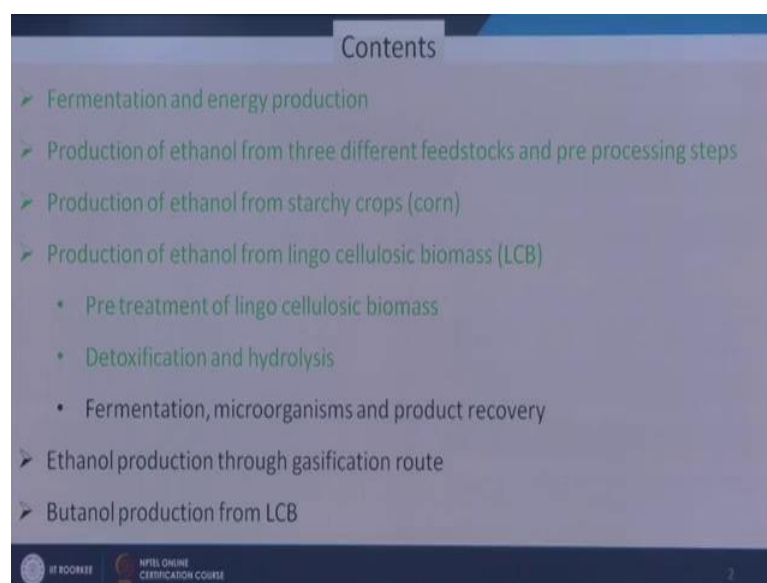


Waste to energy conversion
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Lecture – 30
Energy Production from Organic wastes through Fermentation-1

Good morning. Now we will start discussion on a new module energy production from organic wastes through fermentation. We know that fermentation is a metabolic process in which sugar is converted to acids, gases or alcohol. Basically ethanol and butanol are produced in this suit already we have discussed in the previous module on anaerobic digestion; organic compounds are converted to low molecular weight organic acids through fermentation, and which further converted to methane through methanogenesis steps.

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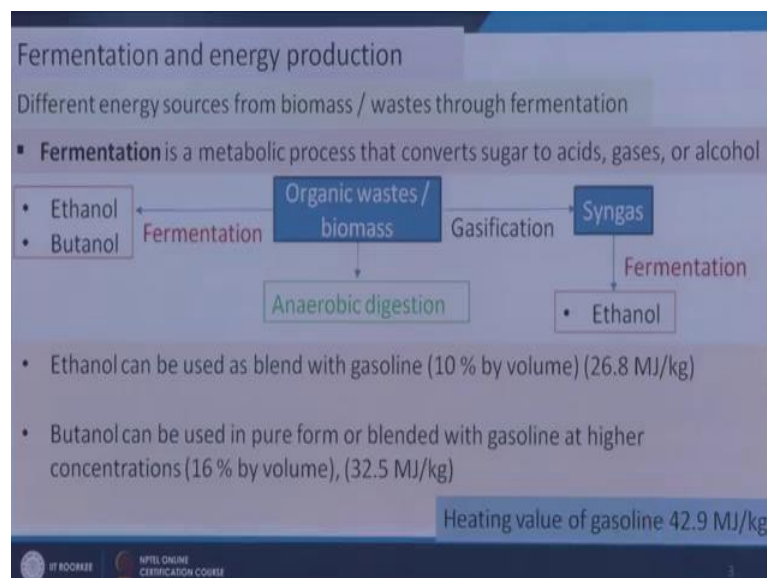


Contents	
➤	Fermentation and energy production
➤	Production of ethanol from three different feedstocks and pre processing steps
➤	Production of ethanol from starchy crops (corn)
➤	Production of ethanol from lingo cellulosic biomass (LCB)
•	Pre-treatment of lingo cellulosic biomass
•	Detoxification and hydrolysis
•	Fermentation, microorganisms and product recovery
➤	Ethanol production through gasification route
➤	Butanol production from LCB

So, in this module we will be concentrated basically on the alcohol production from the organic feed stocks. So, the contents of this module will be fermentation and energy production. Production of ethanol from 3 different feed stocks and preprocessing steps production of ethanol from starchy crops then production of ethanol from lingo cellulosic biomass which will include pretreatment of lingo cellulosic biomass, detoxification and hydrolysis and then fermentation microorganisms and product recovery than ethanol production through gasification route; that means, from syngas to ethanol.

And then finally, butanol production from LCB that is lingo cellulosic biomass. Now we will at first see fermentations and energy productions.

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So, if we use organic wastes or biomass for energy productions we have some options one is directly through fermentation we can get ethanol and butanol. We can make syngas after drying this waste and then gasification, then we will get syngas and syngas can further be converted to ethanol through fermentation process and already we have discussed that anaerobic digestion in which fermentation process converts the organic compounds to acids and then which is further converted to methane. So, we have not concentrating here we will be concentrating basically ethanol and butanol production through these 2 routes.

Now, ethanol and butanol which is produced through these routes can be used in various applications, but as a fuel these compounds can also be used. Because the heating value of ethanol is 26.8 mega joules per kg which is significant amount and for butanol it is 32.5 mega joules per kg whereas, the gasoline is 42.9 mega joules per kg. So, this 2 can be blended with gasoline and can be used as a fuel. Now we will see the methanol fermentation.

