Organic Chemical Technology
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Lecture - 30
Chemicals from Aromatic Compounds - Phenol

Welcome to the MOOCs course organic chemical technology, the title of today's lecture is chemicals from aromatic compounds phenol. First, we have a recapitulation of what we have discussed in the previous lecture of this particular chapter, which is on chemicals from aromatics. We started discussing on listing out what are the main aromatics which can be used as raw materials for production of different types of synthetic chemicals, where we listed out like a benzene, toluene, xylene and then naphthalene are the ones which are important aromatics from which we can produce a number of different types of synthetic chemicals, right? So, if you have these things, you can produce different types of chemicals, but how to produce them, these raw material itself how to produce them because they are not available naturally in the nature, okay? You have to produce them as well, right?

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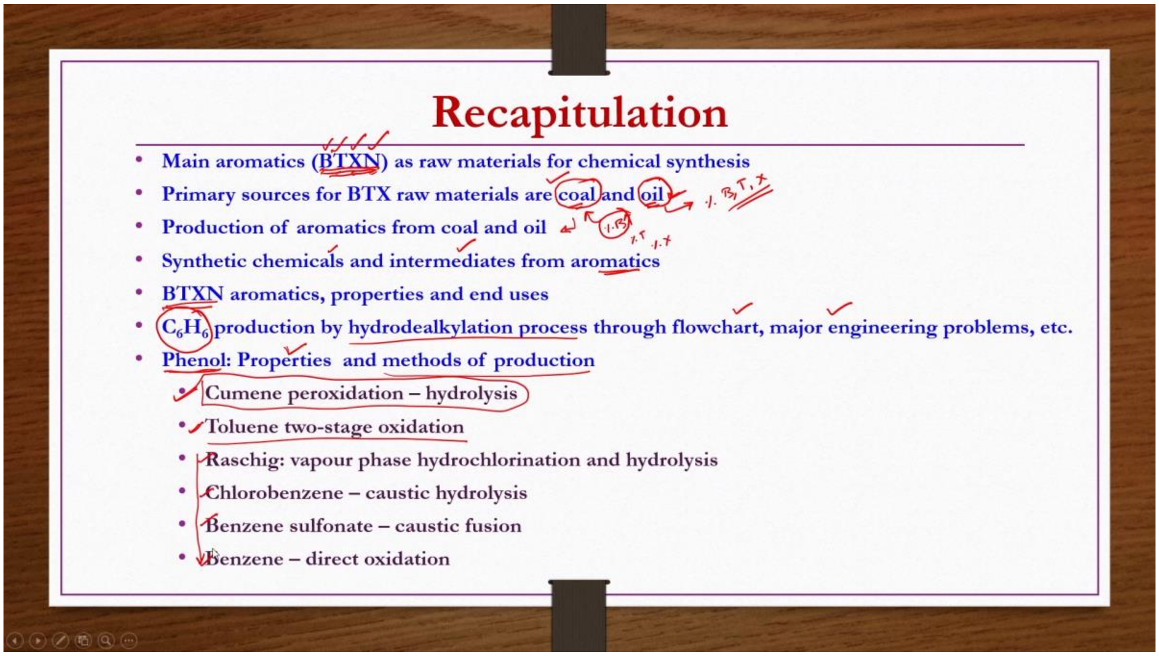

Recapitulation

- 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 by hydrodealkylation process through flowchart, major engineering problems, etc.
- Phenol: Properties and methods of production
  - Cumene peroxidation – hydrolysis
  - Toluene two-stage oxidation
  - Raschig: vapour phase hydrochlorination and hydrolysis
  - Chlorobenzene – caustic hydrolysis
  - Benzene sulfonate – caustic fusion
  - Benzene – direct oxidation

For that we listed out there are 2 sources, coal and then oil are the 2 sources from the oil different methods that we have already seen in the previous couple of chapters where we have done different types of steam cracking operations etc. When we do that, when we can get sometimes you know different types of aromatics along with the other components as well. Like coal also, you know when you do the carbonation of the coal, so then we get the volatiles which may be having the tarry components also, you can take off those tarry components from the volatiles by electrostatic precipitators, then whatever the volatiles are there that you can do the subsequent processing like you know, treating with the H2SO4 and other fractionating kind of processes, then you can get a fraction which is completely having the aromatics, okay? So, the aromatics that we produce by different sources of oil, then we get almost equivalent percentage of yield of B, T and X whereas when we did carbonation of coal to get aromatics, then we realized that the percentage of B is very high, substantially high approximately 60% whereas this percent of T and X are something like you know 7 to 12% or something like that, one of the components are even 4%, such low percentages we get you know from the coal. That is basically from the coal, you can get more of the benzene whereas from the oil, you can get you know all 3 components benzene, toluene, xylene in almost equivalent fractions. Production of aromatics from coal and oil that is whatever just now we discussed, so those processes we have discussed. Then we listed out different types of chemicals and intermediates, those can be prepared or manufactured by using these aromatics as raw materials, the big list we have seen. So that gives the importance of these aromatics to produce different types of synthetic chemicals, right? We also discussed properties and end uses of these 4 different types of aromatics. Then first we discussed the production of benzene by hydrodealkylation process through standard way of properties, flowchart and major engineering problems, consumption pattern, etc., right? Then we started discussing on the production of phenol synthetic chemical from aromatics. So, before discussing methods of production, we have discussed its properties, etc. Then we listed out different possible methods of production of phenol using aromatics or the raw materials. There are n number of methods are available, but 6 are very competitive economically. Techno-economically, 6 processes are competitive, those are listed below that is cumene peroxide hydrolysis process, toluene two-stage oxidation process, raschig vapor phase hydrochlorination and hydrolysis process and then chlorobenzene caustic hydrolysis process, then benzene sulfonate caustic fusion process and then finally benzene direct oxidation process. Now out of these 6 methods, this method or this method to produce phenol we have seen in detail as we have been discussing for any component. Now, we are going to discuss the production of phenol by this method that is toluene two-stage oxidation. After completing this, we are also going to discuss how to produce phenol by all these remaining processes as well.

As the name suggests, two-stage oxidation process, in this process, oxidation is taking place at 2 different stages, okay? So, why are we using toluene? Because it is very good aromatic, but from the applications point of view, we have found that it is being produced in large quantities that its end uses are limited and then we are not able to consume all of this toluene. For that reason, different other options are there, one of the options is that convert this toluene into the benzene and then try to get different types of end products. So, likewise you can also convert this toluene into the phenol because phenol is also having good number of applications. So, that process we are discussing here. We start with the chemical reactions. First one is the oxidation of toluene to benzoic acid that is you take toluene and then react with oxygen at 150 degrees centigrade in the presence of a cobalt naphthenate catalyst, then you will get benzoic acid and water, right?

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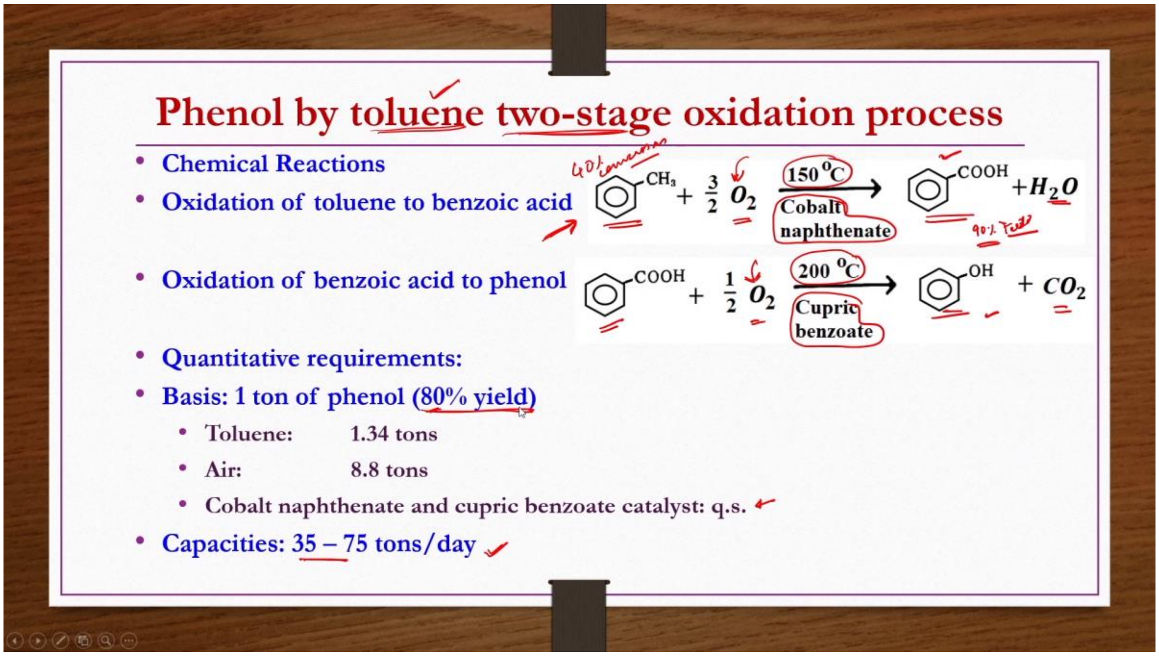

Phenol by toluene two-stage oxidation process

- Chemical Reactions
- Oxidation of toluene to benzoic acid
- Oxidation of benzoic acid to phenol
- Quantitative requirements:
- Basis: 1 ton of phenol (80% yield)
  - Toluene: 1.34 tons
  - Air: 8.8 tons
  - Cobalt naphthenate and cupric benzoate catalyst: q.s.
- Capacities: 35 – 75 tons/day

This benzoic acid if you further do the oxidation, then you get phenol as per the reaction given here. So, that is benzoic acid reacting with oxygen at 200 degrees centigrade in the presence of cupric benzoate catalyst, you will get the phenol, okay? Along with this one, you also get some CO2, right? So now, quantitative requirements, if you want to produce 1 ton of phenol with 80% yield, then toluene you require 1.34 tons and then air you require 8.8 tons, whereas the catalyst cobalt naphthenate and then cupric benzoate catalyst traces are quantity sufficient whatever is required that you have to take. Then capacities 35 to 75 tons per day plants are very common using this particular process to produce phenol, right? So, in this process actually the phenol converting into the benzoic acid by oxygen in the presence of this catalyst cobalt naphthenate at 150 degrees centigrade, you know conversion is limited only up to the 40% only. If not, so many other kind of you know byproducts like benzaldehyde, etc. would also be forming. So, then subsequent purification would become very difficult, that is the reason. In this first reaction, the oxidation of toluene is restricted so that the conversion of toluene is taking place only 40% and then that would be accomplished by using the excess of oxygen, right? So, even though here 40% of toluene conversion is taking place or you are limiting to convert only 40% of toluene, you get you know more than 90% of a benzoic acid yield, right? So, here also this benzoic acid is oxidized with excess of oxygen so that you know sufficient more than you know 90% or 80% yield of phenol will take place. But however, when you take the overall yield, then that yield would be 80%, okay?

