Biomass Conversion and Biorefinery
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Lecture – 34
Concept, Lignocellulosic Biorefinery

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Module	Module Name	Lecture	Title of Lecture
12	Integrated Biorefinery	1	Concept, corn/soybean/sugarcane biorefinery, lignocellulosic biorefinery

Good morning students. We are starting module 12 today and as you know this is the last module of our course and this module is dedicated to integrated biorefinery. So, in today's lecture, we will be discussing about the concept of integrated biorefinery. If you recall, we have already discussed about biorefinery.

We will try to learn what is integrated biorefinery and few examples of already commercialized integrated biorefinery. That will include corn, soybean and sugarcane-based biorefinery as well as lignocellulosic biomass based biorefinery. So, let us begin our discussion.

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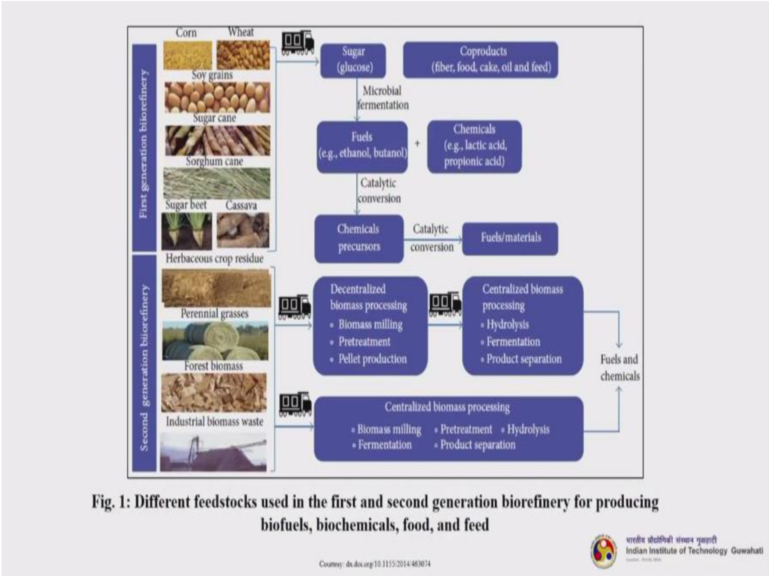

Fig. 1: Different feedstocks used in the first and second generation biorefinery for producing biofuels, biochemicals, food, and feed

If you recall, we have discussed this, but I am just trying to make you aware again that what are the first generation biorefinery and second generation biorefinery. So, this is your first generation biorefinery in which corn, wheat, soy grains, then sugarcane, sorghum cane, sugar beet, cassava all these were being used to produce valuable products. It can be biofuel, some platform chemicals and other value-added products from these biomasses.

Now, when we look for the second generation biorefinery, so there the focus is entirely switched to mostly the lignocellulosic biomass wastes. Perennial grasses, herbaceous crop residue, forest biomass, industrial biomass waste all these things that includes even the municipal solid waste. So, if you look at the first generation biorefinery conceptually what it means actually? So, let us understand that the base or the platform is actually the sugar/glucose.

So, when we go for our microbial fermentation, we get fuels, alcoholic fuels, ethanol, butanol and all these things, plus chemicals i.e., lactic acid, propionic acid, succinic acid. We have discussed all these in detail previously. And then you go for catalytic conversion, so you get chemical precursors. You again further convert them to different types of upgraded fuels and chemicals.

So then we have a decentralized biomass processing. It is very much required, especially if we are talking about the wastes including the lignocellulosic biomass. So biomass milling, pretreatment, pellet production. Then it goes to the processing like hydrolysis, fermentation, product separation. Then we have either fuels and chemicals and we can also centralize biomass processing where all these operations like the pretreatment operation, mechanical aspects as well as hydrolysis, fermentation, product operation, everything is carried out in a centralized way.

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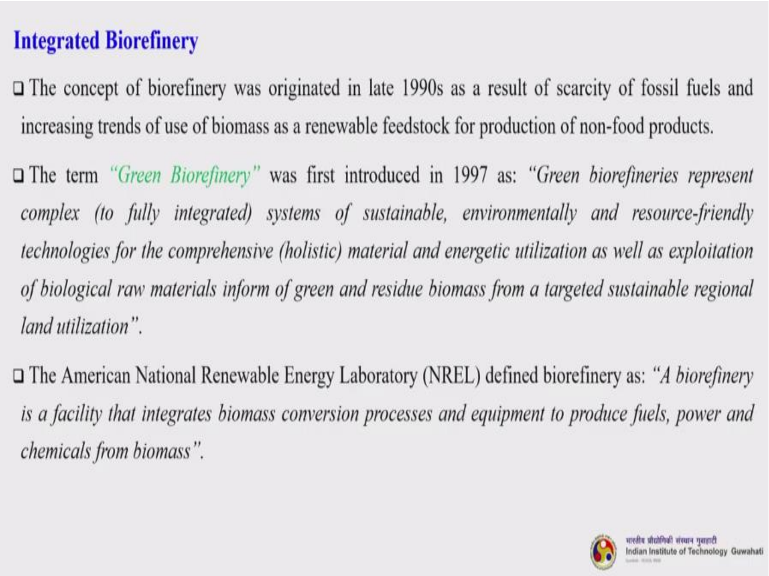

So, let us try to again understand about the integrated biorefinery. So, the concept of biorefinery was originated in the late 90s as a result of scarcity of fossil fuels and increasing trends of use of biomass as a renewable feedstock for the production of non-food products. That term green biorefinery was first introduced in 1997 as: "*Green biorefineries represent complex to fully integrated systems of sustainable, environmentally and resource friendly technologies for the comprehensive material and energetic utilization as well as exploitation of biological raw materials in form of green and residue biomass from a targeted sustainable regional land utilization*". This is what looks to be a big actually terminology, but this is what it was coined as the definition of green biorefinery.

Then American National Renewable Energy Laboratory, the NREL, defined biorefinery as: "A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass."

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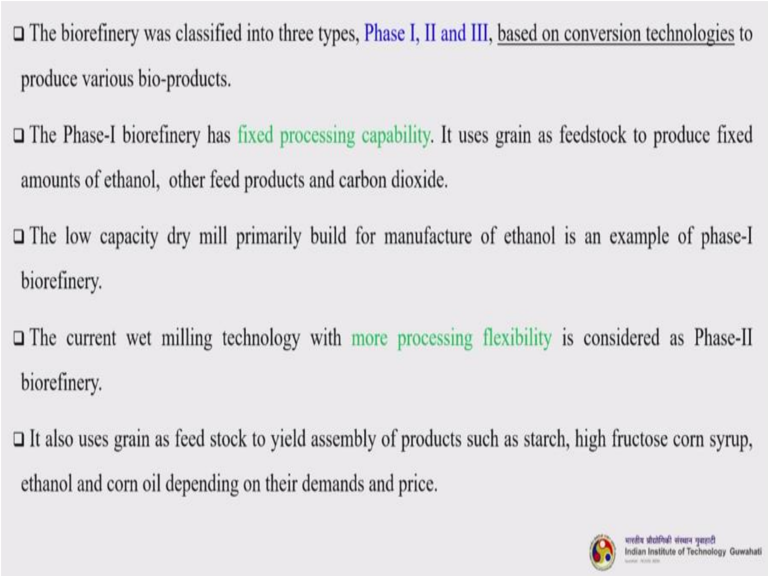

Biorefinery was classified into 3 types. Phase 1, Phase 2 and Phase 3 based on the conversion technologies to produce various bioproducts. So phase 1 biorefinery has a fixed processing capability. So it uses grain as feedstock to produce fixed amounts of ethanol, other feed products and carbon dioxide. The low capacity dry mill primarily build for manufacture of ethanol is an example of the phase 1 biorefinery.

The current wet milling technology with more processing flexibility is considered as phase 2 biorefinery. So phase 2 and phase 1 the difference is that in phase 1 it is fixed processing capability, but in the phase 2 we have more processing flexibility. So, it also uses grain as feedstock to yield assembly products such as starch, high fructose corn syrup, ethanol and corn oil depending on their demands and price.

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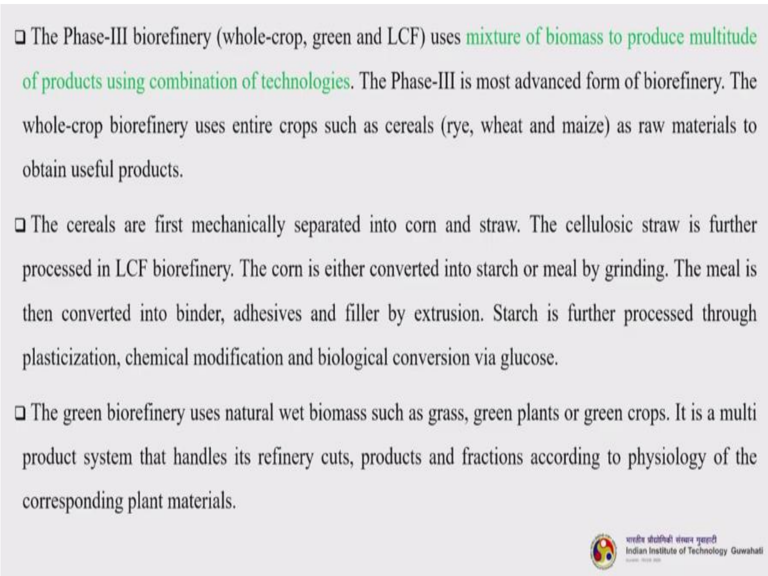

The phase 3 biorefinery which takes into account the whole crop, green and LCF (LCF is the lignocellulosic feedstock) uses mixture of biomass to produce multitude of products using combination of technologies. So in phase 3, we have different types of biomass plus different types of conversion technology plus different types of products. So the phase 3 is most advanced form of biorefinery.