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Fermentation and energy production Ethanol fermentation

- It is a series of chemical reactions for converting sugars to ethanol in the presence of suitable microbial strain, which feed on the sugars.
- Ethanol and carbon dioxide are produced as the sugar is consumed.
The simplified fermentation reaction for a 6-carbon sugar, glucose, is as follows:

$$\text{C}_6\text{H}_{12}\text{O}_6 = 2 \text{CH}_3\text{CH}_2\text{OH} + 2 \text{CO}_2$$

Yeast is normally used for hexose

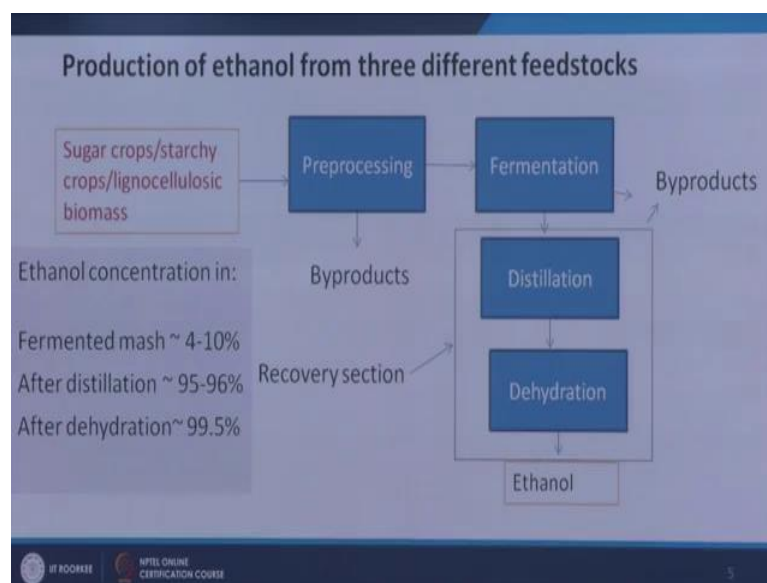
Source of sugar	Sugars may contain
Sugar crops	6 carbons (i.e., Hexose)
Starchy crops	5 carbons (i.e., Pentose)
Lignocellulosic biomass	

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So, what is methanol fermentation? It is a series of biological or chemical reactions for converting sugars to ethanol in presence of suitable microorganisms. And then basically what type of reactions takes place in this case sugar is converted to ethanol and carbon dioxide.

Yeast is normally used for hexose. There are 2 types of sugars may be used pentose and hexose. If hexose is used, then yeast is used and this reaction is representing the ethanol fermentation reaction. So, how this higher form this will come that sugar will come? Sugar can come from 3 types of sources. That is sugar crops starchy crops and lingo cellulosic biomass. So, these 3 types of feed stocks we will be using separately and con discuss separately, how to produce sugar and then the ethanol and sugars may contain 6 carbons and 5 carbons just we have discussed.

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Then production of ethanol from 3 different feed stocks 3 types of different feed stocks basically.

So, sugar crops starchy crops and lingo cellulosic biomass. So, whatever may be the type of feed stocks, if we want to produce ethanol our first step will be preprocessing then we will go for fermentation that is the heart of the reactions or the process. So, the after fermentation the products which will form that has to be purified and the distillation and followed by dehydration is normally followed for the production of ethanol from this feed stocks. So, if sugar is there the preprocessing steps will be very simple then the starchy crops it will be relatively complex and thus lingo cellulosic more complex more steps are required. So, after fermentation ethanol production the concentration here is around 4 to 10 percent distillation gives us ethanol with 95 to 96 percent purity, but we need 99 .5 percent purity for using in blend of gasoline and ethanol.

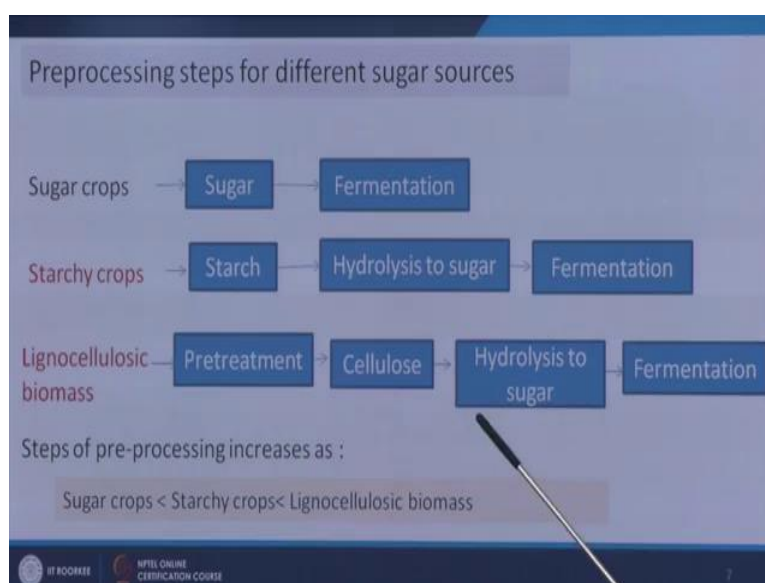
So, some another step that is dehydration step is added for the further purification of this ethanol, particularly to reduce the water content in the methanol which is produced through the distillation process. So, we will discuss later on the detail of dehydration methods. So, ultimately we will get the ethanol and other some bi products we will get. So, this is the process flow sheets now we will consider on preprocessing steps for different types of feed stocks.