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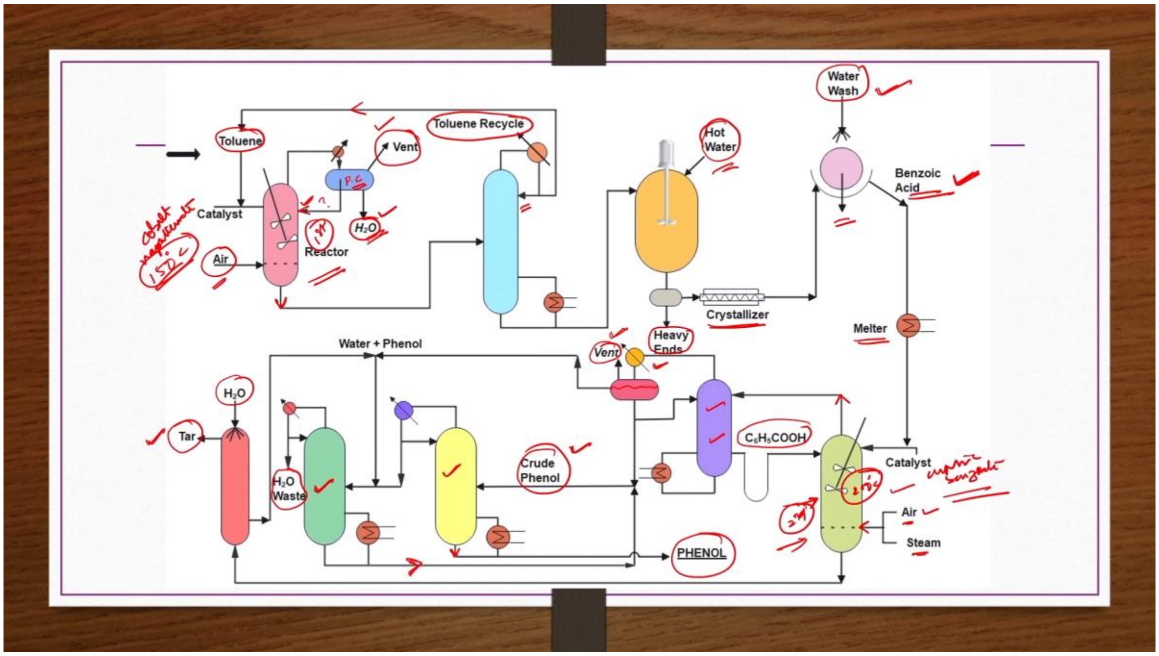

Now, this is the flowchart for the production of a phenol from the toluene by 2-step oxidation process. So, what we do first here, we take a toluene fresh one as well as the recycle one within the process whichever unreacted toluene is there that we recover and then recycle back to the reactor, right? So, this is a liquid phase reactor continuous still tank kind of reactor to this reactor along with the catalyst whatever cobalt naphthenate catalyst is there that one toluene are sent to this liquid phase reactor and then to this reactor from the bottom air is being circulated because we want oxidation of the toluene to take place, right? You can take directly oxygen also if it is available, but it is not required, you can take air, okay? Rather taking oxygen, so that would be sufficient, you do not need to spend too much money on purifying this air to get only oxygen, okay? Now, from this reactor from the top what you get? You get you know water vapors and then there would be some unreacted toluene etc. would be there. That mixture you take it to a condenser, condense this water and then take it as a waste or you know for the utilization within the process if it is required, whereas the unreacted toluene you feed back to the reactor. Whereas from the bottom primarily the liquid whatever that you are getting because it is a liquid phase reactor, so here you are maintaining the temperature of 150 degrees centigrade, right? And then you are using this particular catalyst. So, then after the reaction, some of them would also be there in the vapor phase. So, those you condense and then take out as water, non-condensable gases like nitrogen etc. you take out to vent, whereas the unreacted toluene you feed back to the reactor by this partial reflux and then condenser. Whereas the liquid product from the bottom you get that is mostly would be having the crude benzoic acid plus some amount of unreacted toluene as well, okay? Now, here before doing this, taking this liquid solution like benzoic acid plus toluene mixture to the fractionator, what you have here whatever this partial condenser that you are using from here, not only the unreacted toluene, some of the products are also being sent back to the reactor that depends on the how much conversion you need. In this case, particularly we do not need much of the toluene conversion to take place, it should not be more than 40%. So, it has to be carefully operated, okay? Whereas from the bottom whatever the liquids are there, they would be having benzoic acid and toluene mixture. So, then toluene you can collect from the top because it is a high volatile component compared to the benzoic acid. So, toluene you get in the top column, condense it and then some of it you can take it back to the fractionator in order to improve the separation and then remaining one is you can recycle back to the reactor along with the catalyst and then fresh toluene. Whereas from the bottom whatever you get that is primarily having the benzoic acid though it is not completely pure benzoic acid, basically it would be crude benzoic acid that would be washed with hot water to remove any heavy ends etc. that may be present in the benzoic acid because the purity of benzoic acid is going to dictate the purity of the final phenol that you are going to get because the phenol you are getting from the benzoic acid oxidation process, that is second stage oxidation process. So, for that purpose what you do this benzoic acid is washed with the hot water to remove the heavy ends, then whatever the crude benzoic acid is there that would be crystallized and sent to vacuum filtration process where wash water is used to remove the impurities and then benzoic acid is collected. So, this benzoic acid itself you can take as a product and then do subsequent purification if you are looking for the benzoic acid product, otherwise as in this process we are producing phenol, so this would be further melted using a heat exchange, then mixed with the catalyst. Here which catalyst are we using? We are using cupric benzoic catalyst we are using and then temperature is roughly 200 degrees centigrade is maintained in this reactor. This is also continuous still tank kind of reactor. To this reactor from the top benzoic acid, melted benzoic acid mixed with the catalyst is being fed from the bottom air and then steam are being supplied. So, both of them are supplied or only air may be supplied for the oxidation to take place. Now, here after taking the oxidation you get primarily phenol plus unreacted benzoic acid and then CO2 etc. would also be there because in this process CO2 would also be forming So, that reaction mixture whatever is there that you take to a fractionator column where you maintain operating conditions such a way that from the top you get the CO2, N2 etc. gases from the top after passing through condenser they will be taken out as a vent. Whereas in that vapor if at all some of the product mixture are unreacted, you know benzoic acid etc. is there that would be fed back to the fractionator. From the bottom what you do, you get unreacted benzoic acid if at all it is present more in the product stream, so that you can collect from the bottom and then send back it to the second stage oxidation reactor. This is the second stage oxidation reactor and then this is the first stage oxidation reactor. So, this way the benzoic acid recycling you can do it, whereas from the bottom of the second stage oxidation reactor you can get the tarry heavy and so you may be getting that you can wash with the water and then collect as tar. You can check its contents and then if it is required you can recycle as well. So, after cooling and then passing through this separator where you are separating the vent gases like CO2, N2 etc. Then what you have, you may be having water phenol mixture primarily because water is forming in this reactor and then CO2 is forming in this reactor and then water is forming in the first reactor though most of the water we remove. Subsequently we are doing washing with water and other kind of things, so then some water may also be there. So that here what you do, the water phenol mixture you take it to a fractionator where water is removed and then phenol is collected which is again crude phenol. Rather saying the crude phenol actually phenol is forming azeotrope with water, so that mixture you whatever is there that you take back to the another final fractionator, right? This crude phenol you take to the another final fractionator where you get the pure phenol as the bottom product whereas the water contents along with some fractions of phenol you can collect from the top, you can do the required separation if required otherwise you can send back it to the previous fractionator where water phenol are being separated. So, the purification of phenol is taking place in 2 stages because water phenol are forming azeotrope here, okay? So, this is the overall process. If you see this process details in the text form, then what you have, what we realize from this process is the 2-stage oxidation process. So 2 reactors are required, right? And then so many purification steps are required. So then obviously capital cost is going to be higher for this particular process because of such reasons if you see the capacities of such plants is very less 35 to 75 tons only because so many of the operations are involved not only 2 reactors but also so many separation processes are involved. So, it is going to be economically better if you can develop a process which can convert toluene to phenol in one single step, but however there are no such processes available until now which are commercial.

Coming to the process description, it is a 2-stage oxidation process. In the first stage, fresh plus recycled toluene mixed with a small quantity of cobalt naphthenate catalyst. This mixture charged to a reactor which is a liquid filled tower through which air is passed from the bottom. Reactor is provided with cooling tubes to remove exothermic heat of the reaction. Reactor is running at 150 degrees centigrade and 3 atmosphere. Excess air is used, but toluene conversion is limited up to 40% to avoid excessive side reactions because these side reactions give byproducts such as benzaldehyde, benzyl alcohol, benzyl benzoate, CO, CO2. So, separation of these kind of aromatics again will require lot of process unit operations, etc. So capital cost again may increase. Subsequently operational cost would also be increasing. So, for that purpose, we are limiting toluene conversion only up to 40%. Though we are supplying the excess air for this reaction to occur. With this conversion of toluene, one can obtain 90% yield of benzoic acid. Though 40% toluene is allowed to convert, you get 90% of the benzoic acid yield.

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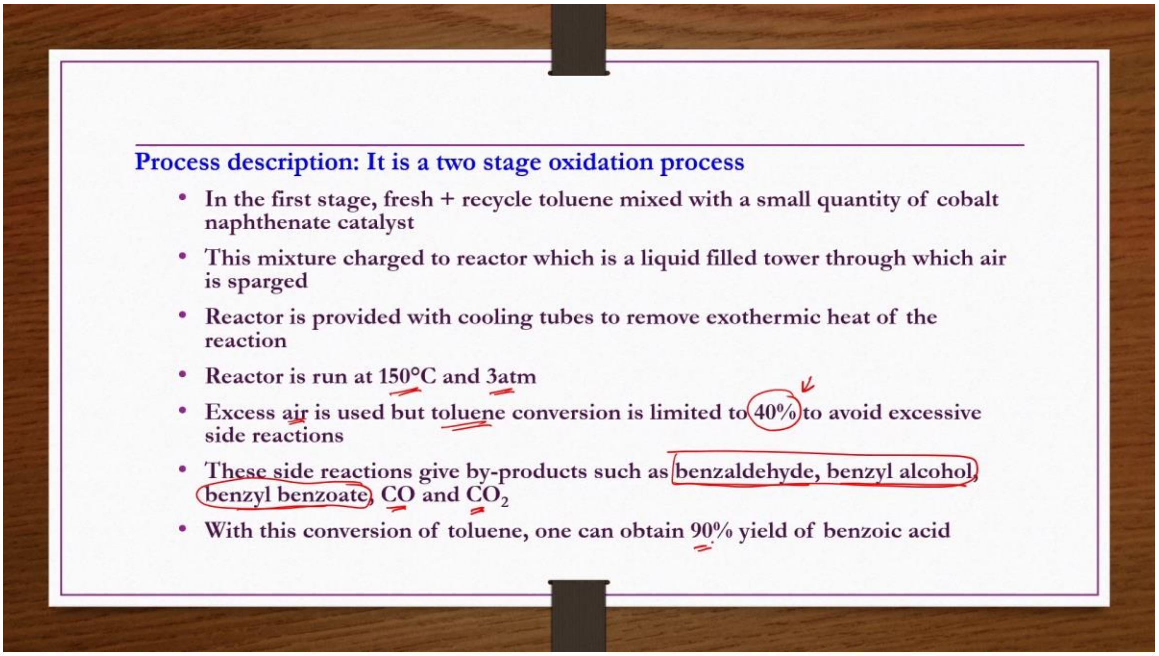

Process description: It is a two stage oxidation process

- In the first stage, fresh + recycle toluene mixed with a small quantity of cobalt naphthenate catalyst
- This mixture charged to reactor which is a liquid filled tower through which air is sparged
- Reactor is provided with cooling tubes to remove exothermic heat of the reaction
- Reactor is run at 150°C and 3atm
- Excess air is used but toluene conversion is limited to 40% to avoid excessive side reactions
- These side reactions give by-products such as benzaldehyde, benzyl alcohol, benzyl benzoate, CO and CO_2
- With this conversion of toluene, one can obtain 90% yield of benzoic acid

Off gases from reactor are vented through a water cooled condenser to remove water and to allow return of toluene. Liquid from reactor continuously passes to distillation column which strips toluene and other volatile byproducts from acid fractions in the bottoms. Purified benzoic acid is separated by extracting the bottoms with hot water, then crystallizing and filtering the crude benzoic acid so that to get it purified. To produce phenol from crude benzoic acid, it is melted, mixed with cupric benzoate catalyst, then charged to air-sparged cooling tubes and mechanical agitation. Other conditions are 220 degrees in degrees and then pressure is 1.3 to 1.7 atmospheres. Excess air is necessary to get 70 to 80% conversion of benzoic acid with a yield of 90% phenol. Overall process yield of 2 steps is about 80% only.

