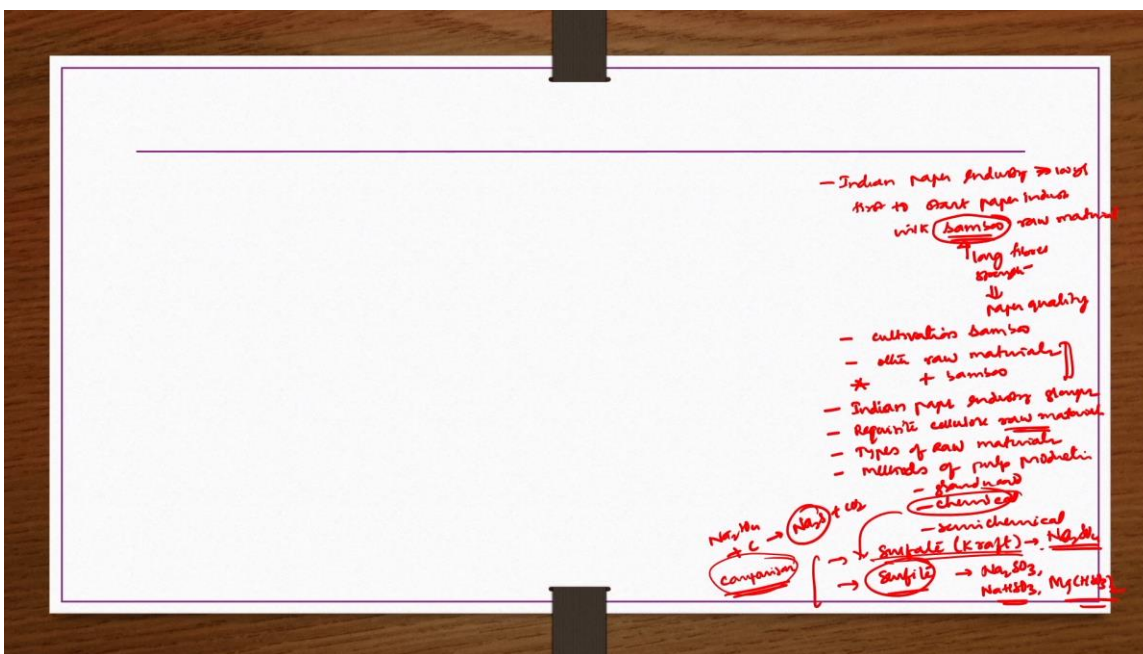


Organic Chemical Technology
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Lecture - 16
Pulp and Paper Industry – 2

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is pulp and paper industry part 2. In the previous class, we started discussing about pulp and paper industry. So before going into the details of today's lecture, we have a recapitulation of what we have discussed in the previous lecture on pulp and paper industry. We started with introduction on Indian chemical industry, especially Indian paper industry. We realized that you know it is more than 100 years old and then first to start paper industry with bamboo raw material. Bamboo raw material has not been used by any other paper industry, any other countries before India. India or Indian paper industry is the first one to use bamboo raw material for the paper production because it is having a value in terms of long fiber and then strength of the fiber is good. So, because of this one whatever the paper quality that you produce is going to be better one. So that is how bamboo is advantageous over other raw materials. But however, cultivation of bamboo to the degree where the demand for the paper can be met is not there. So, there is a gap between the demand and production.

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So, because of that one different other raw materials were tried and then both conventional and non-conventional raw materials can be used. In fact, of course, it has been found that if the other raw materials are blended with bamboo, so then you know better quality paper can also be produced by that way also. Then we have discussed about Indian paper industry groups based on the size of the units and then sources, 6 different of Indian paper industries are there. So those things we have discussed. Then this pulp whatever you produce for making the paper is nothing but the cellulose commercial name of pulp is nothing but the cellulose. So, then requirement of cellulose raw materials also we have discussed that is you know availability throughout the year to the pulp industry and then production cost, the quality of the paper and all those things are you know being affected by the type of raw material that you have taken. So those are the three main deficits of cellulose raw materials we have discussed and then we have discussed types of raw materials like you know soft wood, hard woods, grasses, etc. Those things we have discussed with some example. Then we started discussing on methods of pulp production where we have seen primarily three methods like you know mechanical or ground wood method and then chemical and then semi-chemical methods we have seen. So, this chemical method is again having two methods, two approaches, two processes, sulphate process and then sulphite process. This is this sulphate process is also known as the craft process. Here you know you use sulphates like Na_2SO_4 in the digester. So, but directly you do not use Na_2SO_4 . What is happens like you know Na_2SO_4 reacts with you know carbon that is present in the raw material to give Na_2S plus CO_2 . So, this Na_2S is coming into the digester through the liquors. So that is what we have seen. So that is the reason this process is known as the sulphate process whereas the sulphite process different types of magnetite sulphite process, neutral sulphate process, etc. are available because these are known as the sulphate processes because of you know nature of the you know chemicals that are used in the digestion. So here what we have sodium sulphite you have Na_2SO_3 whereas here Na_2SO_4 in sulphate. You also have you know sodium bisulphite, magnesium bisulphite, etc. Sulphites are being used in this process. So, these process are known as the sulphite processes. Then we have seen the comparison of these processes including different characteristics like you know trade name, type of raw materials and then type of digesters, reaction digestion conditions or temperature, pressure conditions, time of the digestion, etc. All those comparisons also we have seen and then we have also compared the type of pulp that you are going to get brown or white color pulp or you know dull white color pulp and then what are the end products produced from sulphate process as well as the sulphite process we have seen in a comparison table. Then we started discussing on the production of pulp by sulphate process, right? In which there are 5 different steps or important steps are there out of which 4 steps we have already discussed. Now today we are going to the 5th step. However before going to the 5th step of sulphate or craft process we are going to have the recapitulation of those 4 steps once again.

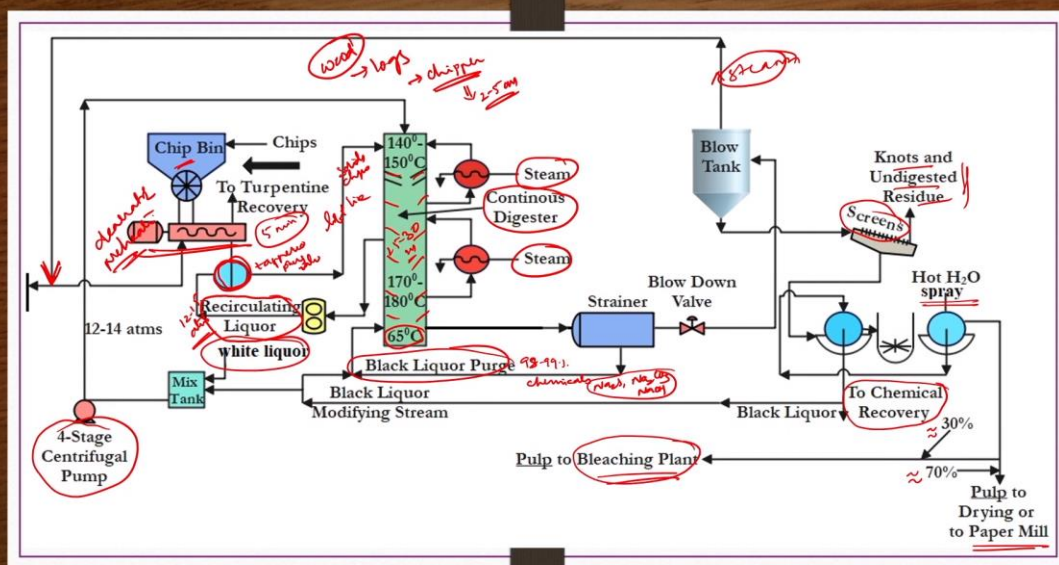
Pulp production by sulphate process, it includes 5 major steps. First one is the digestion of wood based materials. Second one is the modified process for the bagasse and then bleaching of pulp is the third one. Fourth one is finishing operation of pulp if you are producing only pulp if you are not going for the paper from within the same industry and then fifth one is the recovery of chemicals. So, this is what we are going to discuss today.