The whole-crop biorefinery uses entire crops such as cereals, rye, wheat and maize as raw materials to obtain useful products. The cereals are first mechanically separated into corn and straw. The cellulosic straw is further processed in the LCF biorefinery. The corn is either converted into starch or meal by grinding. The meal is then converted into binder, adhesives and filler by extrusion.

Starch is further processed through plasticization, chemical modification and biological conversion via glucose as per the need and demand of course. The green biorefinery uses natural wet biomass such as grass, green plants or green crops. It is a multi-product system that handles its refinery cuts, products and fractions according to physiology of the corresponding plant materials.

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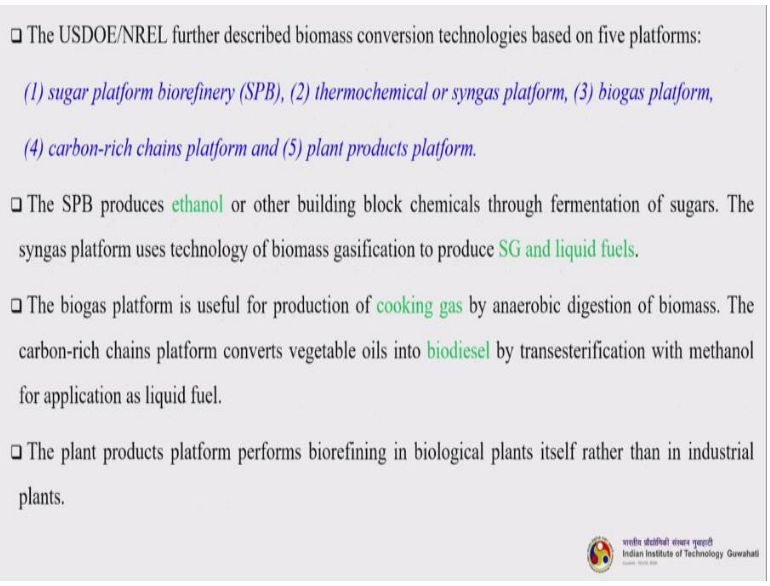

The USDOE, the United States Department of Energy and NREL further described biomass conversion technologies based on 5 platforms. So what are those? The first is the foremost important from where all these biorefinery started is the sugar platform biorefinery. The second is thermochemical or syngas platform. Third is biogas platform, basically anaerobic digestion.

Fourth is the carbon-rich chains platform and fifth is the plant products platform; so entirely LCF based. So SPB produces ethanol and other building block chemicals through fermentation of sugars. The syngas platform uses technology of biomass gasification to produce syngas and liquid fuels. The biogas platform is useful for production of cooking gas by anaerobic digestion, which is very famous in Asian countries including that of India.

The carbon-rich chains platform converts vegetable oils into biodiesel by transesterification with methanol for application as liquid fuel. The plant products platform performs biorefining in biological plants itself rather than in the industrial plants.

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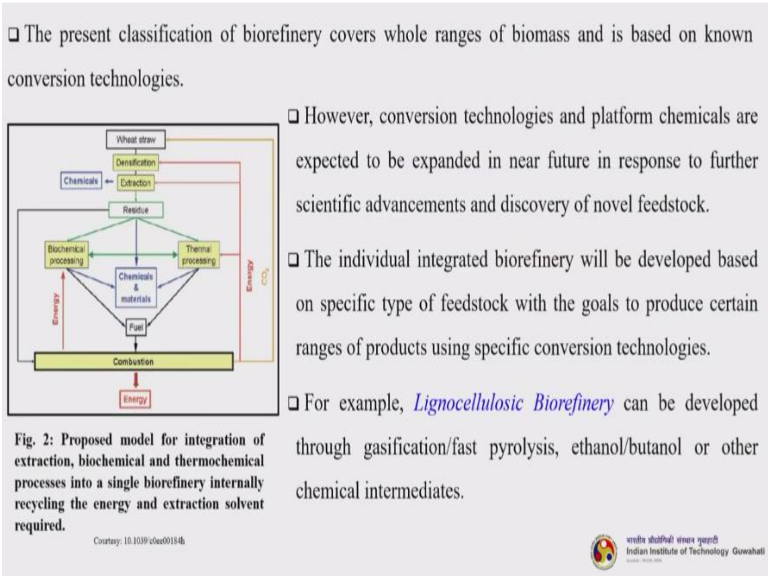

So, the present classification of biorefinery covers whole ranges of biomass and is based on the known conversion technologies. Please look at this particular figure. This is a proposed model for integration of extraction, biochemical and thermochemical processes into a single biorefinery internally recycling the energy and extraction solvent required. So that is what it is integrated biorefinery.

You have multiple feedstocks, we have multiple conversion technologies and you have multiple products. And whatever waste is coming again you are recycling them in the same biorefinery in various forms that is what is integrated biorefinery. So, let us try to understand this wheat straw. It is going through densification, extraction. When you extract, you find some sort of chemicals, useful chemicals.

Whatever the residue left that is being processed in an integrated biorefinery way. It can be converted to chemicals and materials. Then biochemical processing, thermochemical processing both will give us fuel. Now, further conversion we get energy. So, whatever carbon dioxide you are seeing now, whatever carbon dioxide is that is getting generated during the entire processing is again being used or consumed by the wheat to grow itself.

So, this is why the biomass of lignocellulosic biomass play safe or we can say that plays a role in environmental benign technology. So, however conversion technologies and platform chemicals are expected to be expanded in near future in response to further scientific advancements and discovery of novel feedstock. The individual integrated biorefinery will be developed based on specific type of feedstock with the goals to produce certain ranges of products using specific conversion technologies.

For example, lignocellulosic biorefinery can be developed through gasification, fast pyrolysis, ethanol butanol or other chemical intermediates.

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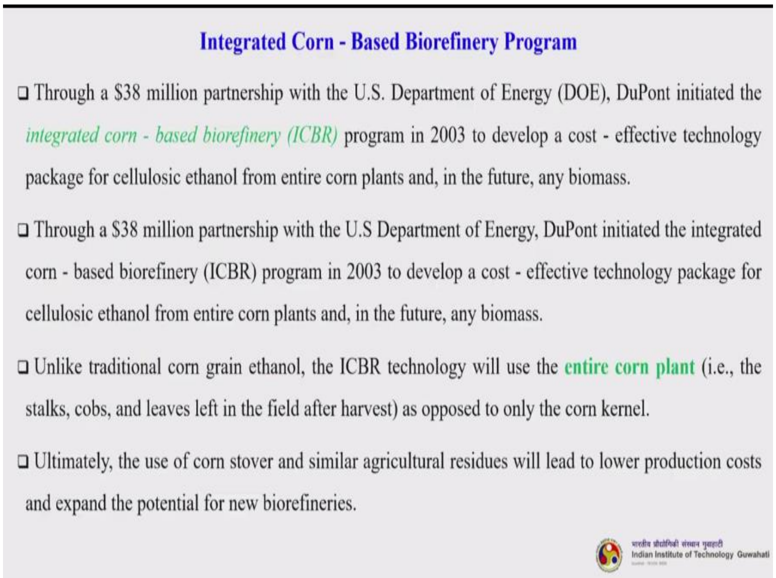

Now, we will discuss few integrated biorefineries. The first one is integrated corn-based biorefinery program. So, through a $38 million partnership with the US Department of Energy, DuPont initiated the integrated corn-based biorefinery program in 2003 to develop a cost effective technology package for cellulosic ethanol from entire corn plants, please note down again entire corn plant, and in the future any biomass.

So, they wish to develop such a protocol which they have already developed so they can process multiple feedstocks. So, through this a $38 million partnership with the US Department of Energy DuPont initiated the integrated biorefinery program for any biomass. Unlike traditional corn grain ethanol, the ICBR technology will use the entire corn plant that is stalks, cobs and leaves left in the field after harvest as opposed to only the corn kernel.

So if you remember the Phase I biorefinery or the corn-based biorefinery used to have only this kernel as their feedstock. Now in the integrated system we have the entire plant, so this is the difference. So, ultimately the use of corn stover and similar agricultural residues will lead to lower production costs and expand the potential for new biorefineries.

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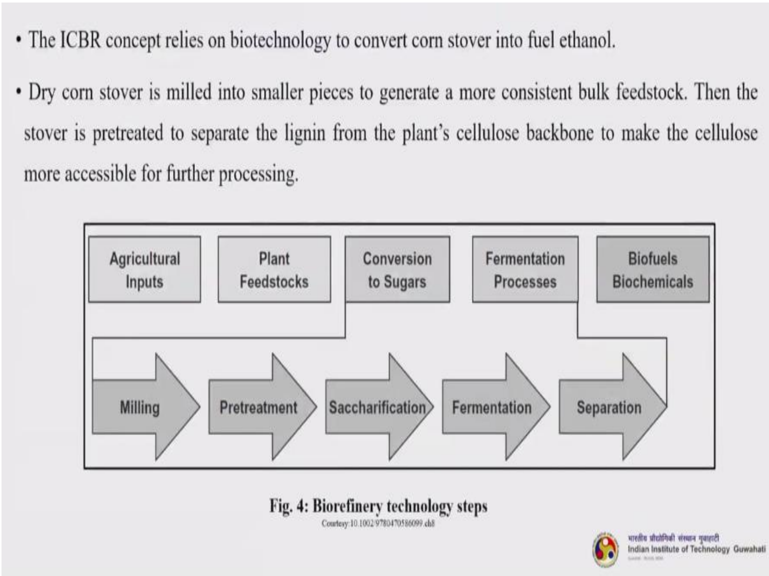

So, the ICBR concept relies on biotechnology to convert corn stover into fuel ethanol. Dry cornstover is milled into smaller pieces to generate more consistent bulk feedstock. Then the stover is pretreated to separate the lignin from the plant cellulosic backbone to make cellulose more accessible for future processing. So, this milling and pretreatment, so these are the processing, preprocessing things.

