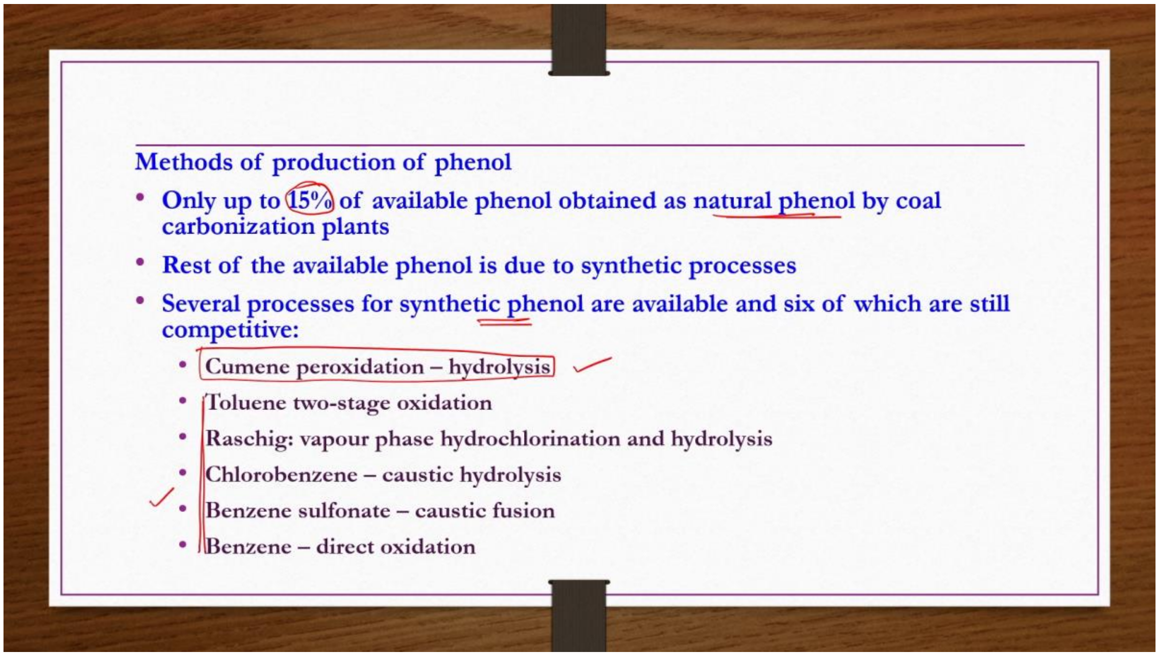

Methods of production of phenol

- Only up to 15% of available phenol obtained as natural phenol by coal carbonization plants
- Rest of the available phenol is due to synthetic processes
- Several processes for synthetic phenol are available and six of which are still competitive:
  - Cumene peroxidation – hydrolysis
  - Toluene two-stage oxidation
  - Raschig: vapour phase hydrochlorination and hydrolysis
  - Chlorobenzene – caustic hydrolysis
  - Benzene sulfonate – caustic fusion
  - Benzene – direct oxidation

Coming to the methods of production of phenol, only 15% of available phenol is obtained as natural phenol by coal carbonation process or coal carbonation plants whereas the remaining is coming from the synthetic processes like by reforming of the petroleum crudes. Several processes for synthetic phenol are available and 6 of which are still competitive, these are nothing but cumene peroxidation hydrolysis process, toluene two stage oxidation process, raschig process which is also known as the vapor phase hydrochlorination and hydrolysis process, chlorobenzene caustic hydrolysis process, benzene sulfonate caustic fusion and then benzene direct oxidation process. So, out of these 6 process, this process we will be discussing in today's lecture whereas the remaining 5 methods to produce phenol will be discussed in the next lecture, okay?

