Biomass Conversion and Biorefinery
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Lecture – 31
Biomass as Feedstock for Synthetic Organic Chemicals, Lactic Acid, Polylactic Acid

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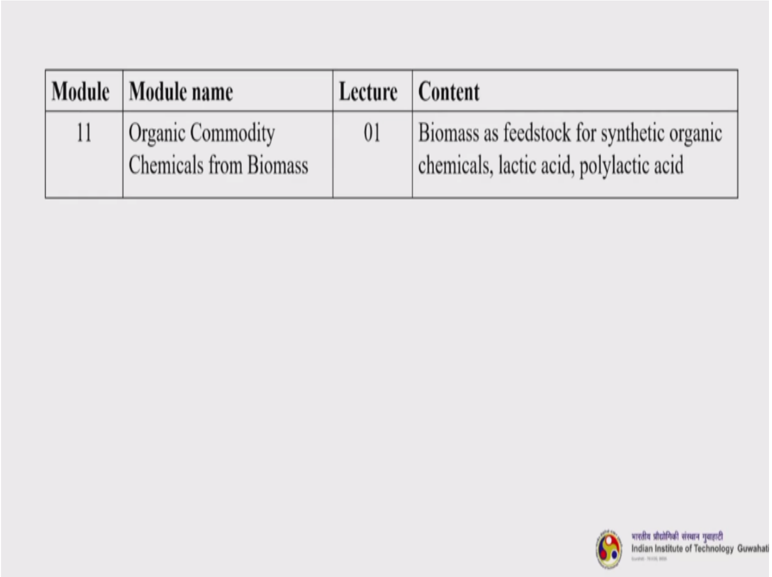

Module	Module name	Lecture	Content
11	Organic Commodity Chemicals from Biomass	01	Biomass as feedstock for synthetic organic chemicals, lactic acid, polylactic acid

Good morning students. Today is lecture 1 under module 11. And as you know that module 11 is dedicated into 3 lectures and we will be actually learning about organic commodity chemicals that are being manufactured from the biomass. And in today's lecture we will talk about synthetic organic chemicals such as lactic acid and polylactic acid (PLA). So, let us begin.

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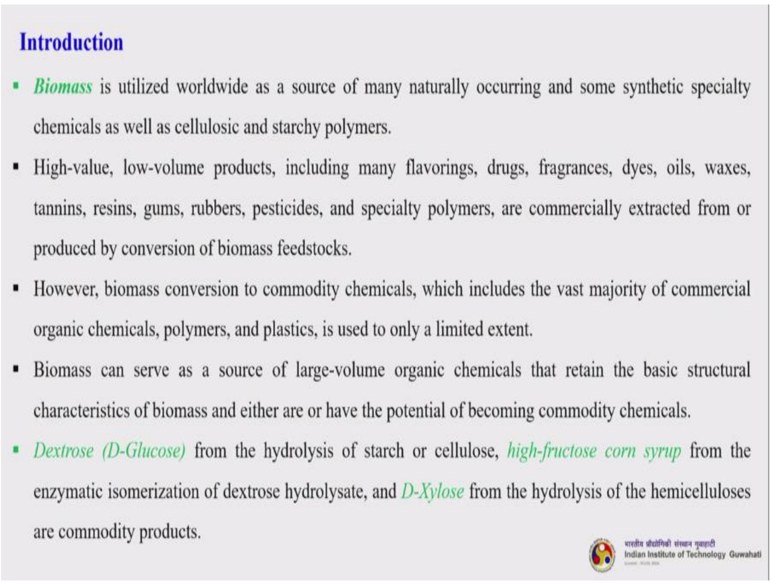

Introduction

- *Biomass* is utilized worldwide as a source of many naturally occurring and some synthetic specialty chemicals as well as cellulosic and starchy polymers.
- High-value, low-volume products, including many flavorings, drugs, fragrances, dyes, oils, waxes, tannins, resins, gums, rubbers, pesticides, and specialty polymers, are commercially extracted from or produced by conversion of biomass feedstocks.
- However, biomass conversion to commodity chemicals, which includes the vast majority of commercial organic chemicals, polymers, and plastics, is used to only a limited extent.
- Biomass can serve as a source of large-volume organic chemicals that retain the basic structural characteristics of biomass and either are or have the potential of becoming commodity chemicals.
- *Dextrose (D-Glucose)* from the hydrolysis of starch or cellulose, *high-fructose corn syrup* from the enzymatic isomerization of dextrose hydrolysate, and *D-Xylose* from the hydrolysis of the hemicelluloses are commodity products.

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So, biomass is utilized worldwide as a source of many naturally occurring and some synthetic speciality chemicals, as well as cellulosic and starchy polymers. High-value, low-volume products including many flavorings, drugs, fragrances, dyes, oil, waxes, tannins, resins, gums, rubbers, pesticides, and specialty polymers are commercially extracted from and produced by conversion of biomass feedstocks.

However, biomass conversion to commodity chemicals which includes the vast majority of commercial organic chemicals, polymers and plastics is used to only a limited extent. Biomass can serve as a source of large volume organic chemicals that retain the basic structural characteristics of biomass and either are or have the potential of becoming commodity chemicals.

One such is actually very famous which is a dextrose or you can say D-glucose from the hydrolysis of starch or cellulose, high-fructose corn syrup from the enzymatic isomerization of dextrose hydrolysate and D-Xylose from the hydrolysis of the hemicelluloses - these are commodity products.

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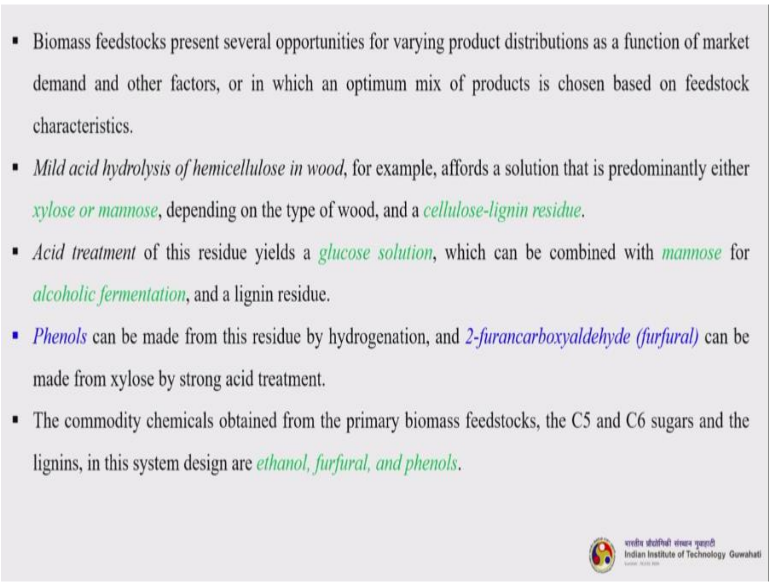

- Biomass feedstocks present several opportunities for varying product distributions as a function of market demand and other factors, or in which an optimum mix of products is chosen based on feedstock characteristics.
- *Mild acid hydrolysis of hemicellulose in wood*, for example, affords a solution that is predominantly either *xylose or mannose*, depending on the type of wood, and a *cellulose-lignin residue*.
- *Acid treatment* of this residue yields a *glucose solution*, which can be combined with *mannose* for *alcoholic fermentation*, and a lignin residue.
- *Phenols* can be made from this residue by hydrogenation, and *2-furancarboxyaldehyde (furfural)* can be made from xylose by strong acid treatment.
- The commodity chemicals obtained from the primary biomass feedstocks, the C5 and C6 sugars and the lignins, in this system design are *ethanol, furfural, and phenols*.

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Biomass feedstocks present several opportunities for varying product distributions as a function of market demand and other factors or in which an optimum mix of products is chosen based on feedstock characteristics. Mild acid hydrolysis of hemicellulose in wood for example affords a solution that is predominantly either xylose or mannose depending on the type of wood and a cellulose-lignin residue.

Now acid treatment of this residue yields a glucose solution which can be combined with mannose for alcoholic fermentation and lignin residue. If you recall, these things we have discussed when we had discussed about fermentation products and all these things, but here we will discuss about speciality chemicals in detail. Now, phenols can be made from this residue by hydrogenation.

And 2-furancarboxyaldehyde, that is furfural, can be made from xylose by strong acid treatment. The commodity chemicals obtained from the primary biomass feedstock, C5 and C6 sugars and lignins in this system design are ethanol, furfural and phenols.

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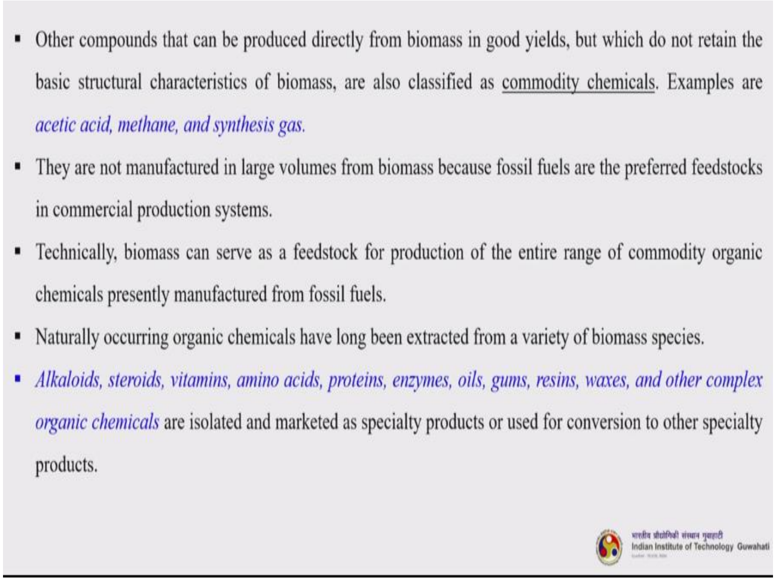

- Other compounds that can be produced directly from biomass in good yields, but which do not retain the basic structural characteristics of biomass, are also classified as commodity chemicals. Examples are *acetic acid, methane, and synthesis gas.*
- They are not manufactured in large volumes from biomass because fossil fuels are the preferred feedstocks in commercial production systems.
- Technically, biomass can serve as a feedstock for production of the entire range of commodity organic chemicals presently manufactured from fossil fuels.
- Naturally occurring organic chemicals have long been extracted from a variety of biomass species.
- *Alkaloids, steroids, vitamins, amino acids, proteins, enzymes, oils, gums, resins, waxes, and other complex organic chemicals* are isolated and marketed as specialty products or used for conversion to other specialty products.

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Other compounds that can be produced directly from biomass in good yields, but which do not retain the basic structural characteristics of biomass are classified as commodity chemicals. So, examples are many, as in the beginning of the class I told you. Some of the major important things are acetic acid, methane and synthesis gas. Now they are not manufactured in large volume from biomass because fossil fuels are the preferred feedstocks in commercial production systems.

But as you know that fossil fuel is depleting and there is a need to look for alternate fuels and of course a route for producing even commodity chemicals, so biomass has taken a center stage of research since almost 20 to 30 years. Now, technically, biomass can serve as a feedstock for production of the entire range of commodity organic chemicals presently manufactured from fossil fuels.

Naturally occurring organic chemicals have long been extracted from a variety of biomass species. Alkaloids, steroids, vitamins, amino acids, proteins, enzymes, oils, gums, resins, waxes and other complex organic chemicals are isolated and marketed as specialty products or used for the conversion to other specialty products.

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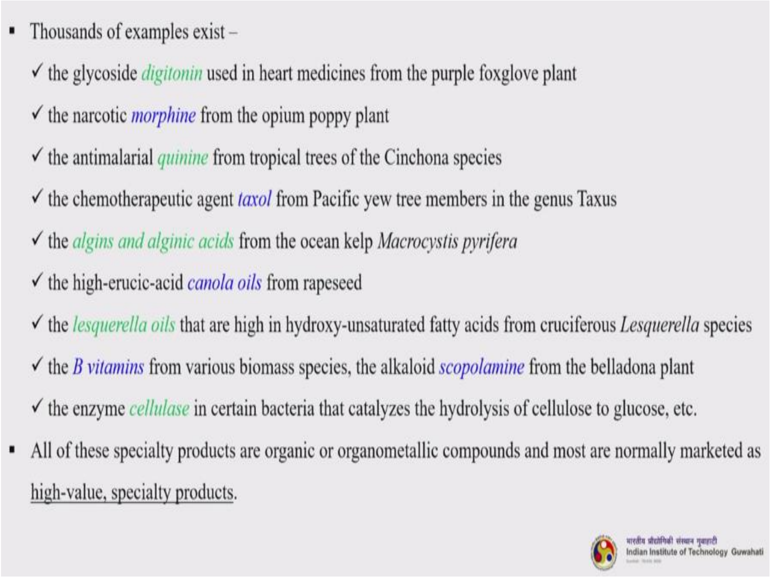

- Thousands of examples exist –
  - ✓ the glycoside *digitonin* used in heart medicines from the purple foxglove plant
  - ✓ the narcotic *morphine* from the opium poppy plant
  - ✓ the antimalarial *quinine* from tropical trees of the Cinchona species
  - ✓ the chemotherapeutic agent *taxol* from Pacific yew tree members in the genus Taxus
  - ✓ the *algins and alginic acids* from the ocean kelp *Macrocystis pyrifera*
  - ✓ the high-erucic-acid *canola oils* from rapeseed
  - ✓ the *lesquerella oils* that are high in hydroxy-unsaturated fatty acids from cruciferous *Lesquerella* species
  - ✓ the *B vitamins* from various biomass species, the alkaloid *scopolamine* from the belladona plant
  - ✓ the enzyme *cellulase* in certain bacteria that catalyzes the hydrolysis of cellulose to glucose, etc.
- All of these specialty products are organic or organometallic compounds and most are normally marketed as high-value, specialty products.

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So thousands of examples exist. Just something I have written here, we will go through it. The glycoside digitonin used in heart medicine from the purple foxglove plant. The narcotic morphine from the opium poppy plant. The antimalarial quinine from the tropical trees of the Cinchona species. The chemotherapeutic agent taxol from Pacific yew tree members of the genus Taxus. The algins and alginic acids from the ocean kelp *Macrocystis pyrifera*.

The high-erucic-acid canola oil from the rapeseed. The lesquerella oils that are high in hydroxy-unsaturated fatty acids from cruciferous *Lesquerella* species. The B vitamins from various biomass species, the alkaloid scopolamine from the belladonna plant. The enzyme cellulase in certain bacteria that catalyzes the hydrolysis of cellulose to glucose, etc. Now all of these specialty products are organic or organometallic compounds.

And most are normally marketed as high value and specialty products. Now, having said that, we just try to understand actually that these are some of the names only, there are many, but again I have told you many times that what happens when you produce something from the biomass. Biomass itself is extremely complex in nature we have learned that.

So, when you degrade it, try to make some value-added products out of them, does not matter whether you use thermochemical conversion process or you use biochemical conversion that is fermentation, the major problem is of course the downstream processing. Another problem is of course the extraction of that particular compound from which you are going to make some value-added products. This is first step.

Second is the purification or downstream processing part so which is extremely, we can say that it is costly with respect to the chemicals required, the equipment that is being required and of course the energy. So, people are working day and night on those aspects. We have already learned some of the latest developments of downstream processing part and again we will also discuss in future about downstream processing.

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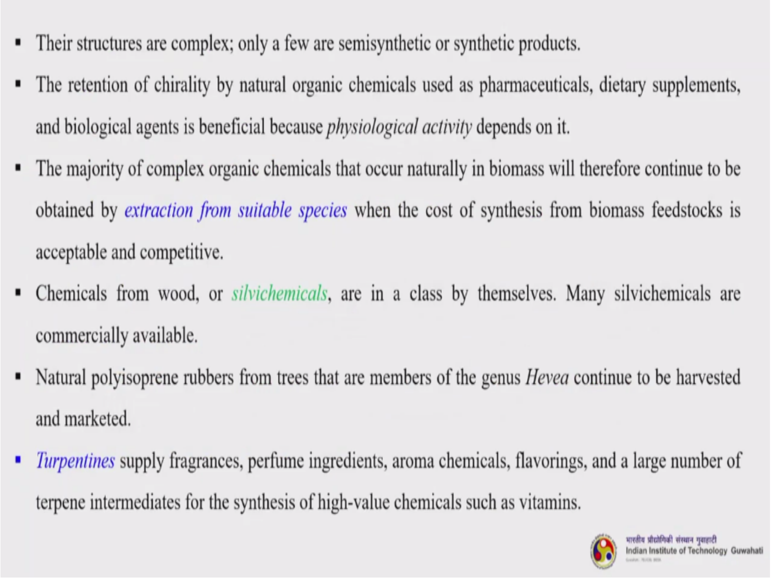

- Their structures are complex; only a few are semisynthetic or synthetic products.
- The retention of chirality by natural organic chemicals used as pharmaceuticals, dietary supplements, and biological agents is beneficial because *physiological activity* depends on it.
- The majority of complex organic chemicals that occur naturally in biomass will therefore continue to be obtained by *extraction from suitable species* when the cost of synthesis from biomass feedstocks is acceptable and competitive.
- Chemicals from wood, or *silvichemicals*, are in a class by themselves. Many silvichemicals are commercially available.
- Natural polyisoprene rubbers from trees that are members of the genus *Hevea* continue to be harvested and marketed.
- *Turpentines* supply fragrances, perfume ingredients, aroma chemicals, flavorings, and a large number of terpene intermediates for the synthesis of high-value chemicals such as vitamins.