You can see the agricultural inputs, plant feedstocks. So, they have to be milled and pretreated. Then the second part is conversion of sugars, so we are doing the saccharification. Then the fermentation will begin. Fermentation process, then the separation which is many times I have told you that this is one of the most energy intensive as well as a costly process the downstream part. So you get biofuels and biochemicals.

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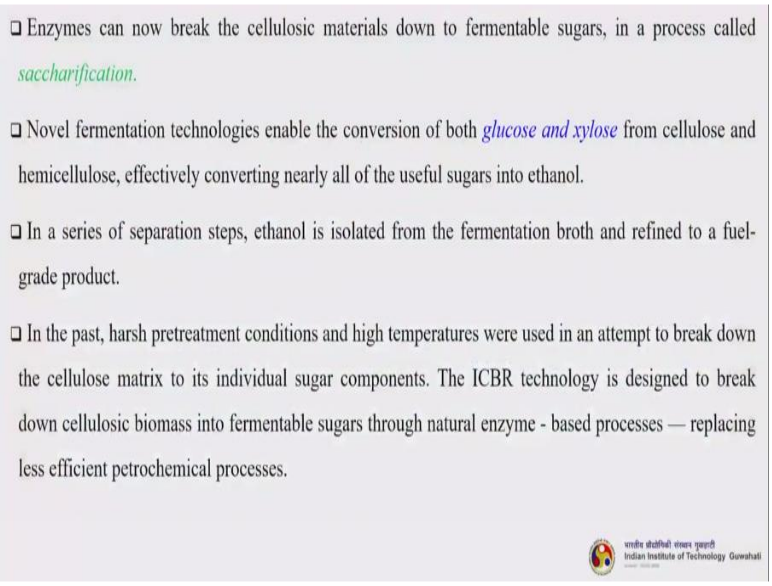

So enzymes can now break the cellulosic material down to fermentable sugars in a process called saccharification. Novel fermentation technologies enable the conversion of both glucose and xylose from cellulose and hemicellulose effectively converting nearly all of the useful sugars into ethanol. In a series of separation steps, ethanol is isolated from the fermentation broth and refined to a fuel-grade product and it is very energy intensive as well as costly process.

So in the past, harsh pretreatment conditions and high temperatures were used in an attempt to break down the cellulose matrix to its individual sugar components. The ICBR technology is designed to break down cellulosic biomass into fermentable sugars through natural enzyme based processes replacing less efficient petrochemical processes.

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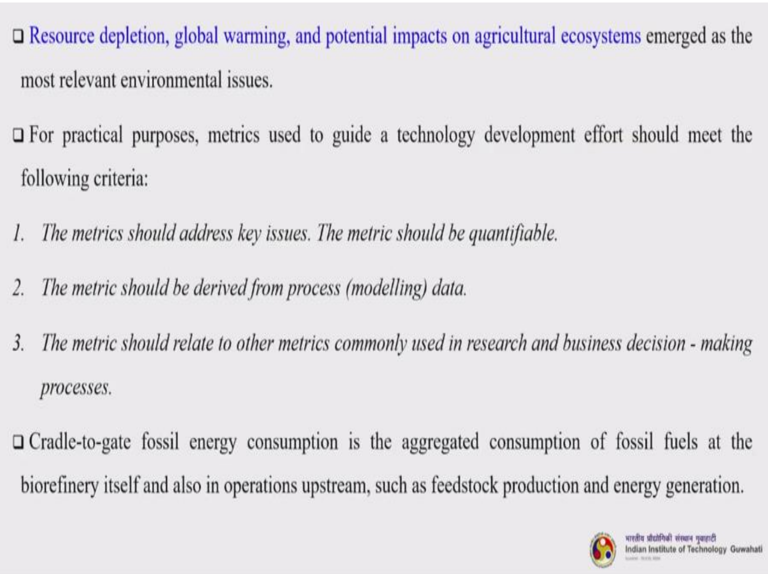

So resource depletion, global warming and potential impacts on agricultural ecosystems emerged as the most relevant environmental issues. For practical purposes, metrics used to guide a technology development effort should meet the following 3 criteria. So first one is the metrics should address the key issues and they should also be quantifiable. The metric should be derived from process data, modelling data.

The metric should relate to other metrics commonly used in research and business decision making processes. Now, cradle-to-gate fossil energy consumption is the aggregated consumption of fossil fuels at the biorefinery itself and also in operations upstream such as feedstock production and energy generation.

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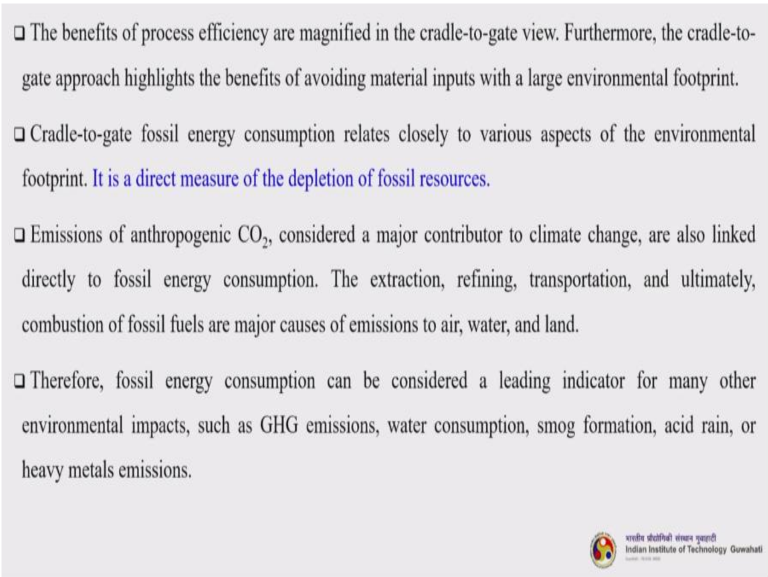

The benefits of process efficiency are magnified in the cradle-to-gate view. Furthermore, the cradle-to-gate approach highlights the benefits of avoiding material inputs with a large environmental footprint. Cradle-to-gate fossil energy consumption relates closely to various aspects of the environmental footprint. So it is a direct measure of the depletion of the fossil resources.

Emission of anthropogenic carbon dioxide, considered a major contributor to climate change, are also linked directly to fossil energy consumption. The extraction, refining, transportation and ultimately combustion of fossil fuels are major causes of emission to air, water and land. Therefore, fossil energy consumption can be considered a leading indicator for many other environmental impacts such as the green house gas emissions, water consumption, smog formation, acid rain or heavy metal emissions.

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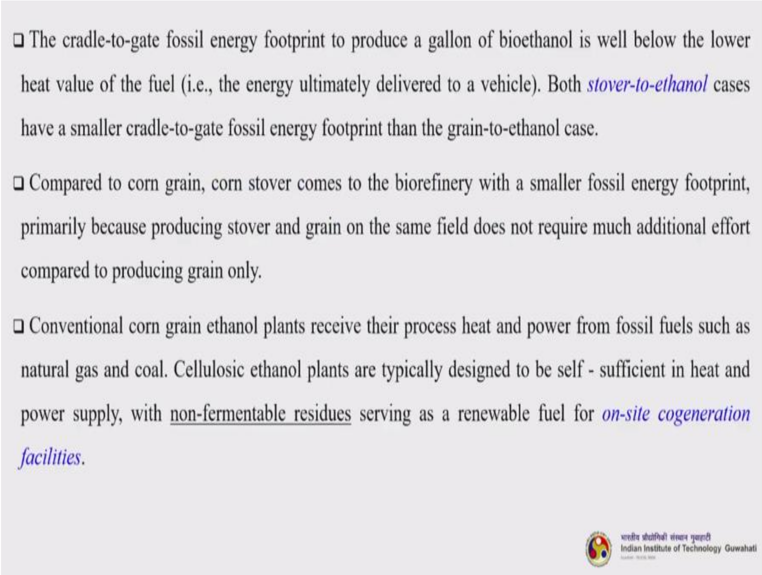

The cradle-to-gate fossil energy footprint to produce a gallon of bioethanol is well below the lower heat value of the fuel, so that is the energy ultimately delivered to a vehicle. Both stover-to-ethanol cases have a smaller cradle-to-gate fossil energy footprint than grain-to-ethanol case. Compared to corn grain, corn stover comes to the biorefinery with a smaller fossil energy footprint.

Primarily because producing stover and grain on the same field does not require much additional effort compared to producing grain only. Conventional corn grain ethanol plants receive their process heat and power from fossil fuels such as natural gas and coal. Cellulosic ethanol plants are primarily designed to be self-sufficient in heat and power supply with non-fermentable residue serving as a renewable fuel for on-site cogeneration facilities, the CHP facilities. We have already discussed about that.