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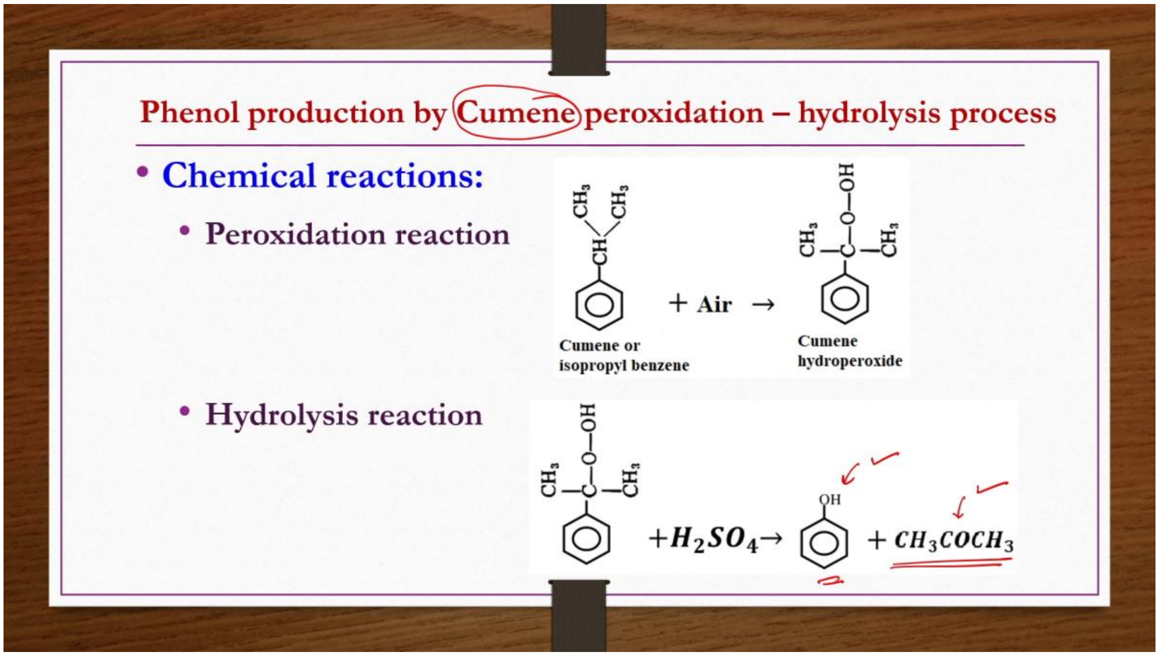

Phenol production by Cumene peroxidation – hydrolysis process

- **Chemical reactions:**
  - Peroxidation reaction
  - Hydrolysis reaction

So, let us start discussion on phenol production by cumene peroxidation and hydrolysis process. Chemical reaction, first whatever the cumene is there that will undergo peroxidation reaction. Cumene or isopropyl benzene will react with air to give the cumene hydroperoxide. This cumene hydroperoxide will undergo hydrolysis reaction using sulfuric acid to give the phenol and then acetone co-product. We have already discussed production of a cumene in the previous lecture, there we discussed that cumene is primarily utilized for the production of phenol in which acetone would be obtained as a co-product. So, in the previous chapter, we have discussed the cumene production. Now, in this chapter, we are using the cumene to produce phenol and then acetone.

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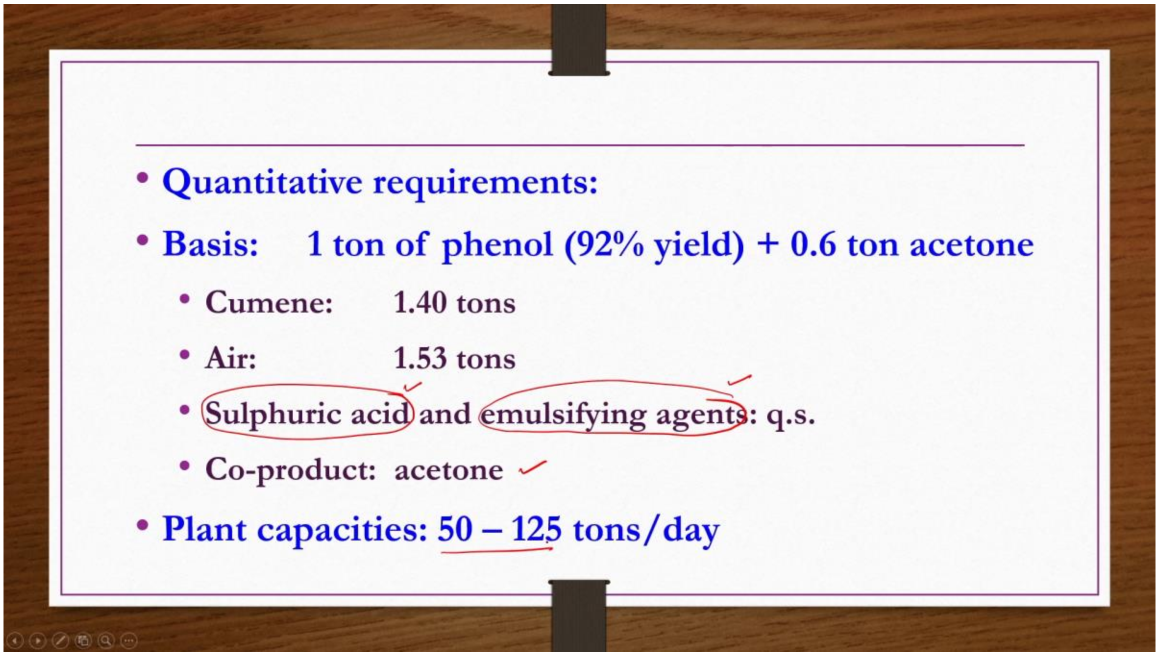