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- The ethanol concentration in the fermented mash can attain a level of only 4% to 10% depending on the operating conditions and the strain of yeast being used.
- Ethanol is therefore recovered through distillation but only hydrous ethanol of about 95-96% can be produced through steam distillation of the fermented mash due to the formation of water-ethanol azeotrope.
- To make ethanol fully miscible with gasoline, it is necessary to further remove the residual water to produce anhydrous ethanol with a concentration of at least 99.5%. To attain this concentration, the hydrous ethanol has to undergo a suitable dehydration process or operation.

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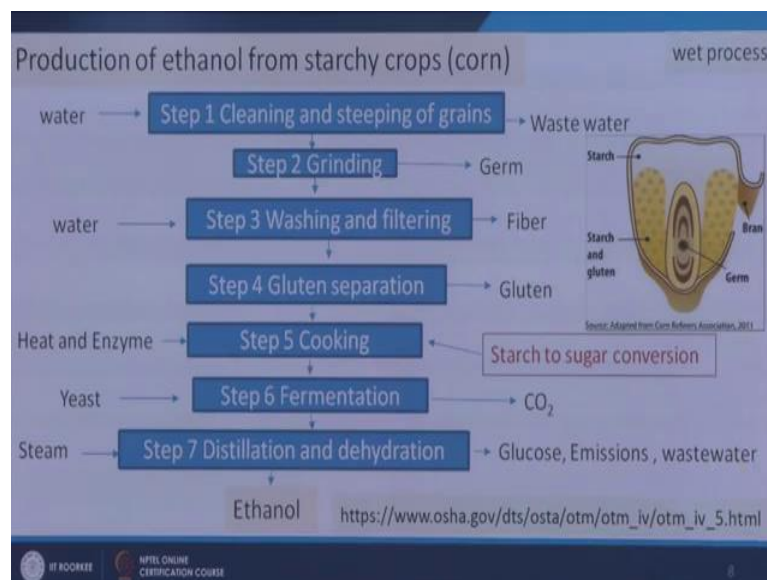


So, this thing already we have discussed. So, if it is a sugar crops, then sugar crops to sugar then sugar to fermentation; simplest method. Then it is starchy crops we will get starch from the starchy crops then starch has to be hydrolyzed to convert it into sugar.

Then sugar will be further fermented. If it is a lingo cellulosic biomass pretreatment is must. Pretreatment then it will give us cellulose and hemi cellulose and then cellulose hemi cellulose will be hydrolyzed to get sugars and then that will be the fermentation

steps. So, the preprocessing steps is varying depending on the feed stocks and sugar crops is less than the starchy crops and then the lingo cellulosic biomass.

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Now, we will concentrate on the production of ethanol from starchy crops. So, one example is your corns. So, in this case the corn, it contains germ, it contains gluten it contains starch and it contains bran. So, these are the composition of the corn.

So, if we want to use these feed stocks for the production of ethanol, there are basically 2 routes one is wet process another is dry process. In the wet process before fermentation different fragments have been separated different parts have been separated from the corn kernel, and then in the dry process the separation does not take place at the initial stage later on the product recovery takes place. So, at first we will see the wet process. So, in the wet process the cleaning and steeping of grains is the first step. So, in this case this is cleaned and this is put in dilute sulphuric acid solution for a longer time, within this period the different parts are more becomes more separable. And then after that steeping it goes through the grinding step. So, grinding step helps to get the jumps out from other materials.

So, germ without any further fragmentations in the germ, so that is the grinding step and then third step is washing and filtering. So, after getting out the germs, washing and filtering will help to get the fiber out. So, once the fiber is out, then all will be in this phase that is solution phase. So, gluten starch etcetera will be there. So, gluten is full of

protein and germ is full of oil. And so starch and gluten that are separated in the gluten separation steps. There are number of steps for this separation after the separation of gluten the remaining solution will be containing starch and that starch has to be converted to sugar and that process is called cooking. So, this cooking means some heat is applied as well as some enzymes are added for the conversion of starch to sugar. And once sugar is produced through this cooking steps then that sugar is sent for the fermentation that it is the step number 6.

So, once the fermentation is over then we have to go for distillations and dehydrations we will get the ethanol. And we can get some here glucose and some emissions and wastewater etcetera. So, these are the flow sheets for the production of ethanol through wet process.