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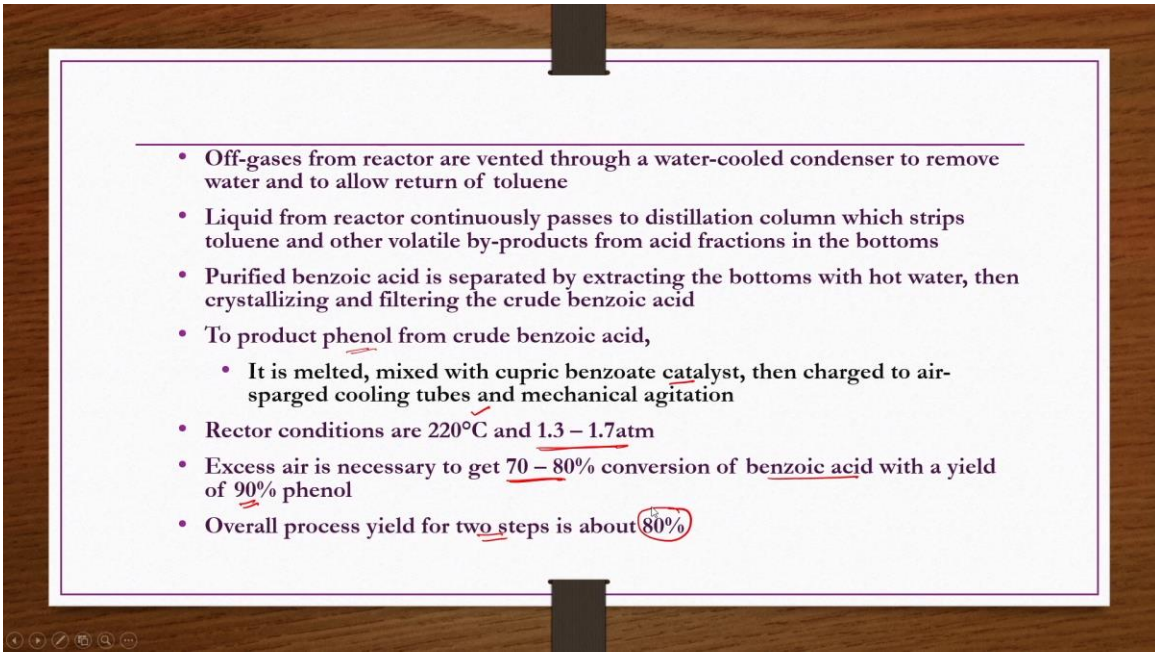

- Off-gases from reactor are vented through a water-cooled condenser to remove water and to allow return of toluene
- Liquid from reactor continuously passes to distillation column which strips toluene and other volatile by-products from acid fractions in the bottoms
- Purified benzoic acid is separated by extracting the bottoms with hot water, then crystallizing and filtering the crude benzoic acid
- To product phenol from crude benzoic acid,
  - It is melted, mixed with cupric benzoate catalyst, then charged to air-sparged cooling tubes and mechanical agitation
- Rector conditions are 220°C and 1.3 – 1.7atm
- Excess air is necessary to get 70 – 80% conversion of benzoic acid with a yield of 90% phenol
- Overall process yield for two steps is about 80%

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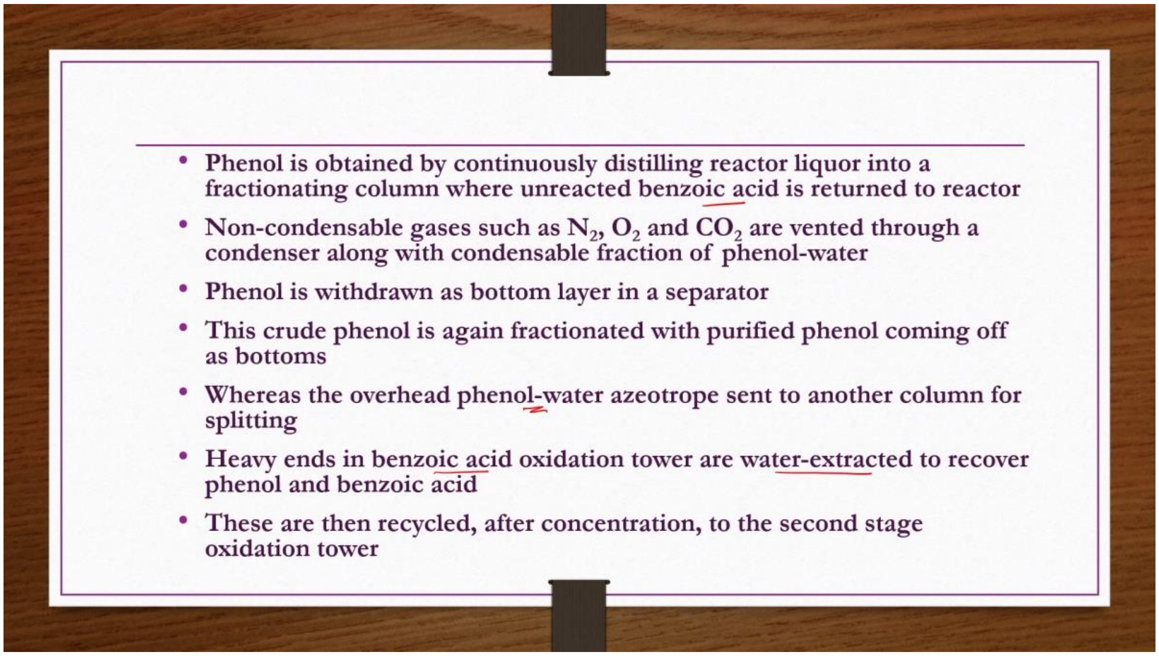

- Phenol is obtained by continuously distilling reactor liquor into a fractionating column where unreacted benzoic acid is returned to reactor
- Non-condensable gases such as N_2, O_2 and CO_2 are vented through a condenser along with condensable fraction of phenol-water
- Phenol is withdrawn as bottom layer in a separator
- This crude phenol is again fractionated with purified phenol coming off as bottoms
- Whereas the overhead phenol-water azeotrope sent to another column for splitting
- Heavy ends in benzoic acid oxidation tower are water-extracted to recover phenol and benzoic acid
- These are then recycled, after concentration, to the second stage oxidation tower

Phenol is obtained by continuously distilling a reactor liquor into a fractionating column where unreacted benzoic acid is returned to reactor. Non-condensable gases such as N2, O2 and CO2 are vented through a condenser along with condensable fractions of phenol water. Phenol is withdrawn as a bottom layer in a separator. This crude phenol is again fractionated with purified phenol coming off as bottoms, whereas the overhead phenol water azeotropes into another column for splitting. Heavy ends in benzoic acid oxidation tower are water extracted to recover phenol and benzoic acid. These are then recycled after concentration and to the second stage oxidation tower as well.

Major engineering problems alternatives, major design problems are efficient gas liquid contacting design because oxidation reaction is required, toluene liquid is interacting with the air which is in the gaseous form. Economic recovery of organics from water containing fractions in the second stage is also one important design problem to consider. Economics of process incentives for switching to toluene as an aromatic source comes from oversupply of a toluene available at low cost from petroleum reforming.

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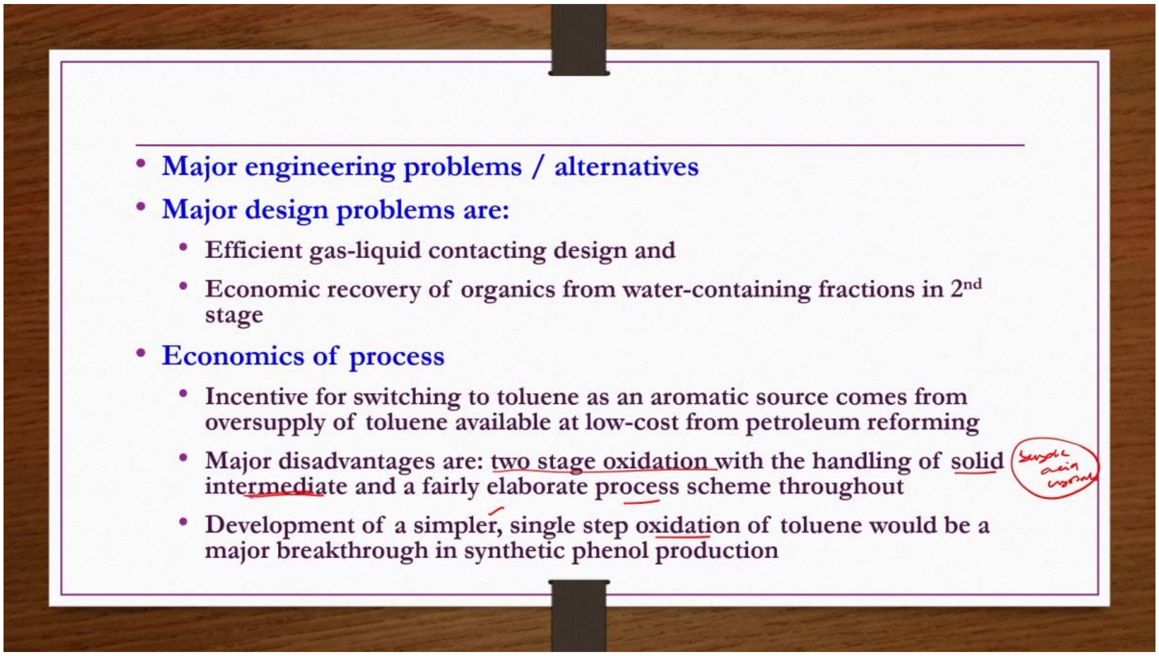

- **Major engineering problems / alternatives**
- **Major design problems are:**
  - Efficient gas-liquid contacting design and
  - Economic recovery of organics from water-containing fractions in 2nd stage
- **Economics of process**
  - Incentive for switching to toluene as an aromatic source comes from oversupply of toluene available at low-cost from petroleum reforming
  - Major disadvantages are: two stage oxidation with the handling of solid intermediate and a fairly elaborate process scheme throughout
  - Development of a simpler, single step oxidation of toluene would be a major breakthrough in synthetic phenol production

Benzoic acid crystals

Major disadvantages are 2-stage oxidation with handling of solid intermediate, not only 2-stage gas liquid reactors are required, but in between also you need to have a provision to handle solids, intermediate solids which are nothing but benzoic acid crystals whatever you are getting. So, that is also one of the disadvantages and fairly elaborate process scheme throughout. We have seen the flowchart, so big so many unit operations are involved to get process done along with the 2 reactors. Development of a simpler single step oxidation of toluene would be a major breakthrough in synthetic phenol production, okay? That is all production of phenol by oxidation of toluene in 2 stages.

Now we discuss Raschig phenol process which is also known as you know hydrochlorination of benzene process. Chemical reactions, first hydrochlorination of benzene to be carried out that is benzene reacting with HCl and then oxygen at 240 degrees centigrade in the presence of ferric chloride or cupric chloride or mixture of these two catalyst, okay? So, as catalyst you can use ferric chloride or cupric chloride or both of them can be added to get a chlorobenzene and then here water is forming. So, excessive water is being formed here, so then after this reaction in a reactor you should have a provision to remove this water as much as possible.

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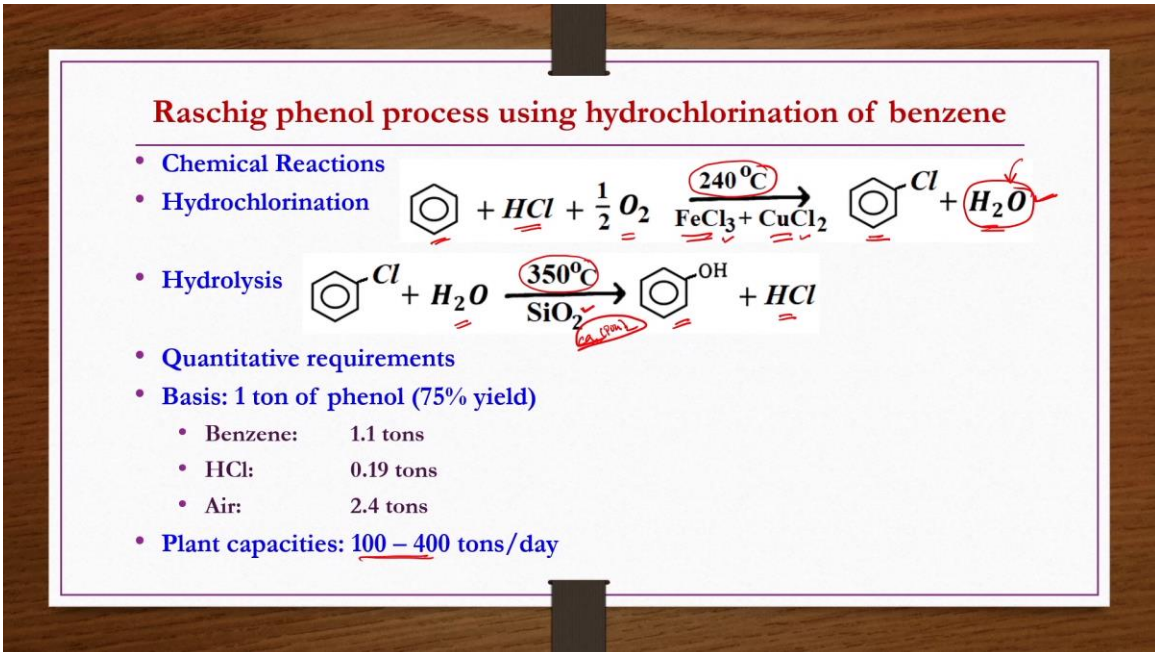

Raschig phenol process using hydrochlorination of benzene

- Chemical Reactions
- Hydrochlorination

- Hydrolysis

- Quantitative requirements
- Basis: 1 ton of phenol (75% yield)
  - Benzene: 1.1 tons
  - HCl: 0.19 tons
  - Air: 2.4 tons
- Plant capacities: 100 – 400 tons/day

Then this chlorobenzene would be undergoing hydrolysis where it is reacting with water at 350 degrees centigrade in the presence of silica catalyst or calcium phosphate is also used as a catalyst, okay? So, when this hydrolysis of a chlorobenzene takes place, you get the phenol and then HCl. Coming to the quantitative requirements to produce 1 ton of phenol at 75% yield, benzene 1.1 tons required, HCl 0.19 tons required, air 2.4 tons required because hydrochlorination is taking place not only with HCl but also it is required oxygen. Plant capacity is usually 100 to 400 tons per day.