- **Quantitative requirements:**
- **Basis: 1 ton of phenol (92% yield) + 0.6 ton acetone**
  - Cumene: 1.40 tons
  - Air: 1.53 tons
  - Sulphuric acid and emulsifying agents: q.s.
  - Co-product: acetone
- **Plant capacities: 50 – 125 tons/day**

Quantitative requirements to produce 1 ton of phenol, 92% yield with 0.6 ton of acetone. How much cumene you require? 1.4 tons, whereas air 1.53 tons required. This cumene hydroperoxidation reaction takes place in the presence of emulsifying agents. So, some quantity of it is required, whereas the hydrolysis of a cumene hydroperoxide will take place in the presence of sulfuric acid. So, some quantity of sulfuric acid is also required. Co-product is acetone, plant capacity is usually 50 to 125 tons per day.

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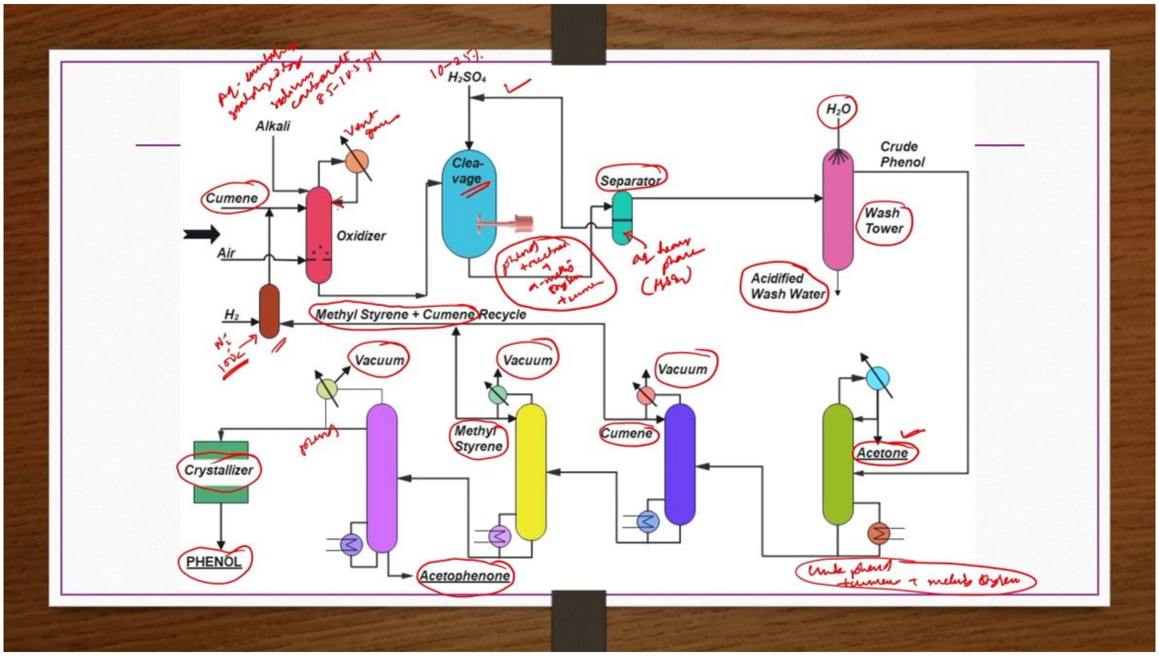