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Pulp production by sulphate process

- **Process description:**
- **Following major steps exist in the manufacturing process of pulp**
 - ✓1) Digestion of wood-base materials
 - ✓2) Modified process for bagasse
 - ✓3) Bleaching of pulp
 - ✓4) Finishing operation of pulp
 - ⑤ Recovery of chemicals

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So, we have already discussed these 4 steps. However, we are going to discuss them once again here. So, let us say flowchart this is what we have whatever the logs are there barked logs etc. that wood chips whatever the wood you take, logs of woods debarked by tumbling and rubbing kind of action then they would be taken to a chipper where heavy revolving knives are there. So, when the material comes into interact when the wood material or logs come into this chipper, you know, they will interact with the strong rotating knives, then those knives will cut down this wood into the flat chips shape of having 2 to 5 centimeters those chips we take into the chip bin. Then through a star wall what we do we take those chips to a deaerator and preheater equipment. That is this one. So, here the purpose is to remove some kind of moisture etc. So, that is done by using this steam that is done by using this steam. So, once doing this process for roughly 5 minutes or so, what we do we take this one to the lift line by this by operating this tapered plug wall. But however, this material whatever is there that is in solid chips, solid chips, you know, they may not able to convey easily for that purpose what you do you recirculate the liquor at 12 to 15 atmosphere pressure. So, then this liquor when it enters the lift line at such pressure, it will also take the chips to the top of the continuous digester. In the continuous digester different sections are there different you know, screens are also available to maintain the flow or the control the drop of the chips from top to down as well as to maintain the temperature, different heat sources are also provided. At the top 140 to 150 degrees centigrade and then at the bottom 65 degrees are maintained or in between around 170 to 180 degrees centigrade are maintained. The height of the column is roughly 25 to 30 meters. So, in this column what are we giving we are also giving a mixture of white liquor and then black liquor. Black liquor is nothing but whatever the liquor that you get in the pulp process after making the pulp you know that liquor is having almost 98 to 99% of chemicals. You know, what chemicals they will have they will have chemicals like you know, required Na_2S , Na_2CO_3 , NaOH etc. such kind of chemicals are there you cannot afford to throw them. So, you have to recover and then these chemicals are also required for the digestion purpose. So, that is the reason. So, the same liquor some of the same black liquor is also sent to the digester so that whatever the chemicals that are present in the black liquor they will cause the required hydrolysis of the wood and then required digestion of the wood that can take place. So, for this purpose some white liquor is also used, you know, black and white liquor are mixed and then sent to the digester using a centrifugal pump. So, but by the time the wood digested wood comes down to the bottom of the continuous digester temperature has to be reduced because you cannot take such high temperature material out of the reactor suddenly. Otherwise, you know what will happen the strength of the pulp would be decreasing or the fiber strength whatever would be there that would be reduced. So that is the reason some of the black liquor is also sent to the bottom of the continuous digester so that to reduce the temperature to 60 degrees centigrade roughly to that one.

So then this mixture is taken to the strainer and from there to the blow tank where further it is, you know, temperature is reduced approximately 30 degrees centigrade or so and then you are recovering heat so that heat is recovered in the form of steam. That same steam what are you doing you are circulating, recirculating back to preheater from the continuous digester whatever the mixture is coming after reducing the temperature that is passed through screens. Here in the screens knots and undigested residues etc. are separated whereas the pulp slurry whatever is there that would be passed through rotary vacuum dryers where hot water is sprayed for the washing of the pulp purpose. So when you wash it so then you get the liquor so that liquor is having chemicals so such chemicals has to be recovered so that is what we are going to discuss in the next slide. So some of the black liquor as mentioned you know sent to the top of the digestion column along with the white liquor whereas the some of the black liquor is sent to the bottom of the digestion column to reduce the temperature of the digestion mixture before taking it to the next level of the strainer. Whereas the pulp whatever you get 70 percent roughly is dried and sent to the paper mill for making the papers whereas the roughly 30 percent is sent to the bleaching plant because pulp is nothing but the commercial cellulose. So different types of cellulosic derivatives can also be made by this pulp. So, for that purpose the required bleaching has to be done after the bleaching they will be you know used for different cellulose derivatives production.

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Pulp production by sulphate process

- **Process description:**
- **Following major steps exist in the manufacturing process of pulp**
 - ✓1) Digestion of wood-base materials
 - ✓2) Modified process for bagasse → Bark → Pith → Delink → wet grinding mill
 - ✓3) Bleaching of pulp → *coordinating agents* ClO_2 → bleach $\text{H}_2\text{O}_2 + \text{NaOH}$ + *stabilizers*
 - ✓4) Finishing operation of pulp → *hydraulic pressure 200-300 atm + vacuum flash dryer + extrusion* → $\frac{\% \text{ solids}}{290\% \text{ solid}}$
 - ✓5) Recovery of chemicals

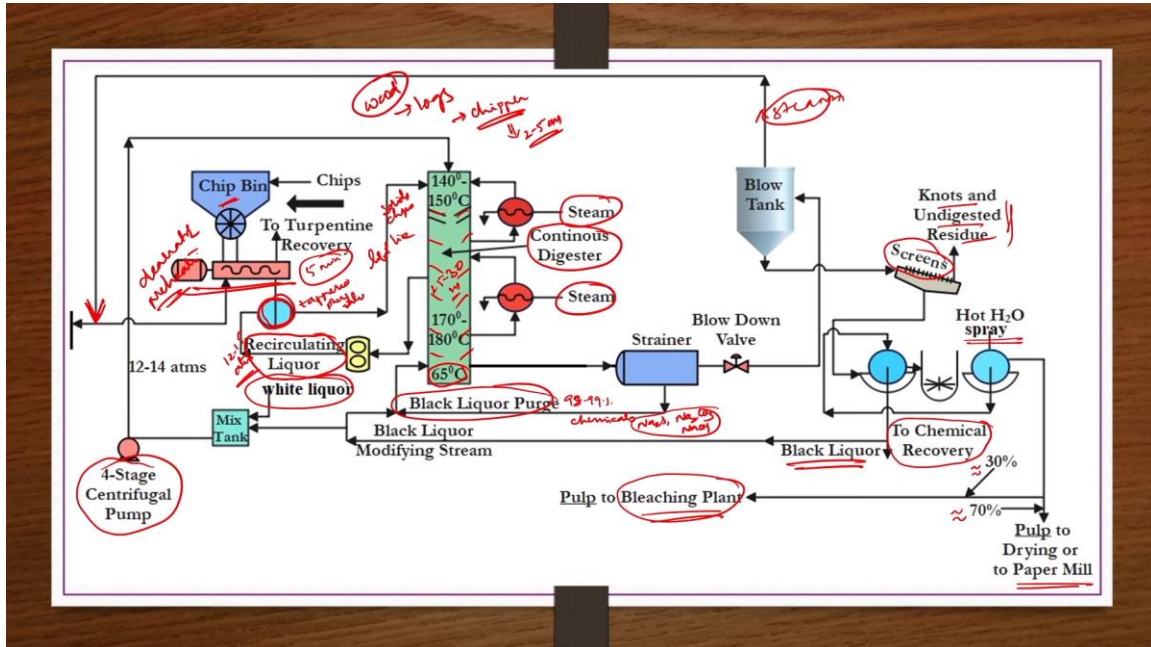
So now this is primarily about the digestion and then coming to the second step that is modified a process for the bagasse whatever the method that we discussed that is discussed for you know primarily for you know wood material but if you have the

