Organic Chemical Technology
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Lecture – 15
Paper and Pulp Industry

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is paper and pulp industry. In this chapter particularly we will be discussing about the production of pulp by different methods, the comparison between different methods that are available for the production of the pulp followed by the production of paper from the pulp and then recovery of chemicals from the liquor that has been producing the pulp, right? So, that is what we are going to discuss and then we are also going to see the major engineering problems associated with both pulp production as well as the papermaking. In addition, we are going to discuss about the cellulose and its derivatives as well because cellulose is nothing but or maybe other way pulp is nothing but commercial cellulose. So, that is the reason cellulose and its derivatives part should also come into the chapter of pulp and paper industry. So, that is what we are going to discuss in this particular chapter. However, before going to the details of such technological details of pulp and paper

production and then chemical recovery, etc., those part, we will be having a brief introduction about the pulp and paper industries.

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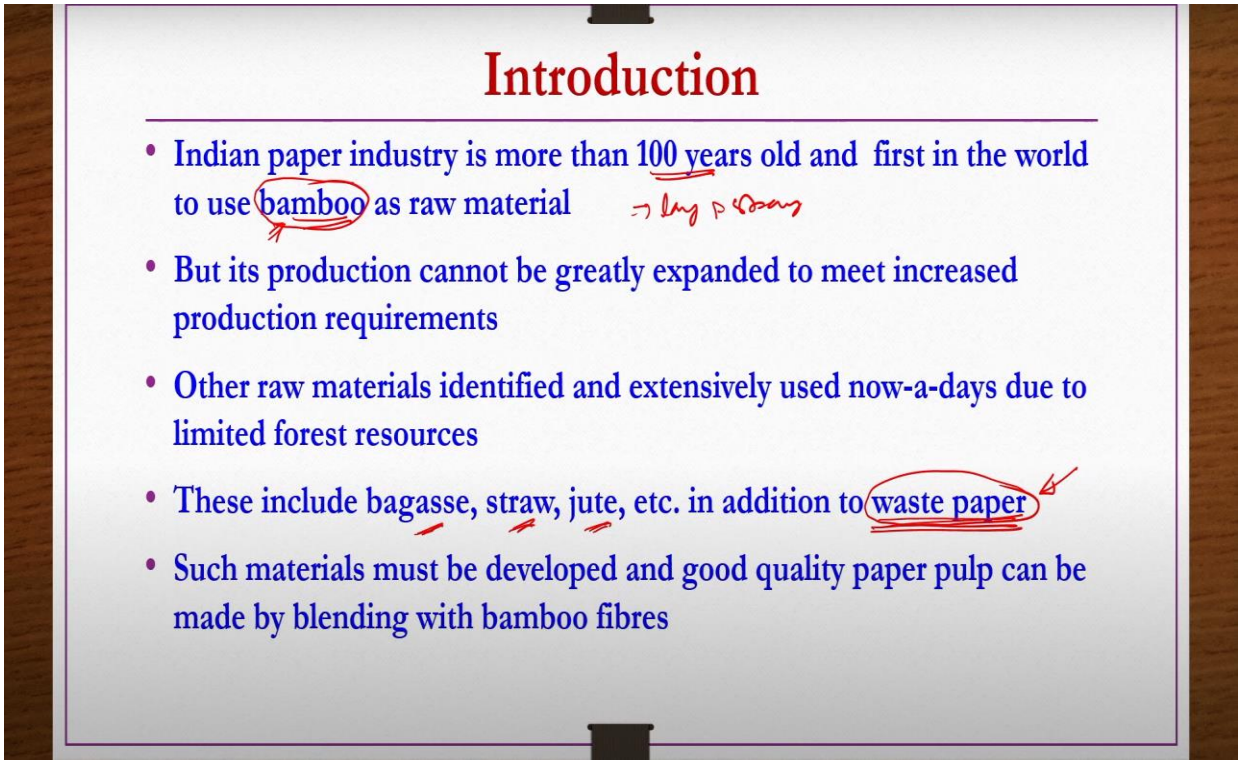

Indian paper industry is more than 100 years old and is the first one in the world to use bamboo as raw material because different types of foods are in general used as a raw material for the production of the pulp followed by the paper. So, those things anyway we are going to discuss, but bamboo was not used earlier by the other industries, especially other countries. Indian paper industry is the first one to use bamboo as raw material. What is so great about the bamboo as raw material because it is the only one that gives long and strong fibers to get the cellulose. If the fibers and then corresponding cellulose that you get during the pulping process, if it is long and then strong enough, if it is more in cellulose content and negligible lignin contents, then obviously the quality of the paper is going to be the better one. That is the good thing about this bamboo as raw material. But however, the demand for the paper is so much higher that having so many bamboo plants is not possible, cultivation of the bamboo has not been taken to that level.

So, because of that one, its production cannot be greatly expanded to meet increased production requirements. However, you know other raw materials identified and extensively used nowadays due to limited forest resources, they include bagasse from the sugar industry, straws, rice straw, wheat straw, etc., jutes, etc., in addition to waste paper also. Waste paper that means like the paper that has been utilized for different purposes, academic, non-academic, commercial purpose, etc.

Then after the use, then what happens that paper if it is not at all useful in future, then that paper you can regard as waste paper including the newspapers, etc. also you can regard as a waste paper. So, such paper can also be utilized as a raw material and then that can be re-pulped and then the chemicals, pigments such as like you know color pigments because when you use the paper, whether you are writing or printing, you may be using different colors. So, those color pigments has to be removed before it is re-pulping. So, once those color pigments are removed, then such waste paper can also be utilized as a raw material for pulping and then making other papers.

But, however, availability of such waste papers are in less quantity. So then because of that reason, you know what we have, we can have such kind of paper industries only in the small units or small scales only. So now, obviously we understand that the bamboo is a better raw material because of the length and then strength of the cellulose that you are going to get, but availability of bamboo is not that much. So, then what you can do? You can develop such kind of raw materials like bagasse, straw, etc. and then you blend. You blend along with the bamboo and then try to produce a better quality paper, okay? That is also possible. Such materials must be developed and good quality paper pulp can be made by blending with bamboo fibers, right?

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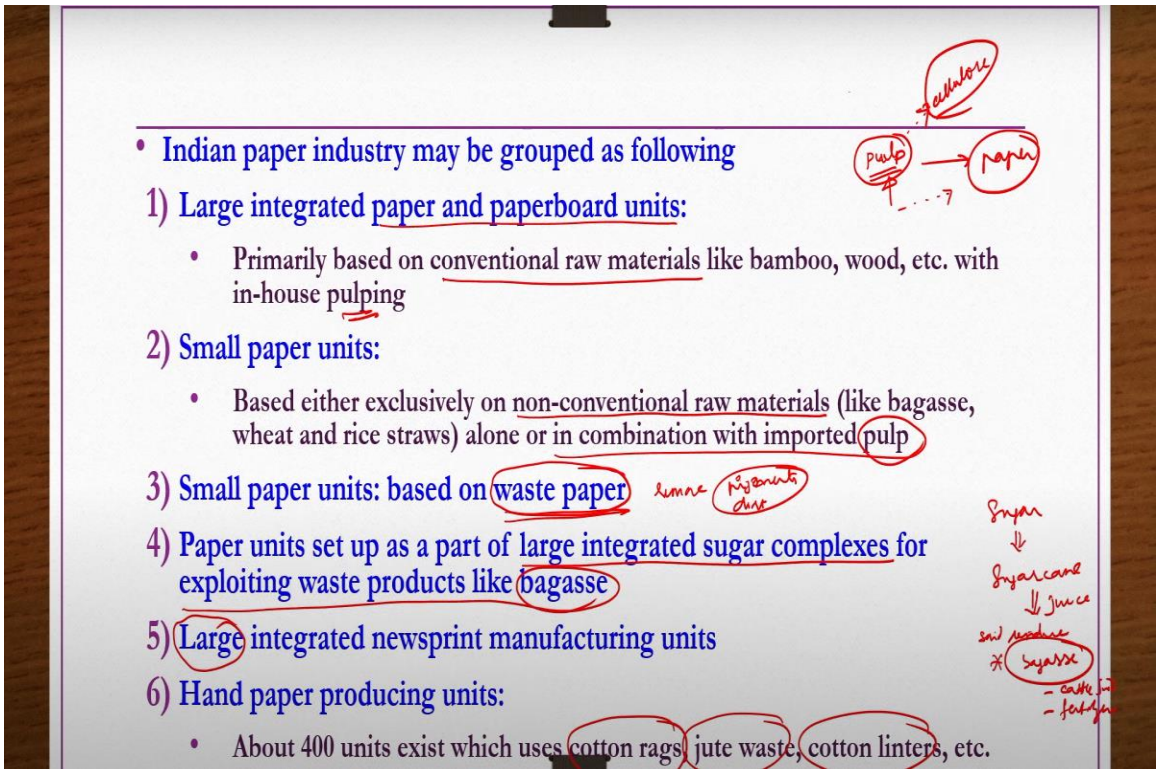

Now, we discuss about the grouping of Indian paper industry. Actually Indian paper industry can be grouped by different ways like one is by the method of the production, other one is by end use, other one is by the resources like raw material, etc. like this, different ways it is possible to group even the size of the plant, right? So all those matters may be included and then different types of grouping can be done. whatever, the grouping that we are going to discuss here, they are primarily based on the size of the units as well as the source of the such kind of industries, okay? So, on the basis of the size as well as the availability of the resources, Indian paper industry can be grouped as 6 different types.

The first one is large integrated paper and paper board units. In general, what happens in paper making? Many paper making industries they do not make pulp required for the paper making. What they do? They buy pulp from some other industries and then they try to make paper, right? So that means indirectly the pulp has been made by some other industry and then that pulp is being used for the paper making because this pulp is nothing but mostly commercial cellulose. So, this commercial cellulose may also be utilized for the

other purpose also. So, that is the reason many industries they target just only up to the pulp, right? Because from the pulp if you wanted to make paper, you can make paper.

If you wanted to make other cellulose derivatives, you can make those kinds of cellulose derivatives also. So, the utilization or in application spectrum is wide from the pulp. So that is the reason many industry restrict themselves up to the pulp making and then paper industries they buy pulp from the other industries and then try to make papers. But however, if they are integrated in one single industry itself, so that is going to be large in size. So that is the reason the first category is large integrated paper and paper board units.

Primarily these are based on the conventional raw materials like bamboo, wood, etc. with in-house pulping. Pulping also it has been done in the plant itself. So, they do not depend on the other industry for the pulp. Small paper units, they are either exclusively based on non-conventional raw materials like bagasse, wheat straw, rice straw, etc. alone or maybe they can be used in combination with imported pulp, imported in the sense from the other sources of pulp industries, okay? So, such units are usually smaller units, smaller paper units, maybe such units classified as smaller paper units. And then another one is again a small paper units, but that is based on waste paper alone. It is not based on the fresh raw material whether conventional or non-conventional. It is based on the waste paper, that waste paper remove pigments or dirt, etc. if at all other ingredients are there or impurities are there, those things you have to remove and then that waste paper you have to repulp and then make a paper.

So, since the availability of waste paper is limited, the size of the units are also limited, but that is the reason these units are also known as the small paper units. And then paper units set up as part of large integrated sugar complexes for exploiting waste products like bagasse. In the sugar and starch industries, what we have seen when you make sugar from the sugar cane, primarily what we have studied in the sugar manufacturing, sugar cane is there that you extract the juice, juice extraction is taking place and then that juice is being concentrated to certain higher concentration and then crystallization of that concentrated juice into the sugar crystals is been taking place. That is what we learned in the sugar and starch industries when we were discussing about the sugar. In the sugar, getting from the

sugar cane, what we get that solid waste whatever is there, solid residue after getting or extracting all the juice that we call as bagasse.

This is primarily used for the cattle food or as fertilizers in some forms, agricultural fields that is what used, but we also seen that this can also be used as a raw material for making paper. So, if you are making paper units within the sugar complexes and that is going to be better one. That is one category of Indian paper industry. Next is large integrated newsprint manufacturing units. Actually nowadays news in print media, the quantity is less compared to the decade or couple of decades before. So then in the present days context, we cannot say large but still integrated newsprint manufacturing units if you consider, that is going to be sufficiently large if you compare all of them. If you compare with the small paper units, they will be still larger. So we can call them large integrated newsprint manufacturing units. Next is the hand paper producing units. Different types of hand papers are produced which are used for the interior designing purposes. Some those kind of applications it is used. There are hundreds of such units which use cotton racks, jute waste and cotton linters etc as raw material. So, this is one of the way of classifying the Indian paper industries. Of course, you can classify in different ways as well.