Now, we discussed the flowchart for the production of phenol from the cumene. In this flowchart, we can see that cumene is being mixed with the cumene and methyl styrene recycle stream, but this methyl styrene and cumene recycle stream whatever is there that is first hydrogenated using hydrogen in the presence of a nickel catalyst at approximately 100 degree centigrade. The purpose of this mild hydrogenation of methyl styrene and then recycle, cumene recycle stream is to make whatever the unsaturates or whatever alpha methyl styrene is there, those things would be made saturated and then mixed with the cumene and then sent to the oxidizer along with the air. So, when these are being sent to the oxidizer, what we do? We add aqueous emulsifying agent or emulsifier will be added which is stabilized by alkali like sodium carbonate having pH 8.5 to 10.5, so that this oxidation of a cumene takes place and then you get the cumene hydroperoxide. After the reaction, what happens? Whatever the gases are there, they would be condensed and then if at all any hydrocarbons are there, they would be recycled back to the reactor whereas after recovering the hydrocarbons, vent gases are taken off.

From the bottom of the oxidizer what you get? You get primarily cumene hydroperoxide along with the unreacted cumene, etc., some amount of methyl styrene, etc. may be there. So, that would be taken to cleavage tank where weak H2SO4 having 10 to 25% H2SO4 is utilized to do the hydrolysis of this cumene hydroperoxide so that you get the so called phenol plus acetone but also some alpha methyl styrene would also be there plus unreacted cumene, etc. would also be there. So, all these mixture you get after the hydrolysis reaction. This mixture now passes through a separator here. What it does? It separates the aqueous heavier phase at the bottom and then that is primarily containing the H_2SO_4, dilute H_2SO_4 that would be recycled back to the cleavage tank, right? whereas the top organic phase whatever is there that would be having the crude phenol, acetone and then some impurities that would be taken to a wash tower where you know mixture is washed with water so that to remove if at all any traces of acid still present in the mixture, okay? After removing the acid crude phenol is taken to a distillation column where highly volatile acetone is collected as a top product. Some of the top product after condensation is also being refluxed back to the distillation column to improve the purity of acetone, right? After removal of this one whatever the bottom product is there that would be crude phenol along with the cumene, unreacted cumene plus methyl styrene, etc. these kind of products would be there. But what happens this mixture if you heat it they will be decomposing so for that reason you will be using vacuum fractionators, 3 vacuum fractionators would be utilized.

In the first vacuum fractionator you separate cumene as a top product and then you pass it through the hydro treatment reactor to make it you know saturated and then mixed with the cumene and then sent to the reactor. Whatever the bottoms of the first vacuum fractionator would be there they would be taken to the second vacuum fractionator where methyl styrene would be collected as the top product and then that would be you know mixed with the cumene recycle and then that recycle stream is sent to the hydrogenator after saturating this recycle stream that would be mixed with the cumene and then sent to the oxidizer. Whereas the bottoms from the second vacuum fractionator whatever are there that would be primarily having the phenol with little amount of acetophenone. So that acetophenone is collected from the bottom as a heavier product whereas from the top you will be getting a phenol as a product. That phenol may be further purified by passing through a crystallizer to get the pure phenol of high grade high purity.