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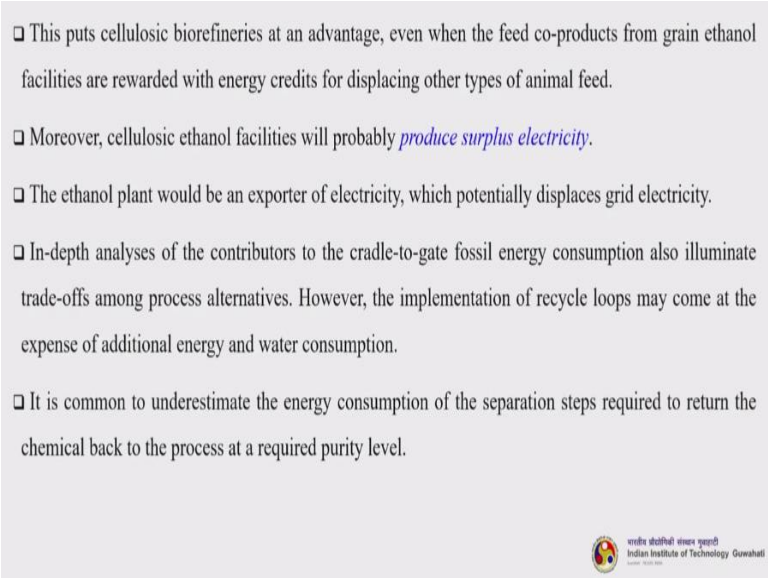

And this puts cellulosic biorefineries at an advantage even when the feed co-products from grain ethanol facilities are rewarded with energy credits for displacing other types of animal feed. Moreover, cellulosic ethanol facilities will probably produce surplus electricity. The ethanol plant would be an exporter of electricity, which potentially displaces grid electricity.

In-depth analysis of the contributors to the cradle-to-gate fossil energy consumption also illuminate trade-offs among process alternatives. However, the implementation of recycle loops may come at the expense of additional energy and water consumption. It is common to underestimate the energy consumption of the separation steps required to return the chemical back to the process at a required purity level.

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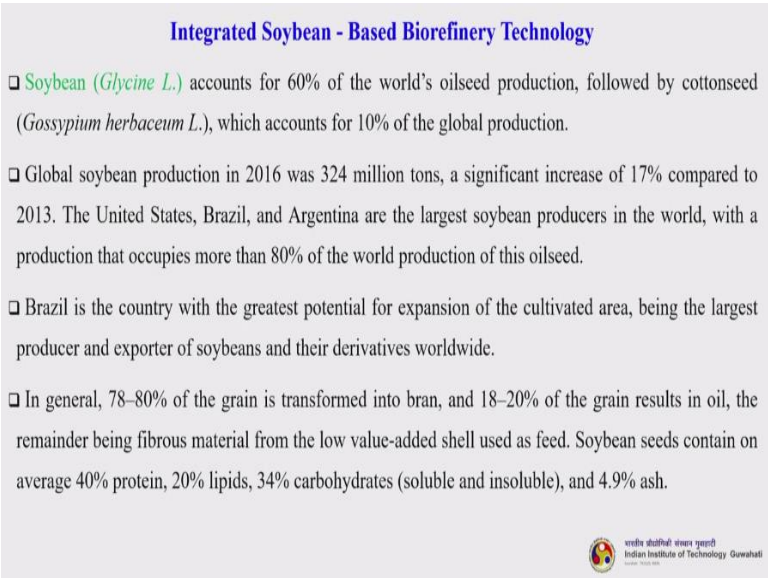

So, now we will talk about another biorefinery technology/integrated biorefinery that is based on soybean. So, integrated soybean-based biorefinery technology. Soybean accounts for 60% of world's oil seed production followed by cotton seed which accounts for 10% of the global production. Global soybean production in 2016 was 324 million tons, a significant increase of 17% compared to 2013.

The United States, Brazil and Argentina are the largest soybean producers in the world with the production that occupies more than 80% of the world production of this oilseed. Brazil is the country with the greatest potential for expansion of the cultivated area, being the largest producer and exporter of soybeans and their derivatives worldwide. In general, 78 to 80% of the grain is transformed into bran and 18 to 20% of the grain results in oil, the remainder being fibrous material from the low value-added shell used as feed. Soybean seeds contain on an average 40% protein, 20% lipids, 35% carbohydrates both soluble and insoluble fraction and 4.9% ash.

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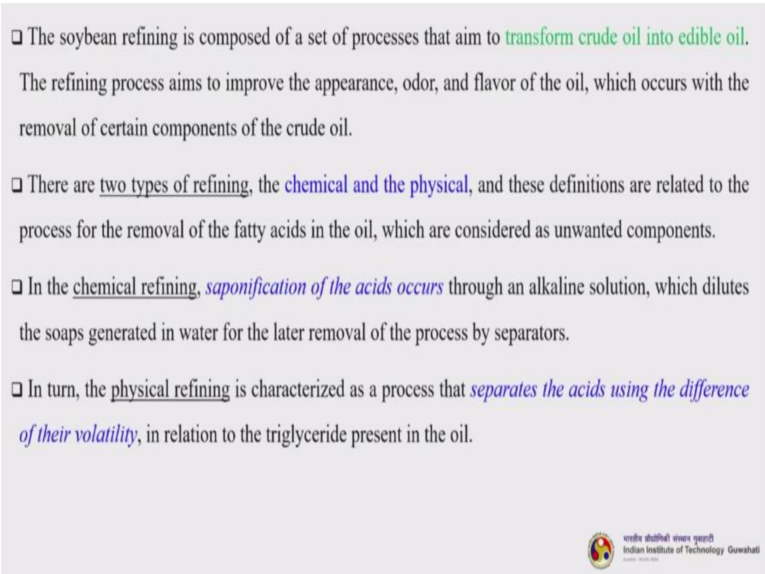

The soybean refining is composed of a set of processes that aim to transform crude oil into the edible oil. The refining process improve the appearance, odor and flavor of oil, which occurs with the removal of certain components of the crude oil. Now, there are two types of refining process. The first is chemical and second is the physical one and these definitions are related to the process for the removal of the fatty acids in the oil, which are considered as unwanted components when you talk about final consumption. So, in the chemical refining saponification of the acids occur through an alkaline solution which dilutes the soaps generated in water for the later removal of the process by various separators. In turn, the physical refining is characterized as a process that separates the acids using the difference of their volatility in relation to that triglyceride present in the oil.

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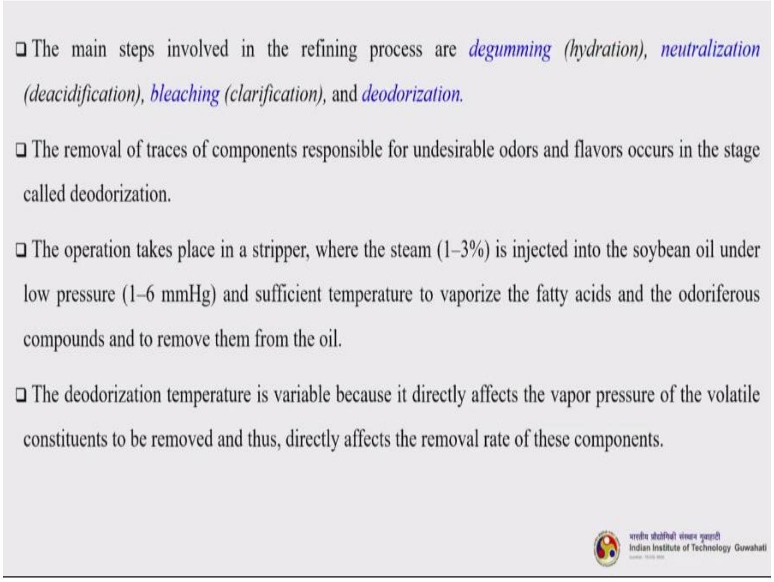

The main steps involved in the refining process are degumming - which is actually hydration, the neutralization - which is a deacidification step, bleaching - which is a clarification process, and then deodorization. The removal of traces of components responsible for undesirable odors and flavours occur in the stage called deodorization. The operation takes place in a stripper where the steam usually 1 to 3% is injected into the soybean oil under low pressure (almost 1 to 6 mmHg) and sufficient temperature to vaporize the fatty acids and odoriferous ferrous compounds and to remove them from the oil. So, they are more volatile and they will immediately vaporize. The deodorization temperature is variable because it directly affects the vapor pressure of the volatile constituents to be removed and thus directly affects the removal rate of these components.

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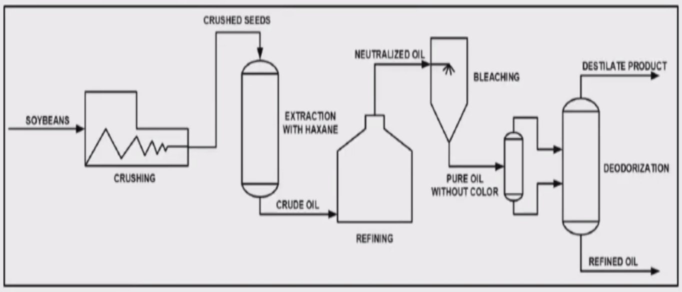

Fig. 5: Simplified flowchart for refining soybean oil

Courtesy: 10.5772/intechopen.88111

So, this is a simplified flowchart for the refining of soybean oil. So, you can see that this is the preprocessing step. Soybean goes through a mechanical preprocessing steps like crushing, milling, whatever it is. Then the crushed seeds go to the extraction unit. Usually hexane being used as the extracting solvent. So you get the crude oil. Now, that crude oil goes to the refining purposes. So, various steps are there.