bagasse then what happened you know dirt and pith may be there. So, you need to do deep pithing so how it is done it can be done by wet grinding. Wet grinding mills are wet grinding hammer mills etc you can use. So, when you take this material bagasse material and then you use the water and do the wet grinding. So, when you do the wet grinding when your hammers give the impact on the bagasse you know the cellulosic fibers whatever are there they will not shredded they will not be broken down rather pits whatever are there they will be you know diluted or washed out with the water. So that way you can remove such kind of pith etc and then once removing this pith that you can use for the you know sulphate process as we have done for the wood base raw materials just now as we have discussed it. Then next important step is the bleaching of the pulp. Bleaching of the pulp is in general done by using oxidizing agents. Usually chlorine dioxide is used but you know by using chlorine dioxide what happens you know the dioxins kind of impurities or you know undesired chemicals formation taking place. So that is the reason people started using hydrogen peroxide but hydrogen peroxide combined with NaOH it has proved to be better digesting agent but however in the mixture in order to maintain the H_2O_2 concentration up to the desired level you know sodium silicates are also added. Na_2SiO_3 are also added in order to maintain the balance of H_2O_2 . So this is how bleaching of the pulp is done. So once the bleaching has been done you can assume that you know on the almost all colors have been removed almost like you know white color pulp you can get. So that pulp you have to do the finishing operation. Finishing operation is the removal of the water because whatever the pulp that you get it is having so much of water. So how you do? You do with the hydraulic press or pressing by hydraulic press at 200 to 300 atmospheres or even high pressure. Then after that you know whatever the material is coming after the hydraulic press that dewatered pulp you can further dry in vacuum flash dryers. Further if you wanted to do dewatering what you can do? You can do so called you know extrusion in the form of tablets and then pills etc those kind of forms they can be made. So, these processes you know selection of these processes depends on the what is the percentage of solids that you like to have in the pulp. So, all these steps are required to do if you wanted to have you know more than 90% solids in the pulp with less water or moisture. If you are happy with 40 to 50% of the solids in the pulp then if you do only hydraulic press that would itself is sufficient enough.

So now the next step is the recovery of chemicals as we have seen whatever the liquor that is having you know it is having chemicals like Na_2S , Na_2CO_3 , NaOH etc depending on the process and then raw materials that have been used. So and then they are present in large quantity like 98 to 99% of black liquor is you know chemicals only. So, you cannot afford releasing such chemicals because of the environmental concern as well as from the economics point of view because you need large quantity of these chemicals. If you are throwing without recovering so then your plant is not going to be economically feasible. So that is the reason you must recover these chemicals and then whatever the white liquor

is there you have to reuse for the digestion purpose, okay? So that the process goes continuously.

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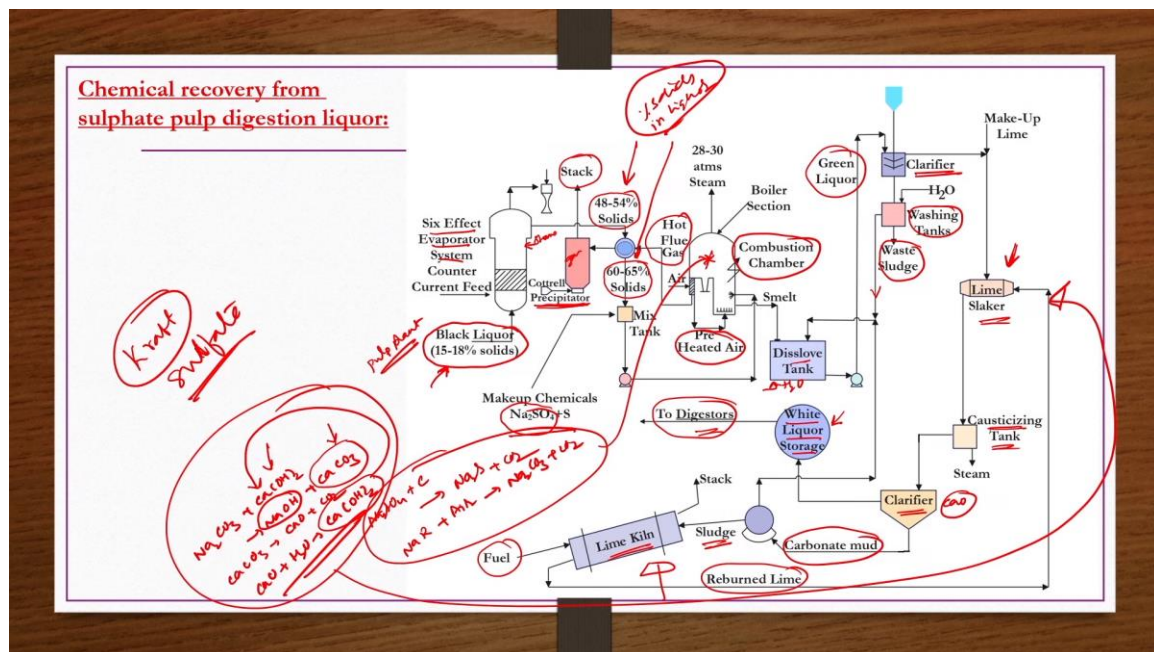
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- **5) Recovery of chemicals:**
- Black liquor from blow tank contains 98-99% of digestion chemicals which must be recovered
 - To avoid water and air pollution problems and
 - To provide a balanced economy of operation
- Multiple effect evaporation using 5-6 stages of calandria equipment followed by disk evaporators concentrates the liquor
 - From 15-18% solids to the point where combustion can be sustained in a smelting waste heat boiler (C, H, O)
 - This concentration is around 60% solids
- Organic carbon burns in the smelting furnace, supplying the necessary heat and CO₂ to produce an inorganic molten slag or smelt → recycle chemicals

Now recovery of chemicals, black liquor from a blow tank contains 98 to 99% of digestion chemicals which must be recovered in order to avoid water and air pollution

problems and to provide a balanced economy of operation because such large amount of chemicals if you are releasing or wasting so that is not going to be economical. How such kind of recovery is done? It is done by several steps. First step is multi-effect evaporation using 5 to 6 stages of calendria equipment followed by disc operators which concentrate the liquor, okay? Initial liquor whatever you feed is having 15 to 18% of solids in the black liquor. In the black liquor initially 15 to 18% solids are there, right? So, whereas the colors or chemicals you know 98 to 99% are there. So, from 15 to 18% solids to the point where combustion can be sustained in a smelting waste heat boiler to that level you know concentration of the solids increased. Actually, the solids are nothing but some kind of you know cellulosic or non-cellulosic component that has not been converted into the pulp, okay? So that means that those components must be having carbon atoms because those cellulosic or non-cellulosic components of wood material whatever is there so that is nothing but you know biopolymer. So, in the biopolymers you have the organic components as having the C, H, O etc. So, but that can be combustible if you know sufficient amount of solids are there. 15 to 18% of solids are only there in the liquor so then that is not going to be combustible. Even if it is combustible that combustion cannot be sustained. So that would be increased to 40 to 65% and then that would whatever the black liquor having 40 to 60% that would be sent to a smelting furnace, right? So, increasing the solids concentration from 15 to 18% to a range of 40 to 60% is done in multiple effect evaporation process, okay? Organic carbon burns in the smelting furnace supplying the necessary heat and CO₂ to produce an inorganic molten slag or smelt. So, this is the one from which you recover the chemicals, inorganic chemicals, okay?