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So, these commodity chemicals, their structures are complex, only a few are semisynthetic or synthetic products. The retention of chirality by natural organic chemicals used as pharmaceuticals, dietary supplements and biological agents is beneficial because physiological activity depends on it. Now, the majority of complex organic chemicals that occur naturally in biomass will therefore continue to be obtained by extraction of suitable species.

This is what I was just mentioning. The need for development of a particular protocol to extract suitable species and that too in a cost beneficial or economical way when the cost of synthesis from the biomass feedstocks is acceptable and competitive. So, cost is very important that has to be taken care of when you go for making commercial products. Now, chemicals from wood or silvichemicals are in class by themselves.

So many silvichemicals are commercially available. Natural polyisoprene rubbers from trees that are members of the genus *Hevea* continue to be harvested and marketed - that is in large scale. Now turpentine supply fragrances, perfume ingredients, aroma chemicals, flavorings, and a large number of terpene intermediates for the synthesis of high-value chemicals such as vitamins.

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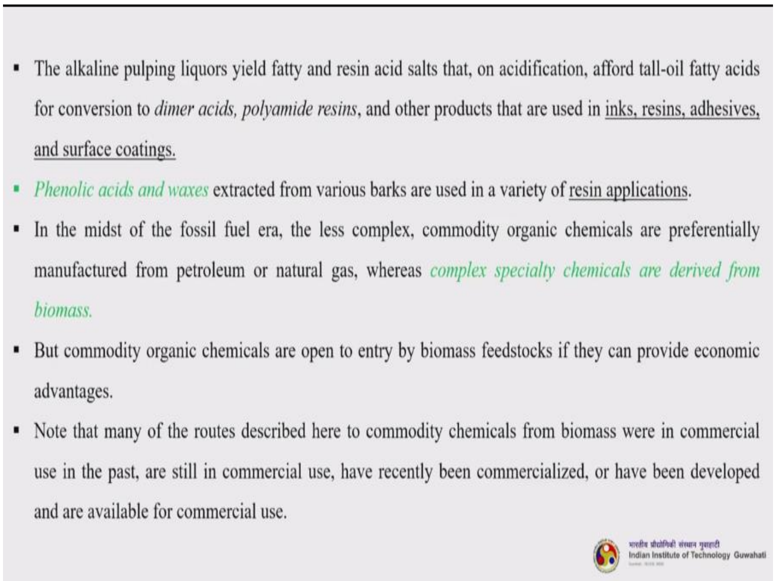

- The alkaline pulping liquors yield fatty and resin acid salts that, on acidification, afford tall-oil fatty acids for conversion to *dimer acids, polyamide resins*, and other products that are used in inks, resins, adhesives, and surface coatings.
- *Phenolic acids and waxes* extracted from various barks are used in a variety of resin applications.
- In the midst of the fossil fuel era, the less complex, commodity organic chemicals are preferentially manufactured from petroleum or natural gas, whereas *complex specialty chemicals are derived from biomass.*
- But commodity organic chemicals are open to entry by biomass feedstocks if they can provide economic advantages.
- Note that many of the routes described here to commodity chemicals from biomass were in commercial use in the past, are still in commercial use, have recently been commercialized, or have been developed and are available for commercial use.

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Synthetic terpene resins prepared by cationic polymerization of terpene hydrocarbons are used in hot-melt and pressure-sensitive adhesives. Wood pulps are sources of specialty sugars used in drugs, sweeteners, plasticizers and surfactants. In addition to the commercial regenerated cellulose described previously, wood pulps are used for production of cellulose esters such as the acetates and butyrates for fibers, films and moldings and for production of ethers such as ethyl cellulose, carboxymethylcellulose and hydroxyethyl cellulose for use as gums and thickening agents. The alkaline pulping liquors are usually combusted to recover the pulping chemicals and energy for recycle but the alkali lignins are also separated for use in formulating resins, rubbers and emulsions.

Dimethyl sulfide, dimethyl sulfoxide and dimethyl sulfone are recovered from the volatile fraction of the kraft black liquors from the sulfate pulping. The sulfonated lignins in sulfite pulping liquors are a source of semisynthetic vanillin and are separated for use in formulating adhesives, binders, dispersants, tanning agents and similar products.

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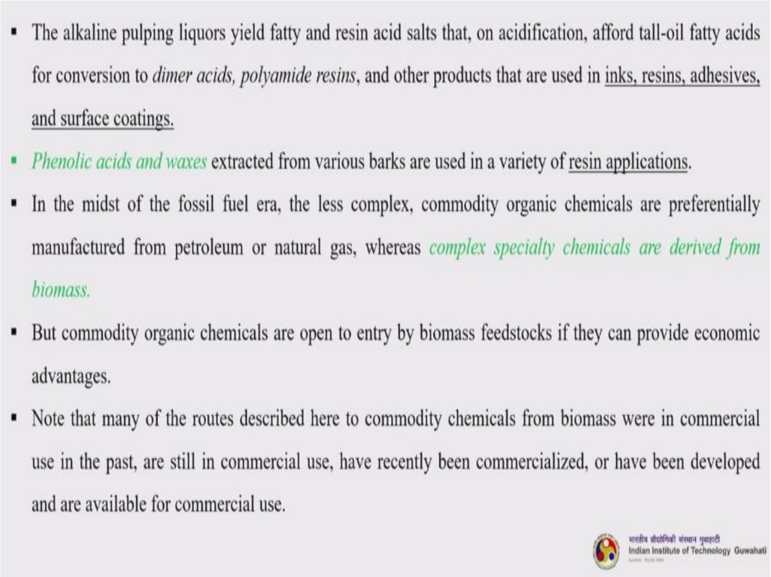

- The alkaline pulping liquors yield fatty and resin acid salts that, on acidification, afford tall-oil fatty acids for conversion to *dimer acids, polyamide resins*, and other products that are used in inks, resins, adhesives, and surface coatings.
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The alkaline pulping liquors yield fatty and resin acid salts that on acidification afford tall-oil fatty acids for conversion to dimer acids, polyamide resins and other products that are used in inks, resins, adhesives and surface coatings. Now phenolic acids and waxes extracted from various barks are used in a variety of resin applications. In the midst of the fossil fuel era, the less complex commodity organic chemicals are preferentially manufactured from petroleum or natural gas.

Whereas complex speciality chemicals are derived from biomass. But commodity organic chemicals are open to entry by biomass feedstocks if they can provide economic advantage. Again the same thing that economic advantage is coming into picture. So, when you talk about economic advantage vis a vis biomass, again I am just trying to repeat it that two things are very important, the species which you want to extract from the biomass that step has to be economical.

Then second is that, once that is produced, mostly they will be in aqueous phase, then you have to go for purification that is the downstream part. So, both these steps are the major contributor to the overall cost of the final product. So, note that many of the routes described here to commodity chemicals from biomass were in commercial use in the past, are still in commercial use, have recently been commercialized or have been developed and are available for commercial use.

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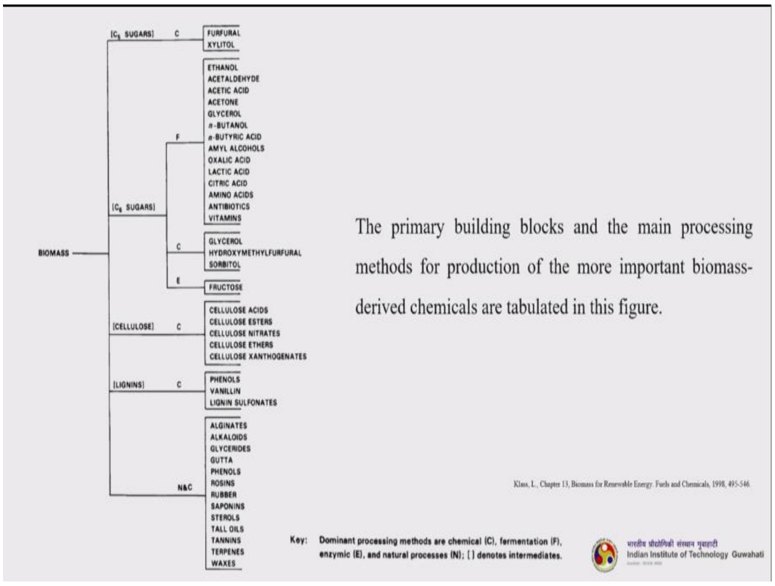

The primary building blocks and the main processing methods for production of the more important biomass-derived chemicals are tabulated in this figure.

Klass, L., Chapter 13, Biomass for Renewable Energy. Fuels and Chemicals, 1998, 495-546.

Key: Dominant processing methods are chemical (C), fermentation (F), enzymic (E), and natural processes (N); [ ] denotes intermediates.

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So this is actually you can see what are the different types of products or value-added products that can be derived from the biomass. These are all commodity chemicals only, we are not talking about other things like directly used biofuel and all. So, you can see that C 5 sugar, C6 sugar, cellulose, lignin and other things, nitrogen and carbon. So, from the C5 sugars we can have furfural and xylitol.

From C6 sugars you can have so many things, ethanol and so many other things of course, ethanol of course goes to your biofuel production, but we are discussing about commodity chemicals. So, you can see all the chemicals here, the different types of acids, we can have glycerol and all these things as their byproduct can also be converted to some other value-added products. Then you can have fructose very important.

Similarly from cellulose we can have different types of acids, esters, nitrates, ethers. Then from lignins, the main thing is of course phenol, phenolic compounds and vanillin and lignin sulfonate, then there are so many other things also. So the primary building blocks and the main processing methods for production of the more important biomass derived chemicals are given here.

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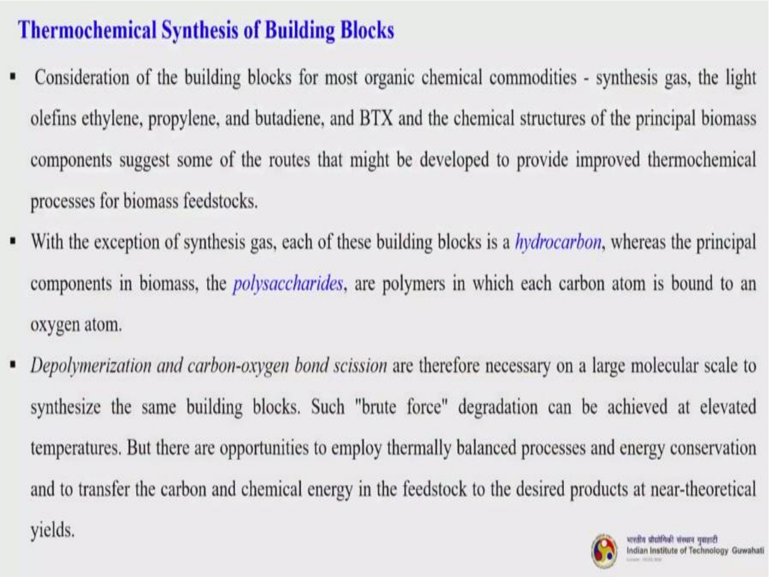

Thermochemical Synthesis of Building Blocks

- Consideration of the building blocks for most organic chemical commodities - synthesis gas, the light olefins ethylene, propylene, and butadiene, and BTX and the chemical structures of the principal biomass components suggest some of the routes that might be developed to provide improved thermochemical processes for biomass feedstocks.
- With the exception of synthesis gas, each of these building blocks is a *hydrocarbon*, whereas the principal components in biomass, the *polysaccharides*, are polymers in which each carbon atom is bound to an oxygen atom.
- *Depolymerization and carbon-oxygen bond scission* are therefore necessary on a large molecular scale to synthesize the same building blocks. Such "brute force" degradation can be achieved at elevated temperatures. But there are opportunities to employ thermally balanced processes and energy conservation and to transfer the carbon and chemical energy in the feedstock to the desired products at near-theoretical yields.

So, we will see the different commodity chemicals by various routes. First, we will talk about the thermochemical synthesis. Consideration of the building blocks for most organic chemical commodities, the synthesis gas, the light olefin, ethylene, propylene, butadiene and BTX and the chemical structures of the principal biomass component suggests some of the routes that might be developed to provide improved thermochemical processes for biomass feedstocks.

With the exception of synthesis gas, each of these building blocks is a hydrocarbon, whereas the principal components in biomass, the polysaccharides, are polymers in which each carbon atom is bound to an oxygen atom. Depolymerization and carbon-oxygen bond scission are therefore necessary on a large molecular scale to synthesize the same building blocks. Such brute force degradation can be achieved at elevated temperatures.

But there are opportunities to employ thermally balanced processes and energy conservation and to transfer the carbon and chemical energy in the feedstock to the desired products at a near theoretical yield.

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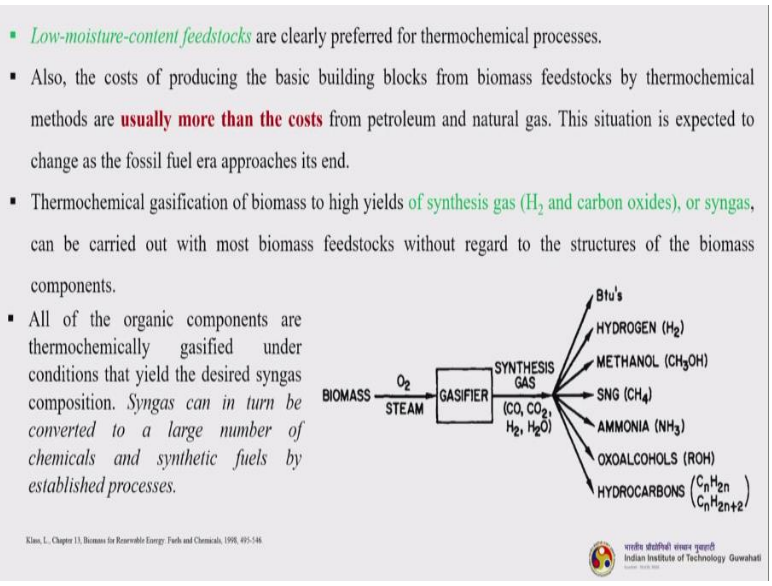

- *Low-moisture-content feedstocks* are clearly preferred for thermochemical processes.
- Also, the costs of producing the basic building blocks from biomass feedstocks by thermochemical methods are **usually more than the costs** from petroleum and natural gas. This situation is expected to change as the fossil fuel era approaches its end.
- Thermochemical gasification of biomass to high yields of synthesis gas (H_2 and carbon oxides), or syngas, can be carried out with most biomass feedstocks without regard to the structures of the biomass components.
- All of the organic components are thermochemically gasified under conditions that yield the desired syngas composition. *Syngas can in turn be converted to a large number of chemicals and synthetic fuels by established processes.*

Klass, L., Chapter 13, Biomass for Renewable Energy: Fuels and Chemicals, 1998, 495-546

Low-moisture-content feedstocks are clearly preferred for thermochemical processes. This we have understood earlier also when we discussed about thermochemical conversion processes in detail such as gasification and pyrolysis. Now, also the costs of producing the basic building blocks from biomass feedstocks by thermochemical methods are usually more than the costs from petroleum and natural gas and that is the problem.

Now, this situation is expected to change as the fossil fuel era approaches its end. Now, when that happens, you will never think about cost. However, cost is always an important factor when you talk about commercial production in a sustainable way. Now thermochemical gasification of biomass to high yields of synthesis gas or syngas can be carried out with most biomass feedstocks without regard to the structure of the biomass components.

All of the organic components are thermochemical gasified under conditions that yield the desired syngas composition. Syngas in turn can be converted to a large number of chemicals and synthetic fuels by established processes; such as, you can see the scheme such as the Btu’s, hydrogen, methanol, SNG, ammonia, oxoalcohols and different types of hydrocarbons.

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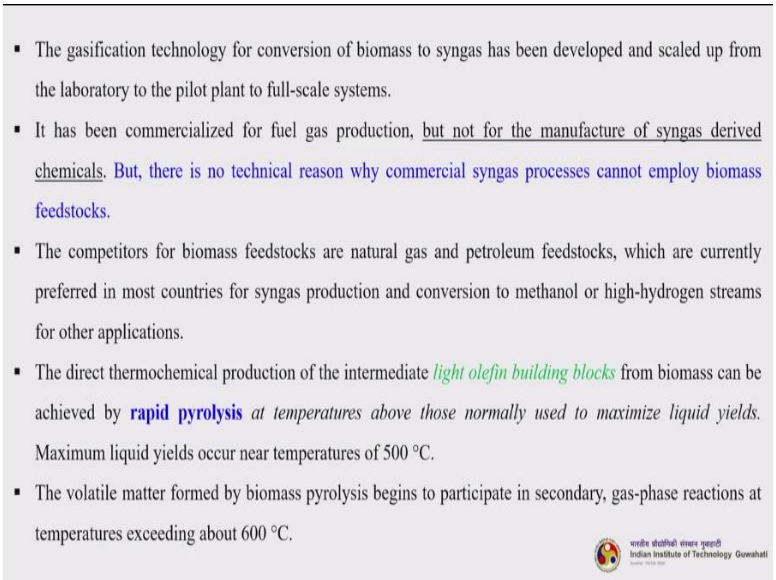

- The gasification technology for conversion of biomass to syngas has been developed and scaled up from the laboratory to the pilot plant to full-scale systems.
- It has been commercialized for fuel gas production, but not for the manufacture of syngas derived chemicals. But, there is no technical reason why commercial syngas processes cannot employ biomass feedstocks.
- The competitors for biomass feedstocks are natural gas and petroleum feedstocks, which are currently preferred in most countries for syngas production and conversion to methanol or high-hydrogen streams for other applications.
- The direct thermochemical production of the intermediate *light olefin building blocks* from biomass can be achieved by **rapid pyrolysis** *at temperatures above those normally used to maximize liquid yields.* Maximum liquid yields occur near temperatures of 500 °C.
- The volatile matter formed by biomass pyrolysis begins to participate in secondary, gas-phase reactions at temperatures exceeding about 600 °C.