This is only shown in schematic only the main steps. Under that refining there are various steps. Extraction also not single extractor, there may be many series of extractors. Then the neutralized oil, it goes to the bleacher where bleaching is taking place. Then whatever you get is pure oil without color. Now, this is finally being fed to a distillation unit where we get the distillate product and refined oil. So, this is the process called actually deodorization.

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- The usage of oil for the fuel synthesis is based on the transformation of triglycerides in esters. The most common way to synthesize those substances is by the *transesterification of the refined oil*.
- Although the regular transesterification process provides high conversion rates and have a relatively operational simplicity, some problems comes along, such as

(1) *low energetic and production efficiency*
(2) *need to adjust the raw material*
(3) *the use of high toxicity intermediate products*
(4) *generation of a significant by-product volume (glycerol) with a level of contamination that requires high investments to its use or discharge*
(5) *the use of methanol which, besides toxic, needs fossil fuels, as raw material, to be produced in the form of energy*
(6) *difficulty in recycling the catalyst*
(7) *need to remove the glycerol from biodiesel and*
(8) *high environmental impact associated.*

So the usage of oil for the fuel synthesis is based on the transformation of triglycerides in esters. The most common ways to synthesize those substance is by the transesterification of the refined oil. Although the regular transesterification process provides high conversion rates and have a relatively operational simplicity, some problem comes along such as low energetic and production efficiency; need to adjust the raw material; the use of high toxicity intermediate products - very big problem the third one; then the generation of a significant byproduct volume as for example glycerol - with a level of contamination that requires high investment to its use or discharge; the use of methanol, which besides toxic needs fossil fuels as raw material to be produced in the form of energy; difficulty in recycling the catalyst, again it is a challenge still remains mostly for the engineering people including the chemical engineers; need to remove the glycerol from biodiesel; and, high environmental impact that is associated with this entire processing.

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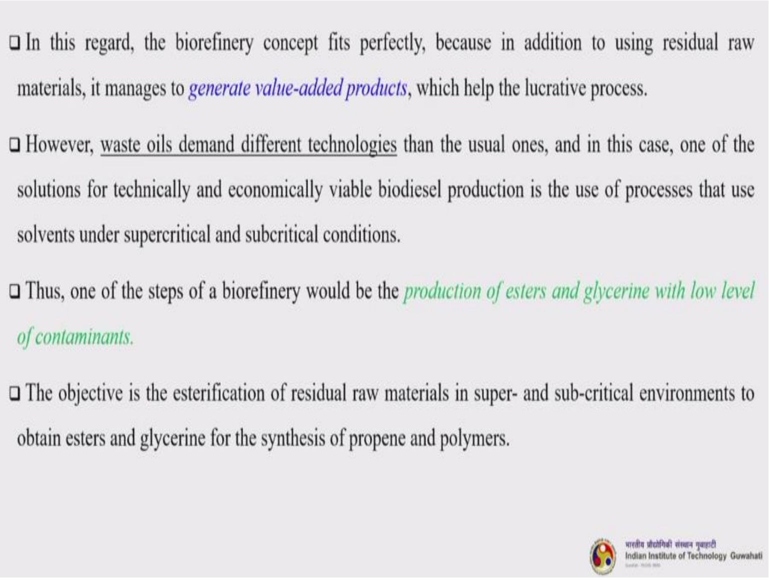

So in this regard, the biorefinery concept fits perfectly because in addition to using residual raw materials, it manages to generate value-added products, not only one but many which help the lucrative process. However, waste oils demand different technologies than the usual ones. And in this case, one of the solutions for technically and economically viable biodiesel production is the use of processes that use solvents under supercritical and subcritical conditions.

But again, I am telling that supercritical systems is a costly process, subcritical is fairly less costly than that. Thus one of the steps for a biorefinery would be the production of esters and glycerin with low level of contaminants. The objective is the esterification of residual raw materials in super and subcritical environments to obtain esters and glycerin for the synthesis of propene and various other polymers.

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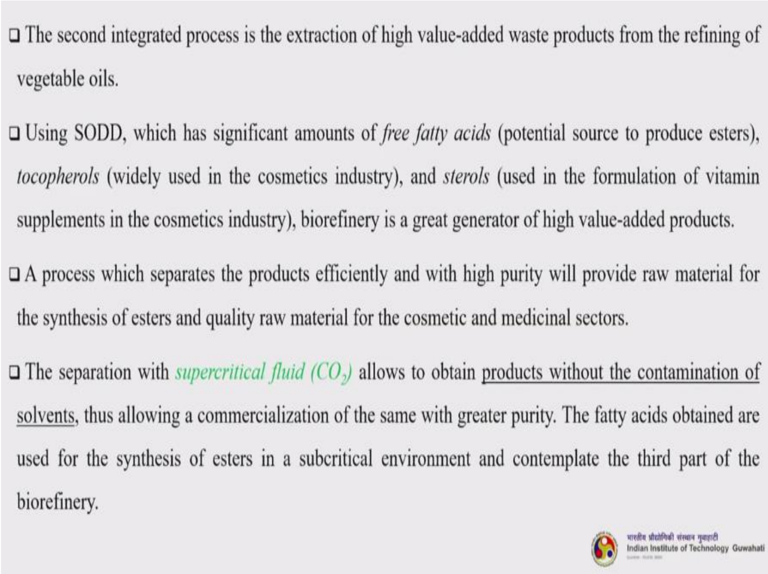

The second integrated process is the extraction of high value-added waste products from the refining of vegetable oils. Using the SODD, which has significant amount of free fatty acids that is it can become a potential source to produce esters, then tocopherols which are widely used in the cosmetic industry, then sterols used in the formulation of vitamin supplements in cosmetic industry, biorefinery is a great generator of high value-added products.

A process which separates the products efficiently and with high purity will provide raw material for the synthesis of esters and quality raw materials for the cosmetic and medicinal sectors. The separation with supercritical fluid, mostly carbon dioxide being used as the fluid, allows to obtain products without the contamination of solvents, thus allowing a commercialization of the same with greater purity.

The fatty acids obtained are used for the synthesis of esters in a subcritical environment and contemplate the third part of the biorefinery.

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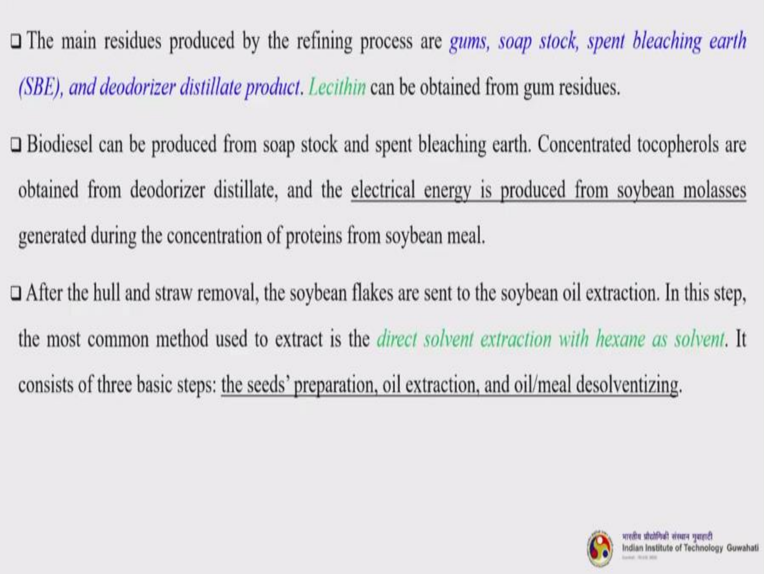

The main residue produced by the refining process are gums, soap stocks, spent bleaching earth that is called as the SBE, deodorizer distillate product, and another one is lecithin that can be obtained from the gum residues. Biodiesel can be produced from the soap stock and spent bleaching earth. Concentrated tocopherols are obtained from deodorizer distillate, and the electrical energy is produced from the soybean molasses generated during the concentration of proteins from soybean meal.

After the hull and straw removal, the soybean flakes are sent to the soybean oil extraction. Now, in this step the most common method used to extract is the direct solvent extraction with hexane as solvent which I have already shown you in that schematic diagram. Now, it consists of 3 basic steps. The seeds preparation, oil extraction and oil/meal desolventizing.