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So, flowchart we discuss here first you know before going to the remaining steps. So here what we have? We have a black liquor which is coming out from the pulp plant or after pulping whatever the black liquor you get that is having now 15 to 18% solids. That solids fed to multi effect evaporator in a counter current system. What do you mean by counter current system? Actually, in evaporator you know removing the moisture content water content is being done actually that is done by supplying the steam, right? That steam and then this black liquor feed are entering in counter current direction so that to improve the interaction between them, right? So, in this process whatever the water vapors etc. are released they will be collected from the top and then checked for their concentration and then accordingly discarded, right? Whereas the material that whatever the black liquor going out from the multi effect evaporator that would be having around 48 to 54% solids. This would be passed through rotary dryer, right? That rotary dryer drying of the black liquor would be done in that rotary dryer so that solid concentration increases to 60 to 65%. How it is done because here also a kind of removal of water is taking place for that purpose hot flue gases which are coming from this smelting process or smelting furnace they are being used, right? So, in this process whatever the vapors or gases etc. are there they will be taken to a Cottrell precipitator in order to check the solids content. If this more solids contents are there in these gases or vapors they will be collected in the precipitator whereas the gases only sent to the stack, okay? Such solids you collected and then you can use it for different purpose based on the quality and then quantity etc., okay? So, but they would be in general very minor quantities less than 1% or something like that. Then these solids are black liquor actually what do you mean by these solids etc. here? You know percentage of solids in liquor, right? So, liquor which is having now 60 to 65% solids is mixed with makeup chemicals like Na_2SO_4 plus sulphur etc. This is we are talking about the craft process. So Na_2SO_4 has been added here, okay? Sulfate process. So in the mix tank the liquor which is having 60 to 65% solids would be mixed up with the makeup chemicals like Na_2SO_4 , sulphur etc. and then that would be fed to smelting furnace. The combustion chamber of that smelting furnace is shown here. So, this furnace preheated air is supplied so that the carbonaceous material that is present in the liquor can be combusted, right? For that purpose, this preheated air is supplied, okay? So here whatever this Na_2SO_4 is there that react with the C of the solids that are present in the liquor and then that will form Na_2S plus CO_2 . So, in the smelter other reactions also takes place. Let us say NaR which is nothing but lignin salt that will react with the preheated air to get Na_2CO_3 plus CO_2 etc., right? In the subsequent causticizing section other reactions takes place where Na_2CO_3 reacts with calcium hydroxide to give NaOH plus calcium carbonate. This calcium carbonate will decompose into calcium oxide plus carbon dioxide. Calcium oxide further reacts with water to give calcium hydroxide. So the purpose of these reactions, the process is that whatever the NaOH required for the digestion purpose that we are getting here itself within the process. That is the reason though for a ton of pulp production you may be

requiring only 40 to 50 kgs of Na_2SO_4 because most of the chemicals are being produced here and then reused, okay? But for this purpose, calcium hydroxide is required that calcium hydroxide also you are getting within the process because whatever the calcium carbonate has formed within the causticizing unit that would be decomposed into calcium oxide and water and then that calcium oxide may be rehydrated to give the calcium hydroxide. This calcium hydroxide again you can reuse to react with sodium carbonate to get the required NaOH for the digestion purpose, okay? So, such in all those reactions takes place here. Actually, in fact here in this combustion chamber only these reactions takes place, okay? Whereas these remaining reactions takes place here in this section, okay? So once the sufficient combustion has been taken place what you can do? You know smelt whatever the molten slag that is formed at the bottom of the smelting furnace that is nothing but inorganic slag. So that you can take to dissolved tank where you add cold water or it interacts with cold water so that you know you get the green liquor, right? So, this green liquor is sent to a clarifier where clear filtrate you take, right? So, whatever the clarified liquor is there that would be taken to a lime slaker and then to causticizing tank where it reacts with calcium hydroxide. Then this process after the causticizing whatever the material is there or the mixture is there that would be taken to the clarifier because here what you get you also have the calcium oxide, etc. So those calcium oxides, etc. you have to remove as carbonate mud and then whatever the clear white liquor is there that you take to the storage or to the digestion tank, okay? So, whatever the calcium oxide, etc. is there that would be processed through rotary filter press to separate out the more liquor if at all it is having some liquor. So that would be taken to the dissolved tank whereas the sludge is there that would be taken to the lime kiln where fuel gases are used to convert this lime into the calcium carbonate and then reburn lime whatever is there that is taken back to the lime slacker storage, okay? Whatever the solids that you get from the clarifier that you wash in washing tanks after washing the sludge whatever is there you filter out and then take it as a waste sludge. But when you do the washing there would be filtrate liquor, wash liquor would be there that wash liquor would be sent back to the dissolved tank again because this wash liquor will also be having some kind of chemicals, okay? So that has to be relooked within the process so that you know as much recovery of chemicals as possible. So, whatever the white liquor that you get here so that would be free from the chemicals. The white liquor we are not calling as water but we are calling it as white liquor because it may be having some amount of pulpy materials without any chemicals, okay? So, since it is having some amount of pulpy materials so that can be taken back to the digester as a recycle process as we have discussed in the previous slide when we are discussing about the digestion of you know wood by craft process just in the previous slide we have discussed it, okay? So, this is how chemical recovery has been done in craft process. This is also part of the craft process or sulfate process. Only thing that you know the recovery chemical recovery part I have shown as a separate flow chart because otherwise both the flow chart if you are combining together

that would become very clumsy and difficult to explain. So, whatever the black liquor that we get from the previous flow chart is sent here in the multiple effect evaporator and this process continues. Whatever the white liquor you get after recovering the chemicals this white liquor is fed back to the digestion tank that we have discussed in the previous flow chart, okay? Otherwise logically both the flow sheets are part of one particular process that is craft sulfate pulp process, okay?