Now, this is the process we have. Here what we are doing? We are taking this purified benzene into a hydrochlorination reactor to which air and then make up HCl along with the recycled HCl are being supplied from the bottom of the reactor, okay? So, when this air, HCl and then benzene interact in this reactor, this reactor is having the catalyst FeCl3 or CuCl2 or both of them and then this reaction is taking place at around 240 degrees centigrade. So, temperature is maintained around this temperature. So, from here you get the chlorobenzene and then there would also be some water and then chloro polybenzene also or poly chlorobenzene should also be forming, right? So, such mixture is taken to a fractionator which is a distillation column. Now here temperature, pressure you maintain such a way that the lighter or more volatile chlorobenzene whatever is there that you can get it as a top product after partially condensing it, whereas the heavier poly chlorobenzene components whatever are forming especially benzene dichloride etcetera or dichlorobenzene etcetera, these kinds of components you know they would be heavier compared to the crude mono chlorobenzene.

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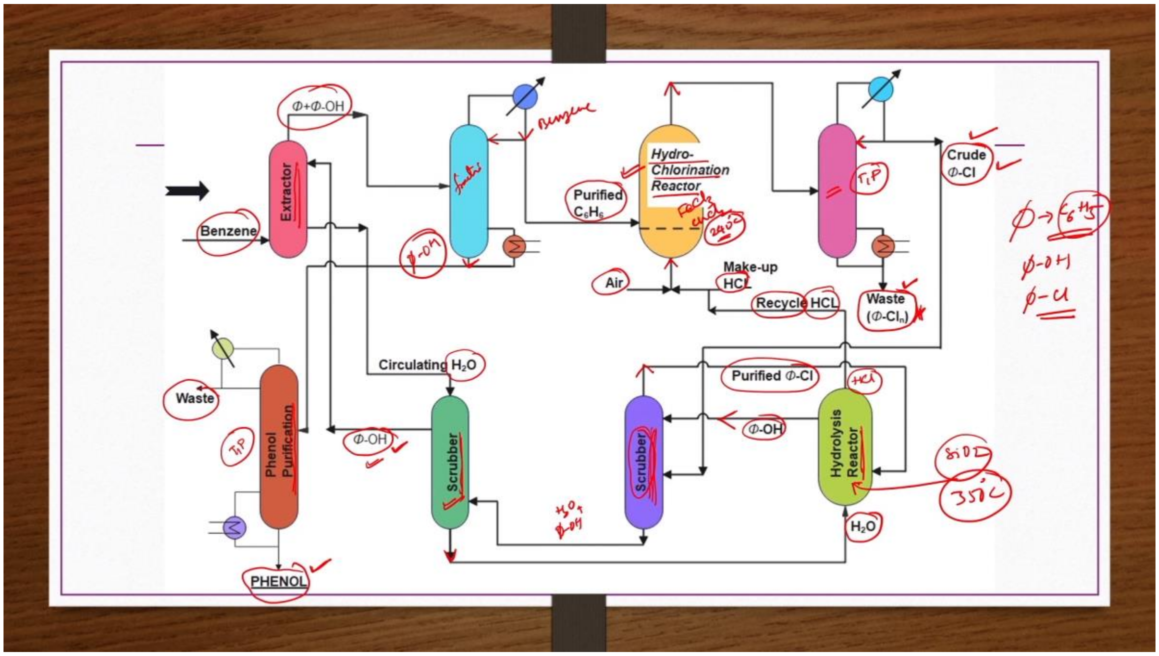

So, those heaviers are collected from the bottom as a wastage, right? So, here in the organic chemistry this ϕ symbol is usually used to represent C6H5 functional. It is not a component whatever the C6H5 radicals are forming that is represented by ϕ. So, let us phenol C6H5OH, so that phenol is written ϕ-OH like this. Mono chlorobenzene C6H5Cl, so that is written as ϕ-Cl. So, ϕ stands for C6H5, right? So that crude mono chlorobenzene is there that you can purify and then do the subsequent reaction that is the process because this mono chlorobenzene is only being hydrolyzed to get the phenol, whereas the dichlorobenzene or other poly chlorobenzene are not required, so then they should be discarded from the bottom as a heavier component, okay? Some of the top product is also recycled back to the fractionator which is a standard process that is partial recycle. This we will do in order to improve the purity of the product we are looking for, okay? So, once you get this mono chlorobenzene that you take to a scrubber, right? So, here mono chlorobenzene is being scrubbed with phenol, so that to get a pure or purified mono chlorobenzene from the top, right? So, that you can take it to the hydrolysis reactor, whereas from the bottom of the scrubber you may be getting you know so called benzene H2O mixture, etc. that would be taken to another scrubber where you recover the phenol from the water because in the scrubber what are you doing? You are using recirculating water H2O for scrubbing purpose. So, from this mixture of phenol and water what you get? You get phenol separated out and then that is sent back to the extractor, you know, where it is being extracted with the benzene that we will see subsequently. From the bottom what you get? You get the water. In that water, you take it to the hydrolysis reactor in which purified mono chlorobenzene is being supplied. So, here what are you doing? Which catalyst you are using SiO2 or calcium phosphate catalyst you are using here in this reactor and then temperature is 350 degrees centigrade is maintained so that the hydrolysis of mono chlorobenzene takes place and then you get the phenol and then you get the required phenol, right? That phenol you can use it to scrub out the mono chlorophenol, whatever the crude mono chlorophenol is there for scrubbing out that one you are using this phenol from here, okay? From the hydrolysis reactor because it is crude one, okay? From the top what are you getting? You are getting HCl vapors, etc. So those you can recycle and then send it back to the hydrochlorination reactor, right? So, after this scrubber, second stage scrubber where you are separating out mostly phenol, that phenol is interacting with the benzene, right? In an extractor to get a mixture of a benzene and phenol that is being sent to another fractionator distillation column so that from the top you can get the more volatile benzene as the product, top product and that purified benzene you can use it in the hydrochlorination reactor. Whereas from the bottom of this fractionator you will be getting phenol, right? That you can take to the phenol purification column and then from here you maintain temperature pressure such a way that more volatile waste, etc. would be separated out from the top whereas the heavier phenol would be collected as a bottom product, pure phenol you collect as a bottom product from the bottom of the phenol purification distillation column, okay? So this is the flowchart for this process.

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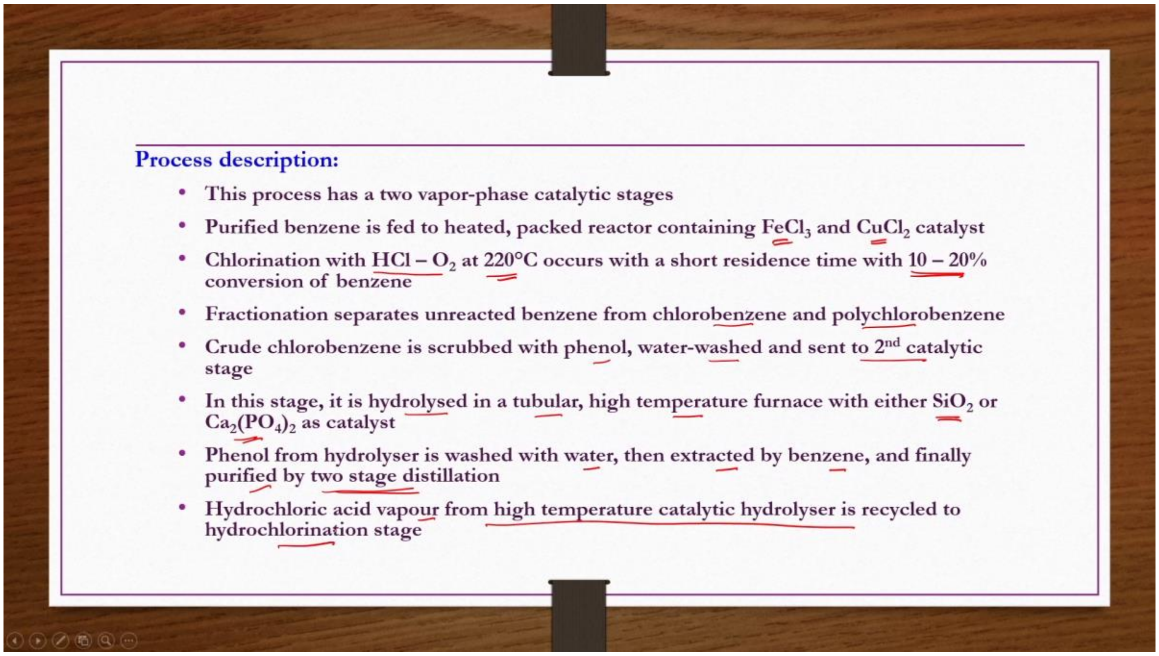

Process description:

- This process has a two vapor-phase catalytic stages
- Purified benzene is fed to heated, packed reactor containing $FeCl_3$ and $CuCl_2$ catalyst
- Chlorination with $HCl - O_2$ at 220°C occurs with a short residence time with 10 – 20% conversion of benzene
- Fractionation separates unreacted benzene from chlorobenzene and polychlorobenzene
- Crude chlorobenzene is scrubbed with phenol, water-washed and sent to 2nd catalytic stage
- In this stage, it is hydrolysed in a tubular, high temperature furnace with either SiO_2 or $Ca_2(PO_4)_2$ as catalyst
- Phenol from hydrolyser is washed with water, then extracted by benzene, and finally purified by two stage distillation
- Hydrochloric acid vapour from high temperature catalytic hydrolyser is recycled to hydrochlorination stage

Now if you see the description, this process has a 2 vapour phase catalytic stages. Unreacted benzene is fed to heated packed reactor containing FeCl3 and CuCl2 catalyst. Chlorination with HClO2 at 220 degrees centigrade occurs with a short residence time with 10 to 20% conversion of benzene. Fractionation separates unreacted benzene from chlorobenzene and then poly chlorobenzene. Crude chlorobenzene is scrubbed with phenol, water washed and sent to second catalytic stage. At this stage, it is hydrolyzed in a tubular high temperature furnace with either SiO2 or calcium phosphate as catalyst. Then phenol from hydrolyzer is washed with water, then extracted with benzene and finally purified by 2 stage distillation column. Hydrochloric acid vapour from high temperature catalytic hydrolyzer is recycled to hydrochlorination stage.