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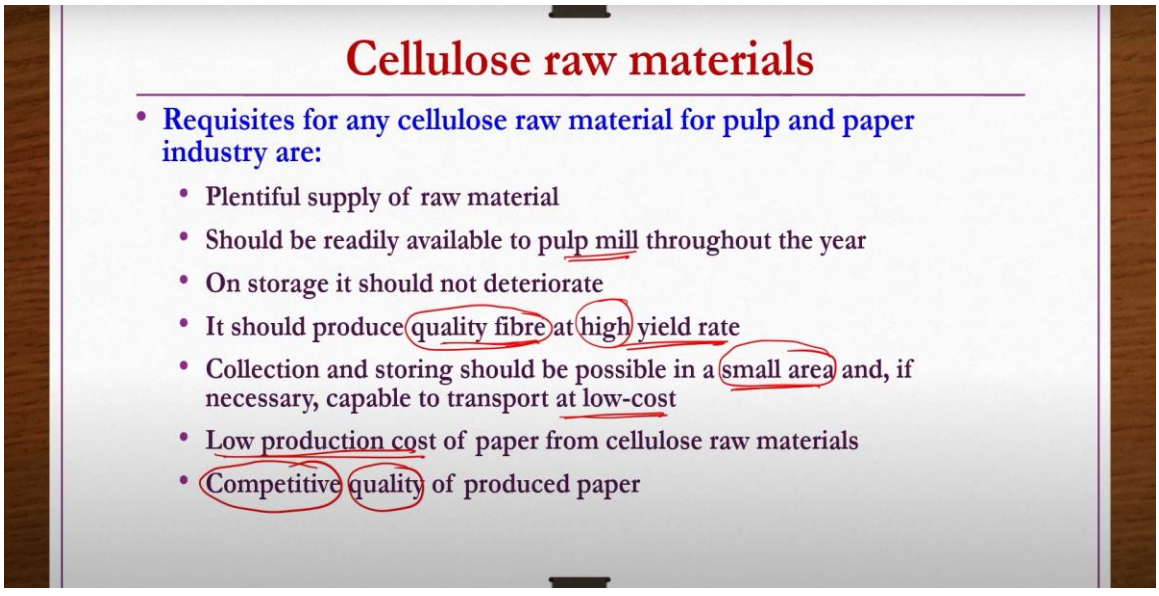

Now, the cellulose raw materials, we discussed about the cellulose raw materials because now what we understand we are going to get a cellulose by pulping of wood or bagasse or you know some other kind of bamboo or any whatever raw materials we are taking. So primarily that cellulose is very essential. Basically from the wood what are you trying to do? You are trying to separate out the lignin and non-cellulosic components and then extract the cellulosic components and those cellulosic components when you extract then you do certain kind of process to get the pulp that is required for pulp making. So that raw material should have proper requisite so that paper industry growth cannot be inhibited or paper industry growth can be continuously there. So, requisites for any cellulose raw material for pulp and paper industry if you see they should be available in plentiful whatever the raw material you take, they should be available plentiful and then not only that one throughout the year they should be available to the pulp mill. It is not that they are available elsewhere but it is not available for the pulp mills for some reason so that is of no use.

So, it should be readily available to pulp mill throughout the year and then sometimes we understand that it is required to store such materials. If you are not directly making paper so then it is required to store such cellulosic raw material. If you are storing or if you need to store them for couple of weeks or for couple of months you know they should not undergo any kind of deterioration that is the other requirement and then they should produce quality fiber at high yield. So, we already seen that bamboo is a good raw material to produce a you know quality fiber. Quality fiber in the sense that should be long enough and then that should have sufficient strength.

Such kind of product you should get and then that also you should get at high yield rate that is also very essential because the demand for the paper is so much higher that if you wanted to meet such demands your production has to increase. So for that all these parameters are essential to be considered. Then, collection and storing should be possible in small area in general. Let us say if you are making paper by procuring pulp from some other sources. So that pulp how much moisture is there or how much solid it is there 40 to 60 percent or 90 percent depending on that one you know your size storing area you know going to be different size of the storing area is going to change accordingly.

So in sometimes it is necessary to transport. So if transport of such kind of material is to be done then that should able to be done at low cost. So these are from the raw material point of view from the product point of view the raw material should have such a kind of characteristic that whatever the paper that is produced that should be produced at low cost. And then the quality of such paper should also be competitive. If the paper quality is not competitive you cannot withstand in the competitive industrial world for long. Then higher priority rate should not be there at all.

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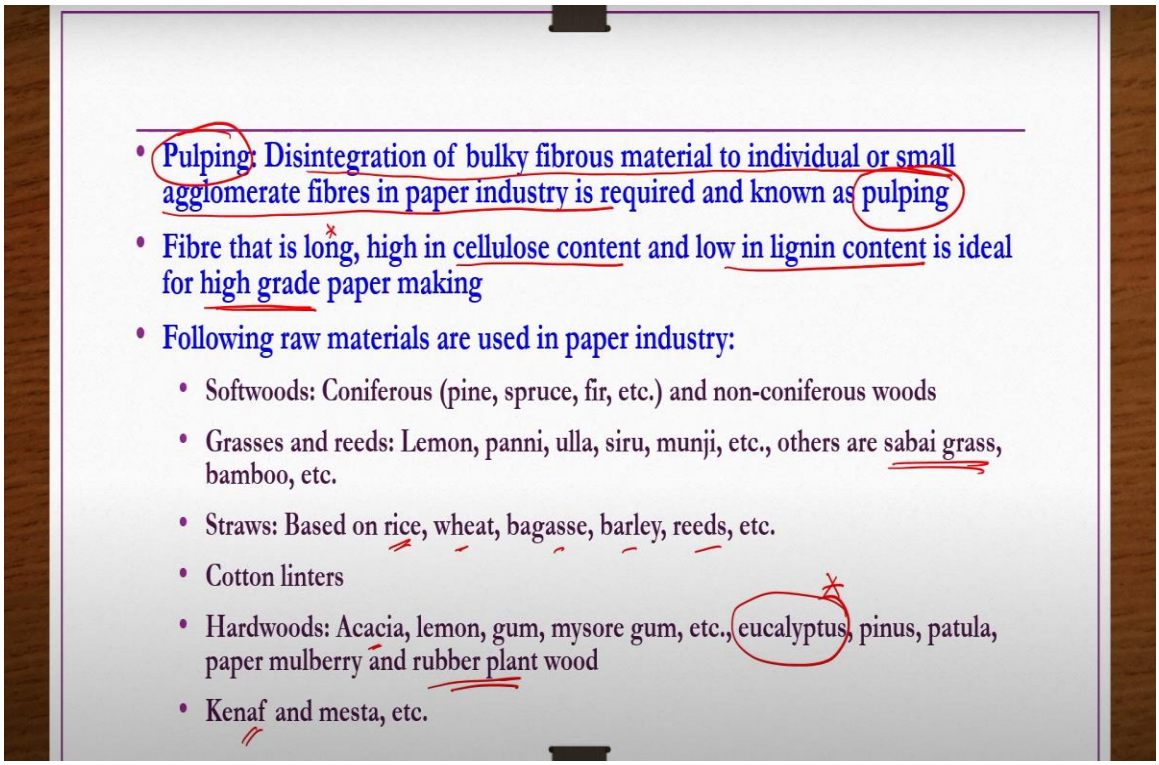

Now let us see what is pulping. So pulping is very much necessary in paper industry. It is nothing but disintegration of bulky fibrous materials to individual or small agglomerate fibers in paper industries. So that is very much essential and then that disintegration of bulky fibrous material into individual or small agglomerates is known as the pulping. It is very much essential in the paper industry. If the pulping is successfully done so then the paper quality is going to be better. As already mentioned fiber that is long high in cellulose content and low in lignin content is very ideal for high grade paper making. Now we see a

few types of raw materials that are used in paper industry like soft wood, hardwood, grass and reeds etc. Different kind of raw materials are there.

It is a classification of raw material actually. Many of these raw materials can be used to get the pulp out of them and then that pulp should be having such kind of characteristic that a proper paper can be made. So let us start with soft woods. Coniferous like pines, spruces, fir etc. such kind of woods. Even non-coniferous woods can also be utilized for making papers or in the paper industries. Then grasses and reeds are also used something like lemon, panni, ulla, siru, munji etc. Some other grasses are sabai grass, bamboo etc. are also used. And then straws are also used as a raw material for making papers based on rice, wheat, bagasse, barley, reeds etc. There are straws used for paper making. Cotton linters are also used. Hardwoods also like acacia, lemon, gum, mysore gum etc. eucalyptus. It is used more. Pines, patula, paper, mulberry and then rubber plant woods etc. are also used for making paper. Some high fiber yielding plants like Kenaf and mesta etc. are also used for making papers. These are the some types of raw materials. There may be other types of raw materials are also possible to make paper. But however, we have listed the most possible ones here.

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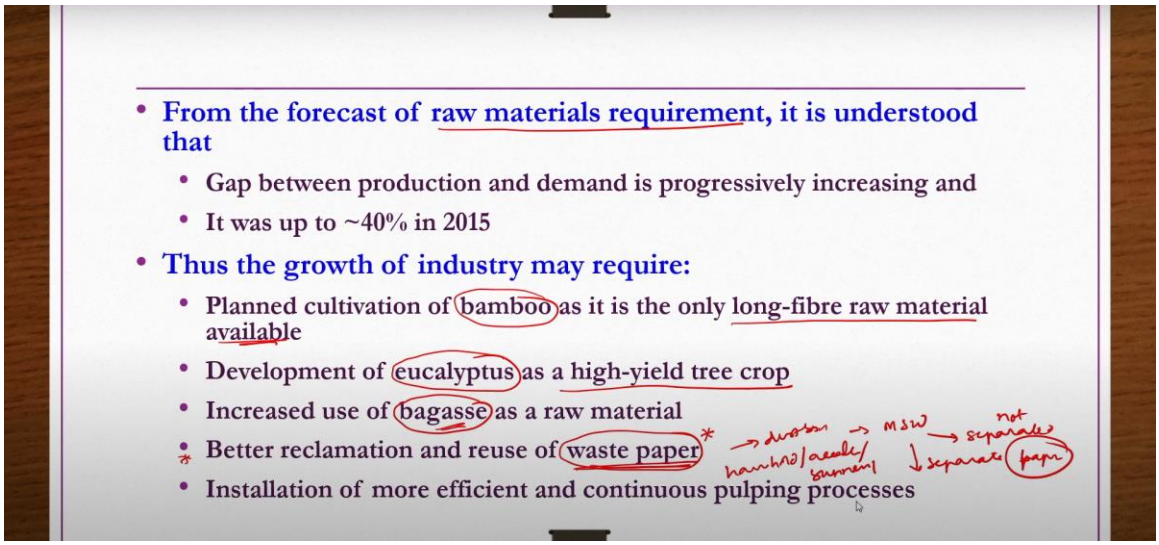

Now, from the raw materials requirement point of view, if you see the gap between production and demand is progressively increasing obviously, and then it was almost like

40 percent in 2015. So, in today's context, it may be even higher, right? So, there should be some kind of measures to take so that the paper industrial growth should not be limited or stopped, okay? So, growth of industry, paper industry may require following actions, right? The very first one is the planned cultivation of bamboo because bamboo is a base raw material for making pulp and paper. As it is the only long fiber raw materials that we are having, then development of eucalyptus also as a high yield tree crop would make this industry progress better. Increased use of bagasse as raw materials because bagasse from the sugar manufacturing from sugar cane industry whatever is there that bagasse is primarily used as a cattle food or as fertilizer in some kind of agricultural fields. If we can use such bagasse also for making pulp and then in a paper then it is going to be very beneficial for the industrial growth point of view, especially paper industry growth point of view.

Better reclamation and reuse of waste paper, actually waste paper in general without being separated they are being thrown in dustbins and then from the dustbins it goes to you know, municipal solid waste where it is if it is not being separated then it is going as a waste. So, what you have to do? You have to do the separate paper, waste paper from such kind of waste or collection from the household academic or you know business fields, you know whatever the paper is there that should be collected separately and then that paper if you reuse after removing the color, imparting pigments etc. from such old paper or waste paper and then you use it as a raw material for production of pulp and paper it is going to be even better. And then it is going to be very essential from environment concern point of view, how many plants we can grow and then cut, it is taking time also.

So, in that time the prices may also go higher. So obviously from the environmental point of view rather cutting trees it is better to use the existing wastage as a resource to produce new product, okay? Like here in waste paper you can use to produce new papers etc., new pulp etc. In fact, you are also recovering some amount of pigment chemicals also you will

be able to recover if you follow this particular step. And then installation of more efficient and continuous pulping processes may also improve the growth of paper industry.