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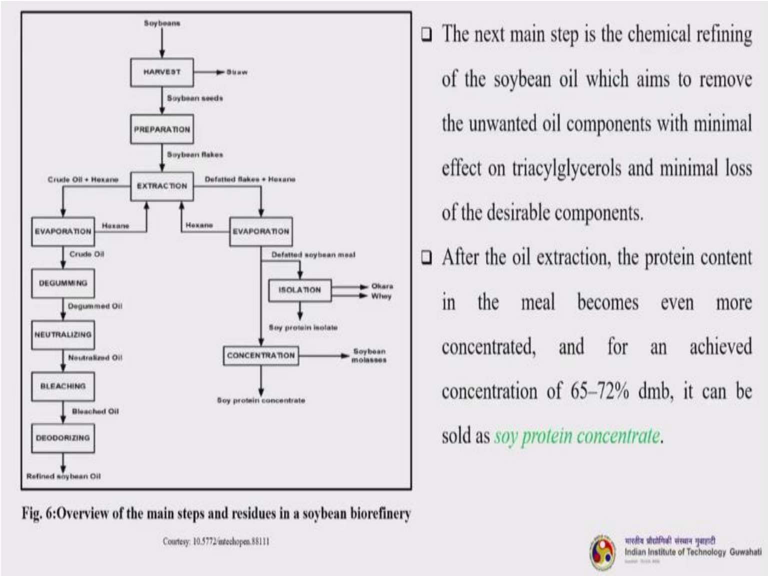

So, this is the overview of the main steps and residues in a soybean biorefinery. You can see this figure. Soybean goes for harvest, of course then you get the straw out of that. It can go to the LCF, lignocellulosic based biorefinery. Then the soybean seeds, it goes through sort of physicochemical processing steps, you get flakes. Now the flakes are sent to the extraction, so where you get crude oil and hexane. So, from here two separate processes.

So, extraction and most of the value-added products. Crude oil plus hexane we get evaporation, hexane recycle. Crude oil then it goes to degumming, you get degummed oil. You send to neutralization, you get neutralized oil. Goes to bleaching, you get bleached oil. Deodorising, you get the final refined soybean oil. Now, the defatted flakes, that means the flakes from which the oil has already been removed but few amount of oil will always be present depending upon what is the process, plus hexane. It will go to evaporation where hexane will be recycled back. It will be recovered and recycled back. Then you get the defatted soyabean meal. You can go for some isolation steps and okara, whey and all these things and you get some soy protein isolate maybe it is in a lower quantity. Then if you go for concentration, you get the soybean molasses which can further go for producing energy and you get the soy protein concentrate.

From this, basically you get the soy protein concetrate. Now, the next main step is the chemical refining of the soybean oil which aims to remove the unwanted oil components with minimal impact on triacylglycerols and minimal loss of the desirable components. After the oil extraction, the protein content in the meal becomes even more concentrated and for an achieved concentration of 65 to 72% dmb it can be sold as soy protein concentrate.

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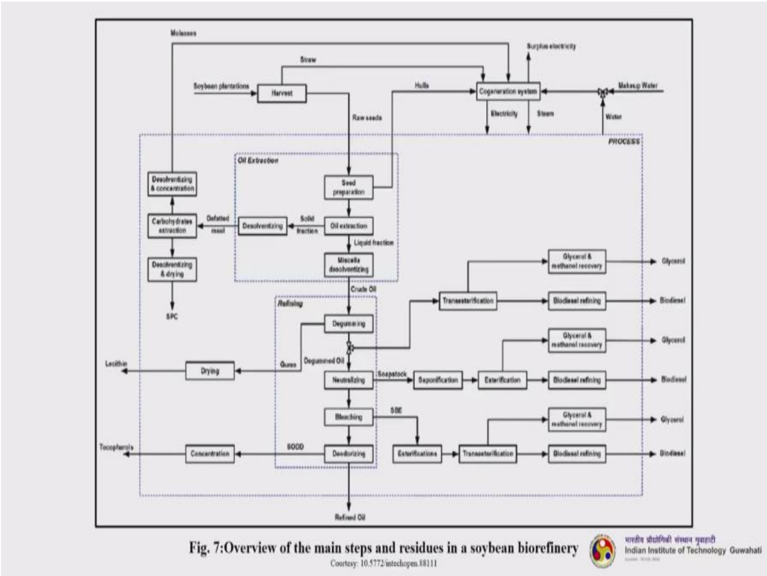

Fig. 7:Overview of the main steps and residues in a soybean biorefinery

Courtesy: 10.5772/intechopen.88111

So, this is an overview of the main steps and residues in soybean biorefinery. So, whatever we have discussed is put in a single slide. So you can go through it later. Here basically what is being done is that entire process; suppose, this is a refining process, this is the oil extraction unit. So, oil extraction, seed preparation, oil extraction, decentralizing, this miscella desolventizing. Then you get the oil, it goes to refining.

Degumming, neutralizing, bleaching, deodorising, you get the refined oil. And apart from that there are so many other processes are also happening together. So, you can see this. This is what is basically different types of byproducts that is coming out when this refining process is going on. All this can be converted into various products. Just see the products, so many different types of products, glycerol, biodiesel. And then we can have other different types of chemical sources and plus energy.

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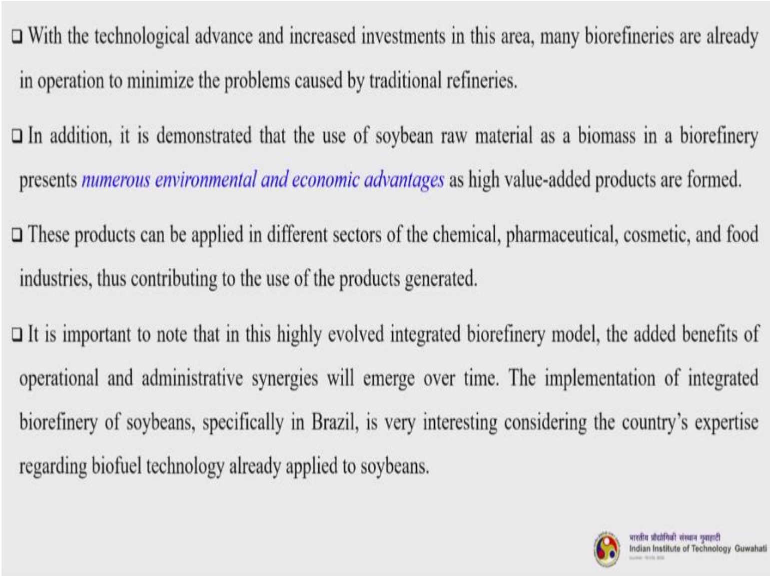

So with the technological advance and increased investment in this area, many bio refineries are already in operation to minimize the problems caused by traditional refineries. In addition, it is demonstrated that the use of soybean raw materials or biomass in a biorefinery presents numerous environmental and economic advantages as high-value added products are formed. These products can be applied in different sectors of the chemical, pharmaceutical, cosmetic and food industries, thus, contributing to the use of the production generated. It is important to note that in this highly evolved integrated biorefinery model, the added benefits of operational and administrative synergies will emerge over time. So, the implementation of the integrated biorefinery of soybeans, especially specifically in the Brazil is very interesting considering the country's expertise regarding the biofuel technology that is already applied to soybeans.

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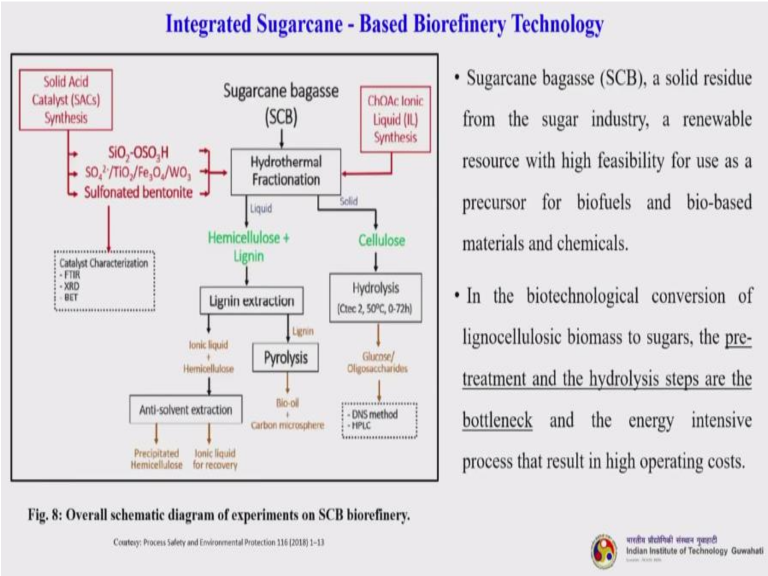

Now, next we are going to talk about the integrated sugarcane-based biorefinery technology. So, this is an overall schematic diagram of the experiments of the sugarcane-based biorefinery. We will discuss. So, let us say you start from here. The sugarcane bagasse/SCB. You go for hydrothermal fractionation. So, you get the liquid part which is composed of the hemicellulose plus lignin here.

Now that goes to the lignin extraction. So, whatever lignin you extract that can be pyrolyzed. So, you get bio-oil and other carbon microsphere. So, you process it using ionic liquid plus hemicellulose, basically ionic liquid based pretreatment. So, you go for some anti-solvent extraction. You will have the ionic liquid recovery, you will have precipitated hemicellulose.

The hemicellulose can futher be converted into ethanol, butanol or any other such uses. So, whatever solid part that is left after removing the liquid one you will have the cellulose. Now, this cellulose can go for hydrolysis. Then we get the glucose, oligosaccharides. It can be converted into various other products such as fuels, basically alcoholic based fuels. So, different types of solid catalysts are being required for this entire processing, heterogeneous catalyst.

So, some of the names are here there, but it is not only these catalysts, there are many catalyst. So, you can develop catalysts characterize. One of the most important part of the entire biorefinery business or even the refinery business is the development of novel catalyst, effiecient catalyst, which is still going on. So, sugarcane bagasse, a solid residue from the sugar industry is a renewable resource with high feasibility for use as a precursor for biofuels and bio-based materials and chemicals.