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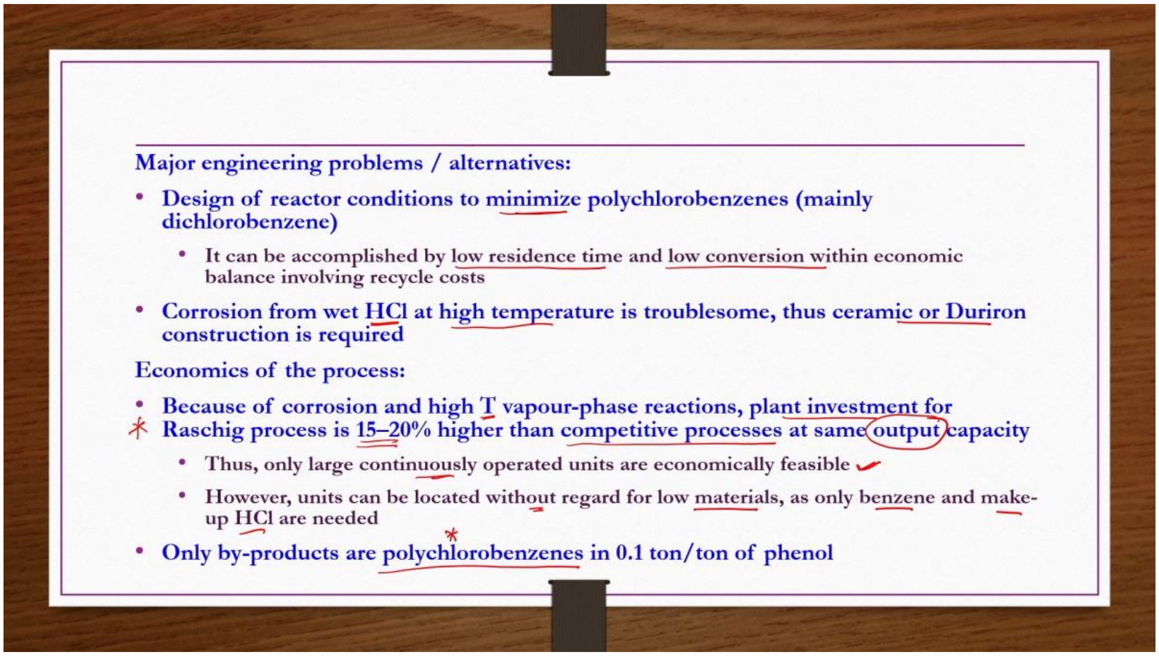

Major engineering problems / alternatives:

- Design of reactor conditions to minimize polychlorobenzenes (mainly dichlorobenzene)
  - It can be accomplished by low residence time and low conversion within economic balance involving recycle costs
- Corrosion from wet HCl at high temperature is troublesome, thus ceramic or Duriron construction is required

Economics of the process:

- Because of corrosion and high T vapour-phase reactions, plant investment for * Raschig process is 15–20% higher than competitive processes at same output capacity
  - Thus, only large continuously operated units are economically feasible
  - However, units can be located without regard for low materials, as only benzene and make-up HCl are needed
- Only by-products are poly*chlorobenzenes in 0.1 ton/ton of phenol

Coming to the major engineering problems or alternatives. One important thing is design of reactor conditions to minimize poly chlorobenzene mainly dichlorobenzene because these are impurities if these are presented, the hydrolysis of chlorobenzene will not take place to produce the phenol. Other problem is the corrosion from HCl, wet HCl, wherever the acids or chlorinated compounds are there, so then usually corrosion may occur if the temperature is high, okay? Whereas ceramic or Duriron construction is required, whereas the design of reactor conditions to minimize poly chlorobenzene can be accomplished by low residence time and then low conversion within economic balance involving recycle cost. Economics of the process because of corrosion and high temperature vapour phase reactions, plant investment for a Raschig process is 15 to 20% higher than other competitive processes at same output capacity. This is a disadvantage of this process. Thus, only large continuously operated units are economically feasible.

However, units can be located without regard for low materials as only benzene and then makeup HCl are needed. Only byproducts are poly chlorobenzene which is advantageous. If you have too many byproducts, then separation units increases, that increases the cost. That is all about Raschig process to produce the phenol.

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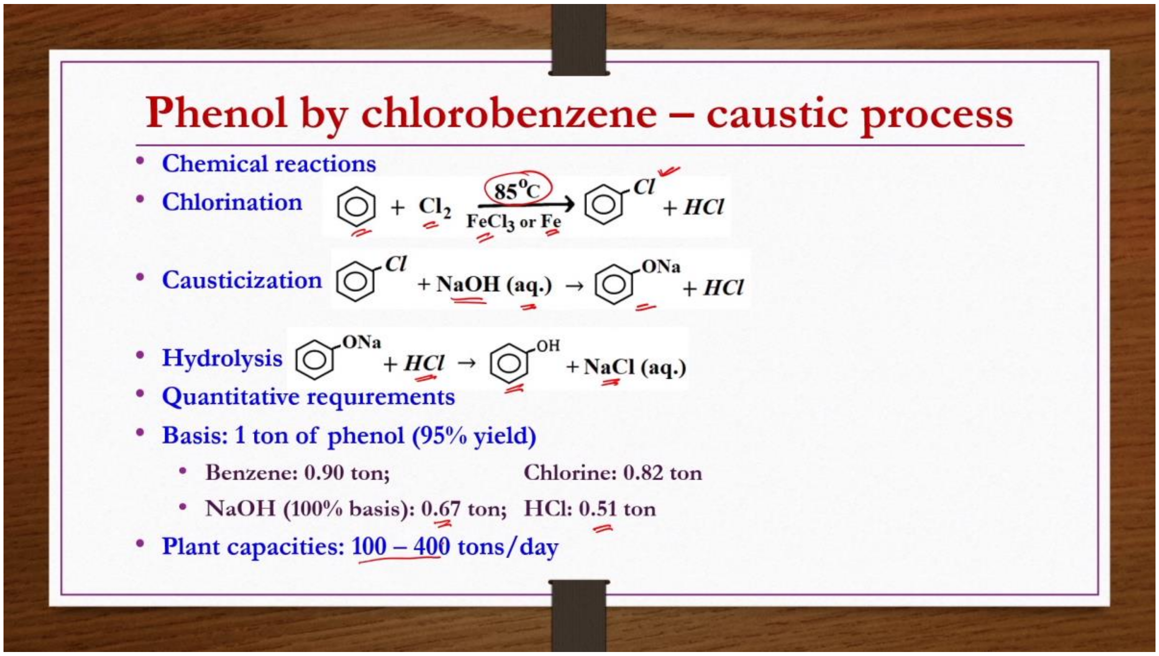

Phenol by chlorobenzene – caustic process

- Chemical reactions
- Chlorination $+ Cl_2 \xrightarrow[FeCl_3 \text{ or } Fe]{85^oC}$ Cl $+ HCl$
- Causticization Cl $+ NaOH \text{ (aq.)} \rightarrow$ ONa $+ HCl$
- Hydrolysis ONa $+ HCl \rightarrow$ OH $+ NaCl \text{ (aq.)}$
- Quantitative requrements
- Basis: 1 ton of phenol (95% yield)
    - Benzene: 0.90 ton; Chlorine: 0.82 ton
    - NaOH (100% basis): 0.67 ton; HCl: 0.51 ton
- Plant capacities: 100 – 400 tons/day

Now we discuss phenol production by chlorobenzene caustic process. As the name indicates, in this process chlorination of benzene as well as the whatever the products are forming, causticizing those products is going to produce phenol. So, what we do? First, we see the process by the reactions. So, first reaction is the chlorination reaction. Here benzene is reacting with the chlorine at 85 degrees centigrade either using direct iron or iron chloride or ferric chloride at least to get the chlorobenzene. In the previous process, in order to get the chlorobenzene, we used HCl. Now we are using directly Cl2. Then this chlorobenzene undergoes causticizing by NaOH aqueous solution to give sodium benzoate. This sodium benzoate would be undergoing hydrolysis using HCl to give phenol and then NaCl, okay? Quantitative requirements, 1 ton of phenol at 95% yield if you want to produce. Benzene 0.9 tons, chlorine 0.82 tons required, whereas 100% base is NaOH 0.67 tons and then HCl 0.51 tons required. Plant capacity is 100 to 400 tons per day, okay?

Coming to the flowchart of phenol production by chlorobenzene caustic process, what we have? We have a chlorinator reactor which is maintained at 85 degrees centigrade to this reactor, benzene along with the catalyst are being fed. Catalyst can be iron or iron chloride. In this chlorinator reactor, Cl2 is already supplied, right? So that whatever the benzene chlorination is taking place and then you can get chlorobenzene from the side stream as a product and then you may also get some kind of vapors like HCl, etc. So those vapors you know you do the partial condensation and then if at all unreacted benzene or some of the product mixtures are there, so they would be fed back to the chlorinator again, whereas some of the HCl is also being taken to HCl of gas from the chlorinator to subsequent steps for the neutralization purpose.

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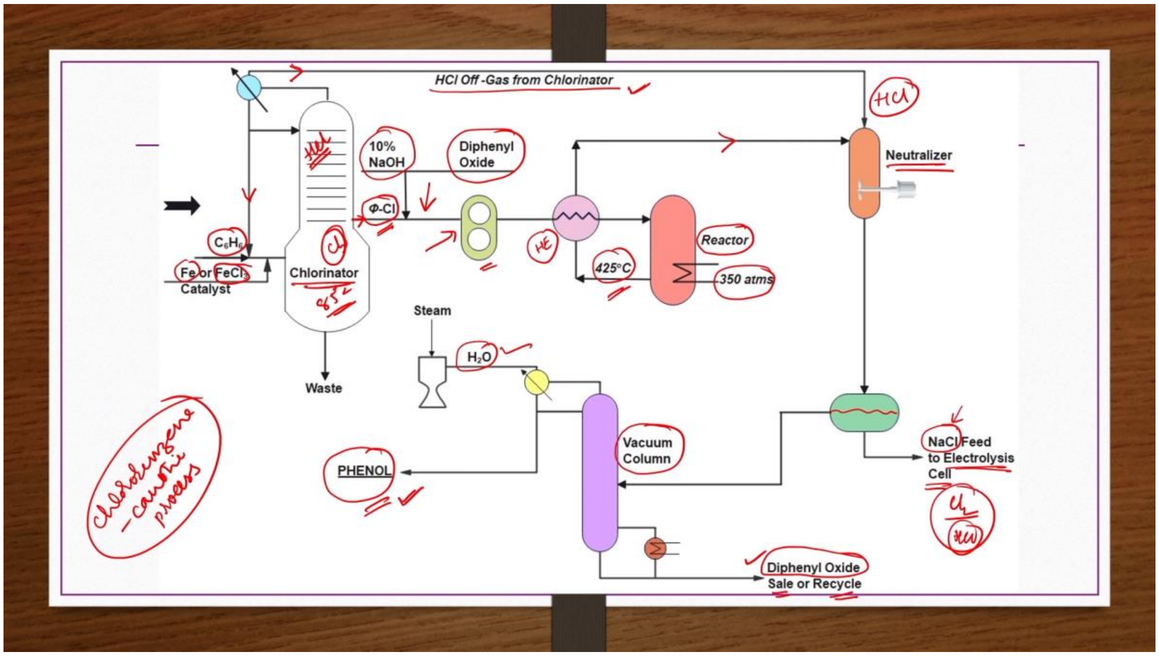

This chlorobenzene whatever we produce from the chlorinator is mixed with sodium hydroxide to undergo some kind of causticization reaction subsequently, but here we also add diphenyl oxide in order to repress the formation of more diphenyl oxide. This mixture of 3 components are compressed and then preheated and then taken to a reactor where the temperature is 425 degrees centigrade and pressure is 350 atmospheres maintained. Here required causticizing reaction takes place and then the product mixture would be at higher temperature, so that would be passed through heat exchange and whatever the heat carried by this product mixture is there that would be utilized by the reactants to get preheated. Then whatever the temperature reduced product mixture is there that is taken to a neutralizer, in this neutralizer we are adding HCl that is we are getting from the chlorinator reactor whatever the vent of gases HCl that we are getting that we are using here to neutralize the sodium benzoate, so that phenol and then NaCl you may be forming. So, the phenol and NaCl you separate here in a separator from the bottom whatever aqueous NaCl is there that you can take as a feed to the electrolysis cell to produce the required chlorine and then HCl etcetera from this electrolysis process itself. Whereas the crude phenol whatever is there that is taken to the vacuum column to separate out the heavier diphenyl oxide from the bottom as one of the product, it can be taken as a product and then used for the marketing otherwise it may be recycled back here along with the mono chlorobenzene and sodium hydroxide before sending to causticizing reactor. From the top of the vacuum column primarily you may be having the phenol and then some water would be there. So, water vapors etcetera would be separated out from the vapors and then pure phenol you can get it as a product.