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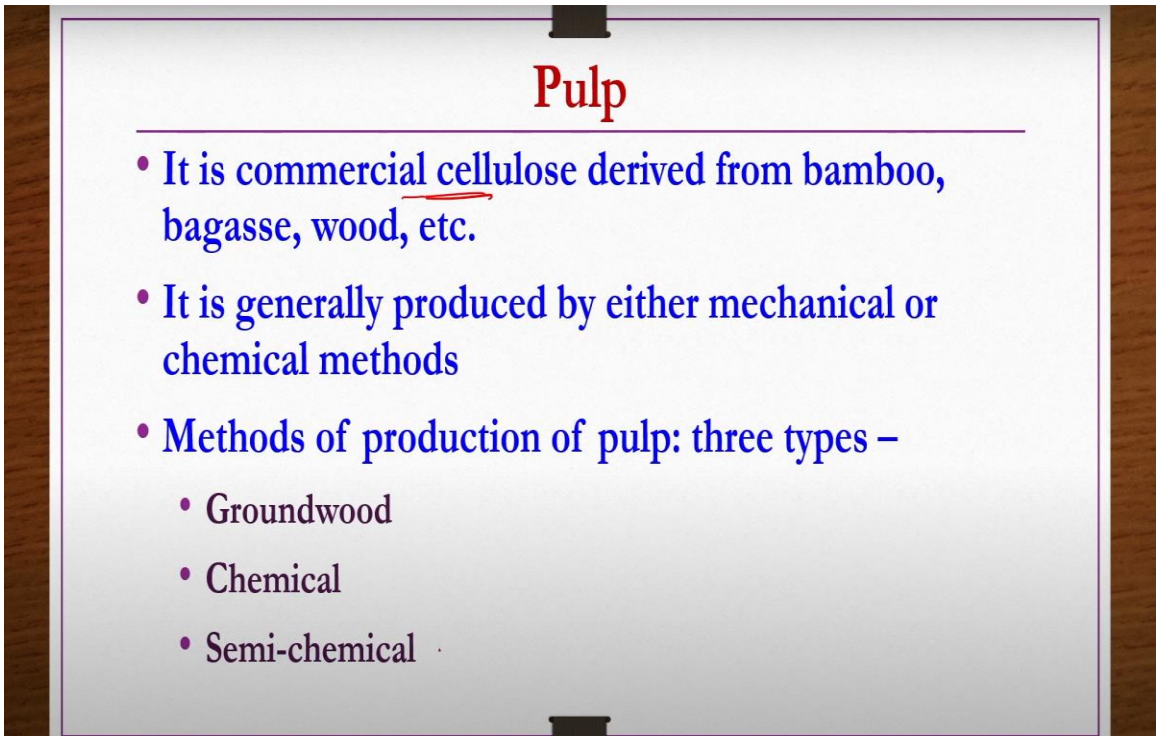

Now, we discuss about pulp. It is nothing but commercial cellulose derived from bamboo, bagasse, wood etc. It is generally produced by either mechanical or chemical methods. If you see the production methods, there are 3 methods are available. The first one is the ground wood method which can also be said as mechanical method because in this method whatever the way that we extract the pulp etc. or fiber etc. from the wood only mechanical methods are involved, no chemical treatments are involved, okay? Second method is the chemical method where some kind of chemical treatment would be required to get the required fibers from the wood and then semi-chemical method where only partial chemical treatment, only marginal chemical treatment would be there and then some kind of

mechanical methods would be used to get the required fibers. So semi-chemical method may be seen as a kind of combination of these 2 methods.

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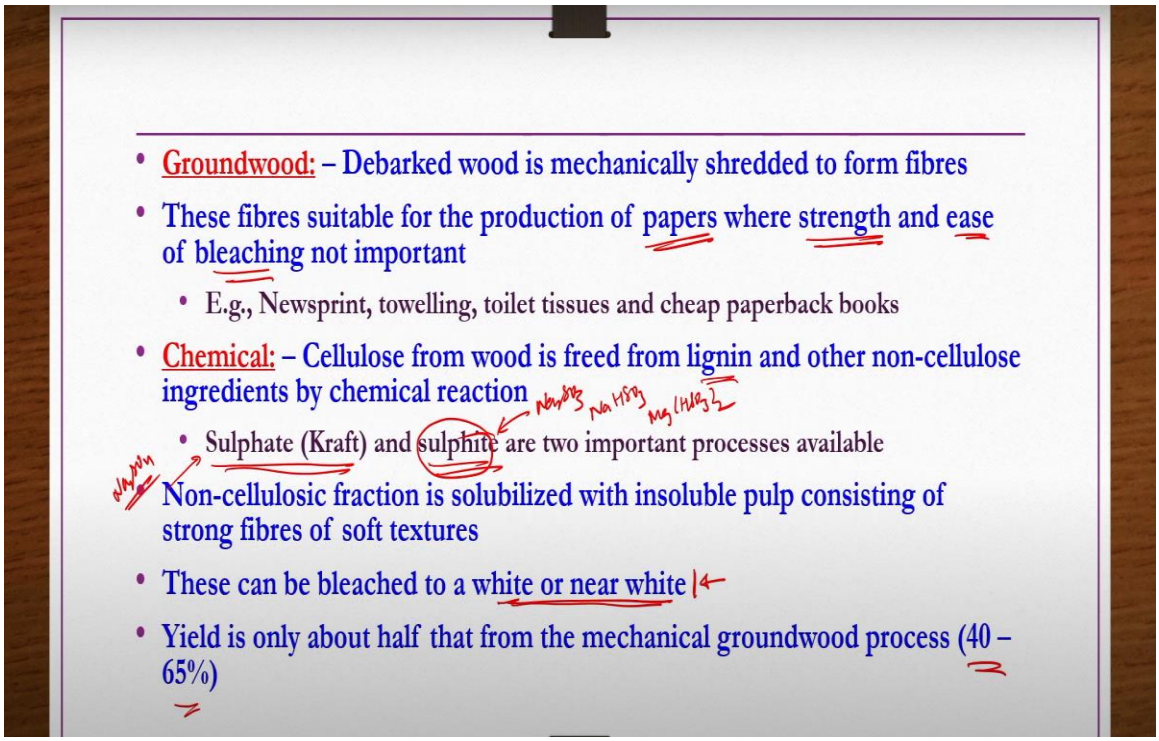

So let us start with one by one method, ground wood method. Here debarked wood is mechanically shredded to form fibers. These fibers are suitable for the production of papers where you do not worry about strength or how is difficult to do the bleaching. Bleaching is very much essential in the pulp and paper industry. So if you are not very much worried, let us say if you are making brown paper etc., those kind of thick brown papers etc., so you do not need to worry about how easy to bleach it or how difficult to bleach it, right? Under such conditions, such fibers may be used to produce such kind of papers. Example newsprint, towelling, toilet tissues and cheap paperback books etc. are produced by the fiber that has been extracted or collected by the ground wood method. Then chemical method, cellulose from wood is freed from lignin and other non-cellulose ingredients by chemical reaction by using mixtures of some chemicals for which there are 2 methods or their important methods, sulphate method which is also known as the Kraft method and sulfite method. The names are because here in the sulphate method, you use Na2SO4

sulphates. In the sulfite method, Na2SO3 sulphates you used or sodium bisulfite or magnesium bisulfite etc., you use in such kind of methods. So that is the reason these methods are known as the sulfite methods, whereas Na2SO4 used such methods are known as the sulphate method or Kraft method. So both chemical processes are existing and both of them are having good applications. Non-cellulosic fraction is solubilized with insoluble pulp consisting of strong fibers of softer textures. These can be bleached to white or near white. When you are doing the bleaching, so then obviously the mechanical strength of the paper in general decreases or mechanical strength of the pulp in general decreases.

So yield is only about half that from the mechanical ground wood process. So yield is approximately 40 to 65 percent only. What does it mean? Whatever the cellulose that is present in the wood, if you are doing the chemical treatment method, you could only collect 40 to 65 percent of that cellulose. You are not able to collect the entire 100 percent of the cellulose that is present in the wood.

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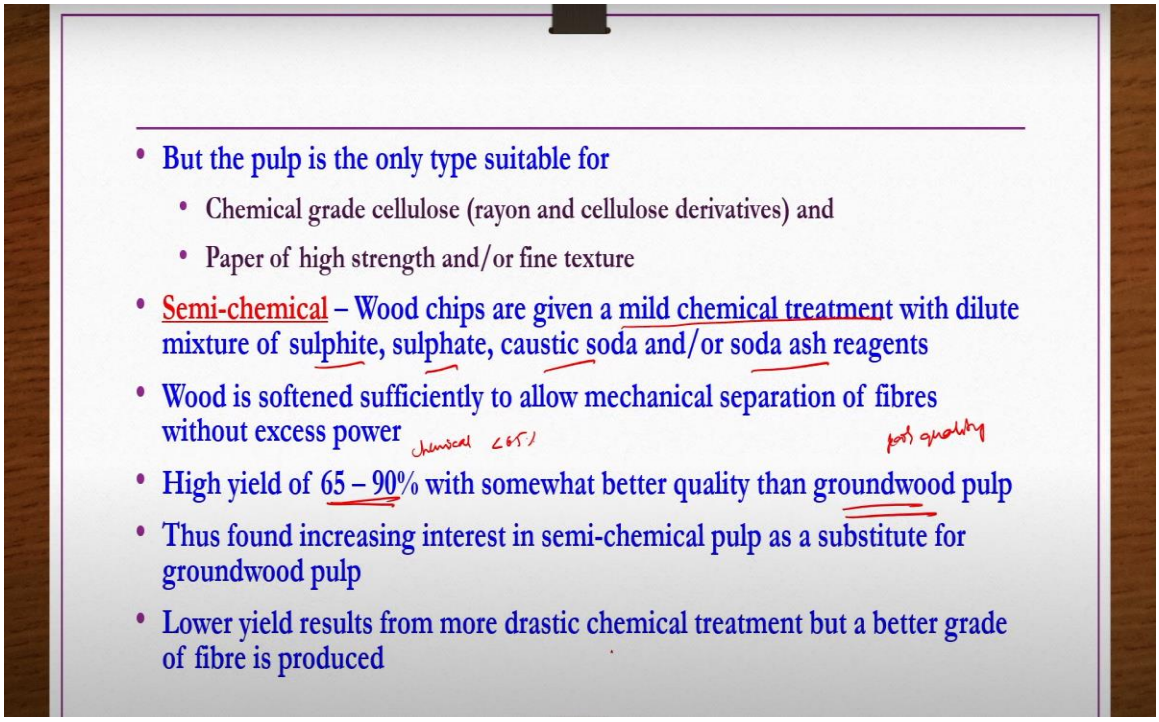

But however, whatever the cellulose that you produce by these chemical methods, they are very good for different applications. That is in other words, whatever the pulp that is

produced by the chemical method is the only type suitable for production of a chemical grade cellulose like in rayon or cellulose derivatives, etc. And then if you are required to make paper of high strength and are fine texture. Next is semi-chemical method. Here as I mentioned it is mild chemical treatment is given to the wood. Then after that some kind of mechanical methods are used. When you give this mild chemical treatment to the wood, then what happen? A kind of loosening of the wood will take place and then extracting or shredding them using the mechanical method should be easier or that can be done with less force or less energy. That is the purpose of this chemical. That is the main difference between the two methods. So though here chemical approach is also involved, mechanical approach is also involved. So it cannot be said as a purely mechanical or purely chemical, it should be said as a semi-chemical method. So wood chips are given a mild chemical treatment with dilute mixture of sulphite, sulphate, caustic soda and or soda as reagents. It is not that all of them are used, depends on the nature of the wood. Some of them are required, maybe mixture of them, some of them are required. In some case, maybe only one would be sufficient.

That depends on the raw material. So the wood is softened sufficiently to allow mechanical separation of fibers without excess power. That is the advantage of this mild chemical treatment in semi-chemical method. Further you get high yield of 65 to 90 percent with somewhat better quality than the groundwood pulp. So now you see the yield is better than the chemical. In chemical methods, yield is only less than 65 percent or something like that, 40 to 65 percent or something like that.

Groundwood, the yield is better but poor quality, strength might not be there or ease of bleaching may not be there in the pulp that is obtained by the groundwood method. So both of such advantages are to some extent overcame by semi-chemical method because of such reasons, it is found increasing interest in semi-chemical pulp as a substitute for groundwood pulp. Lower yield results from more drastic chemical treatment but a better grade of fiber is produced. If you are doing drastic chemical treatment, so then it will

become like chemical method. So then under chemical method, we already know that the yield is lower one though the quality of the paper is better one. So that is what it means by.