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The gasification technology for conversion of biomass to syngas has been developed and scaled up from the laboratory to the pilot plant to full-scale systems. If you recall, we have discussed some of the success stories, how it has been adapted in India as well as other countries. Now, it has been commercialized for fuel production, but not for the manufacture of syngas derived chemicals.

But there is no technical reason why commercial syngas processes cannot employ biomass feedstocks. Time has come that it has to be done. Now, the competitors for biomass feedstocks and natural gas and petroleum feedstocks, which are currently preferred in most countries for syngas production and conversion to methanol or high-hydrogen streams for other applications.

The direct thermochemical production of the intermediate light olefin building blocks from biomass can be achieved by rapid pyrolysis at temperatures above those normally used to maximize liquid yields. Maximum liquid yields occur near temperature of 500 degrees centigrade. The volatile matter formed by biomass pyrolysis begins to participate in secondary gas phase reactions at temperatures exceeding about 600 degree centigrade.

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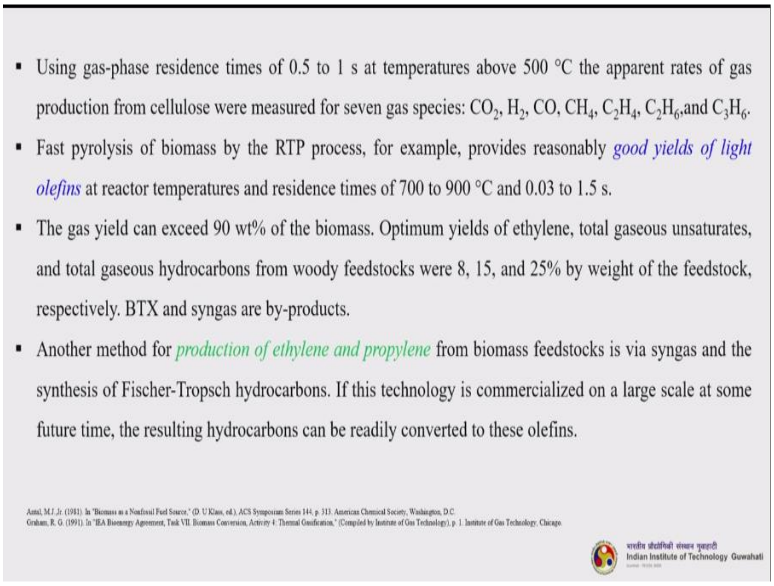

- Using gas-phase residence times of 0.5 to 1 s at temperatures above 500 °C the apparent rates of gas production from cellulose were measured for seven gas species: CO_2, H_2, CO, CH_4, C_2H_4, C_2H_6,and C_3H_6.
- Fast pyrolysis of biomass by the RTP process, for example, provides reasonably *good yields of light olefins* at reactor temperatures and residence times of 700 to 900 °C and 0.03 to 1.5 s.
- The gas yield can exceed 90 wt% of the biomass. Optimum yields of ethylene, total gaseous unsaturates, and total gaseous hydrocarbons from woody feedstocks were 8, 15, and 25% by weight of the feedstock, respectively. BTX and syngas are by-products.
- Another method for *production of ethylene and propylene* from biomass feedstocks is via syngas and the synthesis of Fischer-Tropsch hydrocarbons. If this technology is commercialized on a large scale at some future time, the resulting hydrocarbons can be readily converted to these olefins.

Antal, M.J.,Jr. (1981). In "Biomass as a Nonfossil Fuel Source," (D. L. Klass, ed.), ACS Symposium Series 144, p. 313. American Chemical Society, Washington, D.C.
Graham, R. G. (1991). In "IEA Bioenergy Agreement, Task VII. Biomass Conversion, Activity 4: Thermal Gasification," (Compiled by Institute of Gas Technology), p. 1. Institute of Gas Technology, Chicago.

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Using gas-phase residence times of 0.5 to 1 second at temperatures above 500 degrees centigrade, the apparent rates of gas production from cellulose were measured for seven gas species. Carbon dioxide, hydrogen, carbon monoxide, methane, C_2H_4**,** C_2H_6 and C_3H_6. Now fast pyrolysis of biomass by RTP process for example provides reasonably good yields of light olefins at reactor temperatures and residences time 700 to 900 degrees centigrade and of course 0.03 to 1.5 seconds. You can understand very fast.

Now the gas yield can exceed 90 wt% of the biomass. Optimum yields of ethylene, total gaseous unsaturates and total gaseous hydrocarbons from woody feedstocks were 8,15 and 25% by weight of the feedstock. BTX and syngas are the byproducts. Another method for production of ethylene and propylene from biomass feedstocks is via syngas and the synthesis of Fischer-Tropsch hydrocarbons.

Now, if this technology is commercialized on a large scale at some future time, the resulting hydrocarbons can be readily converted to these olefins and that is going to happen in near future.

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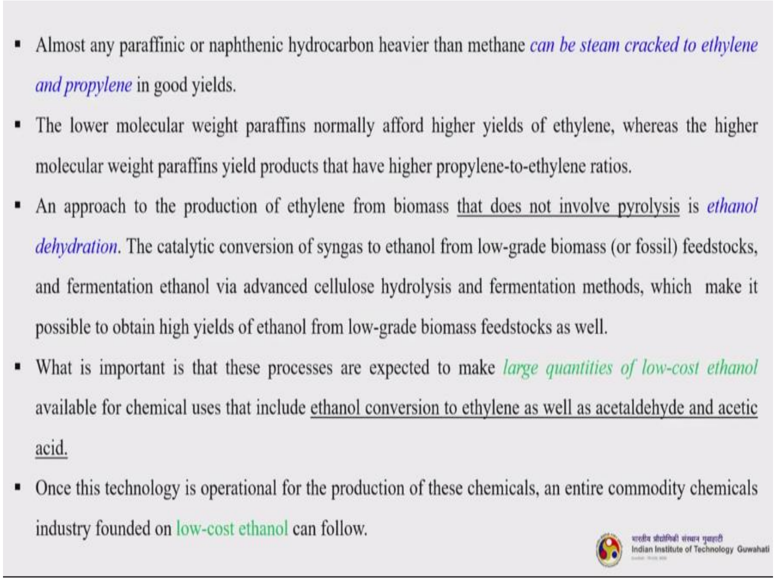

- Almost any paraffinic or naphthenic hydrocarbon heavier than methane *can be steam cracked to ethylene and propylene* in good yields.
- The lower molecular weight paraffins normally afford higher yields of ethylene, whereas the higher molecular weight paraffins yield products that have higher propylene-to-ethylene ratios.
- An approach to the production of ethylene from biomass that does not involve pyrolysis is *ethanol dehydration*. The catalytic conversion of syngas to ethanol from low-grade biomass (or fossil) feedstocks, and fermentation ethanol via advanced cellulose hydrolysis and fermentation methods, which make it possible to obtain high yields of ethanol from low-grade biomass feedstocks as well.
- What is important is that these processes are expected to make *large quantities of low-cost ethanol* available for chemical uses that include ethanol conversion to ethylene as well as acetaldehyde and acetic acid.
- Once this technology is operational for the production of these chemicals, an entire commodity chemicals industry founded on low-cost ethanol can follow.

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So, almost any paraffinic or naphthenic hydrocarbon heavier than methane can be steamed cracked to ethylene and propylene in good yields. Now, the lower molecular weight paraffins normally afford higher yields of ethylene, whereas the higher molecular weight paraffins yield products that have higher propylene to ethylene ratios. An approach to the production of ethylene from biomass that does not involve pyrolysis is of course your ethanol dehydration.

The catalytic conversion of syngas to ethanol from low-grade biomass or even fossil fuel feedstocks and fermentation ethanol via advanced cellulose hydrolysis and fermentation methods which make it possible to obtain high yields of ethanol from low-grade biomass feedstocks as well. It is a good process or technology. So, what is important is that these processes are expected to make large quantities of low-cost ethanol available for chemical uses that include ethanol conversion to ethylene as well as acetaldehyde and acetic acid. Once this technology is operational for the production of these chemicals, an entire commodity chemicals industry founded on low-cost ethanol can follow. A complete biorefinery approach you can say, sustainable biorefinery.

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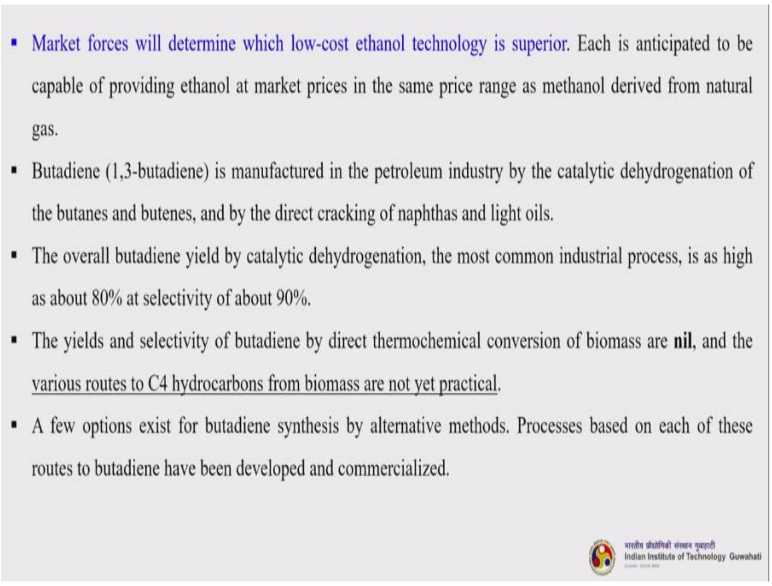

- Market forces will determine which low-cost ethanol technology is superior. Each is anticipated to be capable of providing ethanol at market prices in the same price range as methanol derived from natural gas.
- Butadiene (1,3-butadiene) is manufactured in the petroleum industry by the catalytic dehydrogenation of the butanes and butenes, and by the direct cracking of naphthas and light oils.
- The overall butadiene yield by catalytic dehydrogenation, the most common industrial process, is as high as about 80% at selectivity of about 90%.
- The yields and selectivity of butadiene by direct thermochemical conversion of biomass are **nil**, and the various routes to C4 hydrocarbons from biomass are not yet practical.
- A few options exist for butadiene synthesis by alternative methods. Processes based on each of these routes to butadiene have been developed and commercialized.

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So, markets forces will determine which low-cost ethanol technology is superior. Each is anticipated to be capable of providing ethanol at market prices in the same price range as methanol derived from natural gas. Butadiene is manufactured in the petroleum industry by the catalytic dehydrogenation of the butanes and butenes and by the direct cracking of naphthas and light oils.

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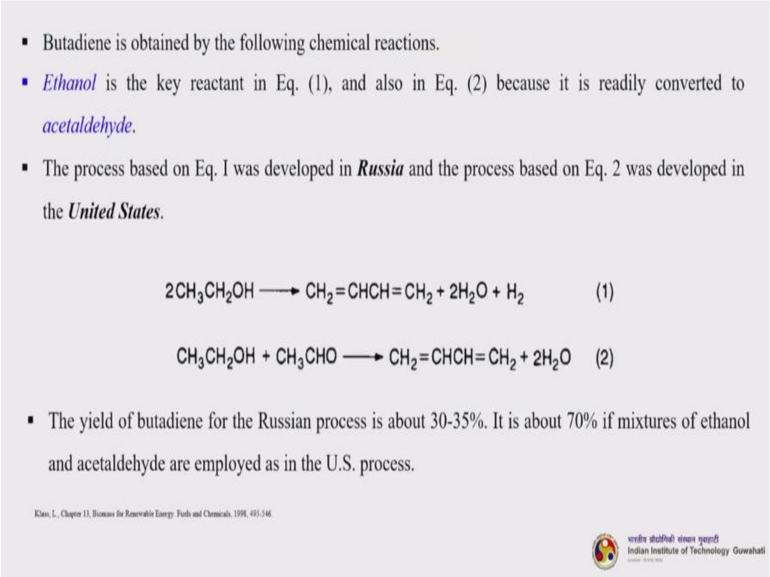

- Butadiene is obtained by the following chemical reactions.
- *Ethanol* is the key reactant in Eq. (1), and also in Eq. (2) because it is readily converted to *acetaldehyde*.
- The process based on Eq. I was developed in ***Russia*** and the process based on Eq. 2 was developed in the ***United States***.

$$2CH_3CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O + H_2 \qquad (1)$$

$$CH_3CH_2OH + CH_3CHO \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O \qquad (2)$$

- The yield of butadiene for the Russian process is about 30-35%. It is about 70% if mixtures of ethanol and acetaldehyde are employed as in the U.S. process.

Klass, L., Chapter 13, Biomass for Renewable Energy. Fuels and Chemicals, 1998, 495-546.

Butadiene is obtained by the following chemical reactions. Ethanol is the key reactant in equation 1 and also in equation 2 because it is readily converted to acetaldehyde. The processes based on equation 1 was developed in Russia and the process based on equation 2 was developed in the United States. These are the 2 reactions you can see. The yield of butadiene for the Russian processes about 30 to 35%. It is about 70% if the mixture of ethanol and acetaldehyde are employed as in the US process.

$$2CH_3CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O + H_2 \qquad (1)$$

$$CH_3CH_2OH + CH_3CHO \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O \qquad (2)$$

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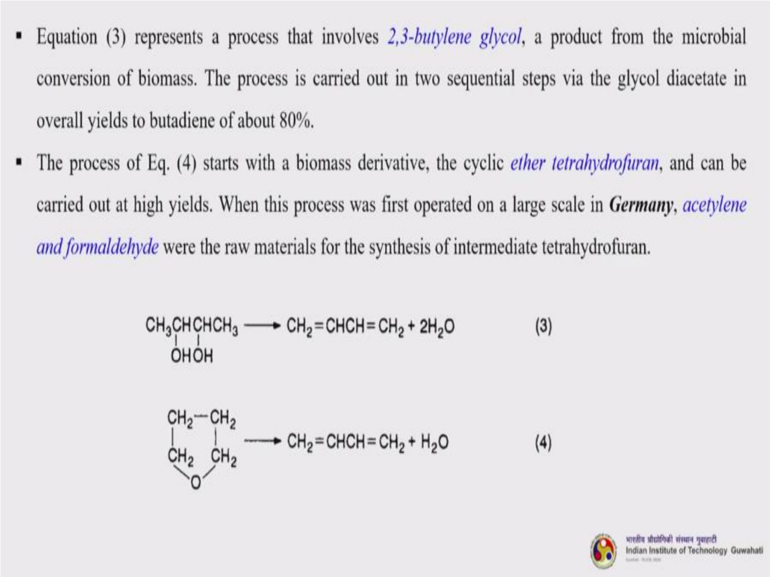
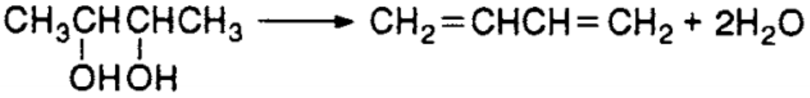


- Equation (3) represents a process that involves *2,3-butylene glycol*, a product from the microbial conversion of biomass. The process is carried out in two sequential steps via the glycol diacetate in overall yields to butadiene of about 80%.
- The process of Eq. (4) starts with a biomass derivative, the cyclic *ether tetrahydrofuran*, and can be carried out at high yields. When this process was first operated on a large scale in ***Germany***, *acetylene and formaldehyde* were the raw materials for the synthesis of intermediate tetrahydrofuran.