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• For smelting purpose, the make-up alkali is supplied via Na_2SO_4 as per reactions:

$$2\text{NaR (lignin salt)} + \text{air} \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2$$

$$\text{Na}_2\text{SO}_4 + 2\text{C (from R)} \rightarrow \text{Na}_2\text{S} + 2\text{CO}_2$$

$$\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2(\text{s}) \leftrightarrow 2\text{NaOH(aq)} + \text{CaCO}_3(\text{s})$$

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$

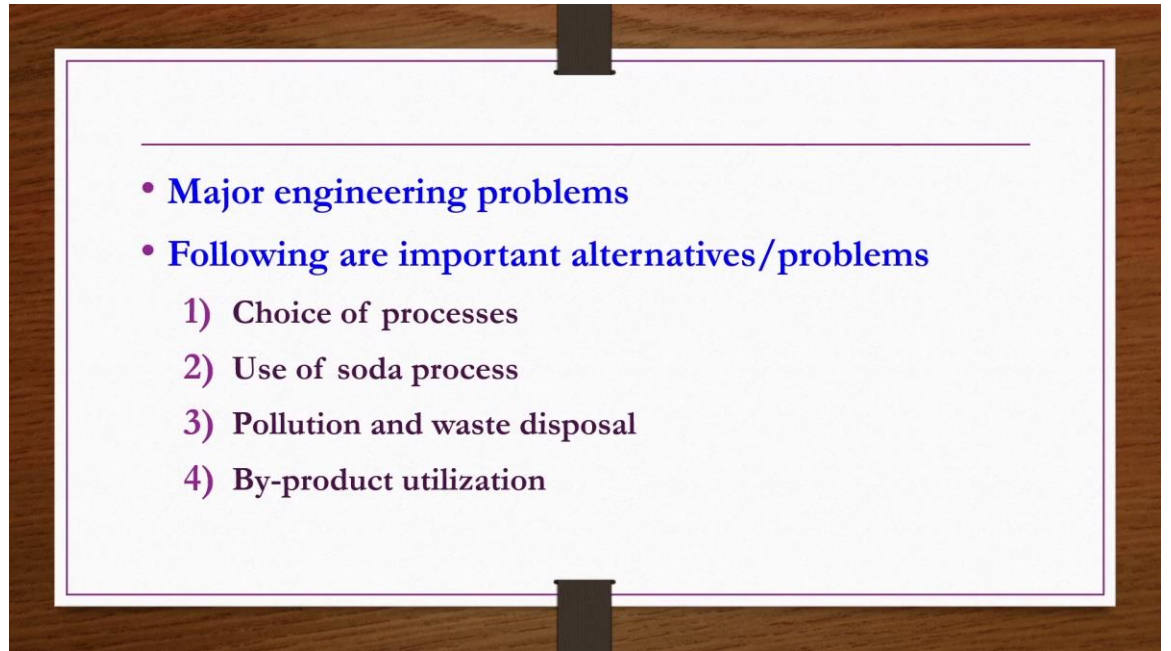
$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$$

- Molten smelt falls into a dissolver where it contacts cold H_2O to yield green liquor solution
- Insoluble impurities such as unburned carbon are settled out and the clear liquor causticized by adding lime
- Filtration removes the calcium carbonate sludge while the filtrate (white liquor) is returned to the digester
- Carbonate sludge is calcined to lime for recycle

For smelting purpose, the makeup alkali is supplied via Na_2SO_4 as per the reactions which I have already explained that is lignin salt react with the preheated air to get Na_2CO_3 and CO_2 . This Na_2CO_3 may be further used you know in the causticizing tank whereas Na_2SO_4 that is fed to the system you know that reacts with the carbon that is present in the solid material that is present in black liquor having 60 to 65 percent solids. So, when it reacts with that carbon it will produce Na_2S . This Na_2CO_3 will react with calcium hydroxide to give sodium hydroxide. This sodium hydroxide again you can reuse for the digestion purpose but this process also forms calcium carbonate which is slightly difficult to remove. For that purpose, what you do? You decompose into the calcium oxide and then carbon dioxide. This calcium oxide further you rehydrate so that to get calcium hydroxide and then that calcium hydroxide you can reuse within the process. So by following these steps what happens? The dependence on the chemicals required for the pulp process would decrease because they are being recovered and within the process they are reused. Molten smelt falls into a dissolver where it contacts cold H_2O to yield green liquor solution. Insoluble impurities such as unburned carbon are settled out and the clear liquor causticized by adding lime. Filtration removes the calcium carbonate

sludge while the filtrate white liquor is returned to the digester so that the digestion may be facilitated in the continuous digestion section. Carbonated sludge is calcium to lime for recycle purpose. This is about the recovery also. So now within the craft process we have seen all the steps. We have seen all 5 steps of digestion of wood based raw material, bleaching of pulp and then use of alternative raw materials. So, what are the modifications required and then finishing of the pulp and then finally recovery of chemicals. So with this craft process is complete.

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- **Major engineering problems**
 - **Following are important alternatives/problems**
 - 1) Choice of processes
 - 2) Use of soda process
 - 3) Pollution and waste disposal
 - 4) By-product utilization

So now what we are going to see? We are going to see major engineering problems associated with the craft or sulphate process for the pulp production. Choice of processes is one important issue to consider. Then use of soda process there is other process other than the sulphate and sulphide process there used to be soda processes earlier. So, what are the issues with the using of soda process we have to discuss. Then pollution and waste disposal. We see that you know in pulp industry pulp and paper industry large amount of water is being used and a large amount of liquor is also being produced. Such large amount of liquor you know after recovering chemical also sometimes somehow you have to dispose. So how to dispose that is also one concern. So, one has to pay attention to that one also. Then byproduct utilization it is possible to have some amount of byproduct recovery like resins etc. or from the lignin to get some value added chemicals etc. Such kind of possibilities are there. So, then we are going to discuss all of them now.

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- **1) Choice of processes**
- **Demand for high-strength good-quality paper products has reduced the choice to**
 - Either chemical sulphite or sulphate process with latter moving out in front
- **Important advantages of sulphate process over sulphite process are**
 - Raw material quality has less significance in the sulphate process
 - Sulphate fibres have superior strength characteristics
- **Newer developments in sulphite processing will help to keep this type of pulping from becoming obsolete**
- **Economics and waste disposal laws have virtually eliminated**
 - Older calcium sulphite process in favour modern sodium- or magnesium-based salts

Choice of processes demand for high strength good quality paper products has reduced the choice to either chemical sulphite or sulphate process whereas the sulphate process is leading the game. So why because you know we have seen you know if you wanted to have high strength good quality paper you know you cannot get such good quality paper by mechanical method. So you have to go for the chemical method. So out of the 2 chemical methods sulphate process is better because the sulphite process you know water pollution issues are there or the chemical recovery is very tough or you know large amount of you know different types of liquors are produced in sulphite processes. So therefore, their recovery is an issue and then because of that one economics is also an issue for the sulphite process because of such reasons sulphate process is leading the race. Important advantages of sulphate process over sulphite process are raw material quality has less significance in the sulphate process. In comparison table we have seen in previous lecture the craft or sulphate process is there it can work with any type of raw material whereas sulphite process is suitable only for the bagasse and then hardwood kind of raw materials only. Sulphate fibers have superior strength characteristics as already mentioned. Newer development in sulphite processing will help to keep this type of pulping from becoming obsolete. Similarly, you have to do some kind of newer development in fact the researchers have developed certain kind of new chemical recovery processes where nowadays sulphite processes are also becoming economical. So, we see some of them now anyway. Economics and waste disposal laws have virtually eliminated and then there used to be other sulphite processes in olden days like calcium

sulphite process. They are now almost like eliminated because of economics and then waste disposal problems because such kind of problems are not existing in modern plants where sodium or magnesium-based salts are being used in the sulphite process.