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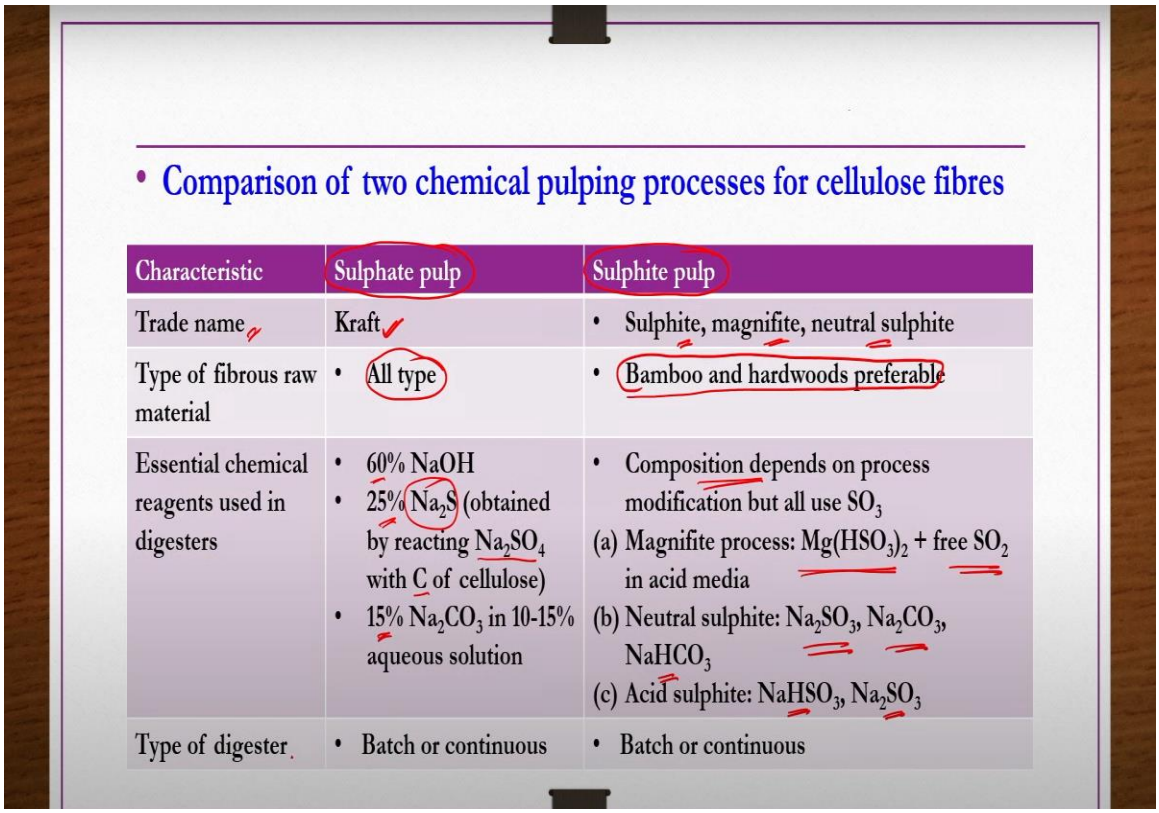

Now we see comparison of two chemical pulping processes for cellulose fibers production like two methods like sulphate and sulfite methods. We see their characteristics, differences, etc. So let us start with trade name. Whatever the sulphate pulp is there, its trade name is the kraft. Whatever the sulfite pulp is there, it is having different trade names like sulfite, magnified, neutral sulfite, etc.

And then type of fibrous raw material required in the kraft method or sulphate pulp method, all type raw materials can be suitable whereas in the sulfite, bamboo and hardwoods are preferable. Next, coming to the essential chemical reagents used in digesters. Kraft method, 60 percent NaOH and 25 percent Na2S obtained by reacting Na2SO4 with C of cellulose, then what you do, you get this Na2S. And then 15 percent Na2CO3 in 10 to 15 percent

aqueous solution or in general used as a reagent. Whereas, coming to the sulfite pulp production process, composition depends on process modification, but all of them use SO3.

So let us say if you have a magnified process, then what you have, magnesium bisulfite plus free SO2 in acid media. If you have neutral sulfite pulp process, then you would use Na2SO3 that is sodium sulfite, sodium carbonate and then sodium bicarbonate. If you are having acid sulfite pulp process, then sodium bisulfite and then sodium sulfite are in general used as a essential chemical reagents. Then coming to the type of digester, you have the batch or continuous, both are suitable for both the processes.

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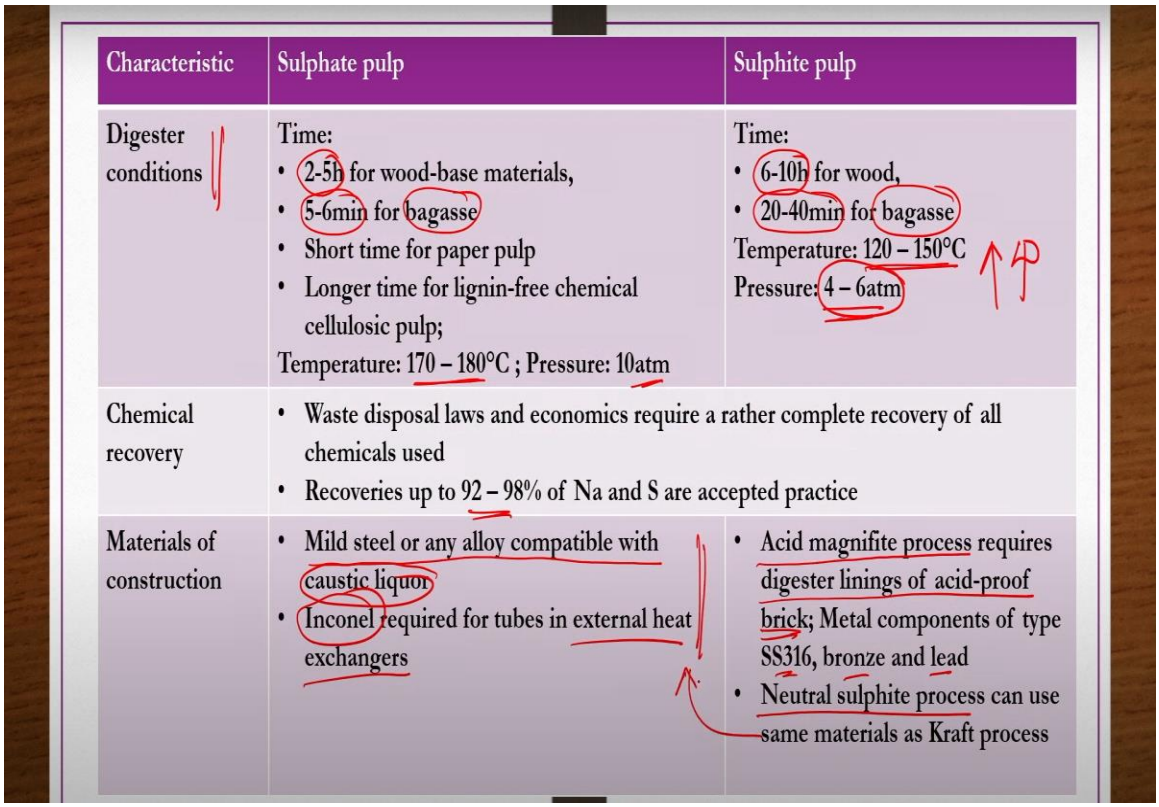

Characteristic	Sulphate pulp	Sulphite pulp
Digester conditions	Time: • 2-5h for wood-base materials, • 5-6min for bagasse • Short time for paper pulp • Longer time for lignin-free chemical cellulosic pulp; Temperature: 170 – 180°C ; Pressure: 10atm	Time: • 6-10h for wood, • 20-40min for bagasse Temperature: 120 – 150°C Pressure: 4 – 6atm
Chemical recovery	• Waste disposal laws and economics require a rather complete recovery of all chemicals used • Recoveries up to 92 – 98% of Na and S are accepted practice	
Materials of construction	• Mild steel or any alloy compatible with caustic liquor • Inconel required for tubes in external heat exchangers	• Acid magnifite process requires digester linings of acid-proof brick; Metal components of type SS316, bronze and lead • Neutral sulphite process can use same materials as Kraft process

About the digester conditions, what you can see here in the sulfite pulp, time required for a given type of raw material is less, whereas time required for the same type of raw material is more in the sulfite pulp. Sulfite let us say if you are having wood based materials, then 2 to 5 hours digestion time is sufficient, whereas in the sulfite pulp making you need 6 to 10 hours. Similarly, if you have bagasse raw material, then 5 to 6 minutes is sufficient in

sulfite pulp making method, whereas if you take the same material and then do the sulfite pulp process, then you need more time, 20 to 40 minutes. This difference is primarily because of the condition that are being used. In the sulfite pulp, you are using 120 to 150 degrees centigrade, whereas in the sulfite pulp process 170 to 180 degrees centigrade can also be used. Pressure 10 atmosphere in sulphate pulp, whereas it is only 4 to 6 atmosphere in the sulfite pulp.

You may be thinking that this you may increase further, this temperature pressure and then reduce the time. No, that is not possible because if these are all the optimized condition, if you play with such condition, the strength of the pulp may not be sufficient enough or maybe subsequent bleaching may not be easy. Such kind of problems may be there or maybe recovery of chemical may not be recovered economically. So, such kind of situations may arise if you use a higher temperature and pressure in the sulfite pulp. If you use the lower temperature and pressure in the sulfite pulp, then it is possible that the yield might not be sufficiently good enough or the lignin removal from the wood may not be completed.

Cellulose whatever you are getting in that one some fractions of lignin may also be there. So, all these factors are there primarily the removal of lignin how efficiently you are doing and then or how efficiently are you maximizing the cellulose recovery and then reducing the lignin content in that one. That is how these conditions are optimized. Coming to the chemical recovery whether the sulphate pulp process or sulphite pulp process waste disposal has to be done as per the laws. Waste disposal laws and economics require a rather complete recovery of all chemicals used up to 90 to 98 percent of recovery of sodium and then sulfur from the waste liquor whatever is there that is sufficient enough and then acceptable in general.

Coming to the materials of construction for the sulphate pulp process mild steel or any alloy compatible with caustic liquor is required. Whereas for the external heat exchangers, inconel material is required for the tubes that are present in the external heat exchangers because of the caustic nature of the liquor that is present. Whereas in sulphite pulp process, let us say if you have acid magnified process it requires digester linings of acid proof brick

because acid is involved in the making of pulp in this acid magnified process and then metal components of type SS 316 bronze and lead are required. Let us say if you have a neutral sulphite process, then you can use the equipment whatever that you use for the sulphate process or the material of construction that you use for the sulphate process, the same thing may be used for the neutral sulphite process.

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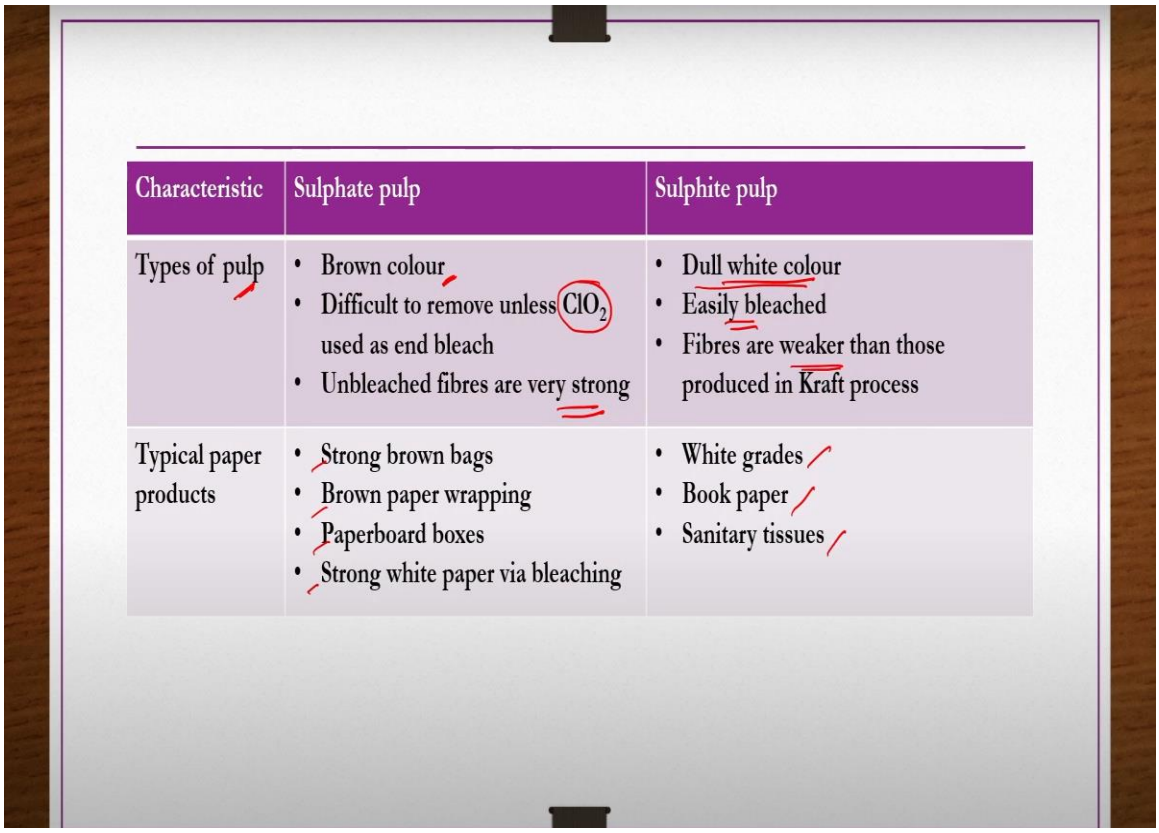

About the product point of view, let us say if you consider types of pulp, then sulphate pulp is brown in color and difficult to remove color unless chlorine dioxide is used as a bleaching agent which is again expensive and then we are going to discuss it has been replaced nowadays by hydrogen peroxide and sodium hydroxide. If you do not do the bleach, then unbleached fibers are very strong, okay? So flexibility may not be there. If the fibers are too strong, then flexibility in the final paper it may not be there, okay? Now coming to the sulphite pulp, it is dull white color. Since the color is almost close to the white color, it can be easily bleached or the bleaching could be done easily without much

effort, okay? Fibers are weaker. Obviously, when the enough bleaching has already been done, so then fibers would become slightly weaker. Now coming to the typical paper products, from the sulphate pulp, you can make strong brown bags, brown paper wrapping, paper board boxes, strong white paper via bleaching, etc. you can produce. From the sulphite pulp, you can make white grade papers, book papers, sanitary tissues, etc. you can make because the fibers are weaker and then they are white in color or dull white in color.