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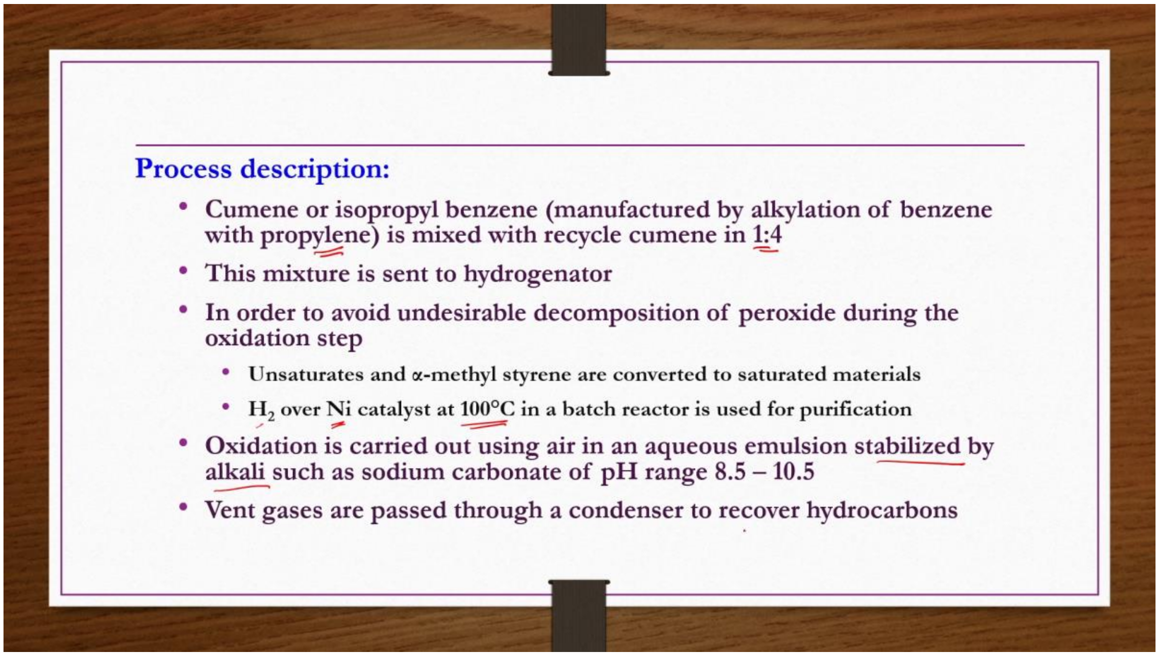

Process description:

- Cumene or isopropyl benzene (manufactured by alkylation of benzene with propylene) is mixed with recycle cumene in 1:4
- This mixture is sent to hydrogenator
- In order to avoid undesirable decomposition of peroxide during the oxidation step
    - Unsaturates and α-methyl styrene are converted to saturated materials
    - H_2 over Ni catalyst at 100°C in a batch reactor is used for purification
- Oxidation is carried out using air in an aqueous emulsion stabilized by alkali such as sodium carbonate of pH range 8.5 – 10.5
- Vent gases are passed through a condenser to recover hydrocarbons

Process description, cumene or isopropyl benzene which is manufactured by alkylation of benzene with propylene that we have already discussed in one of the previous lecture is mixed with a recycle cumene in 1 to 4 ratio. This mixture is sent to hydrogenator in order to avoid undesirable decomposition of peroxide during the oxidation step. Unsaturates and then alpha-meter styrene are converted to the saturated materials in this hydrogenator. For this purpose, hydrogen over nickel catalyst at 100 degree centigrade in a batch reactor used. Oxidation is carried out using air in an aqueous emulsion stabilized by alkali such as sodium carbonate of pH 8.5 to 10.5. Vent gases are passed through a condenser to recover hydrocarbons.

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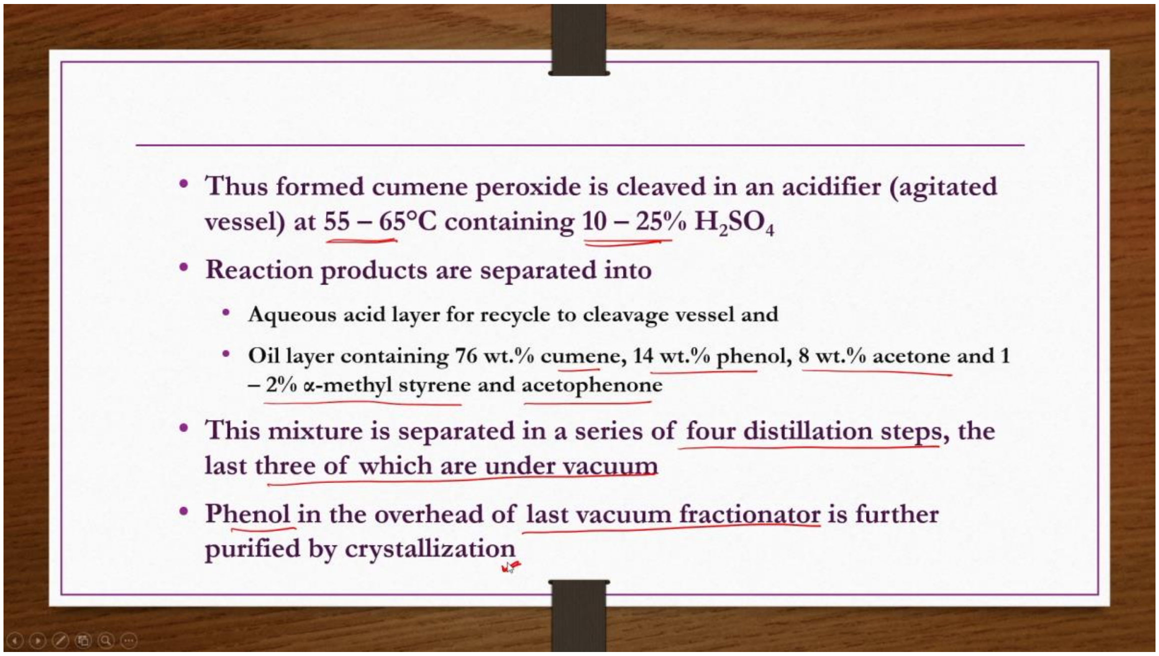