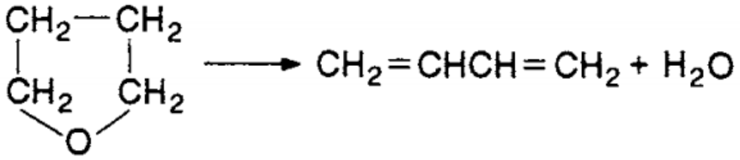
$$CH_3\underset{OH}{CH}\underset{OH}{CH}CH_3 \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O \qquad (3)$$

$$\longrightarrow CH_2{=}CHCH{=}CH_2 + H_2O \qquad (4)$$

Equation 3 represents a process that involves 2, 3 butylene glycol, a product from the microbial conversion of the biomass. The process is carried out in two sequential steps via the glycol diacetate in overall yields to butadiene of about 80%. The process of equation 4 starts with a biomass derivative, the cyclic ether tetrahydrofuran and can be carried out at high yields. When this process was first operated on a large scale in Germany, acetylene and formaldehyde were the raw materials for the synthesis of intermediate tetrahydrofuran.



$$CH_3\underset{OH}{CH}\underset{OH}{CH}CH_3 \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O \qquad (3)$$



(4)

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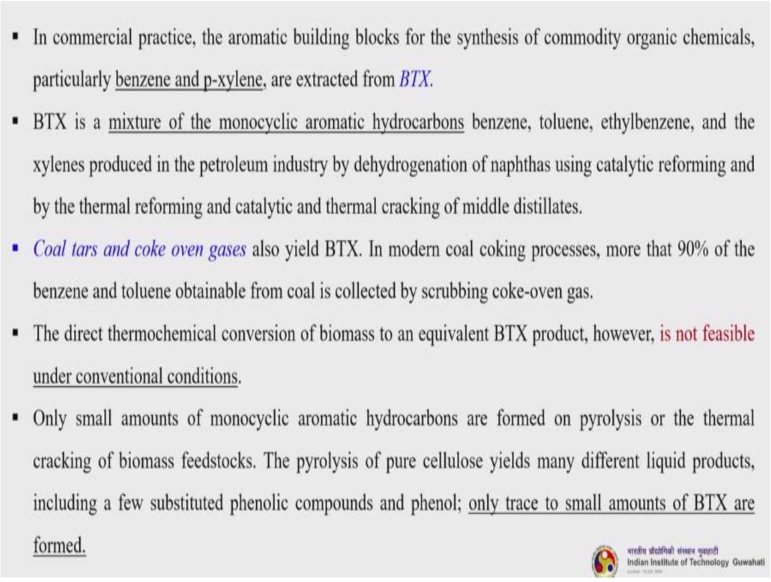

- In commercial practice, the aromatic building blocks for the synthesis of commodity organic chemicals, particularly benzene and p-xylene, are extracted from *BTX*.
- BTX is a mixture of the monocyclic aromatic hydrocarbons benzene, toluene, ethylbenzene, and the xylenes produced in the petroleum industry by dehydrogenation of naphthas using catalytic reforming and by the thermal reforming and catalytic and thermal cracking of middle distillates.
- *Coal tars and coke oven gases* also yield BTX. In modern coal coking processes, more that 90% of the benzene and toluene obtainable from coal is collected by scrubbing coke-oven gas.
- The direct thermochemical conversion of biomass to an equivalent BTX product, however, is not feasible under conventional conditions.
- Only small amounts of monocyclic aromatic hydrocarbons are formed on pyrolysis or the thermal cracking of biomass feedstocks. The pyrolysis of pure cellulose yields many different liquid products, including a few substituted phenolic compounds and phenol; only trace to small amounts of BTX are formed.

In commercial practice, the aromatic building blocks for the synthesis of commodity organic chemicals particularly benzene and p-xylene are extracted from BTX. BTX is a mixture of the monocyclic aromatic hydrocarbon benzenes, toluene, ethylbenzene and xylene produced in the petroleum industry by the dehydrogenation of naphthas using catalytic reforming and by the thermal reforming and catalytic and thermal cracking of middle distillates.

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The pyrolysis of pure cellulose yields many different liquid products including a few substituted phenolic compounds and phenol, only trace to small amounts of BTX are formed.

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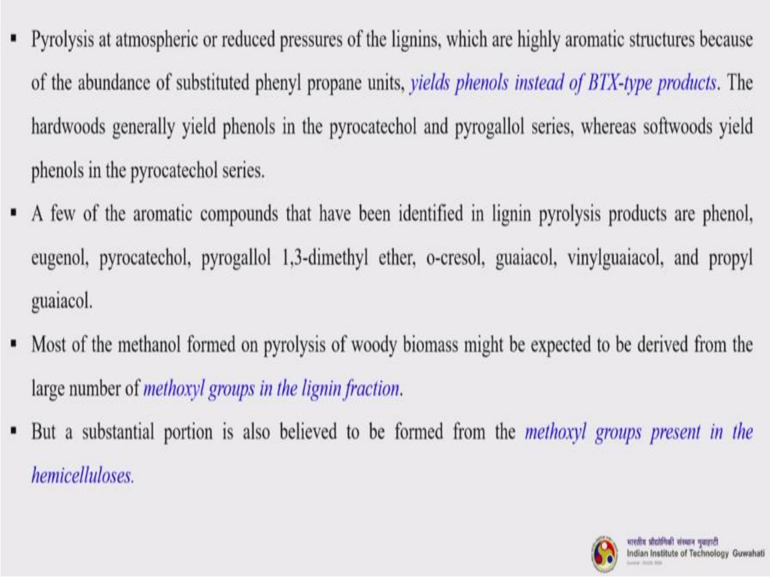

- Pyrolysis at atmospheric or reduced pressures of the lignins, which are highly aromatic structures because of the abundance of substituted phenyl propane units, *yields phenols instead of BTX-type products*. The hardwoods generally yield phenols in the pyrocatechol and pyrogallol series, whereas softwoods yield phenols in the pyrocatechol series.
- A few of the aromatic compounds that have been identified in lignin pyrolysis products are phenol, eugenol, pyrocatechol, pyrogallol 1,3-dimethyl ether, o-cresol, guaiacol, vinylguaiacol, and propyl guaiacol.
- Most of the methanol formed on pyrolysis of woody biomass might be expected to be derived from the large number of *methoxyl groups in the lignin fraction*.
- But a substantial portion is also believed to be formed from the *methoxyl groups present in the hemicelluloses*.

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Pyrolysis at atmospheric or reduced pressure of the lignins, which are highly aromatic structures because of the abundance of the substituted phenly propane units yields phenols instead of the BTX type of products. The hardwoods generally yield phenols in the pyrocatechol and pyrogallol series whereas softwoods yields phenols in the pyrocatechol series.

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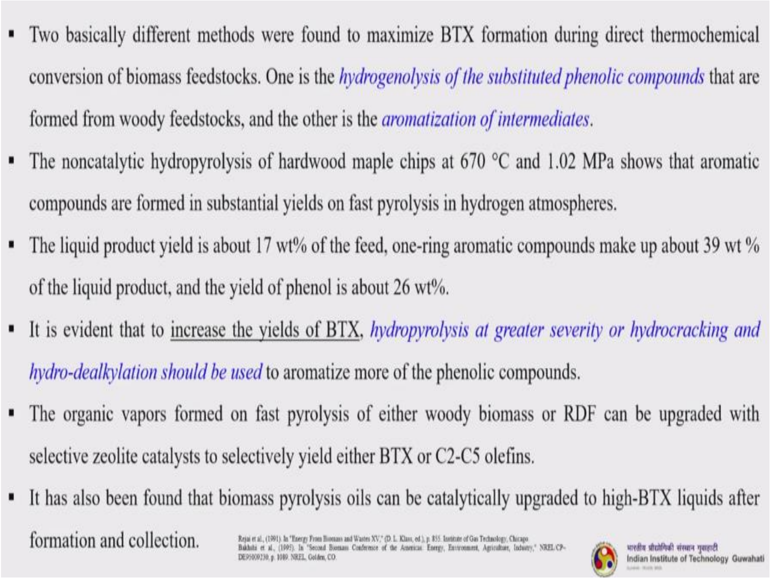

- Two basically different methods were found to maximize BTX formation during direct thermochemical conversion of biomass feedstocks. One is the *hydrogenolysis of the substituted phenolic compounds* that are formed from woody feedstocks, and the other is the *aromatization of intermediates*.
- The noncatalytic hydropyrolysis of hardwood maple chips at 670 °C and 1.02 MPa shows that aromatic compounds are formed in substantial yields on fast pyrolysis in hydrogen atmospheres.
- The liquid product yield is about 17 wt% of the feed, one-ring aromatic compounds make up about 39 wt % of the liquid product, and the yield of phenol is about 26 wt%.
- It is evident that to increase the yields of BTX, *hydropyrolysis at greater severity or hydrocracking and hydro-dealkylation should be used* to aromatize more of the phenolic compounds.
- The organic vapors formed on fast pyrolysis of either woody biomass or RDF can be upgraded with selective zeolite catalysts to selectively yield either BTX or C2-C5 olefins.
- It has also been found that biomass pyrolysis oils can be catalytically upgraded to high-BTX liquids after formation and collection.

Rejai et al., (1991). In "Energy From Biomass and Wastes XV," (D. L. Klass, ed.), p. 855. Institute of Gas Technology, Chicago
Bakhshi et al., (1995). In "Second Biomass Conference of the Americas: Energy, Environment, Agriculture, Industry," NREL/CP-DE95009230, p. 1089. NREL, Golden, CO.

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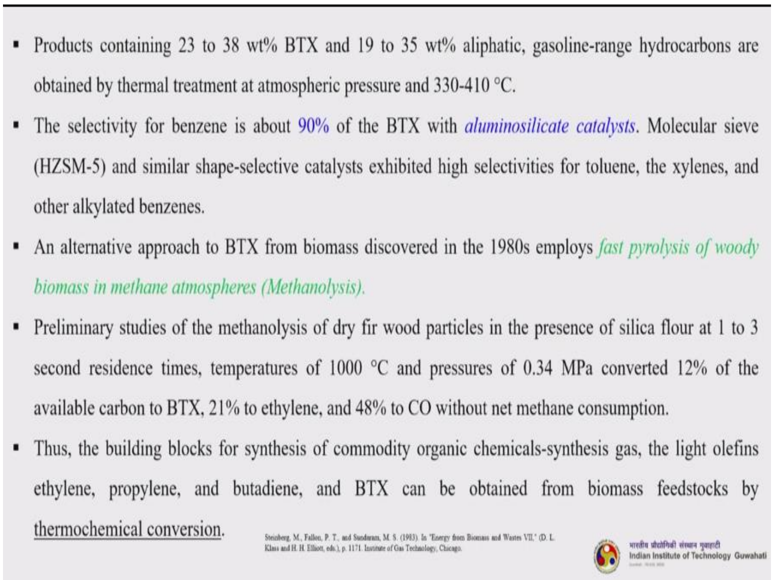

- Products containing 23 to 38 wt% BTX and 19 to 35 wt% aliphatic, gasoline-range hydrocarbons are obtained by thermal treatment at atmospheric pressure and 330-410 °C.
- The selectivity for benzene is about 90% of the BTX with *aluminosilicate catalysts*. Molecular sieve (HZSM-5) and similar shape-selective catalysts exhibited high selectivities for toluene, the xylenes, and other alkylated benzenes.
- An alternative approach to BTX from biomass discovered in the 1980s employs *fast pyrolysis of woody biomass in methane atmospheres (Methanolysis).*
- Preliminary studies of the methanolysis of dry fir wood particles in the presence of silica flour at 1 to 3 second residence times, temperatures of 1000 °C and pressures of 0.34 MPa converted 12% of the available carbon to BTX, 21% to ethylene, and 48% to CO without net methane consumption.
- Thus, the building blocks for synthesis of commodity organic chemicals-synthesis gas, the light olefins ethylene, propylene, and butadiene, and BTX can be obtained from biomass feedstocks by thermochemical conversion.

Steinberg, M., Fallon, P. T., and Sundaram, M. S. (1983). In "Energy from Biomass and Wastes VII," (D. L. Klass and H. H. Elliott, eds.), p. 1171. Institute of Gas Technology, Chicago.

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Thus, the building blocks for synthesis of commodity organic chemical-synthesis gas, the light olefins, ethylene, propylene and butadiene and BTX can be obtained from biomass feedstocks by thermochemical conversion.

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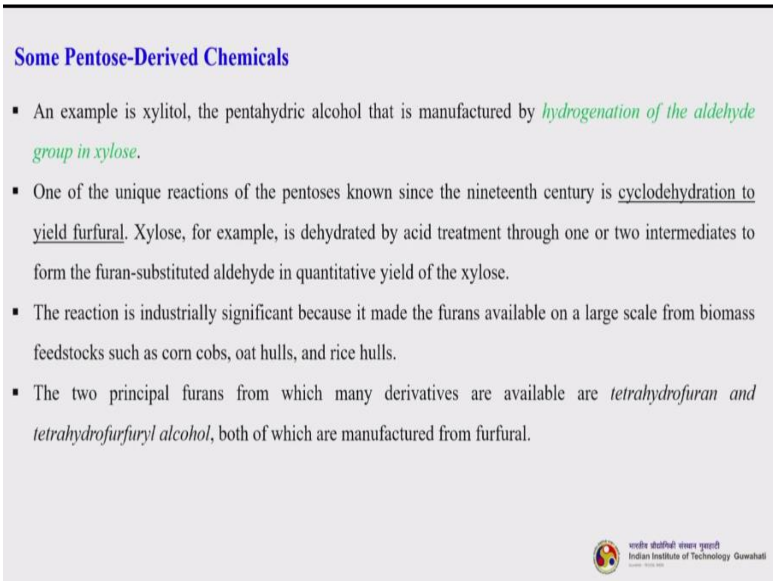

Some Pentose-Derived Chemicals

- An example is xylitol, the pentahydric alcohol that is manufactured by *hydrogenation of the aldehyde group in xylose*.
- One of the unique reactions of the pentoses known since the nineteenth century is cyclodehydration to yield furfural. Xylose, for example, is dehydrated by acid treatment through one or two intermediates to form the furan-substituted aldehyde in quantitative yield of the xylose.
- The reaction is industrially significant because it made the furans available on a large scale from biomass feedstocks such as corn cobs, oat hulls, and rice hulls.
- The two principal furans from which many derivatives are available are *tetrahydrofuran and tetrahydrofurfuryl alcohol*, both of which are manufactured from furfural.

And now we will discuss about some of the pentose-derived commodity chemicals. An example is of course xylitol, the pentahydric alcohol that is manufactured by the hydrogenation of the aldehyde group in the xylose. Now one of the unique reactions of the pentose known since the 19th century is cyclodehydration to yield furfural. Xylose for example is dehydrated by acid treatment through one or two intermediates to form the furan-substituted aldehyde in quantitative yield of the xylose.

The reaction is industrially significant because it made the furans available on a large scale from biomass feedstocks such as corn cobs, oat hulls and rice hulls. Now many other feedstocks has also been used and reported. Now the two principal furans from which many derivatives available are the tetrahydrofuran and tetrahydrofurfuryl alcohol, both of which are manufactured from furfural.

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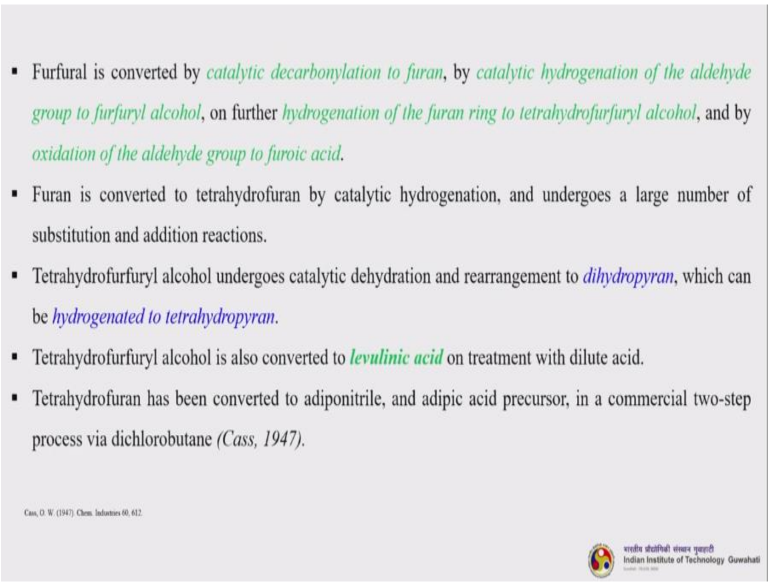

- Furfural is converted by *catalytic decarbonylation to furan*, by *catalytic hydrogenation of the aldehyde group to furfuryl alcohol*, on further *hydrogenation of the furan ring to tetrahydrofurfuryl alcohol*, and by *oxidation of the aldehyde group to furoic acid*.
- Furan is converted to tetrahydrofuran by catalytic hydrogenation, and undergoes a large number of substitution and addition reactions.
- Tetrahydrofurfuryl alcohol undergoes catalytic dehydration and rearrangement to *dihydropyran*, which can be *hydrogenated to tetrahydropyran*.
- Tetrahydrofurfuryl alcohol is also converted to ***levulinic acid*** on treatment with dilute acid.
- Tetrahydrofuran has been converted to adiponitrile, and adipic acid precursor, in a commercial two-step process via dichlorobutane *(Cass, 1947)*.

Cass, O. W. (1947). Chem. Industries 60, 612.

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Furfural is converted by catalytic decarbonylation to furan, by catalytic hydrogenation of the aldehyde group to furfuryl alcohol, on further hydrogenation of the furan ring to the tetrahydrofurfuryl alcohol, and by oxidation of the aldehyde group to furoic acid. Now, furan is converted to tetrahydrofuran by catalytic hydrogenation and undergoes a large number of substitution and addition reactions.

Tetrahydrfurfuryl alcohol undergoes catalytic dehydration and rearrangement to the dihydropyran which can be hydrogenated to tetrahydropyran. Tetrahydrofurfuryl alcohol is also converted to levulinic acid - it is one of the most important commodity chemical - on treatment with dilute acid. Tetrahydrofuran has been converted to adiponitrile and adipic acid precursor in a commercially two-step process via dichlorobutane.