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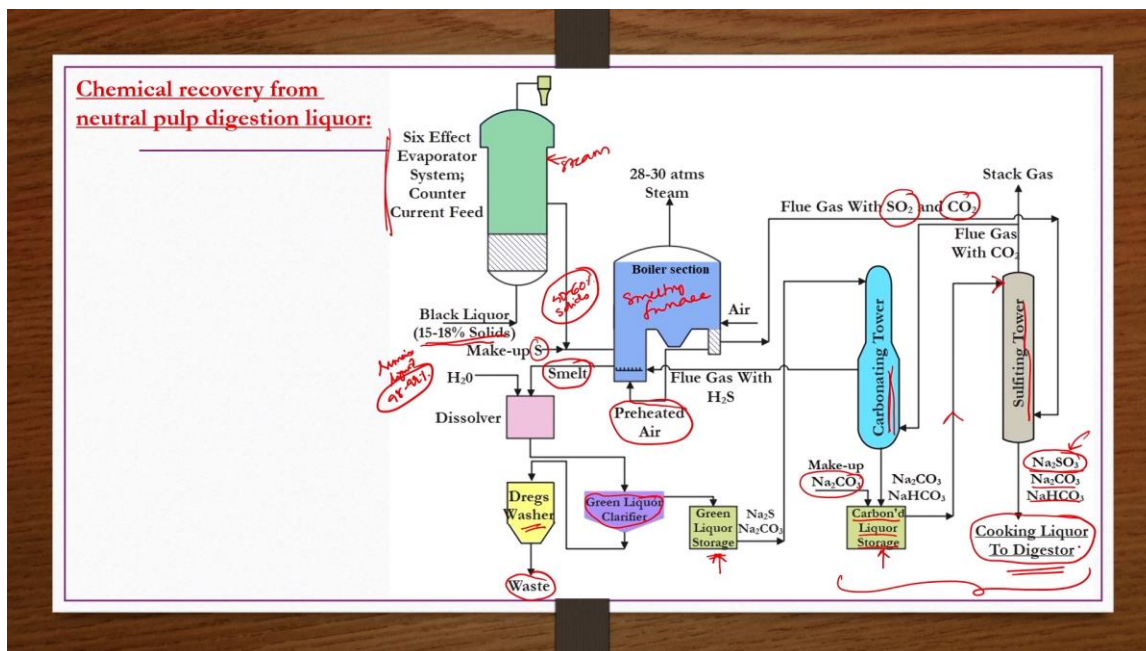
- **These processes also provide**
 - Higher yields
 - Allow more flexibility in raw materials
 - Produce a type of waste liquor wherein the pentosans can be fermented to ethanol
- **Latest trend in large pulping plants is to integrate operations whereby both processes can be used in the same plant** || Neutral sulphite
- **This is possible with the neutral sulphite process (flow chart shown in next slide) since the only change in black liquor recovery is**
 - Carbonation of green liquor followed by oxidation of Na₂S with CO₂ to produce Na₂SO₃ whereas causticization step is omitted

These processes also provide higher yields, allow more flexibility in raw materials, produce a type of waste liquor wherein the pentosans are present they can be fermented to ethanol so that way they are better. Latest trend in large pulping plants is to integrate operations where both processes can be used in the same plant. In the comparison we have seen that if you have neutral sulphite process so then what you can do? You can use the craft plant itself for running the neutral sulphite process such things are possible. This is possible with neutral sulphite process. Since the only change in black liquor is carbonation of green liquor followed by oxidation of Na_2S with CO_2 to produce Na_2SO_3 whereas causticization step which is present in the sulphate process that is omitted. So, this flowchart we are going to see in the next step where primarily what is happening oxidation of Na_2S with CO_2 is taking place so that to get Na_2SO_3 .

How it is that we are going to see in flowchart? Mostly the process is similar like whatever we have seen for the recovery of chemicals from the liquor that is obtained from the craft process, but only thing that there we have causticizing step. Now here rather causticizing you have the sulphiting and carbonating towers. Before that whatever the steps are there they are quite similar. So, whatever the liquor that you get here also roughly 15 to 18 percent solid should be there and then remaining liquid whatever is there that liquid would be containing 98 to 99 percent chemical here also. So, these

chemicals has to be recovered both from the pollution concerns point of view as well as from the economics of the plant.

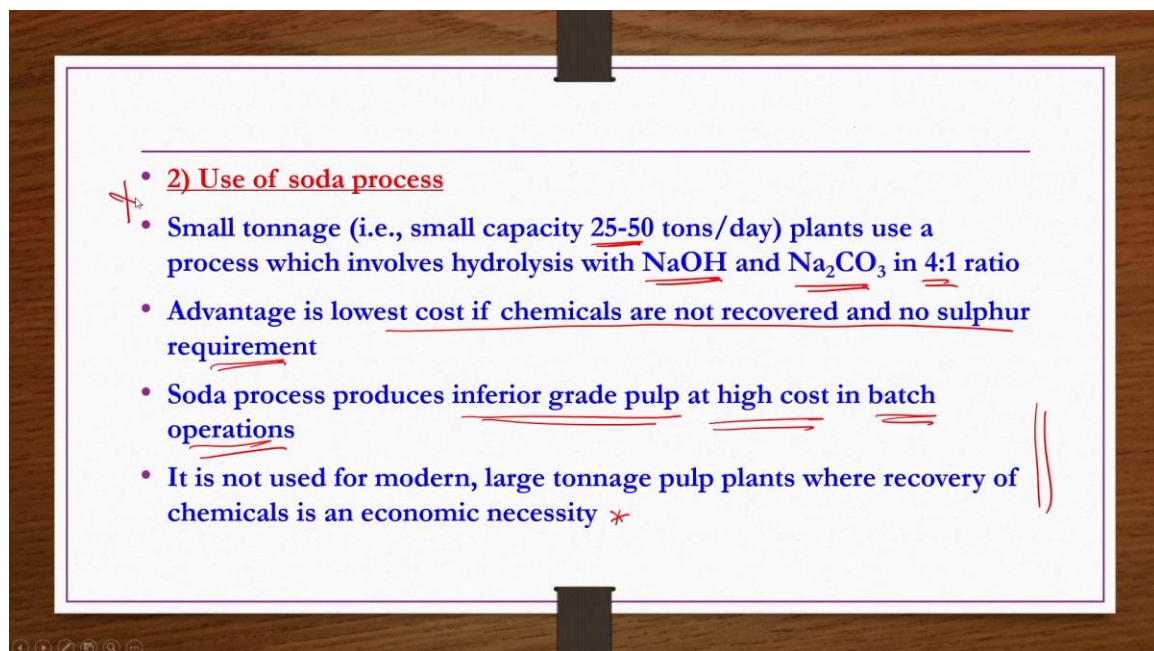
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You cannot afford to have so much of chemicals losing every time. So, for that purpose of recovery this flowchart is here. Now the starting point is here also multi effect evaporator is used so that to increase the solid concentration in the black liquor from 15 to 18 percent to 50 to 60 percent roughly or 45 to 55 percent that can be done by evaporation of the liquid that is present in the liquor and then that evaporation of liquid can be done by heating and then heating is done by the steam. That steam and then liquor are entering the multi effect evaporator in the counter current way. After this multi effect evaporator process whatever liquor you get that would be having you know roughly 50 to 60 percent solids only 40 to 50 percent liquid should be there. So now after improving the solids concentration in the black liquor by evaporating the water you know what you do you mix with the makeup chemicals like sulphur etc. If required you know sodium sulphite etc. may also be added and then that liquor would be sent to the smelting furnace. In the smelting furnace what happened carbonaceous material would be combusted. For that purpose, preheated air is being supplied. When this combustion takes place you get the flue gas as well as the inorganic smelt. So, the flue gas what you do the flue gases having SO₂ and then CO₂ would be sent to a sulphiting tower where whatever the chemicals that are present in the black liquor liquid. So you know mostly they will be converting into the sodium sulphite, sodium carbonate, sodium bicarbonate these kind of chemicals. Of course they will not be in pure conditions but still in the liquor condition. So that you can collect as a cooking liquor and then take it to the digester if required. If