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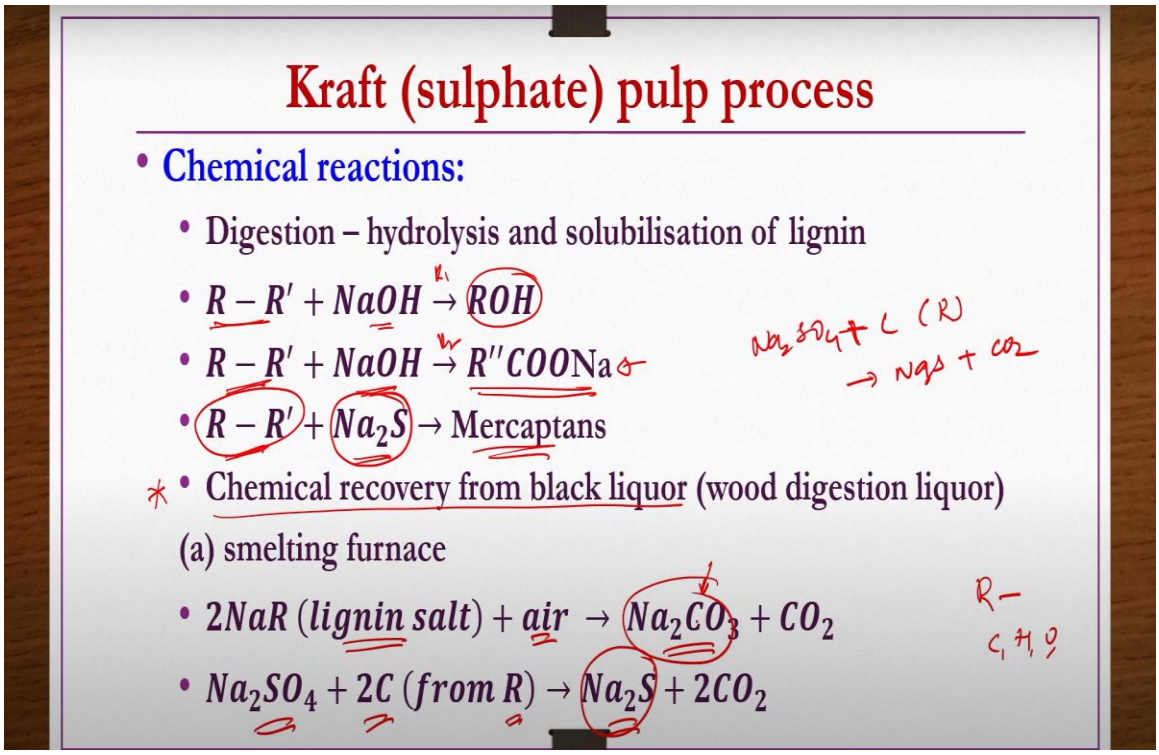

Now we are going to discuss about kraft pulp process which is also known as the sulphate pulp process because of use of Na2SO4 in the process. This process is known as the sulphate pulp process as already mentioned. Its commercial name is Kraft pulp process. If you see the chemical reactions, digestion hydrolysis and solubilization of lignin reactions if you see, let us say whatever the wood material is there that is biopolymer, so then that is represented by R, R prime. If it reacts with NaOH, then you get the cellulose ROH. Cellulose are having such kind of structure, R is different and then different structures is possible that we are going to discuss in cellulose and cellulose derivatives anyway, okay? The same R, R prime whatever the wood or biopolymer is there that reacts with NaOH,

then you can get cellulosic esters like R double prime COO Na that is also possible. The rate of reactions may be different here. So though the reactants are same, you know different products are produced at different rates and different rate constants may be there, okay? Other possibility that the same biopolymer whatever the wood etc. that is taken as raw material that reacts with Na2S which is coming from let us say you have Na2SO4 and then the carbon that is present in R, whatever this R is there that carbon is there, so then what you get? Na2S plus CO2 you get. That Na2S if it is being utilized by this wood raw material again to get mercaptans. Now chemical recovery from black liquor, it is very essential actually you know in the paper making pulp and paper making process, huge quantity of water is used and then huge quantity of liquor is being produced. That liquor is black in color, green in color or brown in color by different types of process that you are going to use. The color is coming because of some kind of chemicals that are present, right? So such chemicals has to be recovered and then white liquor only has to be reused within the digester or after checking the BOD that should be discarded if not useful in the process, right? So chemical recovery from the liquor is very, very important step in the pulp and paper industry.

That is the reason in the pulp and paper manufacturing process, we are separately discussing about the pulp making and then separately discussing about chemical recovery after discussing the pulp process and then separately we are discussing about so called paper making, okay? So in the chemical recovery options, smelting furnace is one of the important step where lignin salt whatever Na or such kind of salts are there, they will react with air or oxygen that has been supplied or preheated air is in general supplied to the smelting furnace. So that preheated air and then this lignin salt will react to give Na2CO3 and carbon dioxide. This can be reused as per the requirement and then sulphate, sodium sulphate whatever is there that will react with the carbon and that is available in the R. R is the chain, organic chain, whatever the organic structures are there, you know, it may be having CH, O, etc., these kind of contents may be there. So that C whatever that is present in R, you know, that would be reacting with Na2SO4 and then you get Na2S plus 2CO2. So you can recover this one, right? They are all present in black liquor in a dangerous form, right? So if you do this kind of reaction, so then what will happen? You can get some kind

of chemicals which you can easily recover. How? That we are going to discuss in the next lecture.

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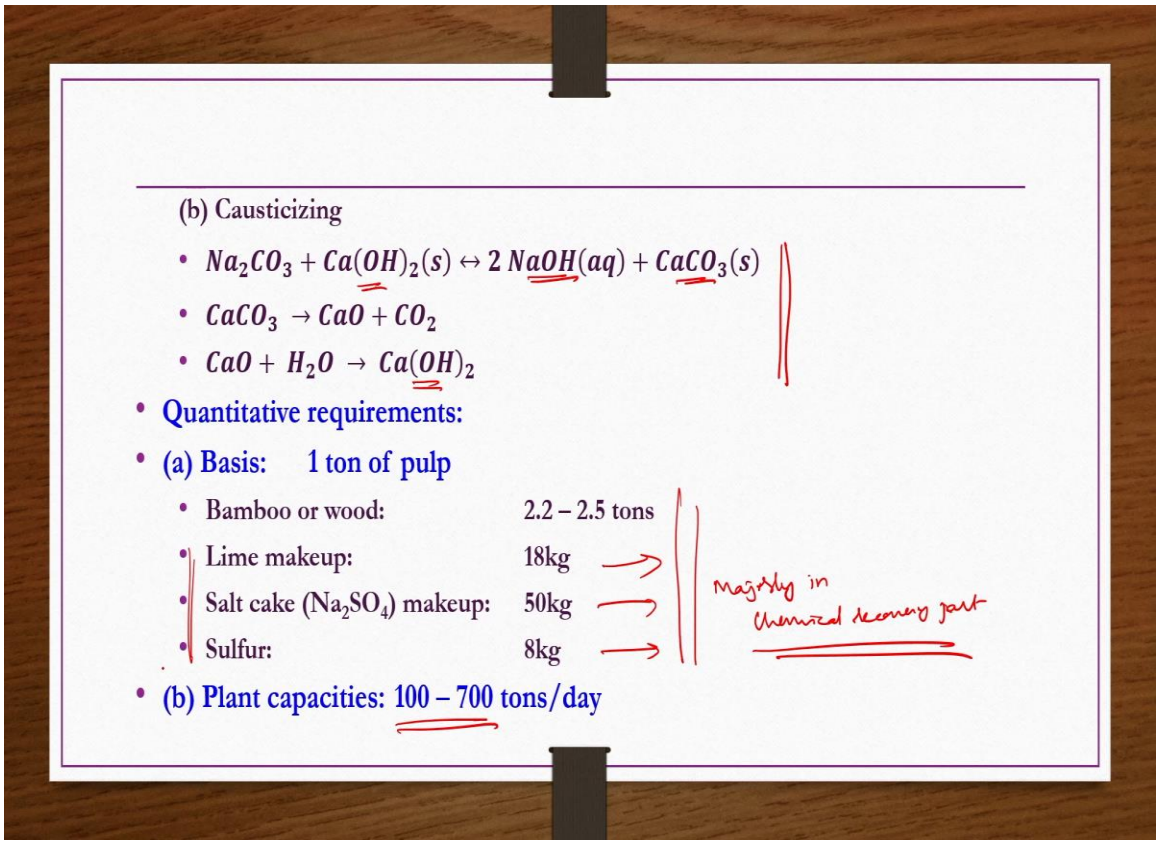

Then in chemical recovery of black liquor, causticizing is another important step. Na2CO3 reacts with calcium hydroxide to give NaOH that can be reused for the digestion purpose and then it also produces calcium carbonate. This calcium carbonate decomposes into calcium oxide and carbon dioxide. Calcium oxide may be reacting with water to give the calcium hydroxide which may be reused to causticize the sodium carbonate. So you know, NaOH whatever required for the digestion that can be, you know, produced from the Na2CO3, that Na2CO3 is being produced, you know, from here, from the lignin salts, right? So whatever the lignin salts that are present in the liquor, you know, you can do the smelting process to get Na2CO3 and then do the causticizing of this Na2CO3 to get the NaOH and then that NaOH you can reuse in the digestion purpose, in the digester, okay? So in this process of getting NaOH from Na2CO3 using calcium hydroxide, you are getting

calcium carbonate that can also be decomposed and then reacted with water to give calcium hydroxide. So again you can reuse within the process for the causticizing purpose. So all these steps we are going to see in a flowchart where we are going to discuss chemical recovery or recovery of chemicals from black liquor, which would be the part of next lecture. Quantitative requirements, basis 1 ton of pulp, bone dry solids basis if you take, then bamboo or wood 2.2 to 2.5 tons, lime make up 18 kgs, salt cake or Na2SO4 make up 50 kgs, sulfur 8 kgs, plant capacity 100 to 700 tons per day. So all these chemicals, you know, whatever the lime etc., salt, sulfur etc. are there, you know, majorly they are used in chemical recovery part. Soon we are going to see in the next slide that you know, this kraft sulphate process whatever are there to make the pulp, several steps are there, right? So one of the important step is the chemical recovery step. So some of these chemicals primarily used there only, but not in the main digester, okay?

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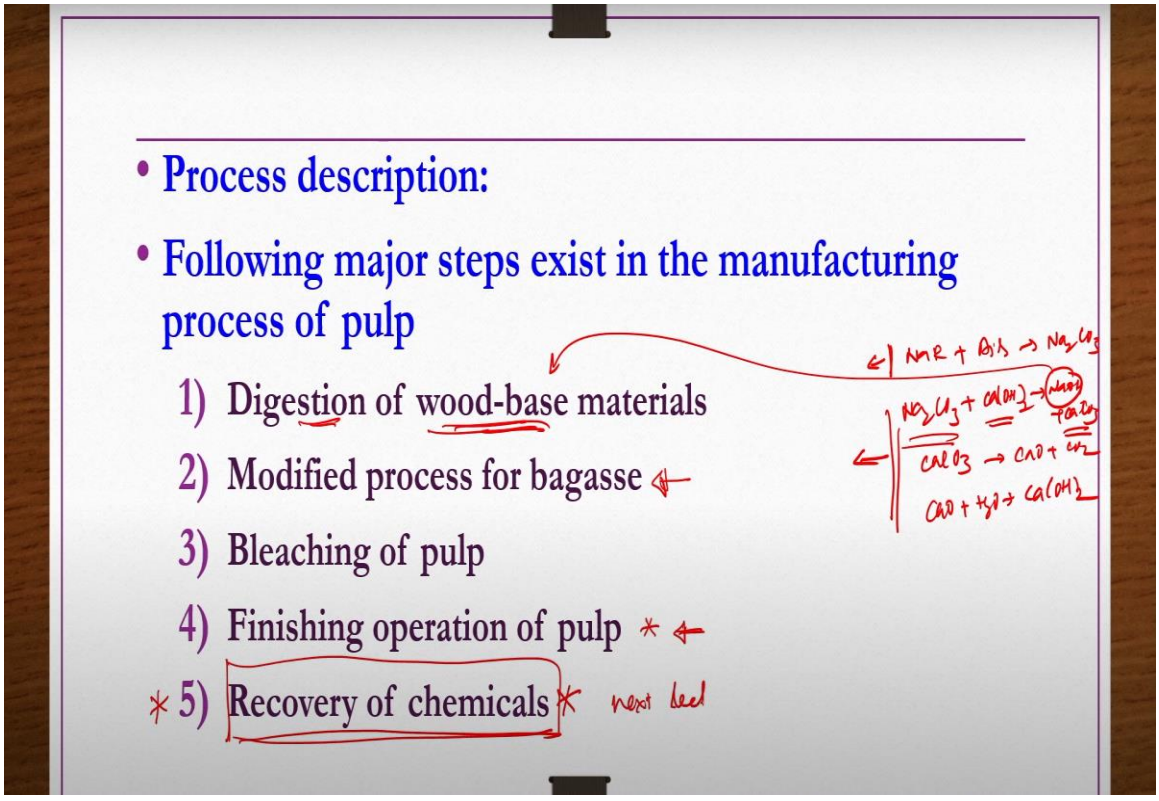

So process description, as I mentioned, major steps that are existing in the process of pulp making using the sulphate process include digestion of wood based raw materials,

digestion. So you need only NaOH that you can get from the black liquor as per the reaction, whatever the NAR is there, that would be reacting with air or oxygen in this smelting process to give Na2CO3. This Na2CO3 reacting with calcium hydroxide to give NaOH plus calcium carbonate, this NaOH is required for the digestion of wood based materials, so that can be used, right? Whereas in order to reduce the wastage or utilization of too much chemical, you know, you try to get the required chemicals, let us say calcium hydroxide is required to get the sodium hydroxide, right? So but you cannot supply too much of external chemicals to recover chemicals from the black liquor. So for that purpose what you do, whatever the produced other chemicals are there, they should be properly utilized. Let us say this calcium carbonate you take and then do the decomposition, you get Ca, CaO, calcium oxide and then carbon dioxide you may get.