In the biotechnological conversion of lignocellulosic biomass to sugars, the pretreatment and the hydrolysis steps are the bottleneck and the energy intensive process that result in high operating costs.

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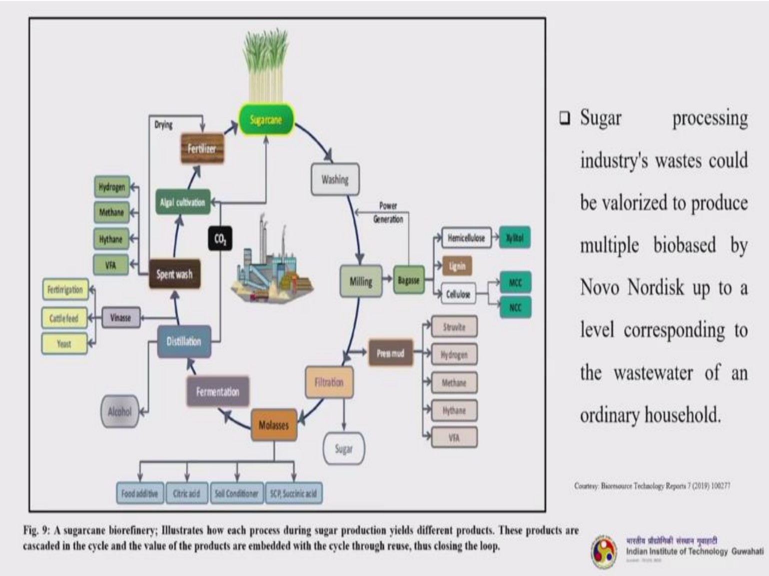

So, this is a sugarcane biorefinery. This is put in a more understandable way. So, you can see that how each process during sugar production yields different products. This is very interesting. So, let us start with this. Sugarcane washing, milling. After milling it is liquid part, it goes to the filtration but the bagasse or the solid part is coming here. It can directly go for power generation, gasification.

Then, if not, you process, you saccharify it, you pretreat it. You get hemicellulose, it produces xylitol. Lignin; lignin can be pyrolized to get various products and bio-oil. Cellulose; you get MCC, NCC. Then whatever the byproduct from milling to filtration, the press mud, it can have so many different things; hythane, methane, hydrogen, struvite and VFA/volatile fatty acids. You do filtration, you get sugar.

Sugar based platform we can start, alcholic fuels and other things. Molasss; the molasses can be fermented and distilled and further things. Otherwise we can have food additives, citric acid, soil conditioner and succinic acid; so many products. Then if you do distillation, you get alcoholic fuel here, alcohols. Whatever carbon dioxide is being generated from here that can go to the algal cultivation.

Algal cultivation ponds, it is an integrated refinery approach. So, many things are happening in a single way. Nothing is being wasted. Whatever byproduct is getting generated, whatever be their quantity, will be converted into some other valuable products. By doing that we generate so many other products or byproducts like let us say waste products like carbon dioxide, water that has to be recycled.

Carbon dioxide, very difficult to trap it. So you can trap it and fed to the algal raceway ponds or photobioreactors. So, you get vinasse from here, so cattle feed, yeast and all these things. Spent wash can be further processed to get hydrogen, methane, hythane and VFA just like the press mud doing here. So, sugarcane processing industry's waste could be valorized to produce multiple biobased products.

This is a classic example by the Novozymes. Novo Nordisk up to a level corresponding to the wastewater of an ordinary household. So this is a very interesting process where each and every byproduct is getting converted to some valuable products.

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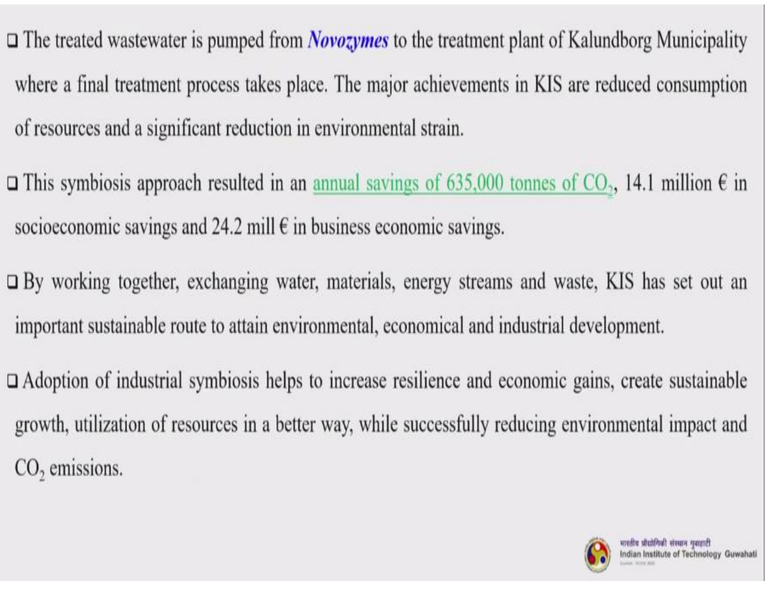

The treated wastewater is pumped from Novozymes (Novozyme is a company that produces enzymes) to the treatment plants of the Kalundborg Municipality where a final treatment process takes place. The major achievements in the KIS are reduced consumption of resources and a significant reduction in the environmental strain. Now this symbiosis approach resulted in an annual savings of 635,000 tons of carbon dioxide.

Huge one, you can understand that because that carbon dioxide is being utilized whatever is being generated by the algae. Now 14.1 million Euro in socioeconomic savings and 24.2 million Euro in business economics savings, so huge savings. By working together, exchanging water, materials and energy streams and waste, KIS has set out an important sustainable route to attain environmental, economical and industrial development.

It is a very classic case study for this integrated sugarcane based biorefinery. Adoption of industrial symbiosis helps to increase resilience and economic gains, create sustainable growth, utilization of resources in a better way, while successfully reducing environmental impact and carbon dioxide emissions.

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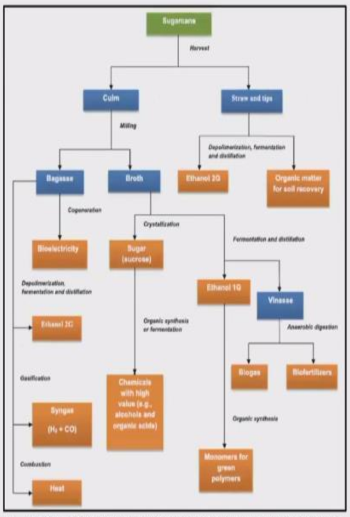

Fig. 10: Simplified flowchart of products (boxes in orange) for a sugarcane-biorefinery

Target compound	Precursor	Route	Status
2,5-Furanodicarboxylic acid	Glucose from cellulose	Organic synthesis Fermentation	In development: improvement of catalysts, biocatalysts, micro-organisms, yield, others
Succinic acid	Xylose from hemicellulose	Fermentation	In development: improvement of micro-organisms and yields
Antioxidants	Lignin	Catalytic cracking	In development: improvement of catalysts, yield, others
Derivatives from cellulose (acids, esters, nitrates, ethers, etc.)	Cellulose	Organic synthesis	Established industrial processes
2G ethanol	Glucose from cellulose Xylose from hemicellulose	Fermentation	In production but with improvement of enzymes, micro-organisms, yields, and cost reduction
Phenols	Lignin	Catalytic cracking	In development: improvement of catalysts, yield, others
Furfural	Xylose from hemicellulose	Organic synthesis	Established industrial processes: still needing to improve catalysts, yields, others
Gas of synthesis ($CO + H_2$)	Lignocellulosic biomass	Gasification	Established industrial processes based on petroleum: still needing to improve yields
5-Hydroxymethylfurfural	Cellulose	Organic synthesis	Established industrial processes: still needing to improve catalysts, yields, others
Sulfonated lignins	Lignin	Organic synthesis	Established industrial processes
Xylitol	Xylose from hemicellulose	Organic synthesis	In development: improvement of catalysts, yield, others

Fig. 11: New products from sugarcane identified as having high potential for biorefineries

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Courtesy: 10.1007/10_2016_70

So, these are the two figures. You can see that the first one is the simplified flowchart of products. So boxes in orange they are products. for a sugarcane biorefinery. So, you start with sugarcane. Harvest it, so culm and straw. So, let us see the culm part. Milling, you get bagasse, broth. So from bagasse to bioelectricity. Now bagasse can produce ethanol 2G through the fermentation pathway.

It can produce syngas through gasification. It can produce heat directly with combustion. Now, the broth can be converted into various one. So, you can get sucrose basically by crystallization, again further organic synthesis you get chemicals with high value, alcohols and organic acids. Now, 1G ethanol to monomers for green polymers and 1G ethanol before that also go and can be converted to the vinasse, so that we will get biogas and biofertilizers.

And whatever left out after taking the culm is basically the straw and tips. So, you can produce ethanol, 2G ethanol and organic matter for soil recovery. So, what we understand is that how many different types of products are getting produced from a single lignocellulosic biomass. So, this is what has actually been described here, but it is written there. So, the target compound, precursor, the route, the status.

So, let us see one. Succinic acid, precursor is the xylose from hemicellulose. The route is the fermentation and what is the status, the status is in development. Improvement of microorganisms and yields is that requirement. Then let us talk about 2G ethanol. So, the precursor is glucose from cellulose, xylose from hemicellulose both. Route is fermentation, So, the status is in production but with the improvement of enzymes, microorganisms, yields and cost reduction is required.