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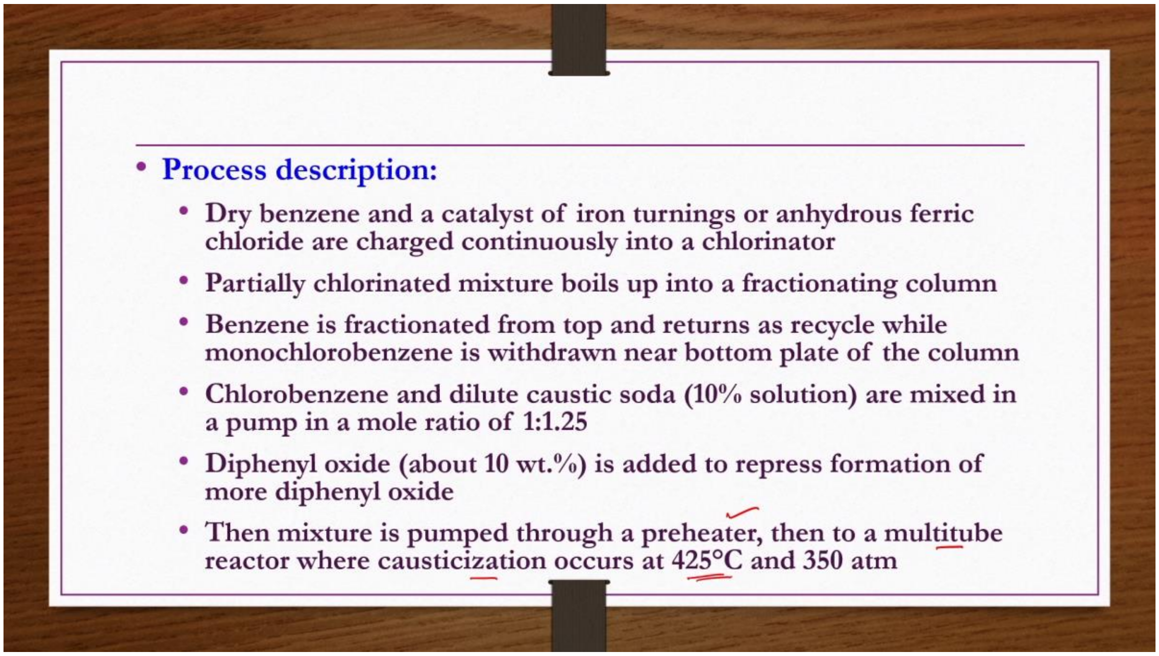

- **Process description:**
  - Dry benzene and a catalyst of iron turnings or anhydrous ferric chloride are charged continuously into a chlorinator
  - Partially chlorinated mixture boils up into a fractionating column
  - Benzene is fractionated from top and returns as recycle while monochlorobenzene is withdrawn near bottom plate of the column
  - Chlorobenzene and dilute caustic soda (10% solution) are mixed in a pump in a mole ratio of 1:1.25
  - Diphenyl oxide (about 10 wt.%) is added to repress formation of more diphenyl oxide
  - Then mixture is pumped through a preheater, then to a multitube reactor where causticization occurs at 425°C and 350 atm

Process description dry benzene and the catalyst of iron turnings or anhydrous ferric chloride are charged continuously into a chlorinator. Partially chlorinated mixture boils up into a fractionating column. Benzene is fractionated from top and then returns as a recycle while mono chlorobenzene is withdrawn near bottom plate of the column. Chlorobenzene and dilute caustic soda 10 percent solution are mixed in a pump in a mole ratio of 1 to 1.25. Diphenyl oxide about 10 weight percent is added to repress formation of a more diphenyl oxide. Then mixture is pumped through a preheater then to a multi-tube reactor where causticization occurs at 425 degrees centigrade and 350 atmosphere.

Residence time is around 15 minutes. Heat is removed from the reactor efflux by heat exchange in feed preheater. Cooled hydrolysate it is acidified in a neutralizer to liberate phenol and sodium chloride which must be separated by distillation. Salt is recycled to an electrolysis unit to produce the needed chlorine and then caustic for the process. Phenol is stripped of diphenyl oxide and other minor byproducts in a vacuum. A portion of diphenyl oxide is returned to causticization tower if required whereas the remainder is redistilled under vacuum for commercial marketing of diphenyl oxide plus other derivatives.

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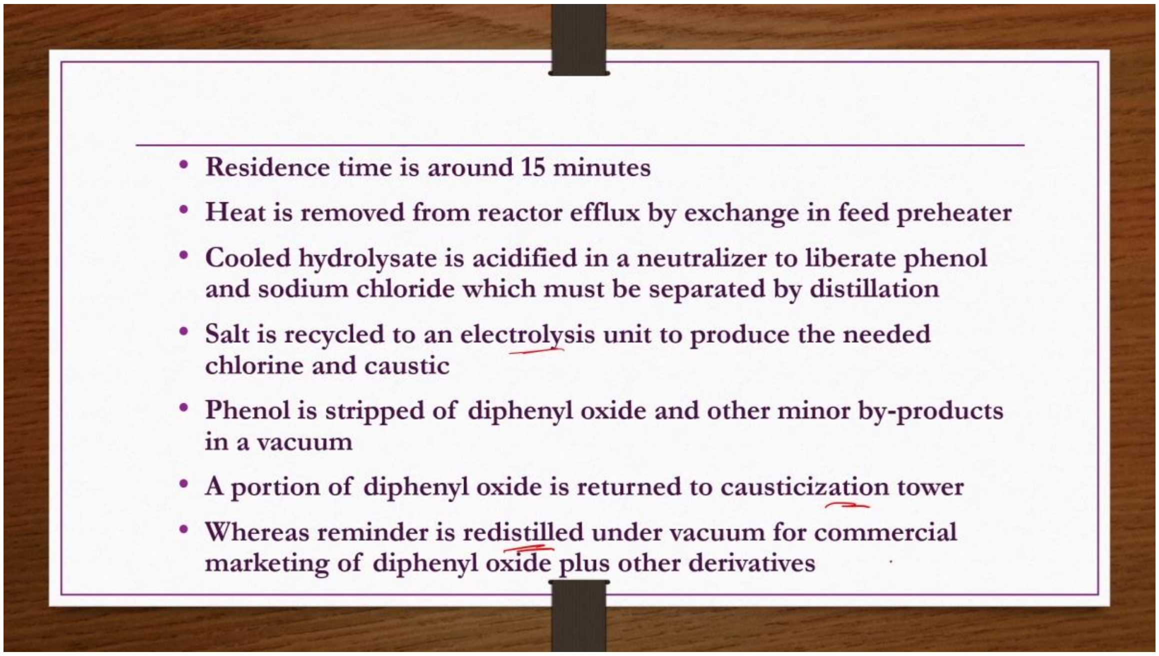

- Residence time is around 15 minutes
- Heat is removed from reactor efflux by exchange in feed preheater
- Cooled hydrolysate is acidified in a neutralizer to liberate phenol and sodium chloride which must be separated by distillation
- Salt is recycled to an electrolysis unit to produce the needed chlorine and caustic
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- A portion of diphenyl oxide is returned to causticization tower
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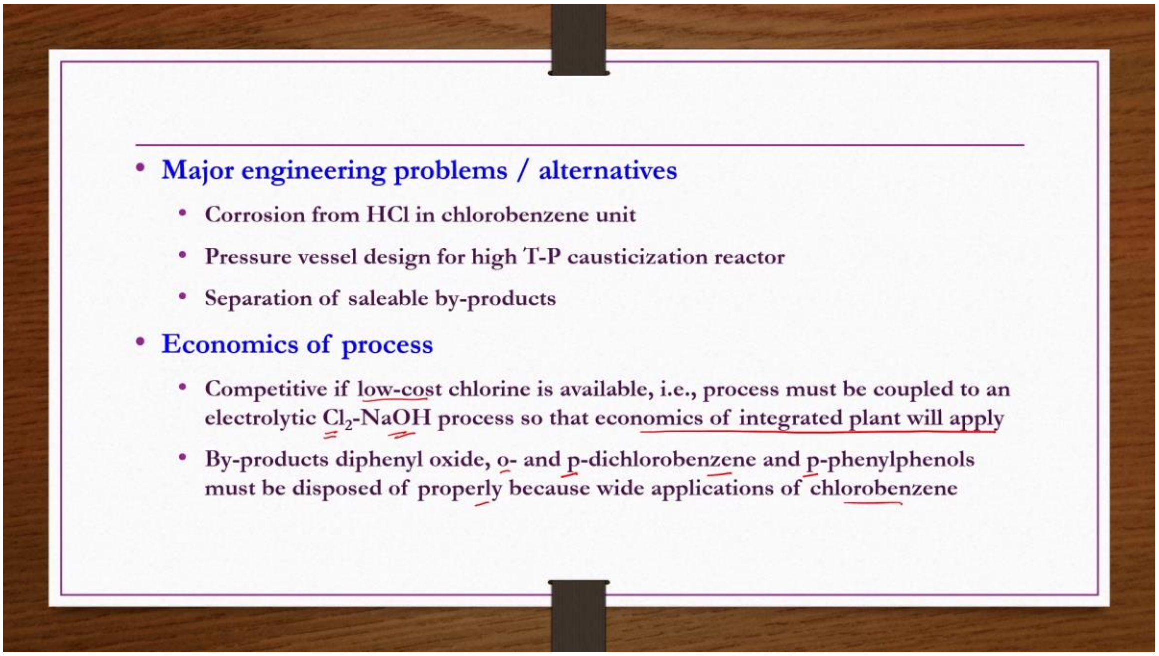

- Major engineering problems / alternatives
  - Corrosion from HCl in chlorobenzene unit
  - Pressure vessel design for high T-P causticization reactor
  - Separation of saleable by-products
- Economics of process
  - Competitive if low-cost chlorine is available, i.e., process must be coupled to an electrolytic Cl_2-NaOH process so that economics of integrated plant will apply
  - By-products diphenyl oxide, o- and p-dichlorobenzene and p-phenylphenols must be disposed of properly because wide applications of chlorobenzene

Coming to the major engineering problems and alternatives, corrosion from HCl in chlorobenzene unit is important issue to be considered. Then pressure vessel design for high temperature pressure causticization reactor is an issue. Then separation of saleable byproducts, how effectively are you separating them is also important. Economics of process, competitive process it is a competitive process if low cost chlorine is available that is process must be coupled to have an Cl2 NaOH process so that economics of integrated plant will apply. Byproduct diphenyl oxide, ortho and para dichlorobenzene and para-phenylphenols must be disposed of properly because of wide applications of chlorobenzene. So that is about the chlorobenzene caustic process to produce the phenol.

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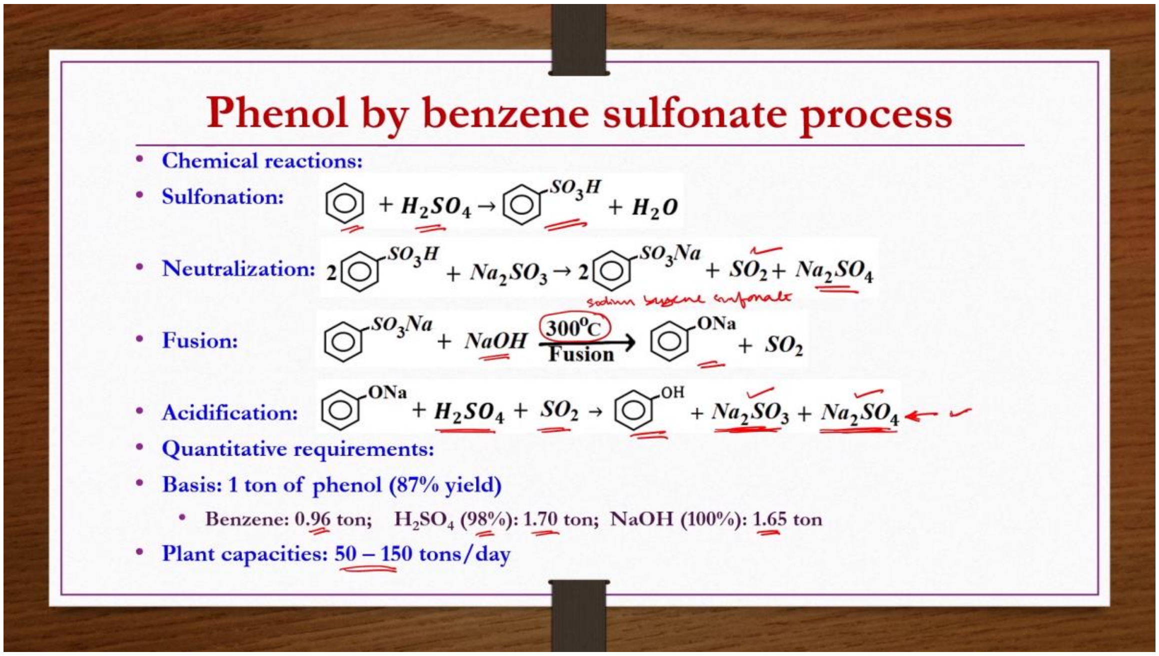