This calcium oxide you react with water to get calcium hydroxide. So these are the causticizing steps, this is the smelting step. So here whatever the NaOH required for the digestion that you are getting from the smelting of a black liquor in the smelting furnace, right? And then whatever the NaOH required for the digestion, directly you are not getting from the smelting process, you are getting Na2CO3 from the smelting furnace reactions, that Na2CO3 reacting with calcium hydroxide that is milk of flame separately provided to get the sodium hydroxide, right? So, that sodium hydroxide you can use here for the digestion purpose. Then modified process for bagasse, the process flowchart whatever we are going to discuss, we are discussing primarily about a wood base. So what should be the modification required for other raw materials like bagasse, that also we will be going to discuss.

Then bleaching of pulp is very much essential to make the paper of sufficient whiteness, etc. or for removing the colors from the pulp, etc., it is very much essential. Then finishing operations of the pulp, okay? Like if you are not making paper, let us say, then the finishing operation of pulp is the final operation whether you are making the pulp in 40 to 60% solids or 90% solids, remaining water, etc., that all should be done according to the steps explained in the finishing operation of the pulp as we are going to discuss. The recovery of chemicals as I mentioned, it is very, very essential both from the economics point of view as well as from the environmental concerns point of view as well. However, this part we

will be discussing in the next lecture. Today's lecture, we will conclude after discussing these 4 steps.

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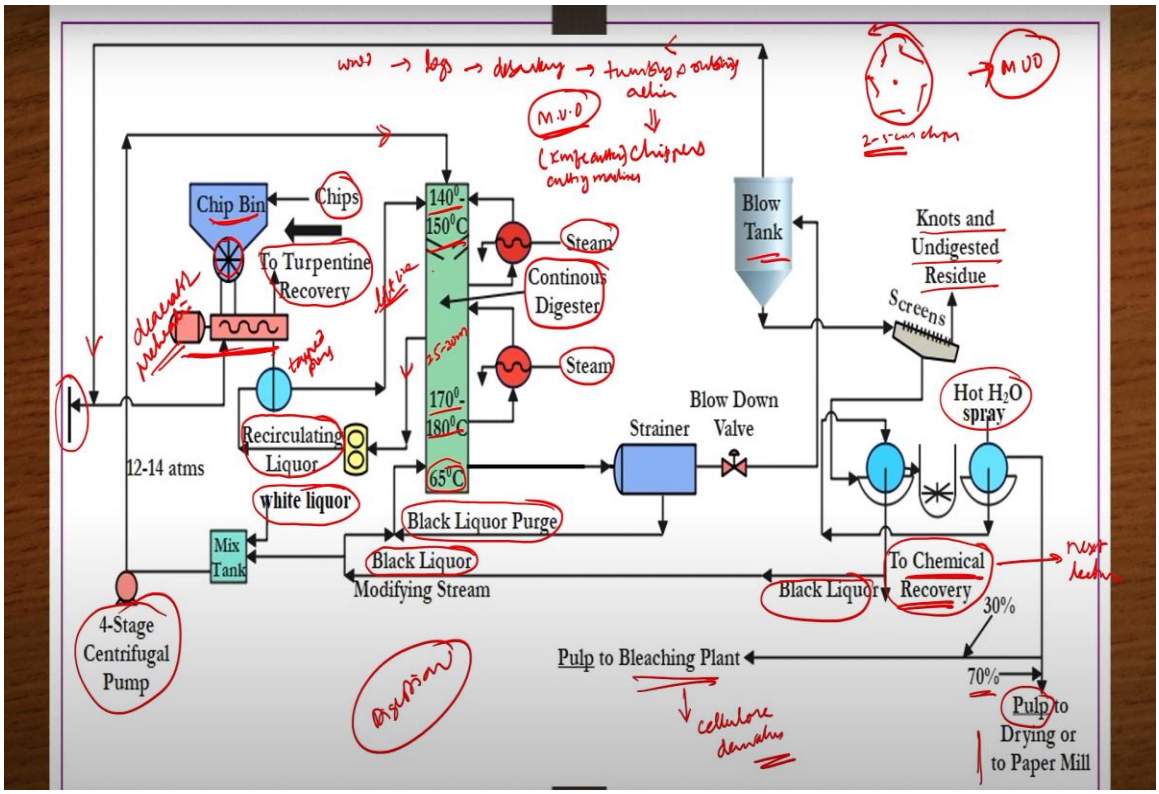

So, let us start with the flowchart of a Kraft sulphate pulp process, right? Here whatever the wood that is there, you know, that actually logs you take, you know, it may be having the box, etc., so debarking of logs has to be done and then you do some kind of tumbling and rubbing actions, right? Then whatever the material that is there after getting this tumbling and rubbing action, you take it to the so called chippers. This chippers is nothing but you know, something like knife cutters or cutting machines. These machines, about these machines and then tumbling and rubbing, about tumbling and rubbing mechanical unit operations, etc., you study in the separate course on mechanical unit operations, which is also available in the NPTEL online portal, okay? So here these knife cutters what happened, let us say you have the drums which are rotating and the inner circumference of drums what you have, you have different types of you know, knives connected like this, right? So these knives what they do, when this drum is rotating, they will also rotate in

different direction without interacting with each other, right? But when the material fed here, so that material wood, material whatever is there, that would be broken down into the small chips, they would be broken down into the small chips like 2 to 5 centimeter chips, etc.

So the size, how much product chip size that you want that depends you know, accordingly you have to rotate the drum and then accordingly you have to have the number of knives and then size of the knives, etc., may be you know, decided accordingly, okay? So cutting machines, you can see details of such cutting machines in mechanical unit operations course available in NPTEL MOOCs portal anyway. Such chips you take to each chip bin, then using a star valve, you send them to this, this is nothing but deaerator, if any air, etc., is present and then preheater. So both operations are done in this deaerator and preheater, right? So after some time when sufficient deaeration and then preheating has been done, that is in order to make sure that moisture, etc., whatever is there that has to be removed, okay? So here whatever the moisture, etc., anything, turpentine recovery, etc., are there, so they would be recovered if at all possible, that depends on the raw material to raw material, right? So after these preheating steps, the material would be taken through rotating tapped plug which is rotating. Using this one, you transfer the material to the lift line, this is the lift line actually, okay? From this lift line, the material goes to the continuous digester, this tall column, green column, whatever is there, that is 25 to 30 meters tall, continuous digester is there.

Since this material whatever chips are there, they are dry, they are solids, they may not easily transported to the continuous digester. So then for that purpose what you do? You send a recirculating liquor along the lift line at certain pressures, so that recirculating liquor will carry and then drop the material or the wood chips at the top of the continuous digester. To this continuous digester what we are getting? We are also feeding liquor, which liquor? White liquor, that is after removing the chemicals from the liquor. So because in this process what you can see, you are getting the black liquor actually. This black liquor has to be treated to recover chemicals, right? So after recovering these chemicals, whatever the clear white liquor is there, that we call white liquor, that you take into the mix tank,

sometimes you know black liquor may also be provided, depending on the pressure requirement or the other conditions within the continuous digester.

So that white liquor mixed with black liquor is also sent to the continuous digester through 4-stage centrifugal pump, right? Now, this continuous digester is provided with steam heating provisions at different levels to maintain different temperature. Let us say at the top you have to maintain 140 to 150 degrees centigrade. At the intermediate level you need to have 170 to 180 degrees centigrade and then at the lowest level you need to have a temperature 65 degrees centigrade, right? So for that purpose this heat recovery system is required or heat reducing system is required. In order to reduce the heat by the time that wood material that is coming to the bottom of the digester, you know the temperature has to be low enough.

It cannot be at 170 or 180 degrees centigrade. If it is at high temperature and then you are sending to the next level, what happens? The paper would not get the required mechanical strength, right? So how to reduce the temperature from 170 to 180 degrees centigrade? For that reason whatever the black liquor is there that is sent to the bottom of the you know this continuous digester. Whereas in the process you know liquor is also collected from the side stream here and then that would be preheated after passing through a heat exchanger and then send it as a recirculating liquor along the lift line to carry forward or carry up the chips of the wood, deaerated and preheated chips of the wood, okay? So this temperature reduced digestion mixture whatever is there that is passed through a strainer where you recover some amount of the black liquor and then that you send back to the continuous digester for the temperature control here. Remember this temperature control is very much essential actually within this pulp. Accordingly your temperature and then time of operation has to be decided. So that to maintain the temperature like this, okay? Now after passing this strainer whatever the digested mixture is there that would be sent to a blow tank through a blow down valve.

What is the purpose of this blow tank? To recover if at all more heat is there because now 65 degrees centigrade the material is coming in. So some more energy is recovered here and then that is stored as steam. So that steam you know that may be reused for the

preheating purpose within this deaerator preheater chamber or that can also be separately collected for some other different purposes, different heating purposes as well, right? So after recovering more heat from the digested pulp you know what you do? That cool down material you pass through screens, separate out the knots and undigested residues and solids, pulp, liquor, mixture whatever is there that you pass through rotary drum filters, right? Where hot water is sprayed for the possible you know cleaning of the pulp, right? About 70% of pulp is dried and sent to paper mill for the paper making whereas the remaining 30% pulp is sent to the bleaching plant and then from here you know one can take them to the cellulose derivative production plants, etc. for this purpose it is taken after the bleaching. Whereas the liquor that is coming out from this rotary drum filtration process whatever there so that black liquor you have to do the chemical recovery.

This chemical recovery we are going to see in the next lecture how to do this one, right? Some part of this black liquor as I already mentioned is mixed with the white liquor and then sent back to the continuous digester again. Some part of the black liquor is sent to the bottom of the continuous digester to cool down the temperature of the mixture at the bottom of the continuous digestion tank, okay? So primarily here what we are seeing only digestion related things we concentrated here. In the next lecture we will be concentrating more on

the chemical recovery related details through different types of flowcharts, okay? Now the steps whatever we discussed in flowchart those things we see here once again.

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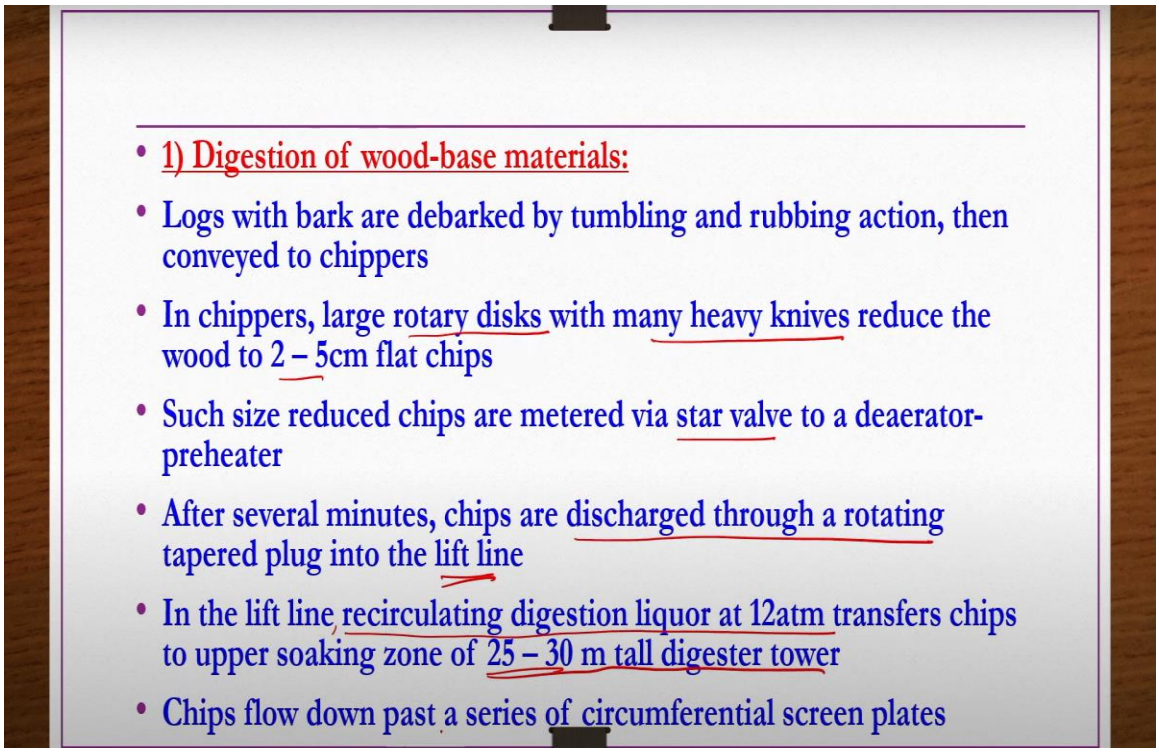

Digestion of wood based materials is the first step out of 5 steps. Logs with bark are debarked by tumbling and rubbing action then conveyed to chippers. In chippers large rotary disc with many heavy knives reduce the wood to 2 to 5 centimeters flat chips. Size reduced chips are metered via star valve to a deaerator preheater. After several minutes of operation in the preheater chips are discharged through a rotating tapered plug into the lift line. Since these are solids they may not be conveyed easily in the lift line. So in order to improve the transportation of solid chips through lift line, recirculating digestion liquor at valve atmosphere is used that transfer chips to upper soaking zone of 25 to 30 meters tall

digester tower. Chips flow down past a series of circumferential screen plates that are present in the continuous digester.