- Thus formed cumene peroxide is cleaved in an acidifier (agitated vessel) at 55 – 65°C containing 10 – 25% H_2SO_4
- Reaction products are separated into
  - Aqueous acid layer for recycle to cleavage vessel and
  - Oil layer containing 76 wt.% cumene, 14 wt.% phenol, 8 wt.% acetone and 1 – 2% α-methyl styrene and acetophenone
- This mixture is separated in a series of four distillation steps, the last three of which are under vacuum
- Phenol in the overhead of last vacuum fractionator is further purified by crystallization

Thus formed cumene peroxide is cleaved in an acidifier which is nothing but agitated vessel at 55 to 65 degrees centigrade using 10 to 25 percent dilute sulfuric acid solution. Reaction products are separated into the aqueous acid layer for recycle to cleavage vessel and then oil top layer containing 76 percent cumene, 14 percent phenol, 8 percent acetone and 1 to 2 percent of alpha-methyl styrene and acetophenone. This mixture is separated in a series of 4 distillation steps, the last 3 of which are under vacuum. Phenol in the overhead of last vacuum fractionator is further purified by crystallization as we have seen in the flowchart.

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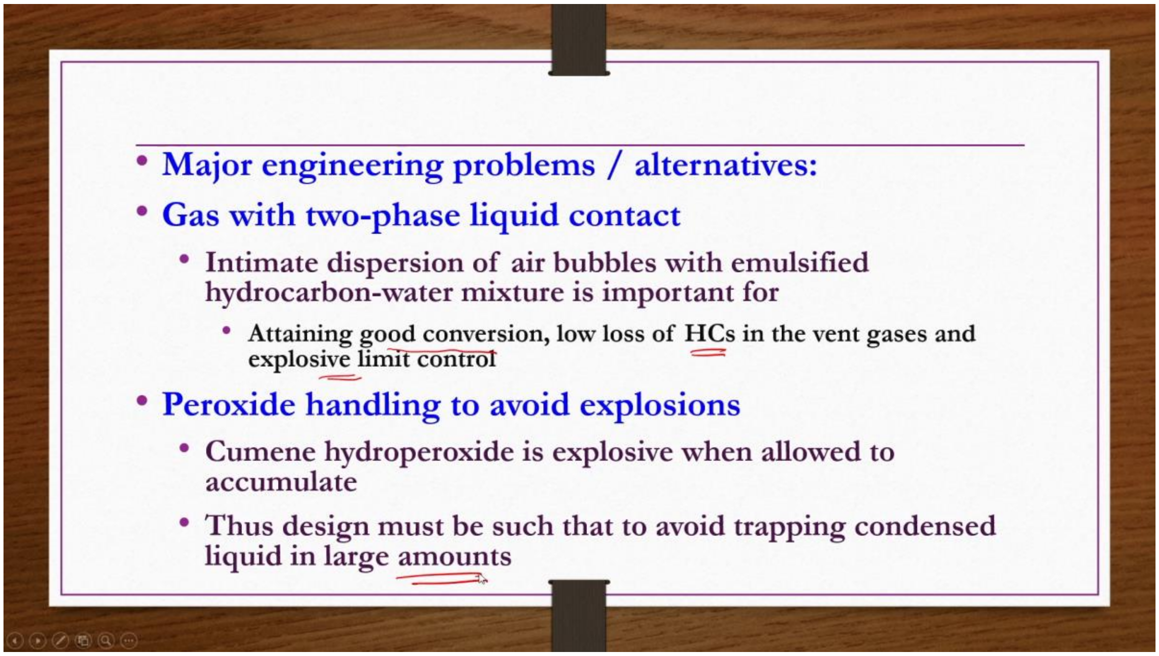