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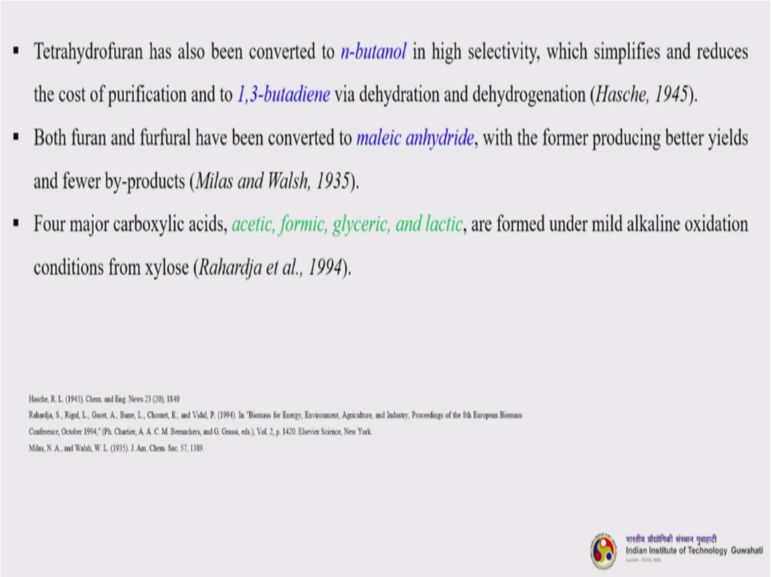

- Tetrahydrofuran has also been converted to *n-butanol* in high selectivity, which simplifies and reduces the cost of purification and to *1,3-butadiene* via dehydration and dehydrogenation (*Hasche, 1945*).
- Both furan and furfural have been converted to *maleic anhydride*, with the former producing better yields and fewer by-products (*Milas and Walsh, 1935*).
- Four major carboxylic acids, *acetic, formic, glyceric, and lactic*, are formed under mild alkaline oxidation conditions from xylose (*Rahardja et al., 1994*).

Hasche, R. L. (1945). Chem. and Eng. News 23 (20), 1840
Rahardja, S., Rigal, L., Gaset, A., Barre, L., Chornet, E., and Vidal, P. (1994). In "Biomass for Energy, Environment, Agriculture, and Industry, Proceedings of the 8th European Biomass Conference, October 1994," (Ph. Chartier, A. A. C. M. Beenackers, and G. Grassi, eds.), Vol. 2, p. 1420. Elsevier Science, New York.
Milas, N. A., and Walsh, W. L. (1935). J. Am. Chem. Sac. 57, 1389.

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Tetrahydrofuran has also been converted to n-butanol in high selectivity which simplifies and reduces the cost of purification and to 1, 3-butadiene via dehydration and dehydrogenation. Both furan and furfural have been converted to maleic anhydride another important class of platform chemicals with the former producing better yields and fewer byproducts. Four major carboxylic acid such as acetic acid, formic acid, glyceric acid and lactic acid are formed under mild alkaline oxidation conditions from xylose.

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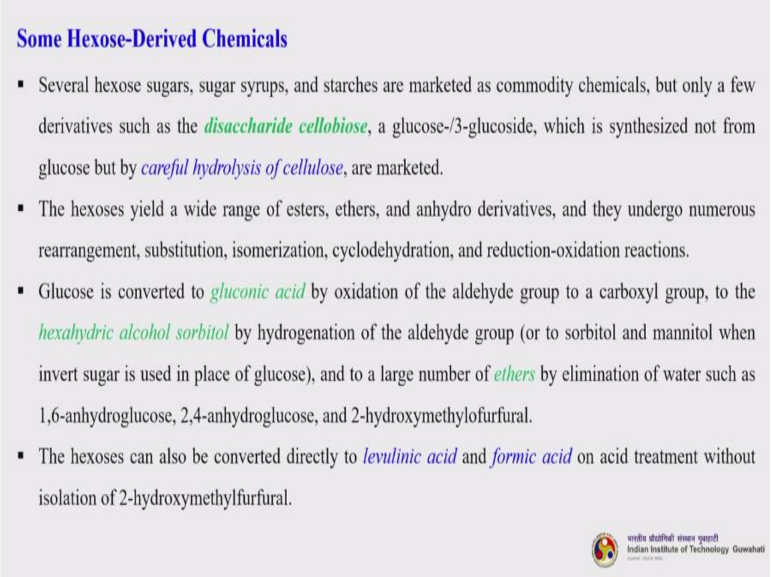

Some Hexose-Derived Chemicals

- Several hexose sugars, sugar syrups, and starches are marketed as commodity chemicals, but only a few derivatives such as the ***disaccharide cellobiose***, a glucose-/3-glucoside, which is synthesized not from glucose but by *careful hydrolysis of cellulose*, are marketed.
- The hexoses yield a wide range of esters, ethers, and anhydro derivatives, and they undergo numerous rearrangement, substitution, isomerization, cyclodehydration, and reduction-oxidation reactions.
- Glucose is converted to *gluconic acid* by oxidation of the aldehyde group to a carboxyl group, to the *hexahydric alcohol sorbitol* by hydrogenation of the aldehyde group (or to sorbitol and mannitol when invert sugar is used in place of glucose), and to a large number of *ethers* by elimination of water such as 1,6-anhydroglucose, 2,4-anhydroglucose, and 2-hydroxymethylofurfural.
- The hexoses can also be converted directly to *levulinic acid* and *formic acid* on acid treatment without isolation of 2-hydroxymethylfurfural.

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So we will now discuss about some of the chemicals from the hexose derived; that is derived from the hexose basically. Several hexose sugars, sugar syrups and starches are marketed as commodity chemicals, but only a few derivatives such as the disaccharide cellobiose, a glucose 3 glucoside, which is synthesized not from glucose but by careful hydrolysis of cellulose, are marketed.

The hexoses yield a wide range of esters, ethers, anhydro derivatives and they undergo numerous rearrangement, substitution, isomerization, cyclodehydration and reduction-oxidation reactions to further produce value-added chemicals. Glucose is converted to gluconic acid by oxidation of the aldehyde group to a carboxylic group and to the hexahydric alcohol, sorbitol by hydrogenation of the aldehyde group (or to sorbitol and mannitol when invert sugar is used in place of glucose), then to a large number of ethers by elimination of water such as 1, 6-anhydroglucose, 2, 4-anhydeoglucose and 2-hydroxymethylofurfural. The hexoses can also be converted directly to levulinic acid and formic acid on acid treatment without isolation of the 2-hydroxymethylfurfural.

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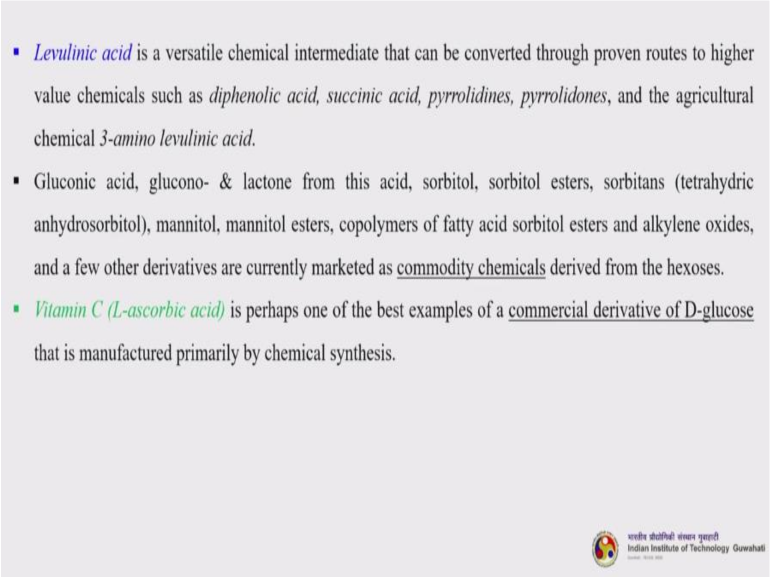

- *Levulinic acid* is a versatile chemical intermediate that can be converted through proven routes to higher value chemicals such as *diphenolic acid, succinic acid, pyrrolidines, pyrrolidones*, and the agricultural chemical *3-amino levulinic acid.*
- Gluconic acid, glucono- & lactone from this acid, sorbitol, sorbitol esters, sorbitans (tetrahydric anhydrosorbitol), mannitol, mannitol esters, copolymers of fatty acid sorbitol esters and alkylene oxides, and a few other derivatives are currently marketed as commodity chemicals derived from the hexoses.
- *Vitamin C (L-ascorbic acid)* is perhaps one of the best examples of a commercial derivative of D-glucose that is manufactured primarily by chemical synthesis.

Levulinic acid is a versatile chemical intermediate that can be converted through proven routes to higher value chemicals such as diphenolic acid, succinic acid, pyrrolidines, pyrrolidones and the agricultural chemical 3-amino levulinic acid. Gluconic acid, glucono and lactone from this acid, then sorbitol, sorbitol esters, sorbitans, mannitol, mannitol esters, copolymers of fatty acid sorbitol esters and alkylene oxides and a few other derivatives are currently marketed as commodity chemicals derived from the hexoses. Vitamin C that is L-ascorbic acid is perhaps one of the best example of a commercial derivative of the D-glucose that is manufactured primarily by chemical synthesis.

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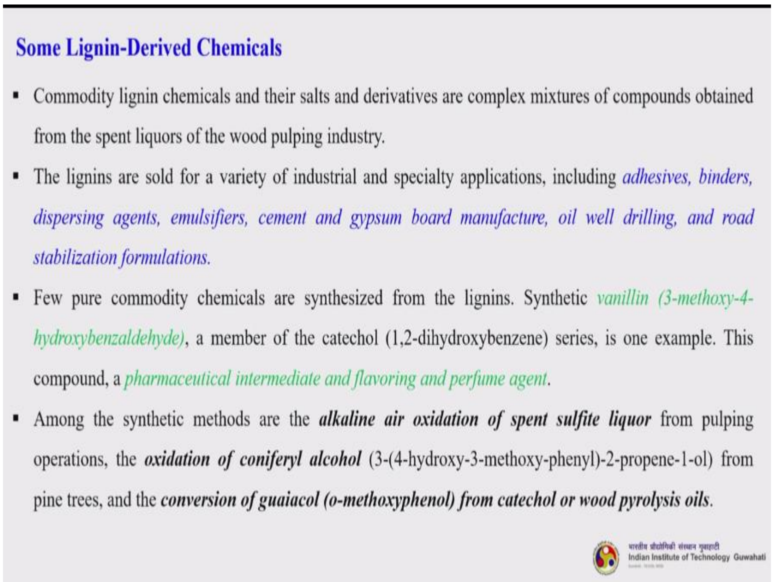

Some Lignin-Derived Chemicals

- Commodity lignin chemicals and their salts and derivatives are complex mixtures of compounds obtained from the spent liquors of the wood pulping industry.
- The lignins are sold for a variety of industrial and specialty applications, including *adhesives, binders, dispersing agents, emulsifiers, cement and gypsum board manufacture, oil well drilling, and road stabilization formulations.*
- Few pure commodity chemicals are synthesized from the lignins. Synthetic *vanillin (3-methoxy-4-hydroxybenzaldehyde)*, a member of the catechol (1,2-dihydroxybenzene) series, is one example. This compound, a *pharmaceutical intermediate and flavoring and perfume agent*.
- Among the synthetic methods are the ***alkaline air oxidation of spent sulfite liquor*** from pulping operations, the ***oxidation of coniferyl alcohol*** (3-(4-hydroxy-3-methoxy-phenyl)-2-propene-1-ol) from pine trees, and the ***conversion of guaiacol (o-methoxyphenol) from catechol or wood pyrolysis oils***.

Now we will talk about some of the lignin-derived chemicals. Now commodity lignin chemicals and their salts and derivatives are complex mixtures of compounds obtained from the spent liquors of the wood pulping industry. The lignins are sold for a variety of industrial and speciality applications including adhesives, binders, dispersing agents, emulsifiers, cement and gypsum board manufacture, oil well drilling and road stabilization formulations.

A few pure commodity chemicals are synthesized from the lignins. Synthetic vanillin, a member of the catechol series is one such example. The compound, a pharmaceutical intermediate and flavoring and perfume agent. Among the synthetic methods are the alkaline air oxidation of the spent sulfite liquor from pulping operations, then the oxidation of the coniferyl alcohol from pine trees, the conversion of guaiacol from catechol or wood pyrolysis oils.

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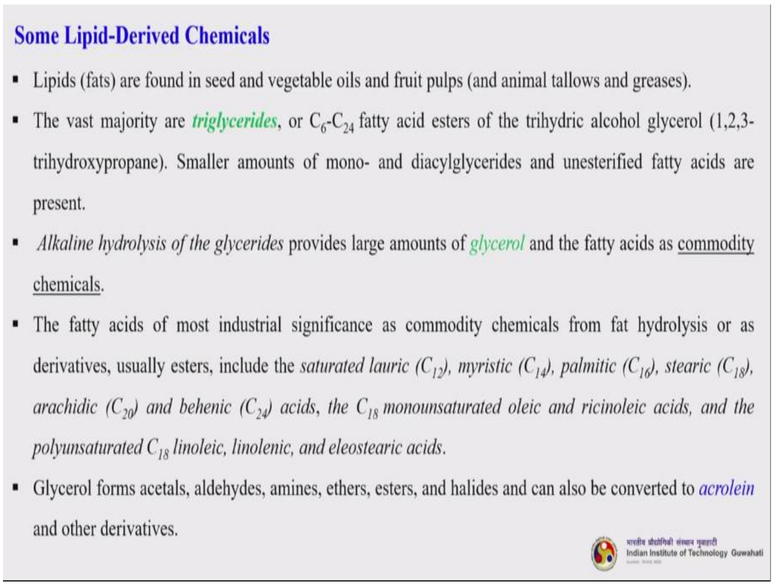

Some Lipid-Derived Chemicals

- Lipids (fats) are found in seed and vegetable oils and fruit pulps (and animal tallows and greases).
- The vast majority are ***triglycerides***, or C_6-C_{24} fatty acid esters of the trihydric alcohol glycerol (1,2,3-trihydroxypropane). Smaller amounts of mono- and diacylglycerides and unesterified fatty acids are present.
- *Alkaline hydrolysis of the glycerides* provides large amounts of *glycerol* and the fatty acids as commodity chemicals.
- The fatty acids of most industrial significance as commodity chemicals from fat hydrolysis or as derivatives, usually esters, include the *saturated lauric* (C_{12}), *myristic* (C_{14}), *palmitic* (C_{16}), *stearic* (C_{18}), *arachidic* (C_{20}) *and behenic* (C_{24}) *acids, the* C_{18} *monounsaturated oleic and ricinoleic acids, and the polyunsaturated* C_{18} *linoleic, linolenic, and eleostearic acids.*
- Glycerol forms acetals, aldehydes, amines, ethers, esters, and halides and can also be converted to *acrolein* and other derivatives.

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Then some lipid-derived chemicals. Lipids or fats are found in seed and vegetable oils and the fruit pupls and of course animal tallows and greases also. The vast majority are triglycerides, C 6 to C 24 fatty acid esters of the trihydric alcohol glycerol. Smaller amounts of the mono and diacylglycerides and unesterified fatty acids are also present. Alkaline hydrolysis of the glycerides provide large amount of glycerol and the fatty acids as commodity chemicals.

The fatty acids of most industrial significance as commodity chemicals from fat hydrolysis, or as derivatives are usually esters that includes the saturated lauric, myristic, palmitic, stearic, arachidic, behenic acid, the C 18 monounsaturated oleic and ricinoleic acid and the polyunsaturated C 18 linoleic, linolenic and eleostearic acids. Now glycerol forms acetals, aldehydes, amines, ethers, esters and halides and can also be converted to acrolein and other derivatives.

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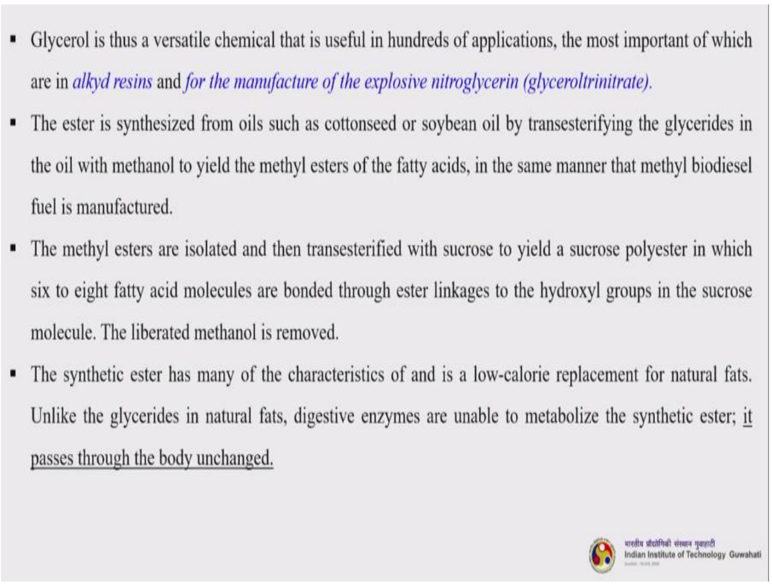

- Glycerol is thus a versatile chemical that is useful in hundreds of applications, the most important of which are in *alkyd resins* and *for the manufacture of the explosive nitroglycerin (glyceroltrinitrate).*
- The ester is synthesized from oils such as cottonseed or soybean oil by transesterifying the glycerides in the oil with methanol to yield the methyl esters of the fatty acids, in the same manner that methyl biodiesel fuel is manufactured.
- The methyl esters are isolated and then transesterified with sucrose to yield a sucrose polyester in which six to eight fatty acid molecules are bonded through ester linkages to the hydroxyl groups in the sucrose molecule. The liberated methanol is removed.
- The synthetic ester has many of the characteristics of and is a low-calorie replacement for natural fats. Unlike the glycerides in natural fats, digestive enzymes are unable to metabolize the synthetic ester; it passes through the body unchanged.