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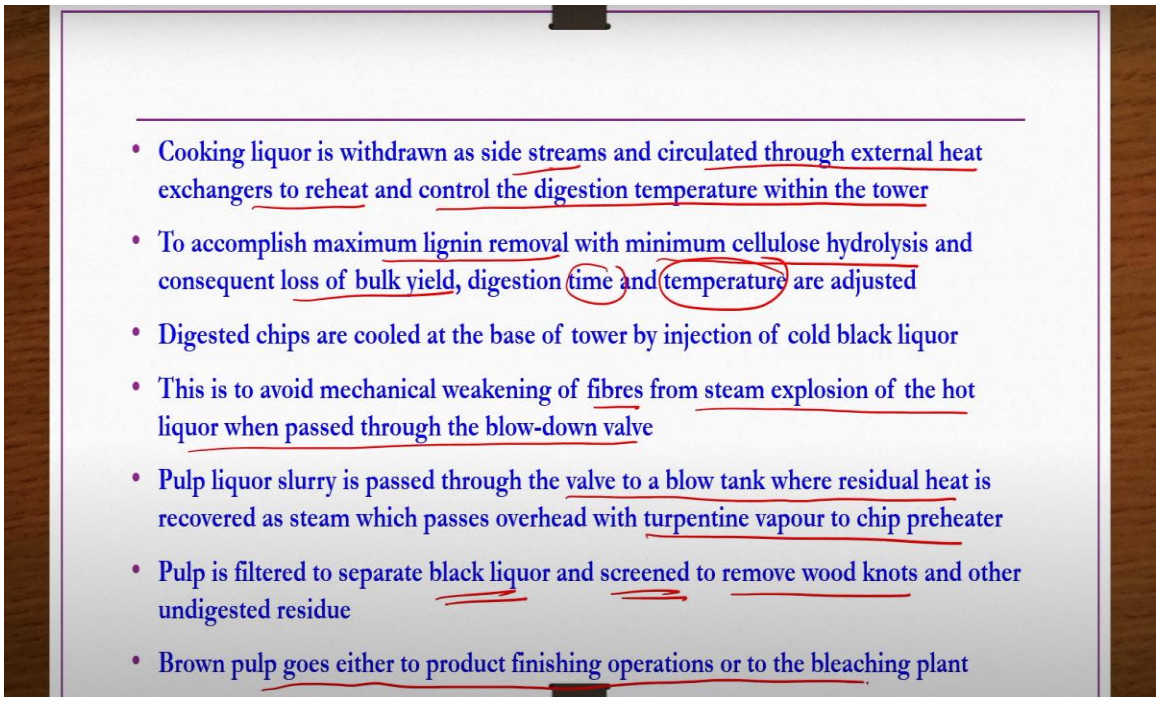

Cooking liquor is withdrawn as side stream and recirculated through external heat exchangers to reheat and control the digestion temperature within the tower and then in order to accomplish maximum lignin removal in the digestion as I already mentioned primarily lignin removal and then increasing the cellulose content that is taking place. With minimum cellulose hydrolysis and consequent loss of bulk yield digestion time and temperature are adjusted. The time and temperature are adjusted such a way that the lignin removal has to be maximum and then cellulose hydrolysis and then loss of bulk yield should be minimum. Digested chips are cooled at the base of tower by injection of cold black liquor.

This is to avoid mechanical weakening of fibers from steam explosion of the hot liquor when passed through blow down valve. Pulp liquor slurry is passed through the valve to blow tank where residual heat is recovered as steam which passes overhead with turpentine vapor to chip preheater. Pulp is filtered and separate black liquor and then screened to

remove wood knots and other undigested residues. Brown pulp goes either to product finishing operations or to the bleaching plant as per the final requirement of the product. What purpose are we using this pulp accordingly? You know either bleaching or you know paper making this pulp has to be sent.

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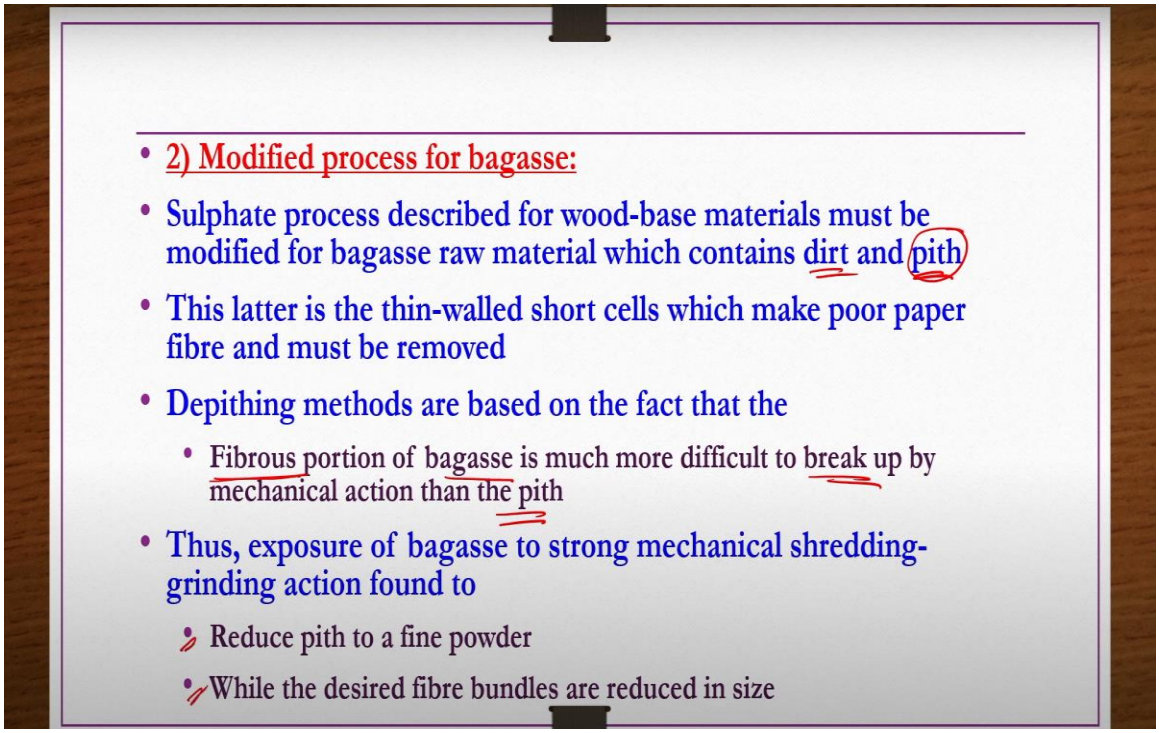

Second step in the kraft process is modified process for bagasse. Whatever the process we discussed in the flow chart is for the wood based raw materials. If your raw material is bagasse then what kind of modifications are required? Sulphate process described for wood based materials must be modified for bagasse raw materials which contains dirt and pith. Actually bamboo is a very good raw material because it gives the long and strong fibers, but it contains lot of dirt and pith. The pith has to be removed.

Actually if you wash the bagasse properly then this pith will go away, but it has to be proper technologically done. Something like wet grinding or wet hammer milling, etc., if you do and then in that process whatever the pith would be there that would be washed away with the water that has been used in the wet grinding mills. This latter is the thin walled short

cells which make poor paper fiber and must be removed. Deep pithing methods are based on the fact that fibrous portion of bagasse is much more difficult to break up by mechanical action than the pith. When you do the hammering kind of process, it is lucky that your fibrous material whatever is there that is not going to be broken down easily compared to the pith. So pith can be easily removed. Thus, exposure of bagasse to strong mechanical shredding grinding action found to reduce pith to a fine powder while the desired fiber bundles are reduced in size. So both the operations have been done by this mechanical shredding method.

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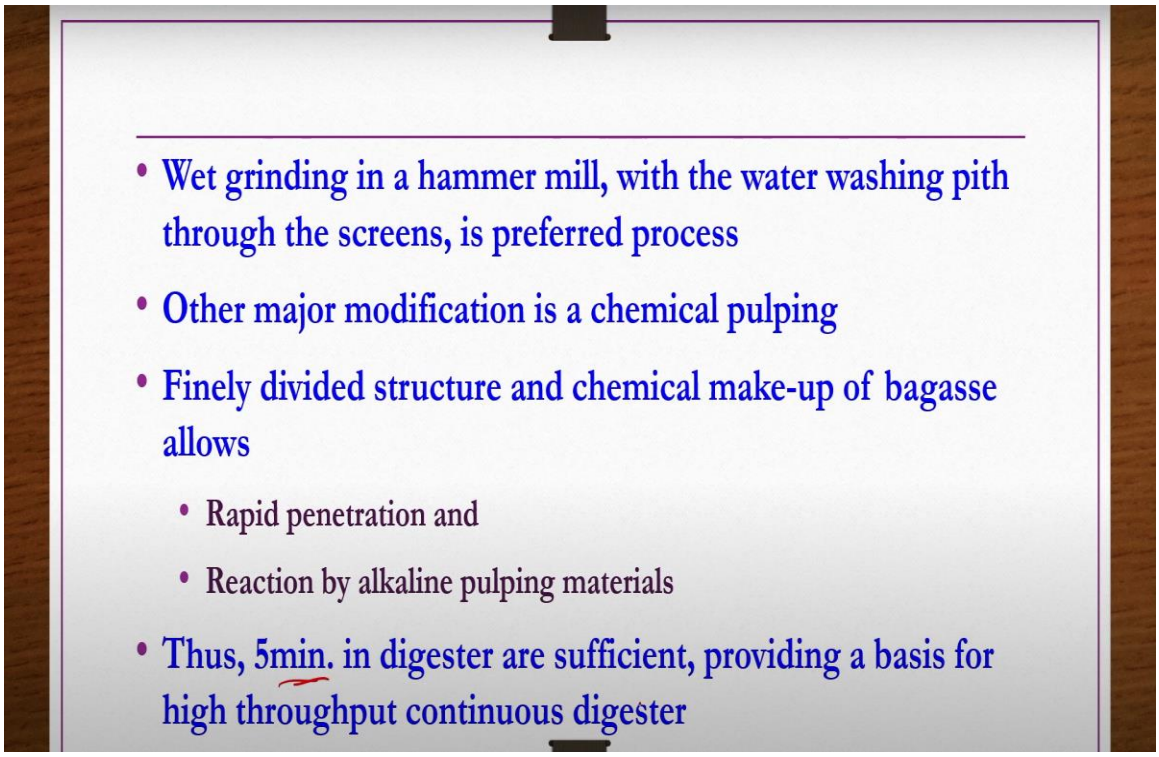

So how it is done? It is done by wet grinding. Wet grinding in hammer mill with water washing pith through the screens is preferred for this purpose. Other major modification is chemical pulping where finely divided structure and chemical makeup of bagasse allows

rapid penetration and reaction by alkaline pulping materials. Thus, 5 minutes in digester are sufficient providing a basis for high throughput continuous digester.