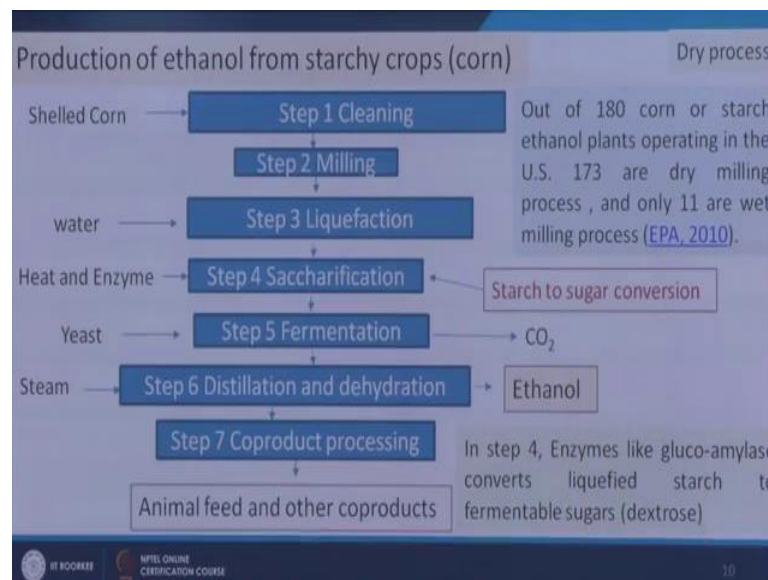
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The slide, titled "Wet process", describes the initial steps of corn processing. It begins with "Steeping in dilute sulphuric acid and water helps disintegrating different parts of the corn kernel". This is followed by "Grinding is used to liberate the intact germ from the kernel. Germ separation is done by a series of hydrocyclones, High oil content of the germ imparts low density, which makes it tend to float in water, enhanced additionally by starch, suspended in water. After a washing of the germ, oil can be extracted (usually with hexane).". The next section, "Fibre separation consists of four steps:", lists "an initial screening of coarse fibre; a milling or grinding step to liberate and disperse all the starch and gluten from the remaining fibre; another washing step and a dewatering and drying step with the addition of corn steep liquor for the production and sale of gluten feed.". It then states, "After the fibre removal, starch, protein and miscellaneous soluble components (e.g. salts, minerals, and vitamins) are left." and includes a callout box stating "alpha-amylase may be used for cooking". The final line on the slide is "Starch is separated from the gluten (protein) in several steps and used for cooking". The slide footer includes the IIT Kharagpur logo and the text "NPTEL ONLINE CERTIFICATION COURSE".

So, some highlights are that grinding is used to liberate intact germ from the kernel. Germ separation is done by a series of hydro cyclones. And the high oil content of the germ imparts low density. So, it comes off. So, and it is separated. And other things the starch and etcetera are available in the lower part and then fiber separation consists of 4 steps that is initial screening of coarse fibers than a milling or grinding step to liberate and disperse all the starch and gluten from the remaining fiber and then another washing step and dewatering and drying step.

So, these are the steps through which the fibers are separated and after the fiber removal starch protein and miscellaneous soluble components these are present in the solution and gluten separation takes place and then finally, cooking process starts and that cooking alpha amylase enzyme is added for the conversion of starch to sugar.

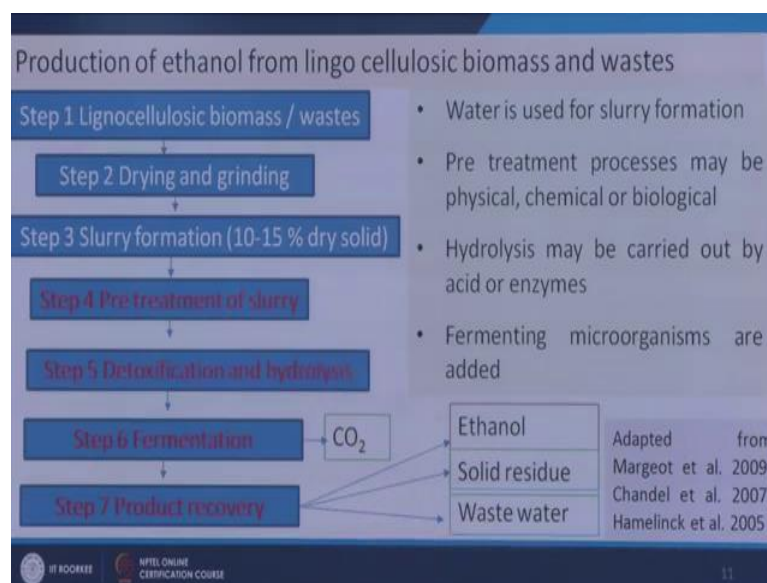
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The dry process does not separate the different components of the corns at the first step before fermentation. So, it after cleaning it goes for milling. So, after milling we get the flour and that is liquefied, we add water here to make a slurry and that is liquefaction then it is going for saccharifications. The liquids slurry is heated and enzymes are added to convert the starch to sugar. So, then sugar is going for fermentation. Then fermentation will give some fermented product and those products will be separated through distillations and dehydration.

So, distillation will give us ethanol and remaining products go for co product processing that have some commercial value on can be used for if other applications like say animal feed and other co products production. So, here the enzymes are like gluco amylase which converts liquefied starch to fermentable sugars. So, this is the dry process for the production of ethanol from starchy materials.

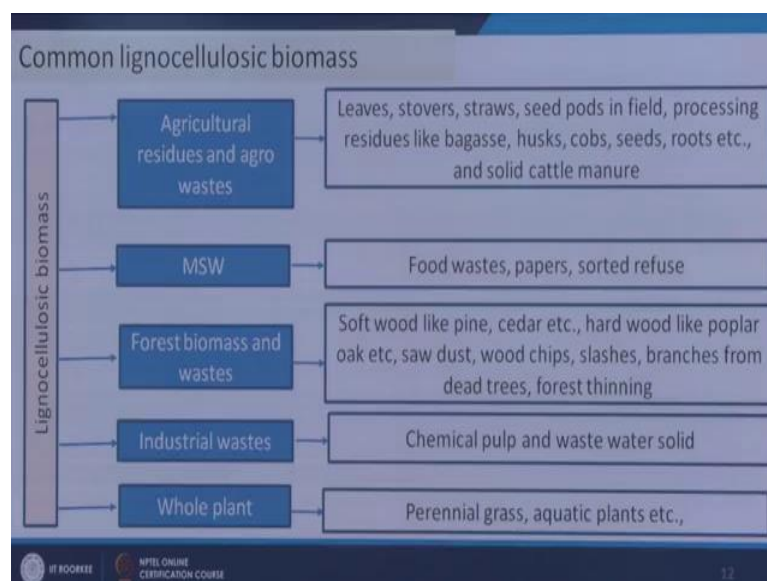
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Now, we will see the flow sheets for the production of ethanol from the lignocellulosic biomass as you have discussed that when the material is lignocellulosic biomass, it will be requiring stringent preprocessing step that is pretreatment. So, lignocellulosic biomass and waste after drying and grinding it will go for slurry formation. And then that is 10 to 15 percent dry solids will be there then it will go for pretreatment step.