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Glycerol is thus a versatile chemical that is useful in hundreds of applications, the most important of which are in alkyd resins and the manufacturer of the explosive nitroglycerin, glyceroltrinitrate. So the ester is synthesize from oils such as cottonseed or soybean oil by transesterifying the glycerides in the oil with a methanol to yield the methyl esters of the fatty acids in the same manner that methyl biodiesel fuel is manufactured.

The methyl esters are isolated and then transesterified with sucrose to yield a sucrose polyester in which 6 to 8 fatty acid molecules are bonded through ester linkages to the hydroxyl groups in the sucrose molecule. The liberated methanol is removed. The synthetic ester has many of the characteristics of and is a low-calorie replacement for natural fats. Unlike the glycerides in natural fats, digestive enzymes are unable to metabolize the synthetic ester, it passes through the body unchanged.

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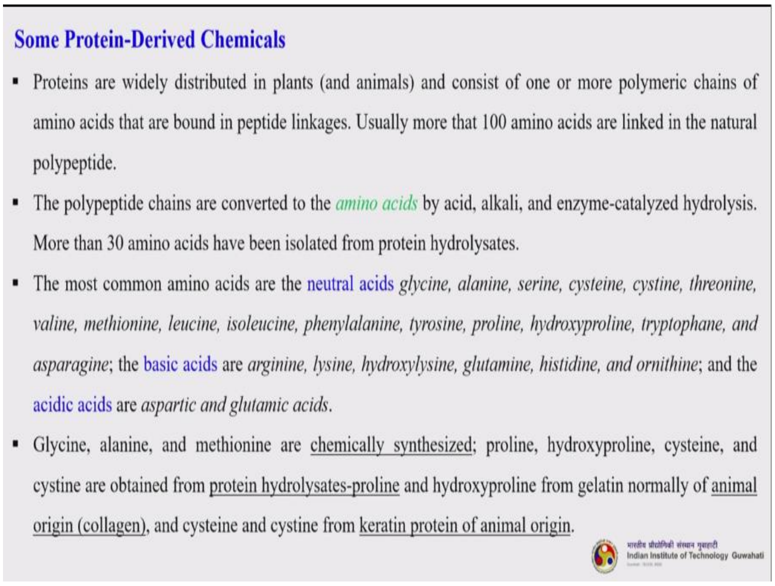

Some Protein-Derived Chemicals

- Proteins are widely distributed in plants (and animals) and consist of one or more polymeric chains of amino acids that are bound in peptide linkages. Usually more that 100 amino acids are linked in the natural polypeptide.
- The polypeptide chains are converted to the *amino acids* by acid, alkali, and enzyme-catalyzed hydrolysis. More than 30 amino acids have been isolated from protein hydrolysates.
- The most common amino acids are the neutral acids *glycine, alanine, serine, cysteine, cystine, threonine, valine, methionine, leucine, isoleucine, phenylalanine, tyrosine, proline, hydroxyproline, tryptophane, and asparagine*; the basic acids are *arginine, lysine, hydroxylysine, glutamine, histidine, and ornithine*; and the acidic acids are *aspartic and glutamic acids*.
- Glycine, alanine, and methionine are chemically synthesized; proline, hydroxyproline, cysteine, and cystine are obtained from protein hydrolysates-proline and hydroxyproline from gelatin normally of animal origin (collagen), and cysteine and cystine from keratin protein of animal origin.

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Now we will talk about some of the protein-derived chemicals. Proteins are widely distributed in plants and animals and consist of one or more polymeric chains of amino acids that are bound in peptide linkages. Usually more than 100 amino acids are linked in the natural polypeptide. The polypeptide chains are converted to the amino acids by acid, alkali and enzyme catalyzed hydrolysis.

More than 30 amino acids have been isolated from protein hydrolysates. The most common amino acids are the neutral acids glycine, alanine, serine, cysteine and then cystine, threonine, valine, methionine, leucine, isoleucine, phenylalanine, then tyrosine, proline, hydroxyproline, tryptophane and asparagine. The basic acids include arginine, lysine, hydroxylysine, glutamine, histidine and ornithine.

And the acidic acids are aspartic and glutamic acids. Glycine, alanine and methionine are chemically synthesized. Proline, hydroxyproline, cysteine and cystine are obtained from the protein hydrolysates. Proline and hydroxyproline from the gelatin normally of animal origin basically from the collagen and cysteine and cystine from keratin protein of the animal origin.

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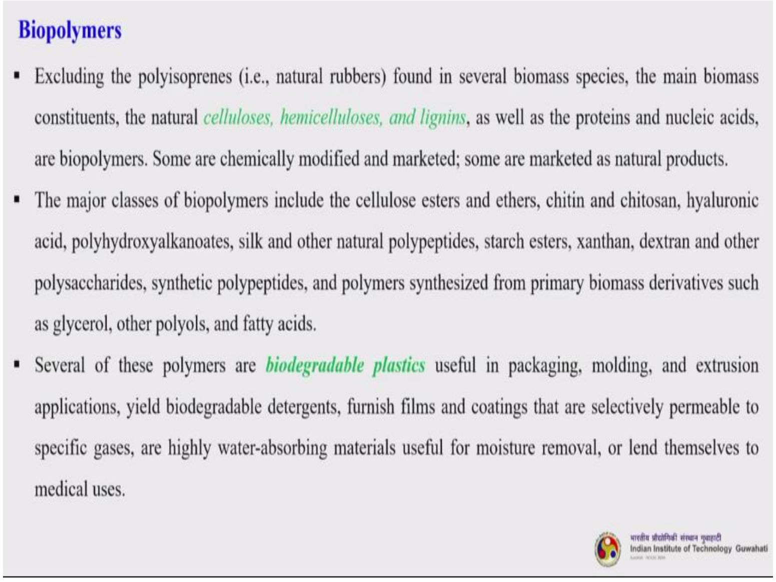

Biopolymers

- Excluding the polyisoprenes (i.e., natural rubbers) found in several biomass species, the main biomass constituents, the natural *celluloses, hemicelluloses, and lignins*, as well as the proteins and nucleic acids, are biopolymers. Some are chemically modified and marketed; some are marketed as natural products.
- The major classes of biopolymers include the cellulose esters and ethers, chitin and chitosan, hyaluronic acid, polyhydroxyalkanoates, silk and other natural polypeptides, starch esters, xanthan, dextran and other polysaccharides, synthetic polypeptides, and polymers synthesized from primary biomass derivatives such as glycerol, other polyols, and fatty acids.
- Several of these polymers are ***biodegradable plastics*** useful in packaging, molding, and extrusion applications, yield biodegradable detergents, furnish films and coatings that are selectively permeable to specific gases, are highly water-absorbing materials useful for moisture removal, or lend themselves to medical uses.

Now we will talk about biopolymers. Now excluding the polyisoprenes that is the natural rubbers found in several biomass species, the main biomass constituents, the natural cellulose, hemicellulose and lignins as well as the proteins and nucleic acids are biopolymers. Some are chemically modified and marketed. Some are marketed as natural products.

The major classes of biopolymers include the cellulose esters and ethers, chitin and chitosan, then hyaluronic acid, polyhydroxyalkanoates, silk and other natural polypeptides, starch esters, xanthan, dextran, and other polysaccharides, synthetic polypeptides and polymers synthesized from primary biomass derivatives such as glycerol and other polyols and fatty acids.

Several of these polymers are biodegradable plastics useful in packaging, molding and extrusion applications, yield biodegradable detergents, furnish films and coatings that are selectively permeable to specific gases and are highly water absorbing materials useful for moisture removal, or lend themselves to medical uses.

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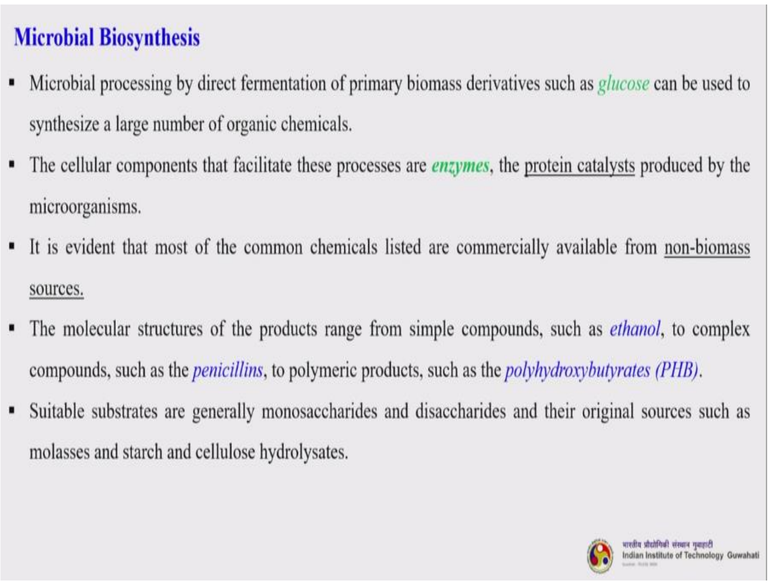

Microbial Biosynthesis

- Microbial processing by direct fermentation of primary biomass derivatives such as *glucose* can be used to synthesize a large number of organic chemicals.
- The cellular components that facilitate these processes are ***enzymes***, the protein catalysts produced by the microorganisms.
- It is evident that most of the common chemicals listed are commercially available from non-biomass sources.
- The molecular structures of the products range from simple compounds, such as *ethanol*, to complex compounds, such as the *penicillins*, to polymeric products, such as the *polyhydroxybutyrates (PHB)*.
- Suitable substrates are generally monosaccharides and disaccharides and their original sources such as molasses and starch and cellulose hydrolysates.

Microbial (Bio)synthesis: Microbial processing by direct fermentation of primary biomass derivatives such as glucose can be used to synthesize a large number of organic chemicals. The cellular components that facilitate these processes are enzymes, the protein catalysts produced by the microorganisms. It is evident that most of the common chemicals listed are commercially available from the non-biomass sources.

The molecular structure of the products range from simple compounds such as ethanol to complex compounds such as penicillins to polymeric products such as polyhydroxybutyrates/PHB. Suitable substrates are generally monosaccharides and disaccharides and their original sources such as molasses, starch, and cellulose hydrolysates.

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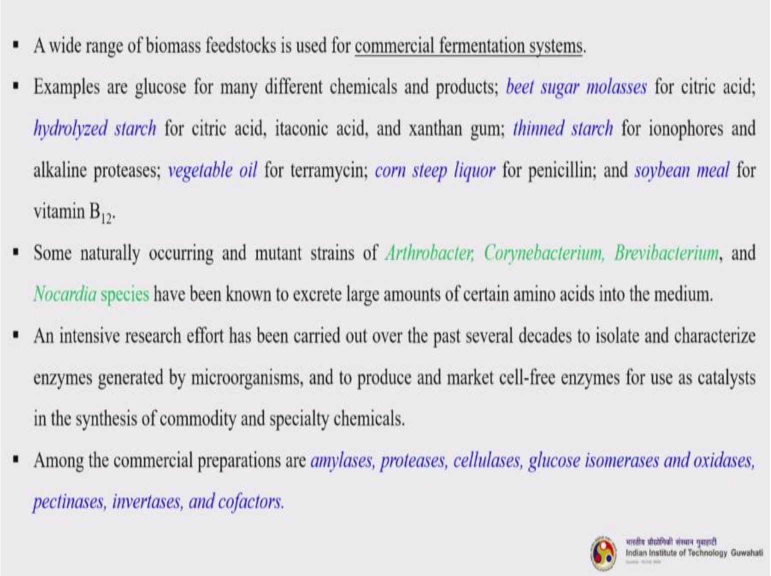

- A wide range of biomass feedstocks is used for commercial fermentation systems.
- Examples are glucose for many different chemicals and products; *beet sugar molasses* for citric acid; *hydrolyzed starch* for citric acid, itaconic acid, and xanthan gum; *thinned starch* for ionophores and alkaline proteases; *vegetable oil* for terramycin; *corn steep liquor* for penicillin; and *soybean meal* for vitamin B_{12}.
- Some naturally occurring and mutant strains of *Arthrobacter, Corynebacterium, Brevibacterium*, and *Nocardia* species have been known to excrete large amounts of certain amino acids into the medium.
- An intensive research effort has been carried out over the past several decades to isolate and characterize enzymes generated by microorganisms, and to produce and market cell-free enzymes for use as catalysts in the synthesis of commodity and specialty chemicals.
- Among the commercial preparations are *amylases, proteases, cellulases, glucose isomerases and oxidases, pectinases, invertases, and cofactors.*

A wide range of biomass feedstocks is used for commercial fermentation systems. Examples are glucose for many different chemicals and products, beet sugar molasses for citric acid, hydrolyzed starch for citric acid, itaconic acid and xantham gum, thinned starch for ionophores and alkaline proteases, vegetable oil for terramycin, corn steep liquor for penicillin, soybean meal for Vitamin B_{12}.

Some naturally occurring and mutant strains of *Arthrobacter*, *Corynebacterium*, *Brevibacterium* and *Nocardia* species have been known to excrete large amounts of certain amino acids into the medium. An intensive research effort has been carried out over the last few decades to isolate and characterize enzymes generated by microorganisms and to produce and market cell-free enzymes for use as catalysts in the synthesis of commodity and speciality chemicals.

Among the commercial preparations are amylases, proteases, cellulases, glucose isomerases and oxidases, pectinases, invertases and cofactors.

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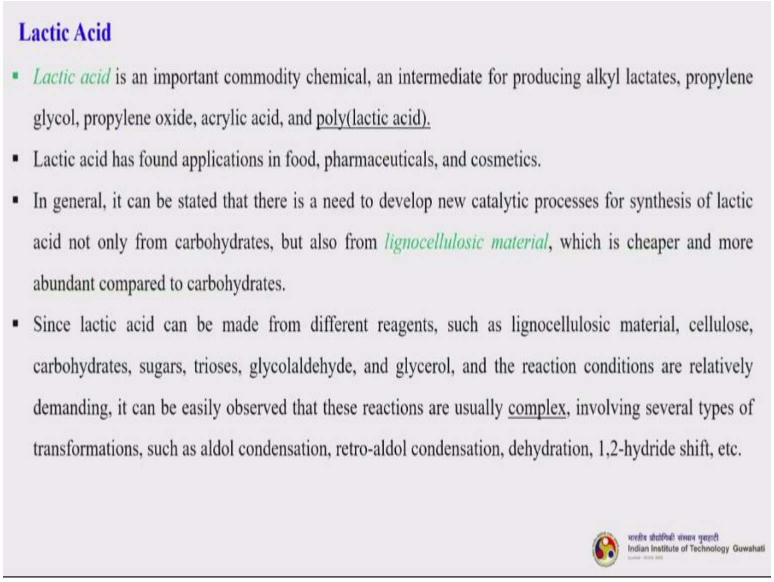

Lactic Acid

- *Lactic acid* is an important commodity chemical, an intermediate for producing alkyl lactates, propylene glycol, propylene oxide, acrylic acid, and poly(lactic acid).
- Lactic acid has found applications in food, pharmaceuticals, and cosmetics.
- In general, it can be stated that there is a need to develop new catalytic processes for synthesis of lactic acid not only from carbohydrates, but also from *lignocellulosic material*, which is cheaper and more abundant compared to carbohydrates.
- Since lactic acid can be made from different reagents, such as lignocellulosic material, cellulose, carbohydrates, sugars, trioses, glycolaldehyde, and glycerol, and the reaction conditions are relatively demanding, it can be easily observed that these reactions are usually complex, involving several types of transformations, such as aldol condensation, retro-aldol condensation, dehydration, 1,2-hydride shift, etc.

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Now we will discuss about lactic acids and of course then polylactic acids, the two most important commercial or commodity chemicals. Lactic acid is an important commodity chemical, an intermediate for producing alkyl lactates, propylene glycol, propylene oxide, acrylic acid and of course PLA the polylactic acid. Lactic acid has found applications in food, pharmaceuticals and cosmetics.

In general, it can be stated that there is a need to develop new catalytic process for synthesis of lactic acid not only from carbohydrates, but also from the lignocellulosic material, which is cheaper and more abundant compared to the carbohydrates. Since lactic acid can be made from different reagents such as lignocellulosic material, cellulose, carbohydrates, sugars, trioses, glycolaldehyde and glycerol, and the reaction conditions are relatively demanding, it can be easily observed that these reactions are usually complex involving several types of transformations such as aldol condensation, retro-aldol condensation, dehydration, 1, 2-hydride shift, etc.