- **Major engineering problems / alternatives:**
- **Gas with two-phase liquid contact**
  - Intimate dispersion of air bubbles with emulsified hydrocarbon-water mixture is important for
    - Attaining good conversion, low loss of HCs in the vent gases and explosive limit control
- **Peroxide handling to avoid explosions**
  - Cumene hydroperoxide is explosive when allowed to accumulate
  - Thus design must be such that to avoid trapping condensed liquid in large amounts

Coming to the major engineering problems or alternatives, gas with a 2 phase liquid contact is one of the important problem. Intimate dispersion of air bubbles with emulsified hydrocarbon water mixture is important because such dispersion does not form easily. If you have this one, what are the advantages? You can attain good conversion, losses of hydrocarbons in the vent gases would be low and then would be under the explosive limit control as well. Other engineering problem is the peroxide handling to avoid explosions. Actually, this cumene peroxide if you accumulate in large quantities that may lead to the explosions. So, you should have a provision that to remove the cumene peroxide as much as possible from the vessels or equipments and then subsequently continuously keep passing rather storing it.

Cumene hydroperoxide is explosive when allowed to accumulate. Thus design must be such that to avoid trapping condensed liquid in large amounts. That is all about the production of phenol from the cumene by its oxidation or hydroperoxidation followed by the hydrolysis of a cumene hydroperoxide to produce phenol and acetone coproducts, right?

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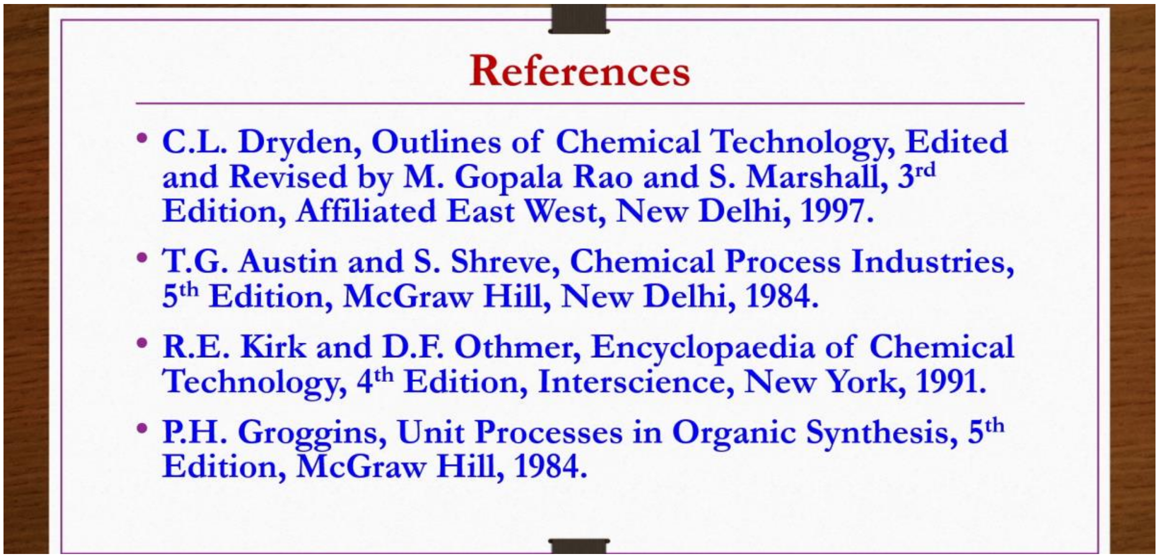

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References for today's lecture are provided here. Thank you