So, that pretreatment can be done by physical means by chemical means or by biological means. And then after pretreatment we will be getting the cellulose and hemicellulose lignin will be separated from this and that cellulose and hemicellulose will go for detoxifications and hydrolysis. And then it will be converted to sugar and then it will go for fermentation for the production of ethanol. And once fermentation is over then we will get different products that has to be recovered that can give us ethanol solid residue and waste water the ethanol is our major concern here. So, in this process water is used for the slurry formation and fermenting microbes are added here that is fermentations microbes are added.

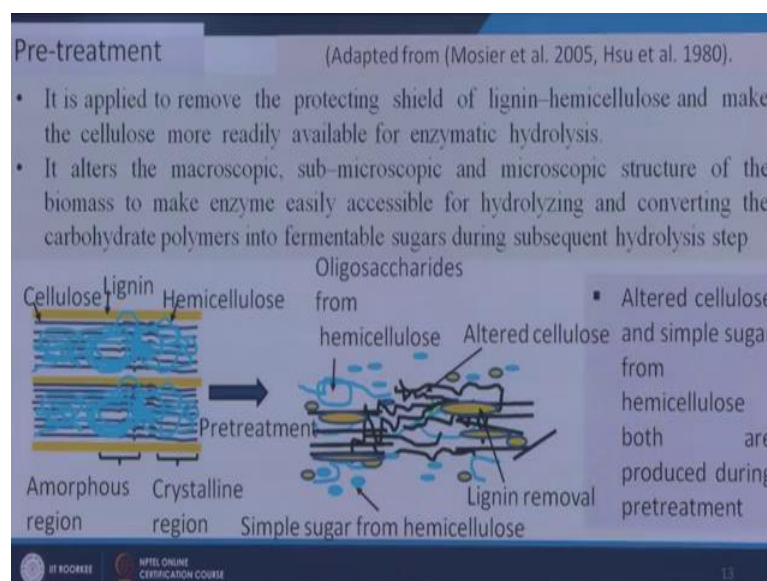
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So, now we will see different types of organic feed stocks are waste which are available for this production of ethanol.

So, here agricultural residues and agro waste, municipal solid waste, forest biomass and wastes and industrial wastes and whole plants, some examples are given here in this slide.

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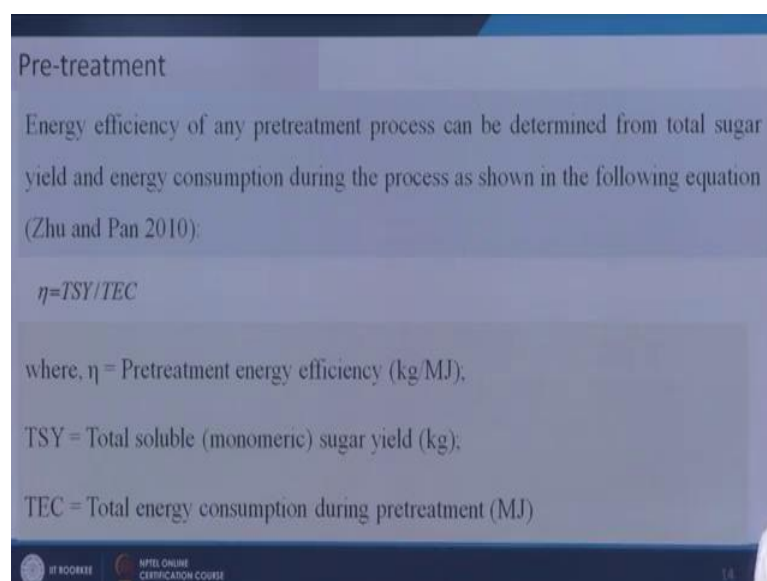
Now, we will discuss this pretreatment step. So, what happens during pretreatment of the lignocellulosic biomass? If we see the lignocellulosic biomass here before

pretreatment, here we are getting lignin we are getting cellulose we are getting hemi cellulose. So, very tightly packed these are very tightly packed. So, we have to break it we have to break it, and we have to separate this cellulose and hemi cellulose from the lignins lignins are not desirable for the biological activity.

So, cellulose is also having some crystalline structure amorphous structure here amorphous crystalline structure and which we these are well structured we have to break the structure of this cellulose. And after pretreatment if we see here the figure the lignin serving separated the hemi cellulose are converted to sugar to some extent and cellulose are broken down into smaller pieces, so altered cellulose. So, see pretreatments alters the cellulose converts the hemi cellulose to some sugar and lignins are also removed. So, this is the main job of the pretreatment process. We do not need more glucose from the cellulose or more sugar from the cellulose in this step. So, this pretreatment step we need the breakdown of these the regular structure of the cellulose and altered cellulose is formed.