the more purification is required then what you do whatever the flue gases with CO₂ only because in the sulphiting tower you do the sulphination so that you get the sulphites etc. So after that primarily flue gases would have CO₂ only those things you take to the carbonating tower where carbonation takes place and then you get sodium carbonate, sodium bicarbonate etc. If required sodium carbonates make up chemicals may be added so that you get a carbonated liquor storage. This liquor what you can do you can send back to sulphiting tower so that whatever the carbonates etc. are there they will be forming sulphites like Na₂SO₃. Whereas the inorganic smelt whatever is there that is taken to a dissolver where cold water is used to dissolve the inorganic smelt. Then you get a green liquor that green liquor would be having the solids as well as you know liquor. So, the waste solids you have to separate out by a clarifier whatever the solids that you get the waste slurry you get that you further wash it with water and then wash water you may be reusing into the dissolver whereas the sludge you know almost like a little water or no water that would be taken as a waste. Whereas the clarified liquid from the liquor clarify or whatever is there that you take it to the green liquor storage which would be having Na₂S, Na₂CO₃ etc. Since Na₂S is there so that you send it back to the carbonating tower and then from there you get the carbonated liquor storage that liquor again you send back to the sulphiting tower so that Na₂SO₃ you get and then that liquor may be reused to the digester. Remember only this liquor is reused in the digester for the sulphite process whereas these things you have to do separate processing otherwise you know you have to do the process continuously until there is no green liquor or almost all chemicals have come into the cooking liquor. So, that cooking liquor you can use or reuse into the digester of a neutral sulphite pulp process.

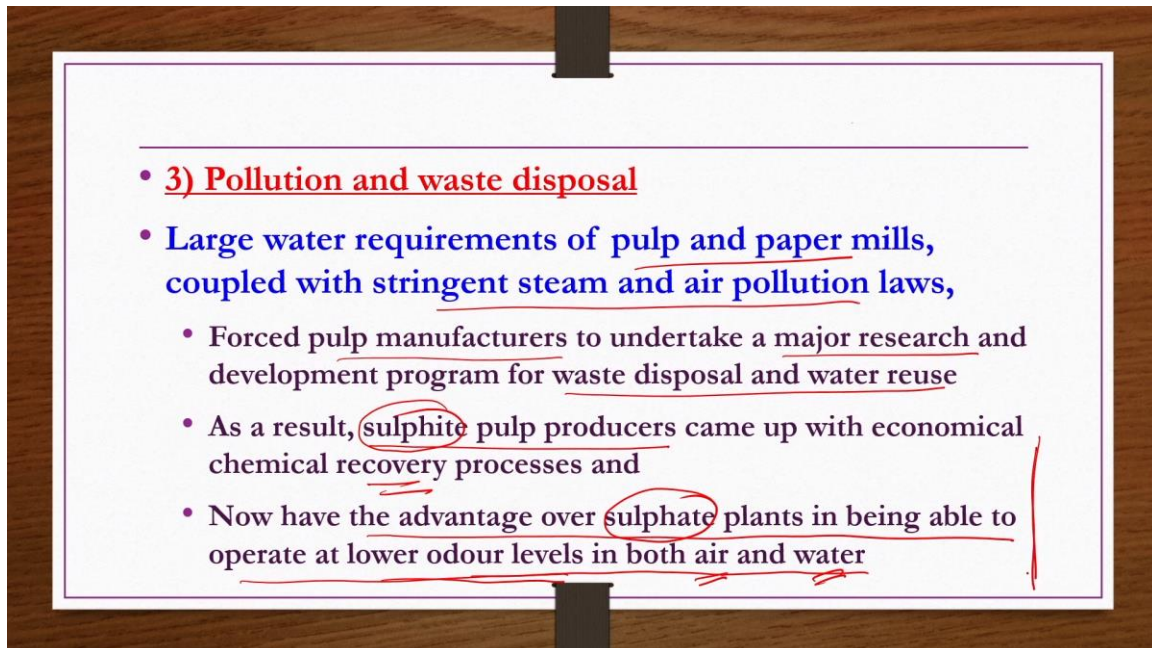
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- **2) Use of soda process**
- Small tonnage (i.e., small capacity 25-50 tons/day) plants use a process which involves hydrolysis with NaOH and Na₂CO₃ in 4:1 ratio
- Advantage is lowest cost if chemicals are not recovered and no sulphur requirement
- Soda process produces inferior grade pulp at high cost in batch operations
- It is not used for modern, large tonnage pulp plants where recovery of chemicals is an economic necessity *

Second engineering problem is use of soda process. Small tonnage that is small capacity 25 to 50 tons per day of plants use process which involves hydrolysis with sodium hydroxide and sodium bicarbonate at 4 by 1 ratio. It is having advantage of lowest cost if chemicals are not recovered and no sulphur requirement is there. Whenever there is a sulphur requirement you know H₂S formation, SO₂ formation would be there then environmental concerns would definitely be there. So, but such problem is not there in the soda process. But soda process produce inferior grade pulp that is the reason it is not used for you know in a large tonnage plants. That also at high cost in batch operations. Continuous process is not possible it has to be done in the batch operation and because of the batch operation the cost is high and then pulp quality is also inferior. It is not used for modern large tonnage pulp plants where recovery of chemicals is an economical necessity because of such reasons. I know this pulp by a use of soda process is not preferred especially for large tonnage plants.

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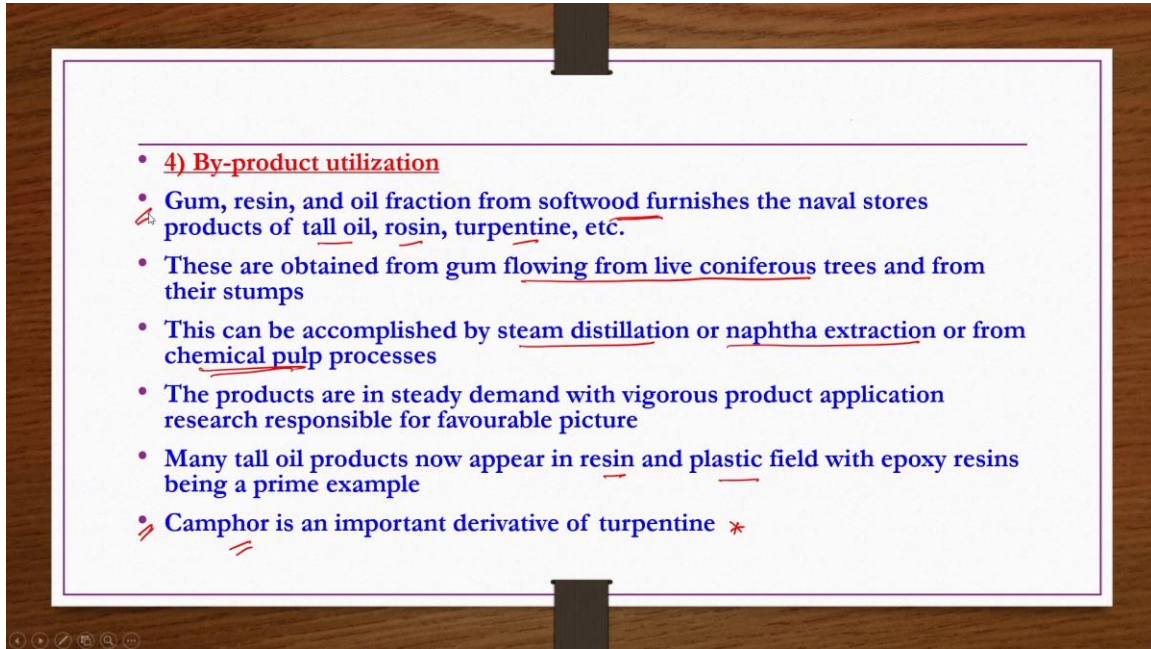