Phenol by benzene sulfonate process

- Chemical reactions:
- Sulfonation: $+ H_2SO_4 \rightarrow$ SO_3H $+ H_2O$
- Neutralization: 2 SO_3H $+ Na_2SO_3 \rightarrow 2$ SO_3Na $+ SO_2 + Na_2SO_4$
  sodium benzene sulfonate
- Fusion: SO_3Na $+ NaOH \xrightarrow[\text{Fusion}]{\boxed{300^oC}}$ ONa $+ SO_2$
- Acidification: ONa $+ H_2SO_4 + SO_2 \rightarrow$ OH $+ Na_2SO_3 + Na_2SO_4$
- Quantitative requirements:
- Basis: 1 ton of phenol (87% yield)
  - Benzene: 0.96 ton; H_2SO_4 (98%): 1.70 ton; NaOH (100%): 1.65 ton
- Plant capacities: 50 – 150 tons/day

Now we discussed the phenol production by benzene sulfonate process. If you look at the reactions, first one is the sulfonation where benzene reacting with H2SO4 to give the benzene sulfonic acid and water. This benzene sulfonic acid would be undergoing neutralization reaction with sodium sulfite to produce sodium benzene sulfonate along with SO2 and then sodium sulfate. Fusion reaction, this sodium benzene sulfonate would be reacting with sodium hydroxide at 300 degrees centigrade to give sodium benzoate along with SO2. This sodium benzoate would be undergoing acidification reaction using H2SO4 and then sulfur dioxide to give phenol along with sodium sulfite and sodium sulfate. These sodium sulfites and sulfates may be recovered and then utilized in the pulp and paper industries, sulfate process and then sulfite processes we have seen, so there this can be utilized. If you can recover them as co-product effectively, then you can use them in pulp and paper industries where we have already discussed sulfite and sulfate processes. So there these chemicals would be utilized. Coming to the quantitative requirements, 1 ton of phenol 85% yield if you take as basis, benzene 0.96 tons required, 93 to 98% H2SO4 is in general used that may be required 1.7 tons and then NaOH 1.65 tons are required. Capacities usually 50 to 150 tons per day plants.

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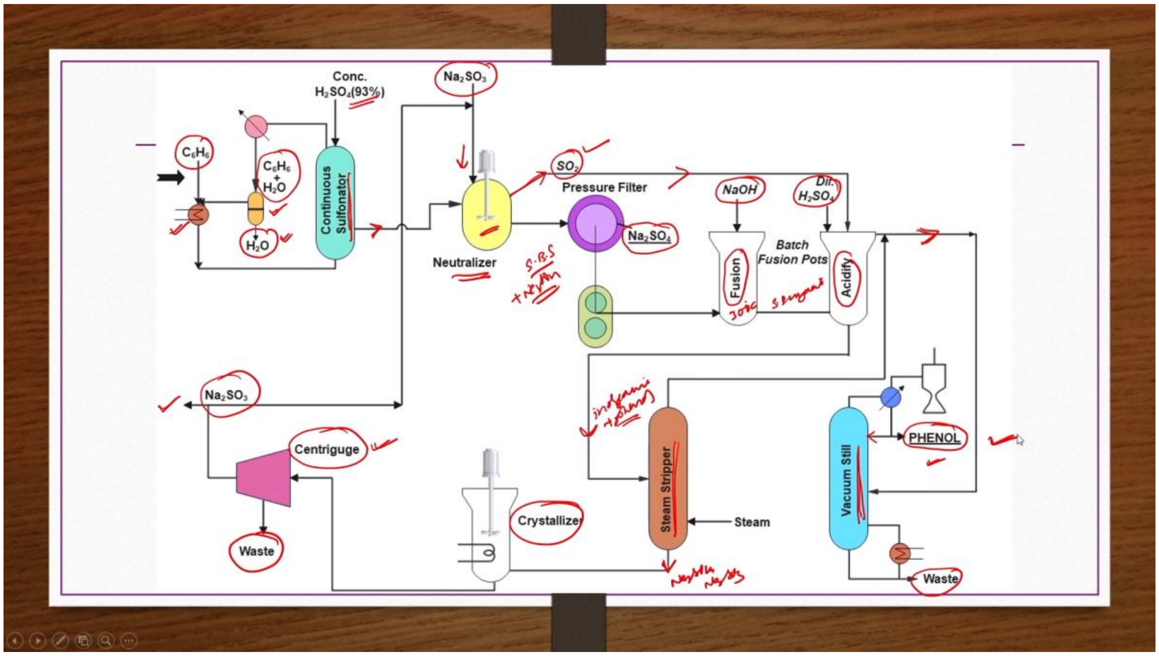

Coming to the flowchart, this is the flowchart for the process. What you do, you take the benzene, then preheat it and then take it to the continuous sulfonator reactor. Here the sulfonation of benzene takes place using 93 to 98% H2SO4 which is being fed to the reactor from the top, right? So, this benzene and H2SO4 interacting counter current way, then you get a product mixture of a benzene sulfonic acid along with the unreacted benzene and then water vapors, etc. So, what you do? You separate out the benzene and then water mixture that you take it to a separator where water is separated out because too much of water is forming, so that will not allow the sulfonation to take place much effectively, right? After separating out the water, whatever the benzene is there that is again mixed with the feed benzene, preheat it and then send it back to the sulfonator reactor. Whatever the benzene sulfonic acid crude, benzene sulfonic acid is there that is taken to a neutralizer where Na2SO3 is being used for the required neutralization purpose. In this process, what you get? SO2 you get and then you get sodium benzene sulfonate plus SO2 plus Na2SO4 you may be getting after the neutralization process. The SO2 you, since it is a gas, you can separate out easily, right? Whereas the sodium benzene sulfonate along with Na2SO4 is there that is taken to a pressure filter where Na2SO4 solids are separated out whereas the clear liquors whatever are there, they would be compressed and then sent to a fusion reactor where the temperature is maintained 300 degrees centigrade in this reactor. This sodium benzene sulfonate is interacting with the sodium hydroxide to give sodium benzoate you can get. That would be taken to acidifying tower where sodium benzoate is interacting with the dilute H2SO4 along with the SO2 that is being obtained from the neutralization step, right? So, here what happens? You get the product streams like crude phenol plus some kind of impurities like Na2SO3, Na2SO4, etc. would also be you may be getting. So, after this acidification tower, whatever the heaviest one are there, so they would be taken to a steam stripper where steam is utilized for the separating out the if at all any phenol etc. that is present because this is mostly having the inorganic components plus slight or small amounts of phenol. So that phenol is recovered by the steam stripper and then mixed with the crude phenol whatever you are taking from the top and then that crude phenol is taken to the vacuum still where wastes are collected from the bottom as a waste whereas the product phenol which is the more volatile compared to the waste that is you get it as top product from the top, okay? So, some amount of phenol is also being refluxed to the vacuum still until you get the required 99 percent purity of the phenol, okay? So, whereas the material that is coming out from the steam stripper would be primarily having you know Na2SO4 or Na2SO3, these kind of components sodium sulfate and then sodium sulfate components would be there. So, these would be taken to a crystallizer. After crystallization, they will be sent to the centrifuge to remove the waste if at all any wastage are present and then you get the pure Na2SO3 as a product that you can feed back to the neutralizer for the required neutralization reaction to take place or you can market it as well. So, this is the process to get the phenol by this you know phenol by benzene sulfonate process.

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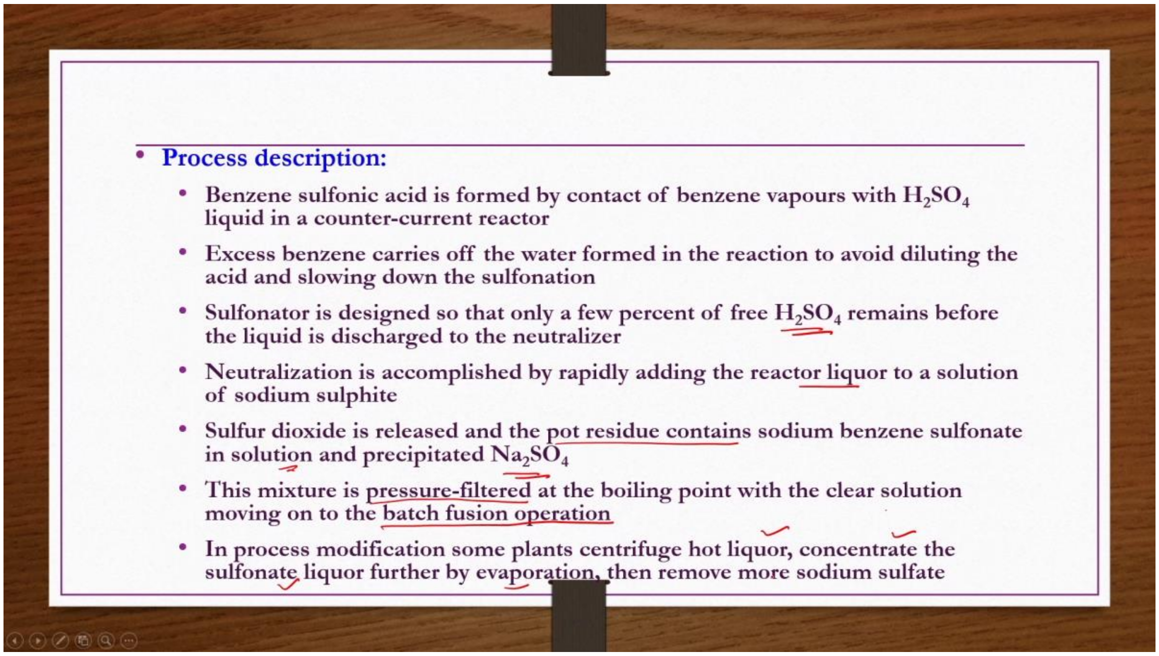

- **Process description:**
  - Benzene sulfonic acid is formed by contact of benzene vapours with H_2SO_4 liquid in a counter-current reactor
  - Excess benzene carries off the water formed in the reaction to avoid diluting the acid and slowing down the sulfonation
  - Sulfonator is designed so that only a few percent of free H_2SO_4 remains before the liquid is discharged to the neutralizer
  - Neutralization is accomplished by rapidly adding the reactor liquor to a solution of sodium sulphite
  - Sulfur dioxide is released and the pot residue contains sodium benzene sulfonate in solution and precipitated Na_2SO_4
  - This mixture is pressure-filtered at the boiling point with the clear solution moving on to the batch fusion operation
  - In process modification some plants centrifuge hot liquor, concentrate the sulfonate liquor further by evaporation, then remove more sodium sulfate

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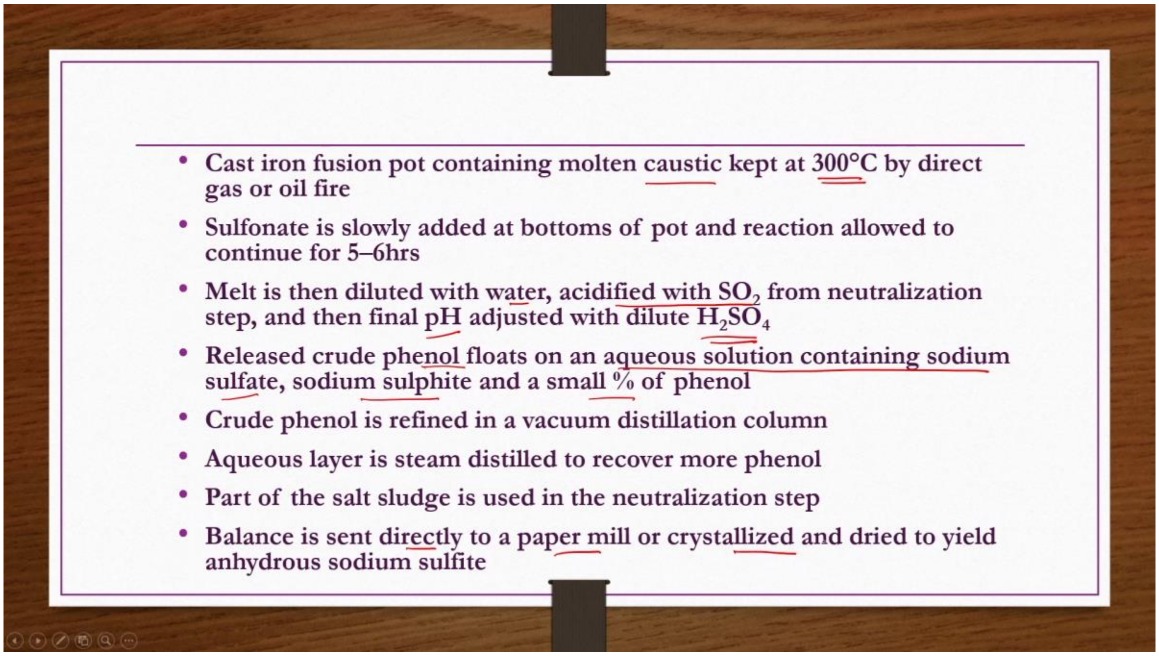