So, altered cellulose and simple sugar from hemi cellulose both are produced during pretreatment steps. So, this is the main objective of this pre pretreatment step, here the macroscopic some microscopic and microscopic structure of the biomass to make it make easily accessible to the microorganisms and enzymes.

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Pre-treatment

Energy efficiency of any pretreatment process can be determined from total sugar yield and energy consumption during the process as shown in the following equation (Zhu and Pan 2010):

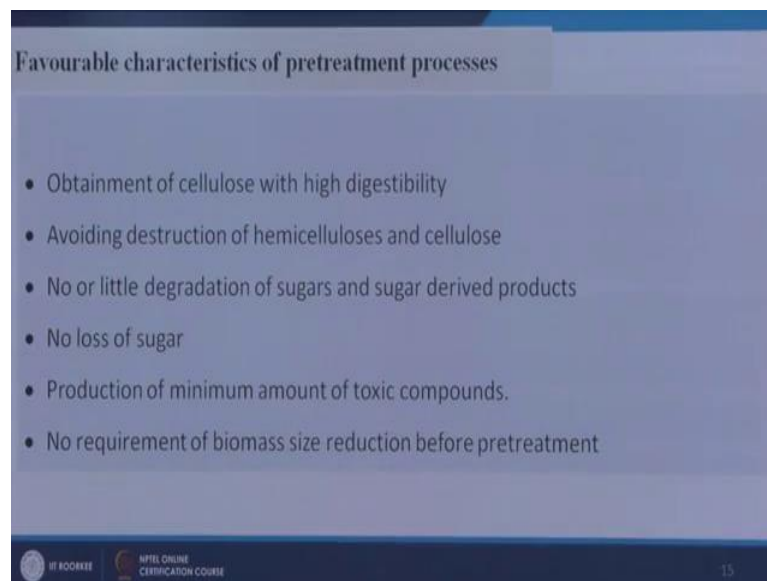
$$\eta = \text{TSY} / \text{TEC}$$

where, η = Pretreatment energy efficiency (kg/MJ),
TSY = Total soluble (monomeric) sugar yield (kg);
TEC = Total energy consumption during pretreatment (MJ)

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So, if this is the role of the pretreatment step how can we define the performance of this pretreatment step or the energy efficiency of any pretreatment step. So, that is defined as efficiency equal to TSY by TEC, what is TSY is the total soluble sugar yield how much total soluble sugar we are getting in kg and total energy consumptions during the pretreatment in mega joule, so kg per mega joule that will be the efficiency of this pretreatment process.

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Favourable characteristics of pretreatment processes

- Obtainment of cellulose with high digestibility
- Avoiding destruction of hemicelluloses and cellulose
- No or little degradation of sugars and sugar derived products
- No loss of sugar
- Production of minimum amount of toxic compounds.
- No requirement of biomass size reduction before pretreatment

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So, during pretreatment process what are the favorable characteristics? Let us see those things, so obtainment of cellulose with high digestibility. So, our main objective is to get more cellulose and not to convert cellulose into sugar in this step. Our objective to remove all lignins, so no or little degradation of sugars and sugar derivative products sugar has to be remained here in significant amount that will be going through the fermentation otherwise we will be losing some sugar avoiding destructions of hemicellulose. And cellulose we cannot allow the destructions of this hemicellulose and cellulose in this step and production of minimum amount of toxic compounds.

So, toxic compounds are also formed during pretreatment steps because the lignins are present. So, some phenolic compounds some organic acids will also be produced those compounds harm the growth of the microorganism. So, that is not desirable. So, our condition should be such that that will not favor this toxic formation.

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Favourable characteristics of pretreatment processes

- Capable of operating in reasonable size and moderate cost reactors.
- No production of solid-waste residues
- Effectiveness at low moisture content.
- Recovery of high amounts of carbohydrates.
- Fermentation compatibility.
- High lignin recovery for conversion into valuable coproducts
- Minimum heat and power requirements

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Then capable of operating in reasonable size and moderate cost reactors no production of solid waste residues, we do need any solidate residues in this step and effectiveness at low moisture content and recovery of high amounts of carbohydrates. So, we have to recover high amounts of carbohydrates through this process, and fermentation compatibility then minimum heat and power requirements. So, these are some characteristics of this process.

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Different types of pre-treatment techniques		
Pre-treatment method	Characteristics	Remarks
Physical	Increases accessible surface area and pore volume decreases the degrees of polymerization of cellulose and its crystallinity	Cutting, grinding
Chemical	Increases delignification, decreases the degree of polymerization and crystallinity of cellulose associated with its swelling, and porosity growth Acid pretreatments solubilizes the hemicellulosic fraction of the biomass and makes the cellulose more accessible to enzymes.	Commonly used acid and base are H_2SO_4 and $NaOH$, respectively. Organic acids such as fumaric or maleic acids are also used as alternatives to enhance cellulose hydrolysis