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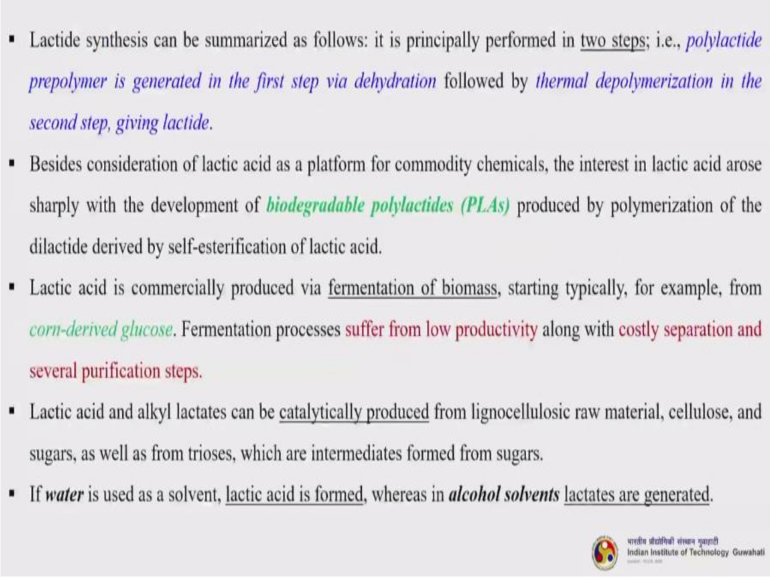

- Lactide synthesis can be summarized as follows: it is principally performed in two steps; i.e., *polylactide prepolymer is generated in the first step via dehydration* followed by *thermal depolymerization in the second step, giving lactide.*
- Besides consideration of lactic acid as a platform for commodity chemicals, the interest in lactic acid arose sharply with the development of ***biodegradable polylactides (PLAs)*** produced by polymerization of the dilactide derived by self-esterification of lactic acid.
- Lactic acid is commercially produced via fermentation of biomass, starting typically, for example, from *corn-derived glucose*. Fermentation processes suffer from low productivity along with costly separation and several purification steps.
- Lactic acid and alkyl lactates can be catalytically produced from lignocellulosic raw material, cellulose, and sugars, as well as from trioses, which are intermediates formed from sugars.
- If ***water*** is used as a solvent, lactic acid is formed, whereas in ***alcohol solvents*** lactates are generated.

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Lactide synthesis can be summarized as follows. It is principally performed in two steps. First polylactide prepolymer is generated in the first step via dehydration followed by thermal depolymerization in the second step, which gives lactide. Besides consideration of lactic acid as a platform for commodity chemicals, the interest in lactic acid arose sharply with the development of the biodegradable polylactides that is the PLA/ olylactic acid produced by polymerization of the dilactide derivative derived by self-esterification of the lactic acid. Now, we will discuss how a PLA is also getting produced. Now lactic acid is commercially produced by fermentation of biomass, starting typically, for example, from corn derived glucose. Fermentation processes suffer from low productivity along with costly separation and several purification steps.

That is the usual drawback of any fermentation process. Now lactic acid and alkyl lactates can be catalytically, produced from lignocellulosic raw material, cellulose and sugars as well as from trioses which are intermediates formed from sugars. If water is used as solvent,lactic acid is formed whereas in alcohol solvents lactates are generated.

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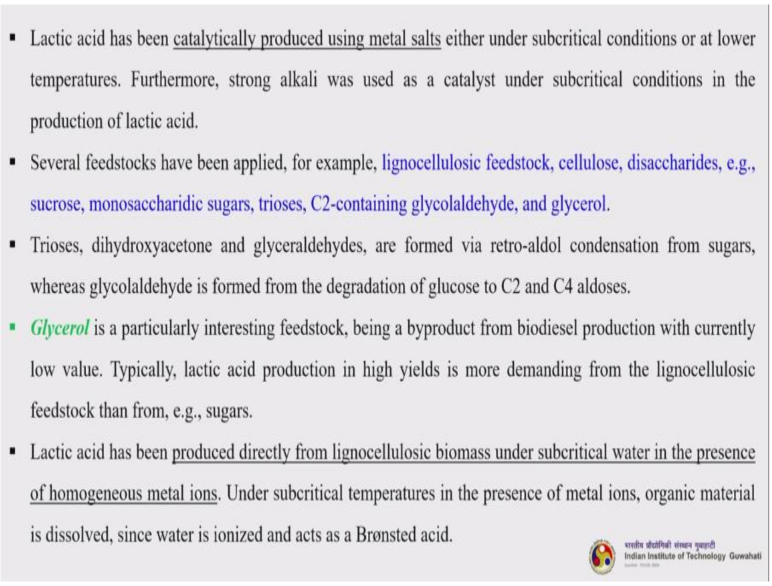

- Lactic acid has been catalytically produced using metal salts either under subcritical conditions or at lower temperatures. Furthermore, strong alkali was used as a catalyst under subcritical conditions in the production of lactic acid.
- Several feedstocks have been applied, for example, lignocellulosic feedstock, cellulose, disaccharides, e.g., sucrose, monosaccharidic sugars, trioses, C2-containing glycolaldehyde, and glycerol.
- Trioses, dihydroxyacetone and glyceraldehydes, are formed via retro-aldol condensation from sugars, whereas glycolaldehyde is formed from the degradation of glucose to C2 and C4 aldoses.
- *Glycerol* is a particularly interesting feedstock, being a byproduct from biodiesel production with currently low value. Typically, lactic acid production in high yields is more demanding from the lignocellulosic feedstock than from, e.g., sugars.
- Lactic acid has been produced directly from lignocellulosic biomass under subcritical water in the presence of homogeneous metal ions. Under subcritical temperatures in the presence of metal ions, organic material is dissolved, since water is ionized and acts as a Brønsted acid.

Lactic acid has been catalytically produced using metal salts either under subcritical conditions or at lower temperatures. Furthermore, strong alkali was used as a catalyst under subcritical conditions in the production of the lactic acid. Several feedstocks has been applied (for example) Lignocellulosic feedstock, cellulose, disaccharides as for example, sucrose, monosaccharidic sugars, trioses, C2-containing glycolaldehyde, even glycerol.

Trioses, dihydroxyacetone and glyceraldehydes are formed via retro-aldol condensation from sugars whereas glycolaldehyde is formed from the degradation of the glucose to C2 and C4 aldoses. Glycerol is a particularly interesting feedstock being a byproduct from the biodiesel production with currently low value. There are a lot of discussion about how to convert glycerin to a value-added products. We have already discussed it.

Now typically, lactic acid production in high yields is more demanding from the lignocellulosic feedstock than from the sugars. Lactic acid has been produced directly from the lignocellulosic biomass under subcritical water in the presence of homogeneous metal ions. Under subcritical temperatures in the presence of metal ions, organic material is dissolved, since water is ionized and act as a Bronsted acid.

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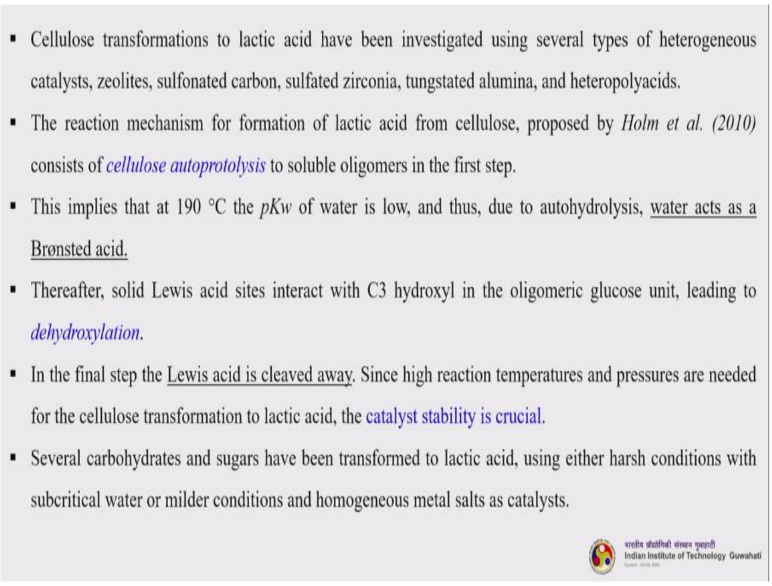

- Cellulose transformations to lactic acid have been investigated using several types of heterogeneous catalysts, zeolites, sulfonated carbon, sulfated zirconia, tungstated alumina, and heteropolyacids.
- The reaction mechanism for formation of lactic acid from cellulose, proposed by *Holm et al. (2010)* consists of *cellulose autoprotolysis* to soluble oligomers in the first step.
- This implies that at 190 °C the *pKw* of water is low, and thus, due to autohydrolysis, water acts as a Brønsted acid.
- Thereafter, solid Lewis acid sites interact with C3 hydroxyl in the oligomeric glucose unit, leading to *dehydroxylation*.
- In the final step the Lewis acid is cleaved away. Since high reaction temperatures and pressures are needed for the cellulose transformation to lactic acid, the catalyst stability is crucial.
- Several carbohydrates and sugars have been transformed to lactic acid, using either harsh conditions with subcritical water or milder conditions and homogeneous metal salts as catalysts.

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And thus due to autohydrolysis water acts as a Bronsted acid. Thereafter solid Lewis acid sites interact with the C3 hydroxyl in the oligomeric glucose unit leading to dehydroxylation. In the final step, the Lewis acid is cleaved away. Since high reaction temperatures and pressures are needed for the cellulose transformation to lactic acid, the catalyst stability is a very crucial factor.

Several carbohydrates and sugars have been transformed to lactic acid using either harsh conditions with subcritical water or milder conditions and homogeneous metal salts as catalysts.

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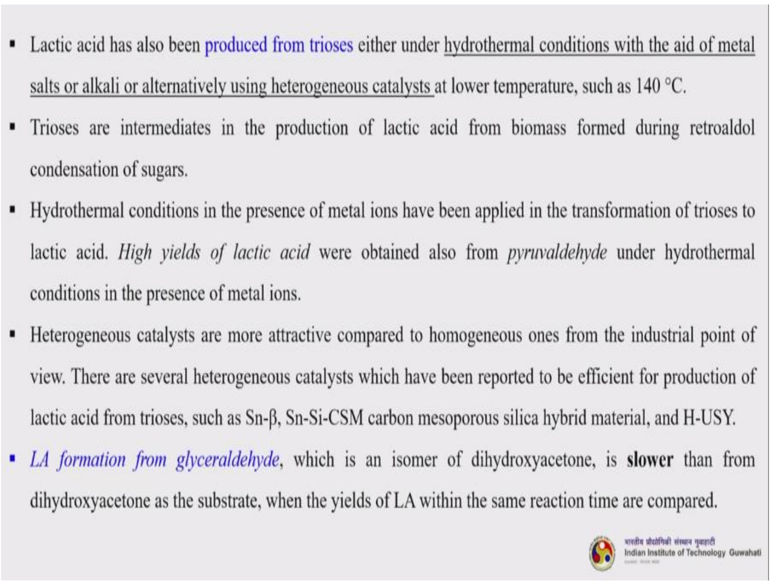

- Lactic acid has also been produced from trioses either under hydrothermal conditions with the aid of metal salts or alkali or alternatively using heterogeneous catalysts at lower temperature, such as 140 °C.
- Trioses are intermediates in the production of lactic acid from biomass formed during retroaldol condensation of sugars.
- Hydrothermal conditions in the presence of metal ions have been applied in the transformation of trioses to lactic acid. *High yields of lactic acid* were obtained also from *pyruvaldehyde* under hydrothermal conditions in the presence of metal ions.
- Heterogeneous catalysts are more attractive compared to homogeneous ones from the industrial point of view. There are several heterogeneous catalysts which have been reported to be efficient for production of lactic acid from trioses, such as Sn-β, Sn-Si-CSM carbon mesoporous silica hybrid material, and H-USY.
- *LA formation from glyceraldehyde*, which is an isomer of dihydroxyacetone, is **slower** than from dihydroxyacetone as the substrate, when the yields of LA within the same reaction time are compared.

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Lactic acid has also been produced from trioses either under hydrothermal conditions with the aid of metal salts or alkali or alternatively using heterogeneous catalyst at lower temperatures such as 140 degree centigrade. Trioses are intermediates in the production of lactic acid from biomass formed during a retroaldol condensation of sugars. Hydrothermal conditions in the presence of metal ions have been applied in the transformation of trioses to lactic acid.

High yields of lactic acid were obtained also from the pyruvaldehyde under hydrothermal conditions in the presence of metal ions. Heterogeneous catalysts are more attractive compared to homogeneous ones (we have understood that, we have discussed why it is so) from the industrial point of view. There are several heterogeneous catalysts which have been reported to be efficient for the production of lactic acid from trioses, such as Sn-beta, Sn-Si-CSM carbon mesoporous silica hybrid material and H-USY. Lactic acid formation from glyceraldehyde which is an isomer of dihydroxyacetone is slower than from dihydroxyacetone as the substrate when the yields of lactic acid within the same reaction time are compared.

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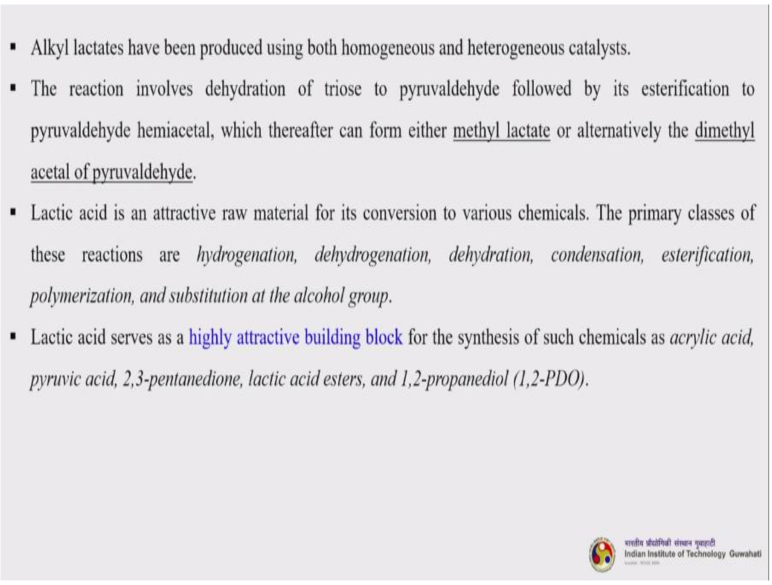

- Alkyl lactates have been produced using both homogeneous and heterogeneous catalysts.
- The reaction involves dehydration of triose to pyruvaldehyde followed by its esterification to pyruvaldehyde hemiacetal, which thereafter can form either methyl lactate or alternatively the dimethyl acetal of pyruvaldehyde.
- Lactic acid is an attractive raw material for its conversion to various chemicals. The primary classes of these reactions are *hydrogenation, dehydrogenation, dehydration, condensation, esterification, polymerization, and substitution at the alcohol group.*
- Lactic acid serves as a highly attractive building block for the synthesis of such chemicals as *acrylic acid, pyruvic acid, 2,3-pentanedione, lactic acid esters, and 1,2-propanediol (1,2-PDO).*

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Alkyl lactates have been produced using both homogeneous and heterogeneous catalysts. The reaction involves dehydration of triose to pyruvaldehyde followed by esterfication of pyruvaldehyde hemiacetal, which thereafter can form either methyl lactate or alternatively the dimethyl acetal of pyruvaldehyde. Now lactic acid is an attractive raw material for its conversion to various chemicals.

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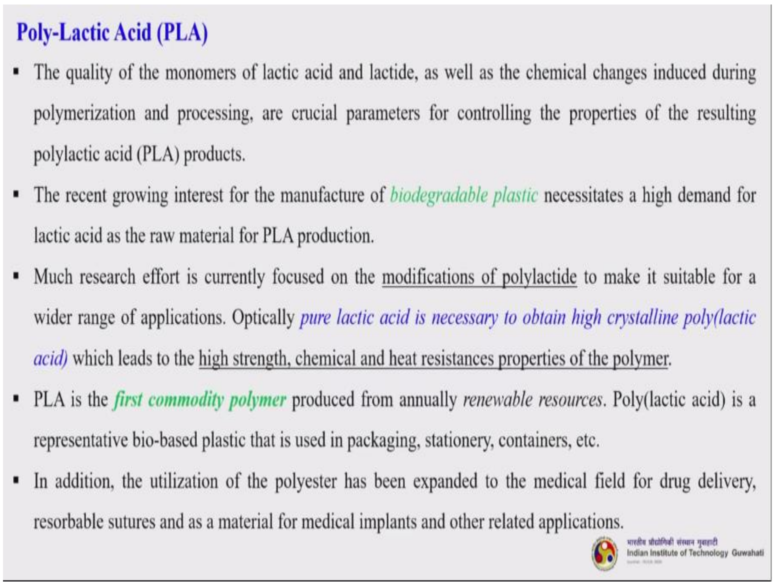

Poly-Lactic Acid (PLA)

- The quality of the monomers of lactic acid and lactide, as well as the chemical changes induced during polymerization and processing, are crucial parameters for controlling the properties of the resulting polylactic acid (PLA) products.
- The recent growing interest for the manufacture of *biodegradable plastic* necessitates a high demand for lactic acid as the raw material for PLA production.
- Much research effort is currently focused on the modifications of polylactide to make it suitable for a wider range of applications. Optically *pure lactic acid is necessary to obtain high crystalline poly(lactic acid)* which leads to the high strength, chemical and heat resistances properties of the polymer.
- PLA is the ***first commodity polymer*** produced from annually *renewable resources*. Poly(lactic acid) is a representative bio-based plastic that is used in packaging, stationery, containers, etc.
- In addition, the utilization of the polyester has been expanded to the medical field for drug delivery, resorbable sutures and as a material for medical implants and other related applications.