- Cast iron fusion pot containing molten caustic kept at 300°C by direct gas or oil fire
- Sulfonate is slowly added at bottoms of pot and reaction allowed to continue for 5–6hrs
- Melt is then diluted with water, acidified with SO_2 from neutralization step, and then final pH adjusted with dilute H_2SO_4
- Released crude phenol floats on an aqueous solution containing sodium sulfate, sodium sulphite and a small % of phenol
- Crude phenol is refined in a vacuum distillation column
- Aqueous layer is steam distilled to recover more phenol
- Part of the salt sludge is used in the neutralization step
- Balance is sent directly to a paper mill or crystallized and dried to yield anhydrous sodium sulfite

Cast iron fusion pot containing molten caustic kept at 300 degrees centigrade by direct gas or oil fire. Sulfonate is slowly added at bottoms of the pot and reaction allowed to continue for 5 to 6 hours. Melt is then diluted with water, acidified with SO2 from neutralization and then final pH adjusted with dilute H2SO4. Released crude phenol floats on an aqueous solution containing sodium sulfate, sodium sulphite and small percentage of phenol. Crude phenol is refined via a vacuum distillation column, aqueous layer is steam distilled to recover more phenol. Part of the salt sludge is used in the neutralization step as well. Balance is sent directly to a paper mill or crystallized and dried to yield anhydrous sodium sulfite for other applications.

Coming to the major engineering problems or alternatives. It is the oldest of 6 processes and operates on large scale batch cycles for all but distillation and sulfonation steps except the distillation and sulfonation steps, all other steps are batch steps or operating on batch cycles.

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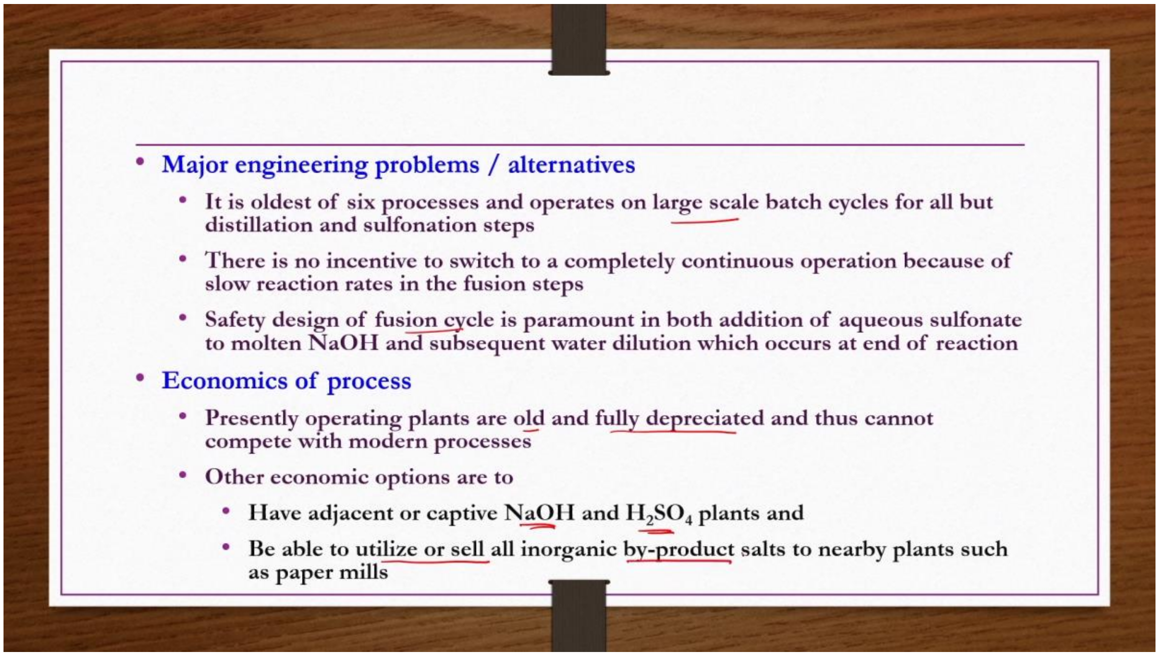

- **Major engineering problems / alternatives**
  - It is oldest of six processes and operates on large scale batch cycles for all but distillation and sulfonation steps
  - There is no incentive to switch to a completely continuous operation because of slow reaction rates in the fusion steps
  - Safety design of fusion cycle is paramount in both addition of aqueous sulfonate to molten NaOH and subsequent water dilution which occurs at end of reaction
- **Economics of process**
  - Presently operating plants are old and fully depreciated and thus cannot compete with modern processes
  - Other economic options are to
    - Have adjacent or captive NaOH and H_2SO_4 plants and
    - Be able to utilize or sell all inorganic by-product salts to nearby plants such as paper mills

There is no incentive to switch to a completely continuous operation because of slow reaction rates in the fusion steps. Safety design of fusion cycle is paramount in both addition of aqueous sulfonate to molten NaOH and subsequent water dilution which occurs at end of reaction. Economics of process, presently operating plants are old and fully depreciated and thus cannot compete with the modern processes. Other economic options are to have adjacent or captive NaOH and H2SO4 plants and then be able to utilize or sell all inorganic byproducts salts to nearby plants such as paper mills.

Now, the last process phenol production that is by direct oxidation of benzene. Chemical reactions, benzene undergo hydrogenation reaction to produce cyclohexane. This cyclohexane undergo oxidation to produce cyclohexanol, cyclohexanone, this is alcohol, this is ketone and then water. This cyclohexanol further undergo dehydrogenation to produce phenol by releasing H2. So, process description, benzene is hydrogenated to cyclohexane. Cyclohexane is then oxidized to produce a mixture of cyclohexanol, cyclohexanone and unreacted cyclohexane. Unreacted cyclohexane is separated and recycled whereas oxygenated fraction is then dehydrogenated to produce phenol over a nickel or platinum catalyst.

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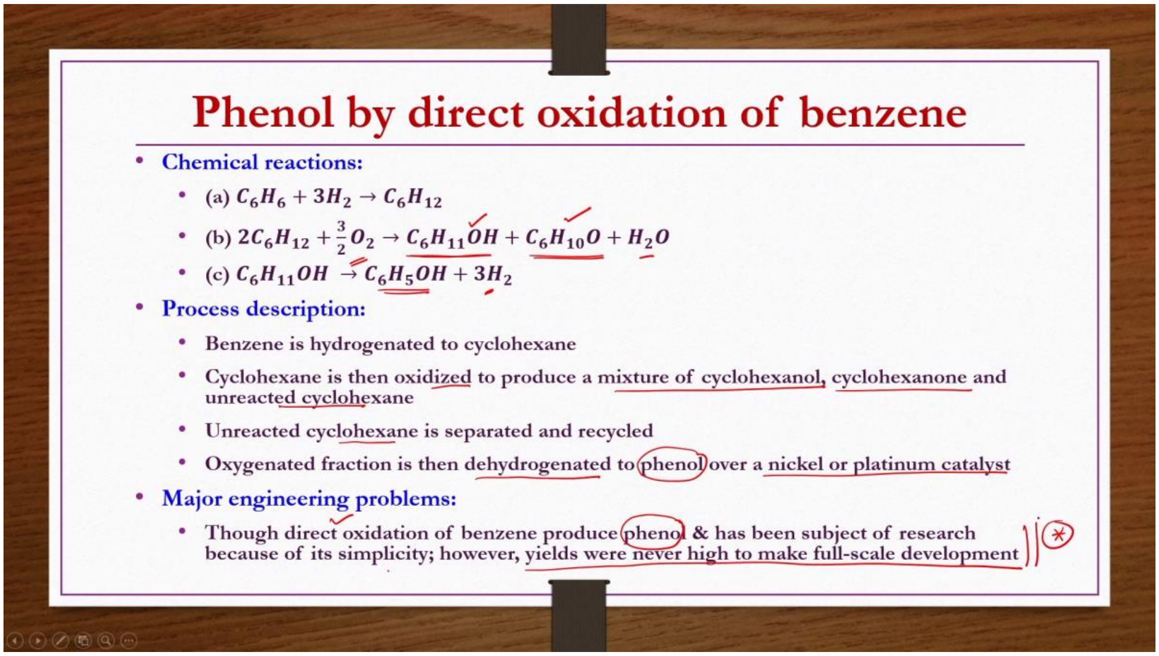

Phenol by direct oxidation of benzene

- Chemical reactions:
  - (a) $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$
  - (b) $2C_6H_{12} + \frac{3}{2}O_2 \rightarrow C_6H_{11}OH + C_6H_{10}O + H_2O$
  - (c) $C_6H_{11}OH \rightarrow C_6H_5OH + 3H_2$
- Process description:
  - Benzene is hydrogenated to cyclohexane
  - Cyclohexane is then oxidized to produce a mixture of cyclohexanol, cyclohexanone and unreacted cyclohexane
  - Unreacted cyclohexane is separated and recycled
  - Oxygenated fraction is then dehydrogenated to phenol over a nickel or platinum catalyst
- Major engineering problems:
  - Though direct oxidation of benzene produce phenol & has been subject of research because of its simplicity; however, yields were never high to make full-scale development

Major engineering problems, though direct oxidation of benzene produces phenol and has been subject of research because of its simplicity. However, the yields were never high to make full scale development. This is one of the important engineering problems. So this is all about production of phenol by different processes. References for today's lecture are presented here. Thank you.

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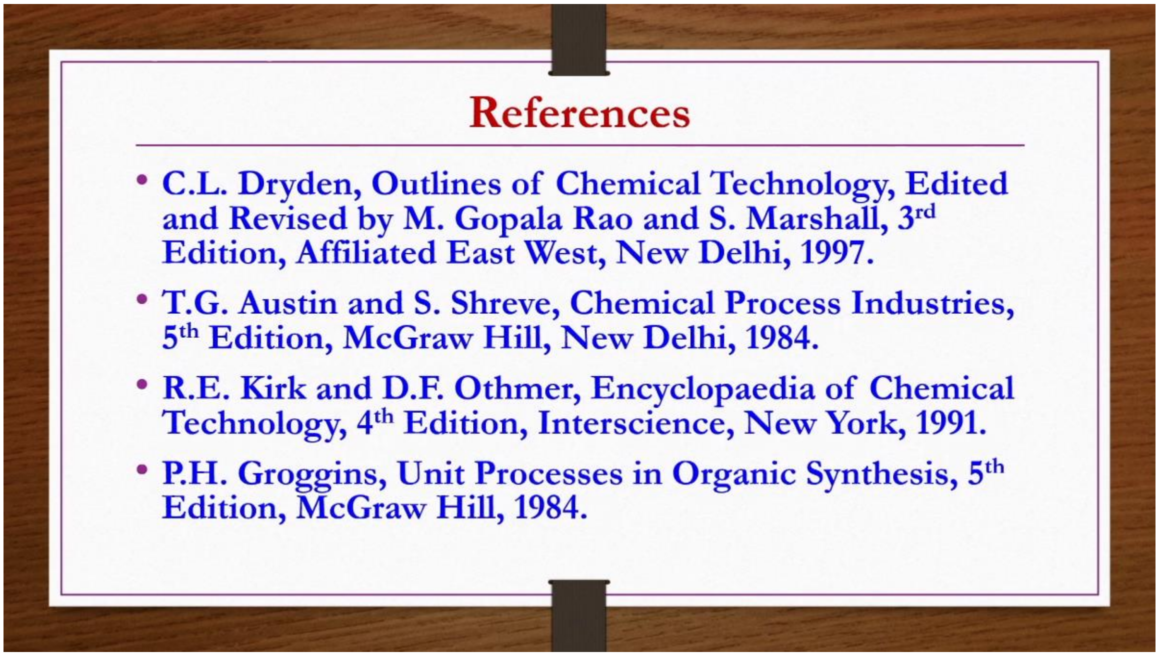

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