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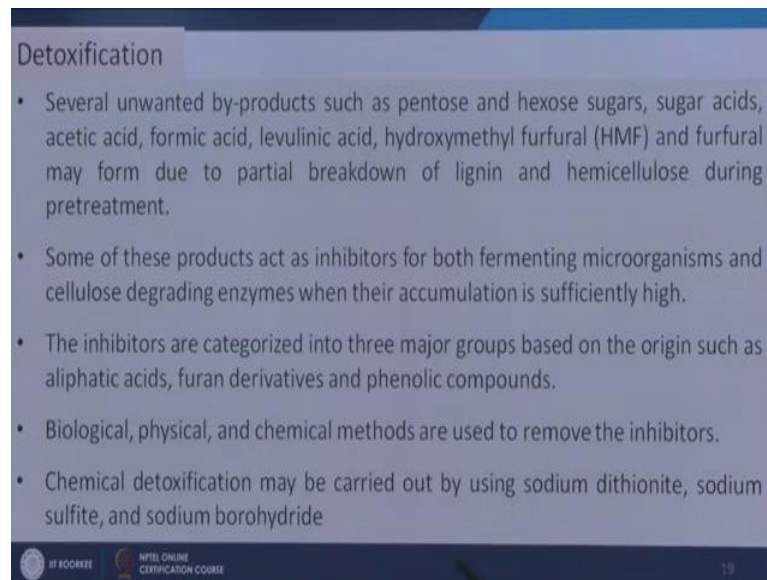
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Pre-treatment method	Characteristics	Remarks
Physicochemical	Exploits the use of conditions and compounds that affect the physical and chemical properties of biomass Increases accessible surface area of the biomass for enzyme accessibility, decreases cellulose crystallinity, removes hemicelluloses and lignin	Steam explosion, ammonia fiber explosion (AFEX), ammonia recycling percolation (ARP), soaking aqueous ammonia (SAA), wet oxidation, CO ₂ explosion
Biological	Alters the structure of lignin and cellulose and separate from the lignocellulosic matrix. Slow rate	White rot, brown rot and soft rot fungi are used Brown rot attacks cellulose while white and soft rots attack both cellulose and lignin

Now, we will see the comparison of different types of pretreatment process. So, one is physical process chemical process and physicochemical and biological process system 4 types of processes have been classified here. So, physical process means cutting and grinding chemical process means acid treatment and alkali treatment. And this is physicochemical process means steam expressions ammonia fiber exploration and ammonia recycling percolations and soaking aqueous ammonia wet oxidation carbon dioxide expressions, and biological methods we use some white rot brown rot and soft rot fungi those are used and brown rot attack cellulose, while white and soft rots attack both cellulose and lignin.

So, these are the type of pretreatment process which are used for the pretreatment of the lingo cellulosic biomass and basically to get the sugar from it cellulose and hemicellulose. So, out of this processes chemical process, is more suitable which gives in which increases the delignification decreases the degree of polymerization. And crystallization of cellulose associated with it is swelling and porosity growth and then acid pretreatments solubilizes the hemicellulosic fractions of the biomass and makes the cellulose more accessible to the enzymes. So, these are the characteristics of these and chemical process is more suitable now we will see the detoxification.

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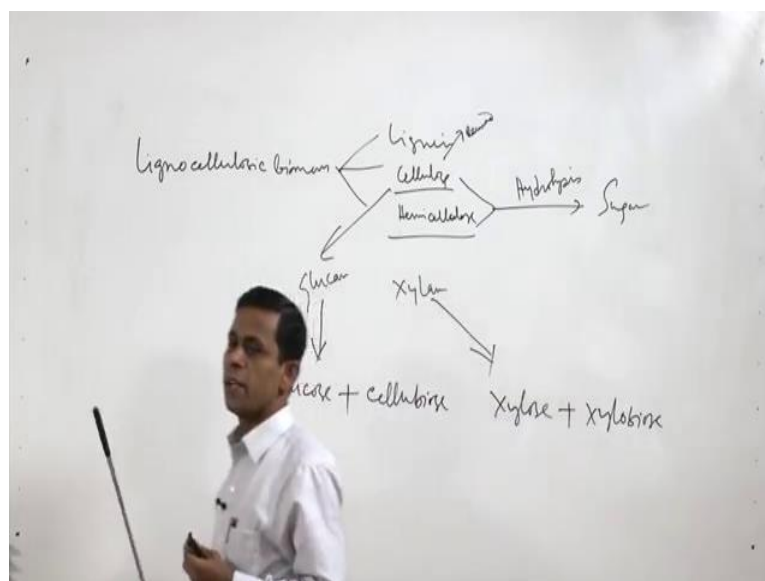
Detoxification

- Several unwanted by-products such as pentose and hexose sugars, sugar acids, acetic acid, formic acid, levulinic acid, hydroxymethyl furfural (HMF) and furfural may form due to partial breakdown of lignin and hemicellulose during pretreatment.
- Some of these products act as inhibitors for both fermenting microorganisms and cellulose degrading enzymes when their accumulation is sufficiently high.
- The inhibitors are categorized into three major groups based on the origin such as aliphatic acids, furan derivatives and phenolic compounds.
- Biological, physical, and chemical methods are used to remove the inhibitors.
- Chemical detoxification may be carried out by using sodium dithionite, sodium sulfite, and sodium borohydride

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So, just now we have seen that in your pretreatment method the lignin compounds are removed. So, during this those some amount of lignin can also produce different types of compounds. Like say furfurals and levulinic acid formic acids and acetic acid all those things are formed in this step. So, we can get these compounds which harms the microbial growth I will as we have already discussed and biological physical and chemical methods are used for the removal of these toxic compounds or inhibitors. So, how this the chemical detoxification may be carried out by using sodium dithionite sodium sulphate and sodium borohydride. So, this 3 compounds can be used during pretreatment steps. So, that detoxification compounds will not be available in the product.