- **3) Pollution and waste disposal**
- **Large water requirements of pulp and paper mills, coupled with stringent steam and air pollution laws,**
 - Forced pulp manufacturers to undertake a major research and development program for waste disposal and water reuse
 - As a result, sulphite pulp producers came up with economical chemical recovery processes and
 - Now have the advantage over sulphate plants in being able to operate at lower odour levels in both air and water

Next is pollution and waste disposal problems. Large water requirements of pulp and paper mills coupled with stringent steam and air pollution laws forced pulp manufacturers to undertake a major research and development program for waste disposal and water reuse. And as a result sulphite pulp producers came up with economic chemical recovery processes and now the advantage over sulphate plants is being able to operate at lower order level in both air and water. So, you know compared to the sulphate plants you know the sulphite plants they are able to develop some kind of new methods for the chemical recovery because of that one the sulphite processes are also able to operate at lower order levels in both air and water. So, air and water pollution is reduced by these new methods

that is what it means to but however we are not going into the details of such processes they are part of the research.

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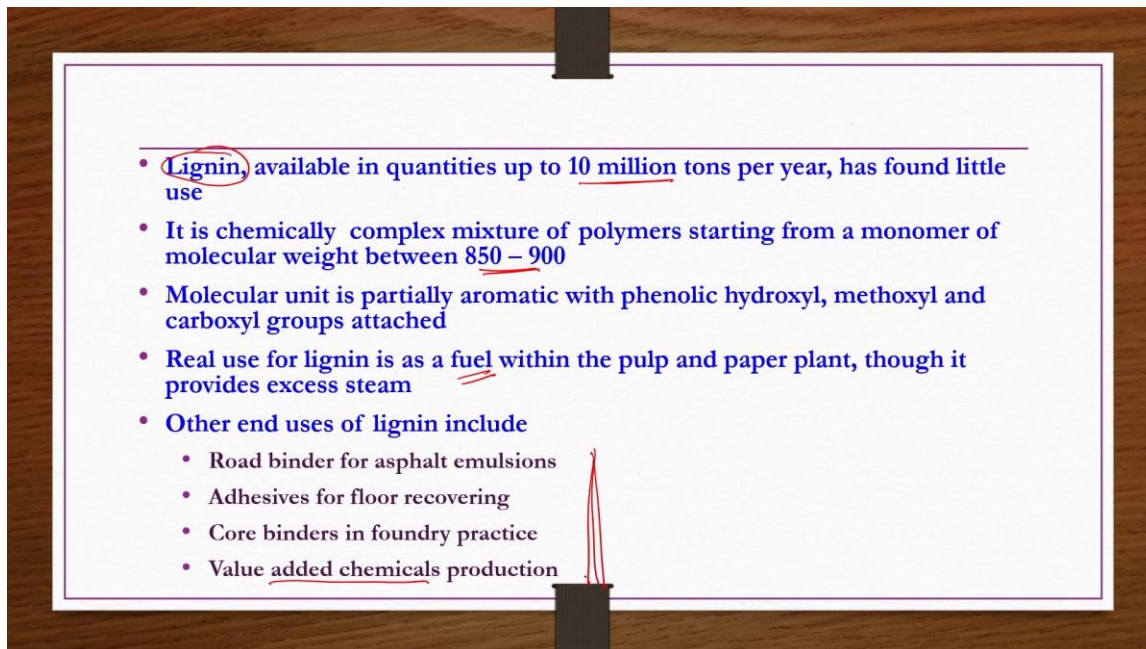


The last major engineering issue of you know pulp production is byproduct utilization. Gum, resin and oil fraction from soft wood furnishes the novel stores products of tall oil, rosins, turpentines etcetera is there. So, one has to see how one can recover them so that you know this byproduct can also give money to the you know pulp and paper industry owners. These are obtained from gum flowing from live coniferous trees and from their stumps. This can be accomplished by steam distillation or naphtha extraction or from chemical pulp processes any of the process can be used. The products are in steady demand with vigorous product application research responsible for favorable picture. Many tall oil products now appear in resin and plastic field with epoxy resins being a prime example and then camphor is an important derivative of turpentine. So, like this whatever possible byproducts are there one has to see how to recover them so that to make the plant more and more economical. Because if you recover more byproducts and then get more money from the byproducts the cost of your main product will reduce and then you know there would be more demand for the you know such kind of products.

Lignin available in quantities up to 10 million tons per year has found little use actually because what we are doing in the digestion section we are primarily you know removing the lignin and then increasing the cellulose content that is what we are trying to do in the digestion section, continuous digester whatever we have taken. That lignin we should able to utilize. There are many ways of utilization of lignin. It is chemically complex

mixture of polymers starting from a monomer of molecular weight between 850 to 900 and then even higher also there.

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So actually, whatever the wood is there that is having the contents like you know cellulose, hemicellulose, lignin and then some kind of other minor chemicals. Primarily, these 3 are important. Cellulose hemicellulose are 2D polymers whereas the lignin is 3D polymer. So, its conversion to products requires large energy because the required activation energy for converting lignin to the product you know very high. So, but however some approaches has to be found or alternative utilization of such lignin has to be found. Otherwise where are you going to dump such large quantity of a lignin. Because it is being produced or piled up 10 million tons per year or even more. Molecular unit is partially aromatic with phenolic hydroxyl, methoxyl and carboxyl groups attached. Real use for lignin is actually as fuel right. You know whichever way possible the solid material that is there after recovering the cellulose contents whatever the lignin solid waste that is there. So that can be used within the process as a solid fuel for the boilers etc. That is the main use actually there itself it can be used. But however, if excess lignin is there that should be utilized for other purposes. What are the other possible applications of lignin? They include a road binder for asphalt emulsions, adhesives for flow recovering, core binders in foundry practices and then value-added chemicals production by different thermochemical biochemical approaches. So, these are not part of our course. So, then we are not going to see how these are being utilized you know or produced using the lignin.

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- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

So, this is all about today's lecture where we discussed in detail about the chemical recovery from the sulphate as well as the sulphite process liquors and then major engineering problems associated with the pulp production processes those things we have seen. So, the references for today's lecture are provided here. Outlines of Chemical Technology by Dryden edited and revised by Gopala Rao and Marshall third edition. Chemical Process Industries by Austin and Shreve fifth edition. Encyclopedia of Chemical Technology by Kirk and Othmer fourth edition. Unit Processes in Organic Synthesis by Groggins fifth edition. Thank you.