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So, now we will discuss about polylactic acid. The quality of the monomers of lactic acid and lactide as well as the chemical changes induced during polymerization and processing are crucial parameters for controlling the properties of the resulting PLA products. The recent growing interest for the manufacture of the biodegradable plastic necessitates a high demand for lactic acid as the raw material for PLA production.

Much research effort is currently focused on the modification of polylactide to make it suitable for a wide range of applications. Optically pure lactic acid is necessary to obtain high crystalline polylactic acid which leads to the high strength, chemical and heat resistance properties of the polymer. So PLA is the first commodity polymer produced from annually renewable sources.

PLA is a representative bio-based plastic that is used in packaging, stationary, containers, etc. In addition, the utilization of the polyester has been expanded to medical field for drug delivery, resorbable sutures, and as a material for medical implants and other related applications.

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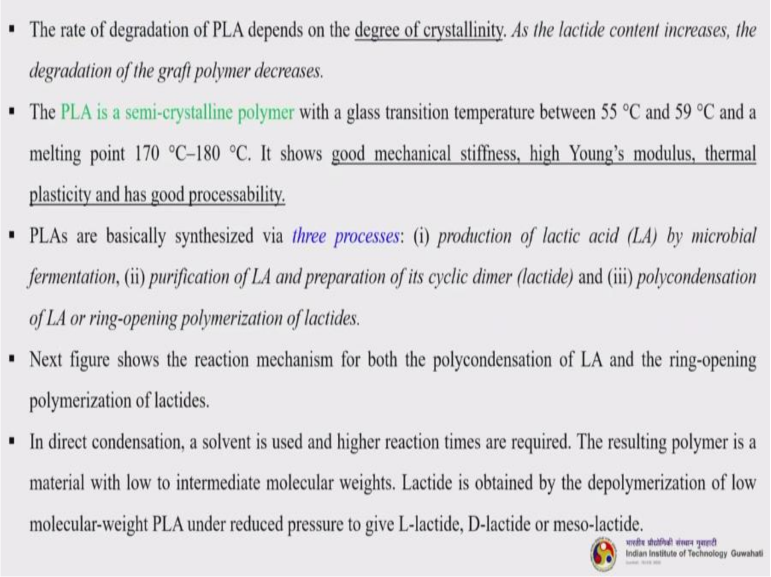

- The rate of degradation of PLA depends on the degree of crystallinity. *As the lactide content increases, the degradation of the graft polymer decreases.*
- The PLA is a semi-crystalline polymer with a glass transition temperature between 55 °C and 59 °C and a melting point 170 °C–180 °C. It shows good mechanical stiffness, high Young's modulus, thermal plasticity and has good processability.
- PLAs are basically synthesized via *three processes*: (i) *production of lactic acid (LA) by microbial fermentation*, (ii) *purification of LA and preparation of its cyclic dimer (lactide)* and (iii) *polycondensation of LA or ring-opening polymerization of lactides.*
- Next figure shows the reaction mechanism for both the polycondensation of LA and the ring-opening polymerization of lactides.
- In direct condensation, a solvent is used and higher reaction times are required. The resulting polymer is a material with low to intermediate molecular weights. Lactide is obtained by the depolymerization of low molecular-weight PLA under reduced pressure to give L-lactide, D-lactide or meso-lactide.

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The rate of degradation of PLA depends on the degree of crystallinity. As the lactide content increases, the degradation of the graft polymer decreases. The PLA is a semi-crystalline polymer with a glass transition temperature between 55 to 59 degrees centigrade and a melting point of 170 to 180 degrees centigrade. It shows good mechanical stiffness, high Young's modulus, thermal plasticity and has a good processability.

PLAs are basically synthesized via three processes. Production of lactic acid by microbial fermentation. Second, purification of lactic acid and preparation of its cyclic dimer that is lactide. Then third polycondensation of lactic acid or ring-opening polymerization of lactides. So, next figure shows the reaction mechanism for both the polycondensation of LA and the ring-opening polymerization of lactides.

In direct condensation, a solvent is used and higher reaction times are required. The resulting polymer is a material with low to intermediate molecular weights. Lactide is obtained by the depolymerization of low molecular weight PLA under reduced pressure to give L-lactide, D-lactide or meso-lactide.

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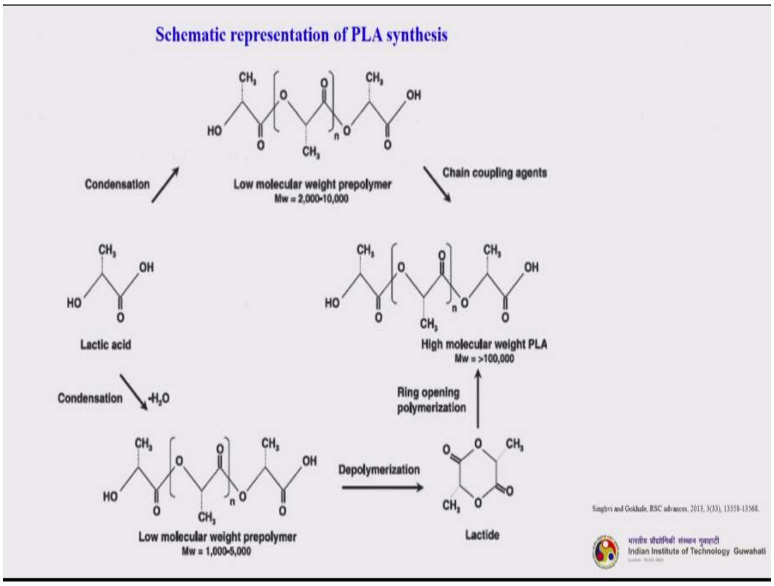
Schematic representation of PLA synthesis

Singhvi and Gokhale, RSC advances, 2013, 3(33), 13558-13568.

So, let us understand what is this scheme basically. It is a schematic representation of the PLA synthesis. We will start with the lactic acid. So, two routes have been shown here. Condensation it gives low molecular weight prepolymer and upon addition of the chain coupling agents it gives the high molecular weight PLA.

Another route is the lactic acid to condensation, then it gives the low molecular weight prepolymer, upon depolymerization then it gives lactide - that is what we just discussed. Now this lactide when you ring opening it; so undergo the ring-opening polymerization reaction it gives 2 PLA, high molecular weight PLA.

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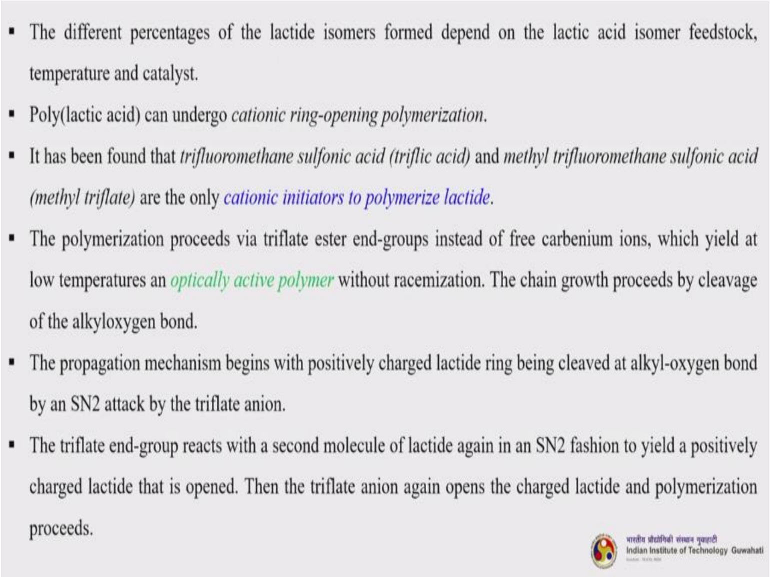

- The different percentages of the lactide isomers formed depend on the lactic acid isomer feedstock, temperature and catalyst.
- Poly(lactic acid) can undergo *cationic ring-opening polymerization.*
- It has been found that *trifluoromethane sulfonic acid (triflic acid)* and *methyl trifluoromethane sulfonic acid (methyl triflate)* are the only *cationic initiators to polymerize lactide*.
- The polymerization proceeds via triflate ester end-groups instead of free carbenium ions, which yield at low temperatures an *optically active polymer* without racemization. The chain growth proceeds by cleavage of the alkyloxygen bond.
- The propagation mechanism begins with positively charged lactide ring being cleaved at alkyl-oxygen bond by an SN2 attack by the triflate anion.
- The triflate end-group reacts with a second molecule of lactide again in an SN2 fashion to yield a positively charged lactide that is opened. Then the triflate anion again opens the charged lactide and polymerization proceeds.

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The different percentages of the lactide isomers formed depend on the lactic acid isomer feedstock, temperature and catalyst. Polylactic acid can undergo cationic ring-opening polymerization. It has been found that trifluoromethane sulfonic acid and methyl trifluoromethane sulfonic acid are the only cationic initiators to polymerize lactide. The polymerization proceeds via triflate ester end groups instead of the free carbenium ions which yield at low temperatures an optically active polymer without racemization.

Now chain the growth proceeds by cleavage of the alkyloxygen bond. The propagation mechanism begins with positively charged lactide ring being cleaved at alkyl-oxygen bond by an SN2 attack by the triflate anion. The triflate end group reacts with the second molecule of the lactide again in an SN2 fashion to yield a positively charged lactide that is opened. Then the triflate anion again opens the charged lactide and polymerization proceeds.

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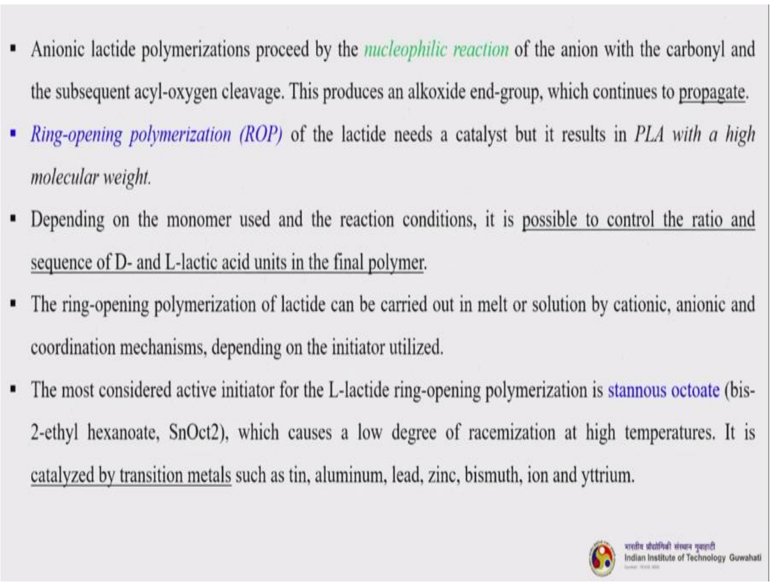

- Anionic lactide polymerizations proceed by the *nucleophilic reaction* of the anion with the carbonyl and the subsequent acyl-oxygen cleavage. This produces an alkoxide end-group, which continues to propagate.
- *Ring-opening polymerization (ROP)* of the lactide needs a catalyst but it results in *PLA with a high molecular weight.*
- Depending on the monomer used and the reaction conditions, it is possible to control the ratio and sequence of D- and L-lactic acid units in the final polymer.
- The ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic and coordination mechanisms, depending on the initiator utilized.
- The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate (bis-2-ethyl hexanoate, SnOct2), which causes a low degree of racemization at high temperatures. It is catalyzed by transition metals such as tin, aluminum, lead, zinc, bismuth, ion and yttrium.

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Anionic lactide polymerization proceed by nucleophilic reaction of the anion with the carbonyl and the subsequent acyl-oxygen cleavage. This produces and alkoxide end group which continues to propagate. Ring-opening polymerization of the lactide needs a catalyst but it results in a PLA with a high molecular weight. Depending upon the monomer used and the reaction conditions, it is possible to control the ratio and sequence of the D and L lactic acid units in the final polymer, some sort of process optimization of the reaction conditions.

The ring-opening polymerization of the lactide can be carried out in melt or solution by cationic, anionic and coordination mechanisms depending on the initiator utilized. The most considered active initiator for the L-lactide ring-opening polymerization is the stannous octoate which causes a low degree of racemization at high temperatures. It is catalyzed by transition metals such as tin, aluminum, lead, zinc, bismuth, iron and yttrium.

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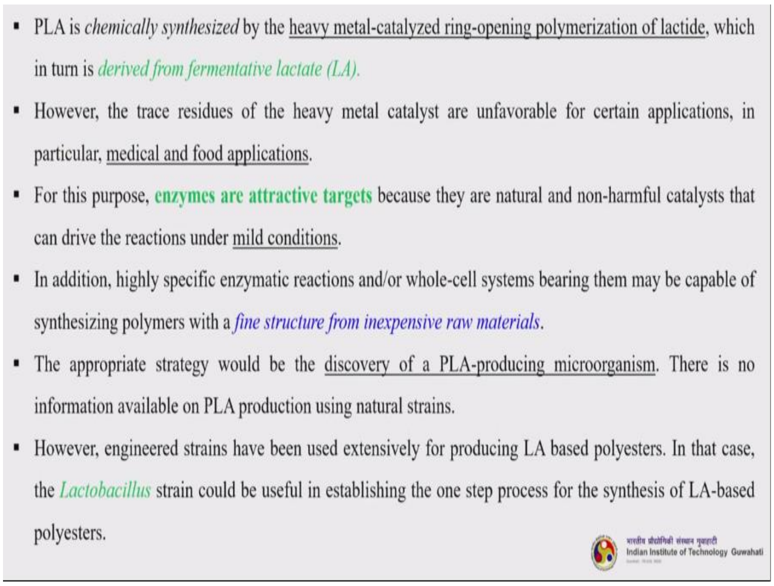

- PLA is *chemically synthesized* by the heavy metal-catalyzed ring-opening polymerization of lactide, which in turn is *derived from fermentative lactate (LA).*
- However, the trace residues of the heavy metal catalyst are unfavorable for certain applications, in particular, medical and food applications.
- For this purpose, **enzymes are attractive targets** because they are natural and non-harmful catalysts that can drive the reactions under mild conditions.
- In addition, highly specific enzymatic reactions and/or whole-cell systems bearing them may be capable of synthesizing polymers with a *fine structure from inexpensive raw materials*.
- The appropriate strategy would be the discovery of a PLA-producing microorganism. There is no information available on PLA production using natural strains.
- However, engineered strains have been used extensively for producing LA based polyesters. In that case, the *Lactobacillus* strain could be useful in establishing the one step process for the synthesis of LA-based polyesters.

PLA is chemically synthesized by heavy metal catalyzed ring-opening polymerization of lactide, which in turn is derived from fermentation lactate. However, the trace residues of the heavy metal catalyst are unfavorable for certain applications, in particular medical and food applications. For this purpose, enzymes are attractive targets because they are natural non-harmful catalysts that can drive the reactions under mild conditions.

In addition, highly specific enzymatic reaction and/or whole cell systems bearing them may be capable of synthesizing polymers with a fine structure from inexpensive raw materials. The appropriate strategy would be the discovery of a PLA producing microorganism. There is no information available on PLA production using natural strains. People are still working on this particular aspect.

However, engineered strains have been used extensively for producing LA based polyesters. In that case, the *Lactobacillus* strains could be useful in establishing the one step process for the synthesis of the LA based polyesters.

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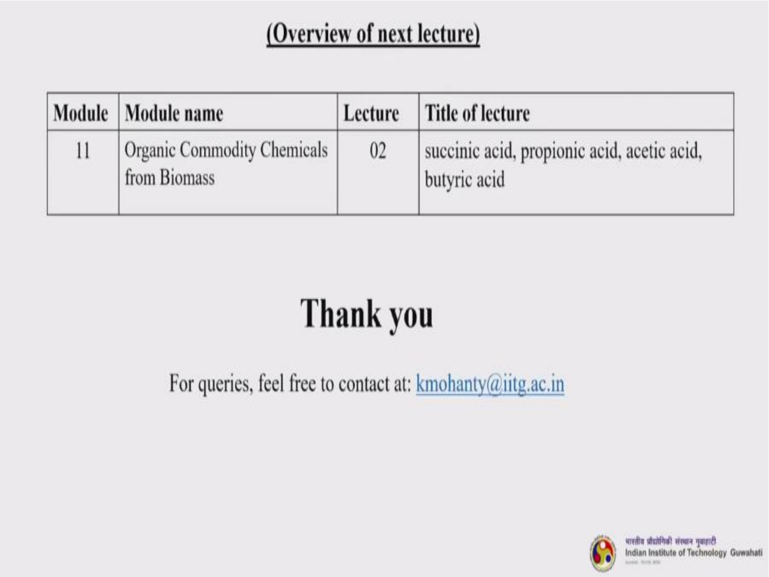

(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
11	Organic Commodity Chemicals from Biomass	02	succinic acid, propionic acid, acetic acid, butyric acid

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

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So with this, I conclude today's lecture. So in our next class, we will be discussing about succinic acid, propionic acid, acetic acid and butyric acid. So thank you very much. In case you have any query, please register in the Swayam portal or you can always drop a mail to me at kmohanty@iitg.ac.in.