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Then we are going to discuss on hydrolysis. So, hydrolysis once the pretreatment is over then the objective of the pretreatment is what to breakdown the lingo cellulosic biomass, in to lignin cell cellulose and hemi cellulose say hemi cellulose. So, next is, this is removed. So, after this removal we will consider these 2 and hydrolysis that will give us sugar that will give us sugar.

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Hydrolysis

The major portions of cellulose and hemicellulose are glucan and xylan, respectively. Digestibility of both glucan and xylan can be determined from the yield of their respective monomers and disaccharides using the equations (Wyman et al. 2005).

$$\text{Digestibility of glucan (\%)} = \frac{\text{Amount of glucose (g)} + 1.053 \times \text{Amount of cellobiose (g)}}{1.111 \times \text{Amount of glucan (g)}} \times 100$$

$$\text{Digestibility of xylan (\%)} = \frac{\text{Amount of xylose (g)} + 1.064 \times \text{Amount of xylobiose (g)}}{1.136 \times \text{Amount of xylan (g)}} \times 100$$

Where, 1.053, 1.111, 1.064, and 1.136 are the hydration factors of cellobiose, glucan, xylobiose and xylan, respectively.

Zhu et al., 2008, Bioresource Technology 99(9): 3817-3828.

So, this is the part the hydrolysis. The major portions of cellulose and hemi cellulose are converted to sugar. So, what is this cellulose and hemi cellulose? This is having glucan

and this having xylan. What is glucan and xylan? Glucan is the polysaccharide and xylan is also polysaccharide the pentose this monomer contents 5 carbon sugar this is 6 carbon sugar, so glucan and xylan respectively.

So, digestibility of both glucan and xylan can be determined from the yield of their respective monomer and disaccharides. What are the disaccharides one is your cellobiose another is your xylobiose? So, xy glucan we will give us one is monosaccharide another is disaccharide. So, monosaccharide is glucose and disaccharide is cellobiose. And what xylan will give us? Xylan will give us xylose and xylobiose it will give us xylose plus xylobiose, it will give us xylose and xylobiose, this monosaccharide disaccharide. So, depending upon the amount of monosaccharide and disaccharide we can get the digestibility of glucan and digestibility of xylan as per the expression given here and this is reported here in this journal into 2008.

So, digestibility of glucan is equal to amount of glucose plus 1.053 into amount of cellobiose in gram unit divided by 1.111 into amount of glucan in gram into 100. So, this is digester how much glucan was present out of those glucan how much glucose and how much cellobiose has been produced. So, this ratio this this express gives us the digestibility. Similarly, for xylan amount of xylose plus one point 0 6 4 into amount of xylobiose divided by 1.136 amount of xylan into hundred this gives us the digestibility of the xylan.

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$$\text{Total Sugar Conversion (\%)} = \frac{\text{Glucose yield} + \text{Xylose yield}}{\text{Theoretical glucose yield} + \text{Theoretical xylose yield}}$$

$$= \frac{([G] - [G]_0) \times V + ([X] - [X]_0) \times V}{\frac{W \times \text{Glucan content}}{0.9} + \frac{W \times \text{Xylan content}}{0.88}}$$

Where,

- [G], is glucose concentration in hydrolysis liquid (mg/mL);
- [G]₀, is the initial glucose concentration, can be assumed as 0 (mg/mL);
- [X], is xylose concentration in hydrolysis liquid (mg/mL);
- [X]₀, is initial xylose concentration, can be assumed as 0 (mg/mL);
- V, is initial volume of biomass slurry (mL);
- W, is the initial dry weight of biomass (mg);
- 0.9, is conversion factor of glucose to equivalent glucan;
- 0.88, is the conversion factor of xylose to equivalent xylan.

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Now, total sugar conversions, how much total sugar is converted we are interested to know that. So, in that case, glucose yield plus xylose yield glucose yield plus yield divided by theoretical glucose yield plus theoretical xylose yield.

What do we mean by theoretical glucose yield and theoretical xylose yield? That means, if we know the glucan content and if we know the xylan content then we can get the theoretical yield of glucose, and theoretical yield of xylan because the relationship is that the theoretical glucose yield is equal to W into glucan content divided by 1.9 and theoretical xylan xylose yield is equal to W into xylan content divided by 0.88. So, if we know the glucose yield that is G is the glucose concentration in hydrolysis liquid that is glucose yield and then 0 or o is the initial glucose concentration initial glucose concentration in this case is how much 0 be because hydrolysis is taking place no glucose was there. So, this minus this into V be the initial volume of the biomass slurry that is m l and then X and X_0 X is what is the xylose concentration is hydrolysis liquid and X_0 is the initial xylose concentration.

So, what is the initial xylan concentration in this case there is also 0 . So, we will be putting this value if we get the analysis of the solution. After this hydrolysis we will get the value of G we will get the value of X and then we will put here and W if we know W is the initial dry weight of biomass then W into glucan content and xylan content also we have to know of this biomass so then or the waste. So, glucan content into W by 1.9 plus xylan content into W by 0.88. So, that will be the theoretical glucan and xylan yield and then this is this in the numerator this is glucose yield plus xylose yield. So, as a whole we will be getting the total sugar conversion. So, after this in this part of this module, so rest part we will discuss in the next part of this module.

Thank you very much for your patience.