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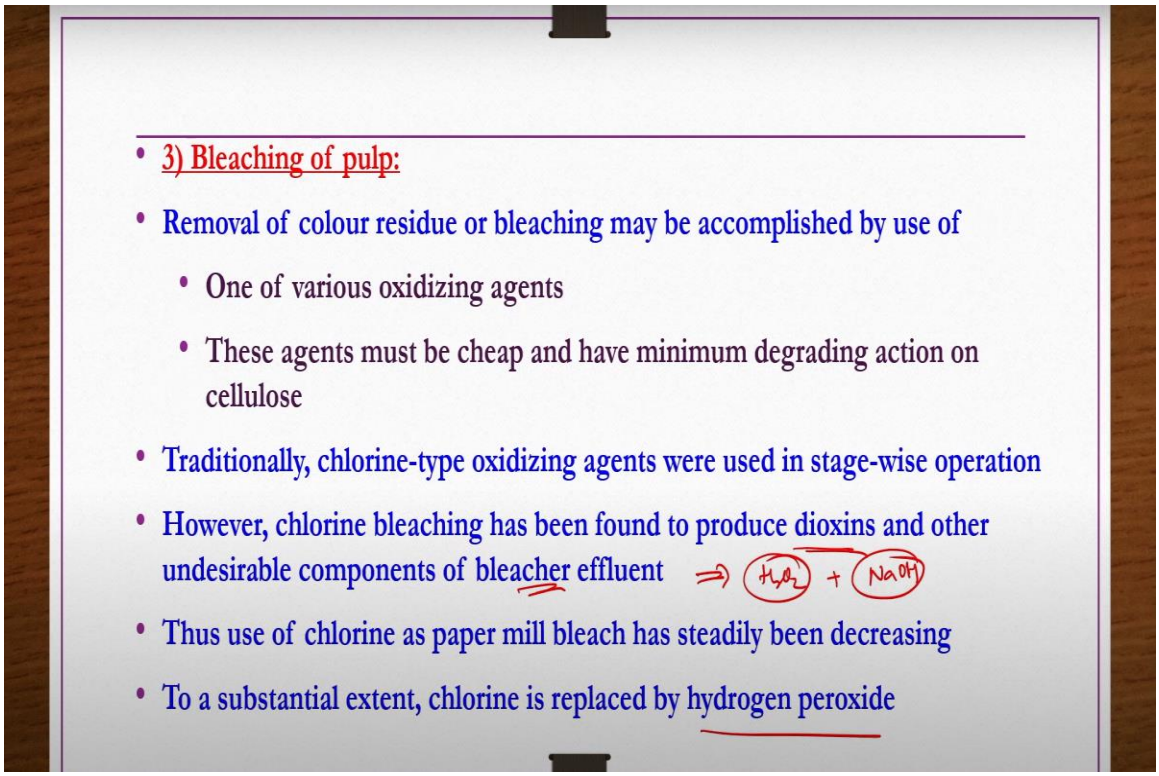

Third step is bleaching of pulp. Removal of color residue or bleaching may be accomplished by the use of different types of oxidizing agents, but such oxidizing agent should be cheaper and then have minimum degrading action such a way one has to use, okay? They should not have degrading action on cellulose. There may be degrading action you cannot avoid, but that should be minimum. Also such agent should be as much cheaper as possible. Traditionally chlorine type oxidizing agents were used in stage wise operations like chlorine dioxide something like that. However, chlorine bleaching has been found to produce dioxins and other undesirable compounds of bleacher effluent. Because of such reasons hydrogen peroxide are primarily used nowadays. Also it is being combined with

NaOH as a bleaching agent. Thus, use of chlorine as paper mill bleach has steadily been decreasing to a substantial extent chlorine is replaced by hydrogen peroxide.

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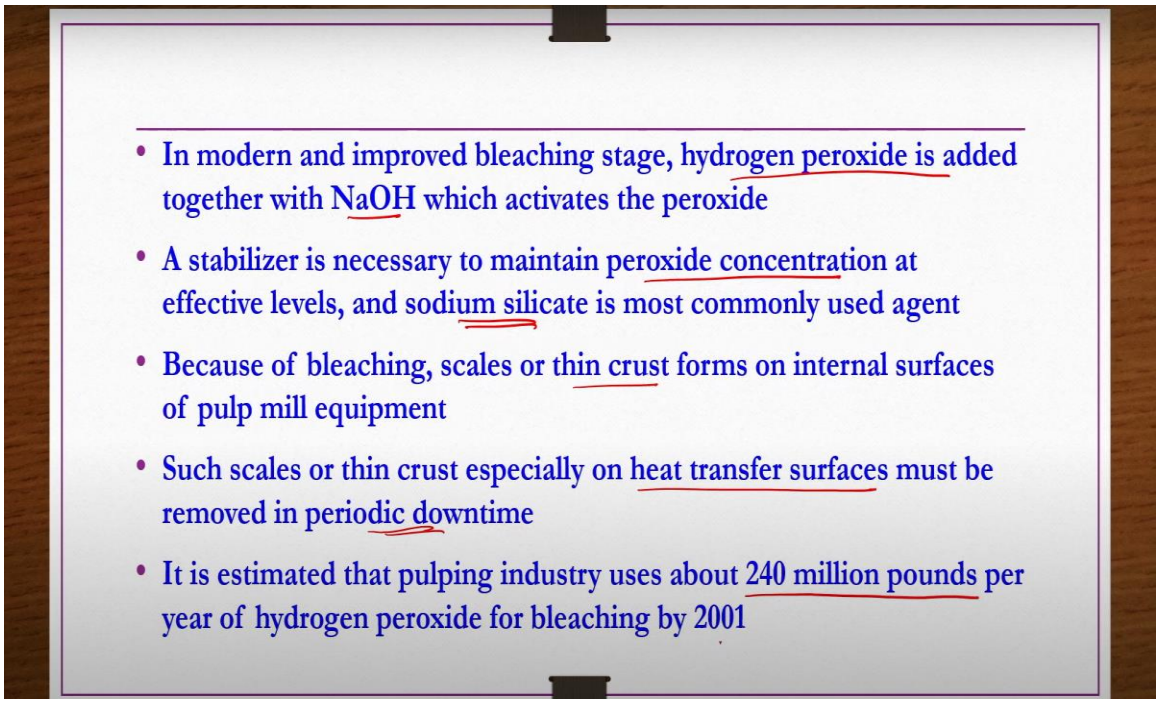

In modern and improved bleaching stage hydrogen peroxide is added together with sodium hydroxide which activates the peroxide, but how much concentration of this NaOH or peroxide is required that has to be balanced. So a stabilizer is necessary to maintain peroxide concentration at effective levels and for that purpose sodium silicate is mostly used. Because of bleaching scales or thin crust forms on internal surfaces of pulp mill equipment especially on heat transfer surfaces whatever the scales or thin crust are formed they must be removed during the periodic downtime of the plant. It is estimated that pulping

industry uses about 240 million pounds per year of hydrogen peroxide for the bleaching by 2001.

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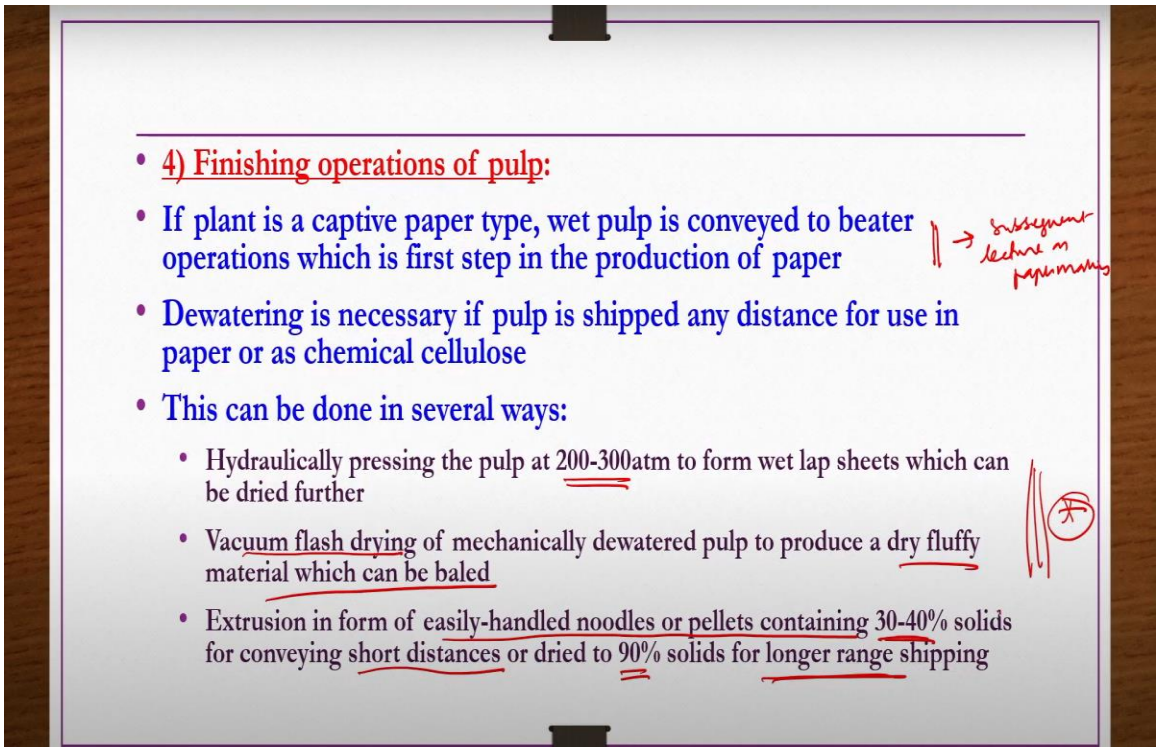

Finishing operations of the pulp, whatever the pulp that is there, so if the plant is captive paper type then wet pulp is conveyed to beater operation which is first step in production of paper. We will be studying about this one in subsequent lectures on paper making. When we talk about paper making, so then this step we can discuss thoroughly, but however dewatering is necessary if pulp is shipped any distance for use in paper or as chemical cellulose for different other applications.

So how it is done? Different methods are there. First one is that hydraulic pressing at higher pressure like 200 to 300 atmosphere to form wet slab sheets which can be dried further. Once doing this hydraulic press what you can do? You can do vacuum flash drying, so that to reduce the water or to make more dewatering of the pulp to produce a dry fluffy material which can be bed. So first you do hydraulic pressing, then you do the vacuum flash drying, so that more and more dewatering can be done. By this time most of the water may be

removed, mostly it is dewatered. Then depending on the application, extrusion in form of easily handled nodules or pellets containing either 30 to 40 percent solids for conveying short distances or dried to 90 percent solids for conveying longer range shipping purpose. So those are the 4 important steps we have discussed. The fifth important step of the recovery of chemicals we are going to discuss in the next lecture, okay?

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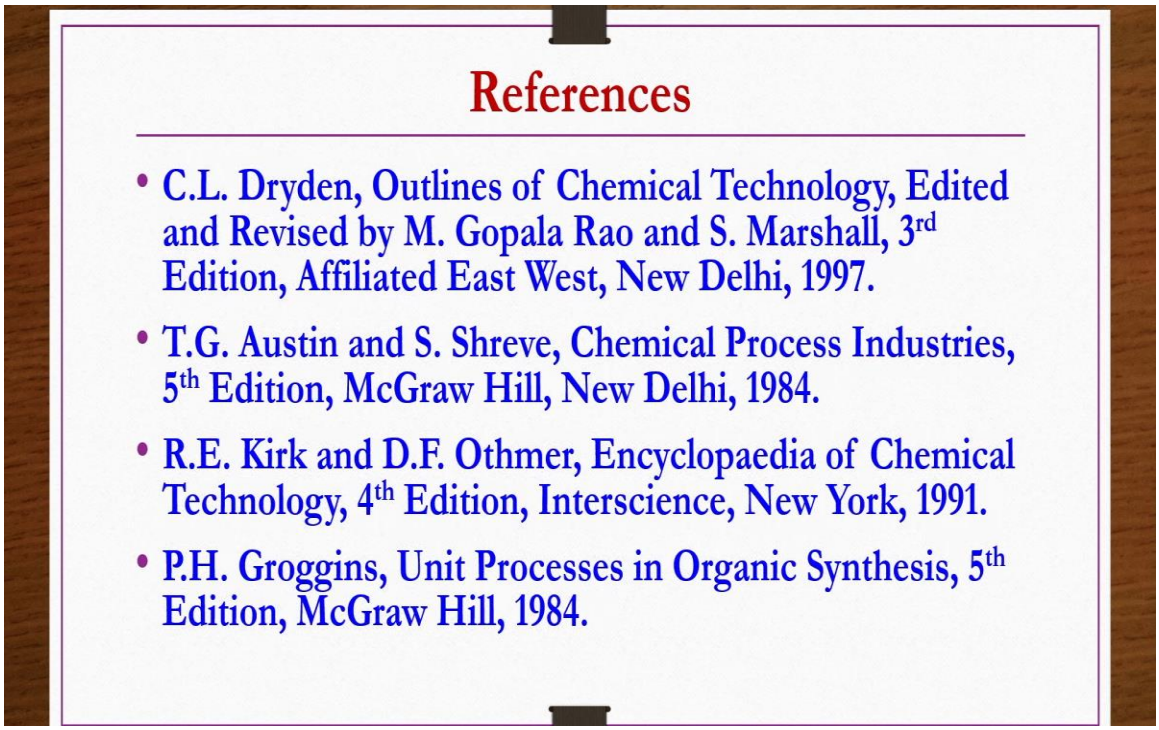

The references for today's lecture are provided here. Thank you