Now, let us talk about 5-hydroxymethylfurfural. It is a very important HMF chemical, it is a fuel additive. So its precursor is cellulose. Its route is organic synthesis. And what about status? It is an established industrial process, still needing to improve catalyst, yields, and others. Then the last one is xylitol. I have skipped some, you can go through later. So, the precursor is the xylose from hemicellulose. Route is organic synthesis. It is in development process stage, improvement of catalysts, yields and others are required.

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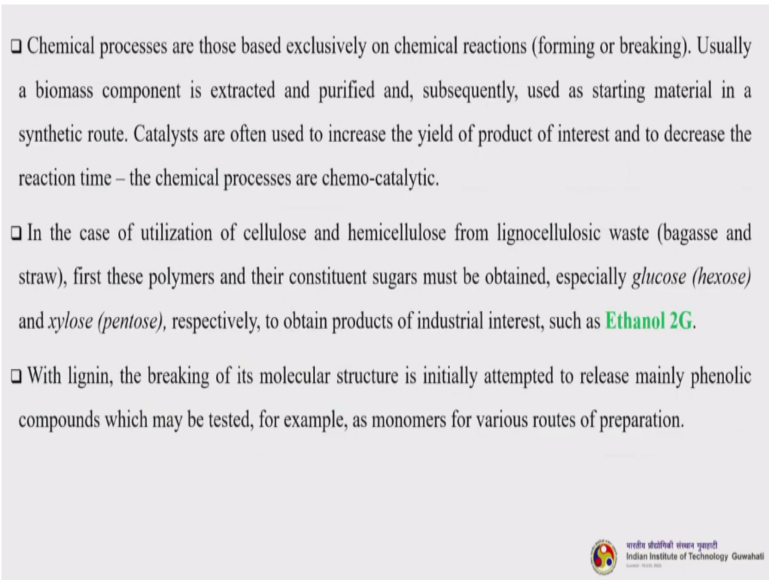

So, chemical processes are those based exclusively on chemical reactions (forming or breaking). Usually a biomass component is extracted and purified and subsequently used as starting material in a synthetic route. Catalysts are often used to increase the yield of product of interest and to decrease the reaction time. The chemical processes are chemo-catalytic. In the case of utilization of cellulose and hemicellulose from lignocellulosic waste, especially bagasse and straw, first these polymers and their constituent sugars must be obtained.

Especially the glucose or hexose or xylose or pentose respectively to obtain products of industrial interest such as 2G ethanol. With lignin, the breaking of its molecular structure is initially attempted to release mainly phenolic compounds, which may be tested for example as monomers for various routes of preparation.

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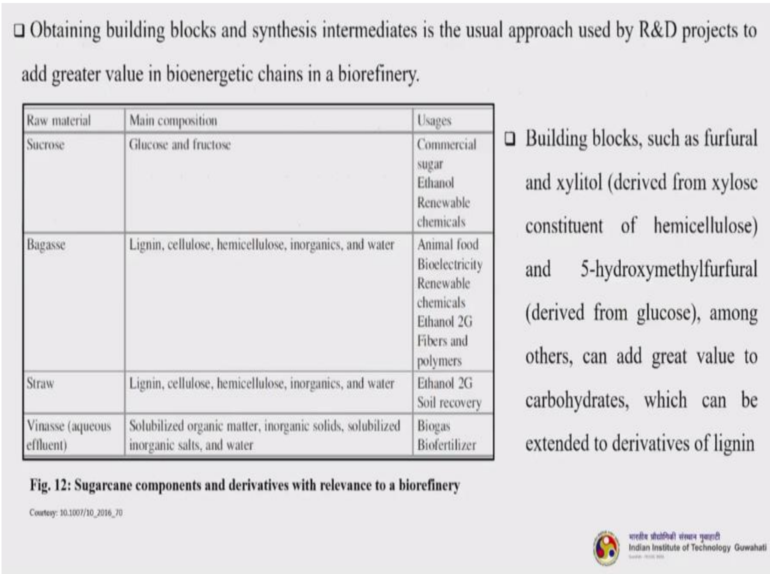

Raw material	Main composition	Usages
Sucrose	Glucose and fructose	Commercial sugar Ethanol Renewable chemicals
Bagasse	Lignin, cellulose, hemicellulose, inorganics, and water	Animal food Bioelectricity Renewable chemicals Ethanol 2G Fibers and polymers
Straw	Lignin, cellulose, hemicellulose, inorganics, and water	Ethanol 2G Soil recovery
Vinasse (aqueous effluent)	Solubilized organic matter, inorganic solids, solubilized inorganic salts, and water	Biogas Biofertilizer

Fig. 12: Sugarcane components and derivatives with relevance to a biorefinery

Courtesy: 10.1007/10_2016_70

So, obtaining building blocks and synthesis intermediates is the usual approach used by the R&D projects to add greater value in bioenergetic chains in a biorefinery. You can see some are listed here. So, the raw materials are sucrose, bagasse, straw and vinasse that is the aqueous effluent. Main composition is glucose and fructose. Usage is commercial sugar, ethanol, renewable chemicals.

Similarly bagasse you get the main composition is the lignin, cellulose, hemicellulose, inorganic and water. So it can go for animal food, bioelectricity production, renewable chemicals, 2G ethanol, fibres and polymers, so many more. So building blocks such as furfural and xylitol and 5-hydroxymethylfufural (HMF), among others can add great value to carbohydrates which can be extended to derivatives of lignin. The reason is that they are high-value chemicals.

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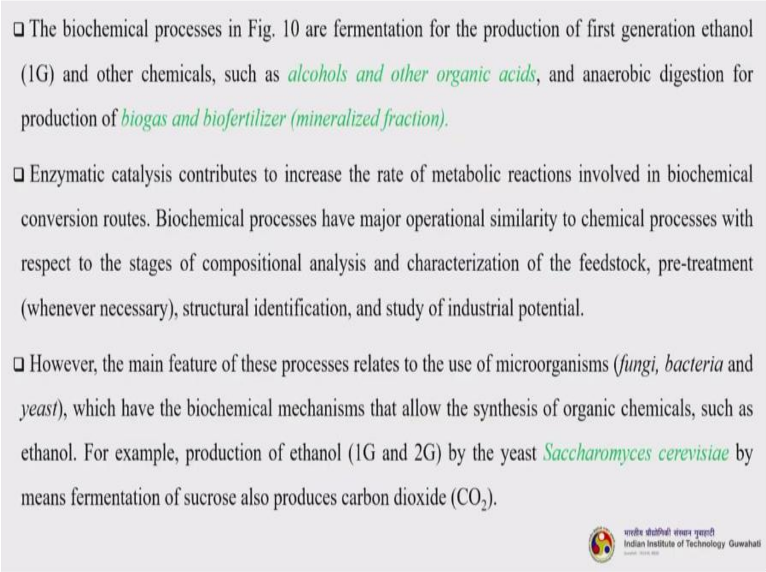

So the biochemical process in figure 10, so we will just go back to figure 10, this one, this process, are fermentation for the production of first generation ethanol and other chemicals such as alcohols and other organic acids and anaerobic digestion for the production of biogas and biofertilizer, that is, the mineralized fraction. Enzymatic catalysis contributes to increase the rate of metabolic reactions involved in biochemical conversion routes.

Biochemical processes have major operational similarity to chemical processes with respect to the stages of compositional analysis and characterization of the feedstock, pretreatment whenever necessary, structural identification and study of industrial potential. The main feature of these processes relates to the use of microorganisms either fungi, bacteria and yeast which have the biochemical mechanisms that allows the synthesis of organic chemicals such as ethanol.

For example, production of ethanol whether it is 1G or 2G by the yeast, *Saccharomyces cerevisiae* by means of fermentation of sucrose also produces carbon dioxide.

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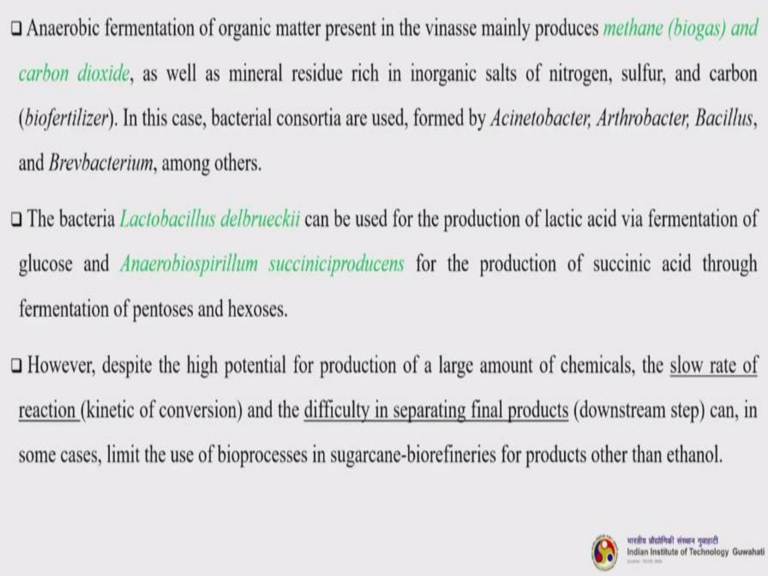

Anaerobic fermentation of organic matter present in the vinasse mainly produces methane and carbon dioxide as well as mineral residue rich in inorganic salts of nitrogen, sulfur and carbon. In this case, bacterial consortia are used formed by *Acinetobacter*, *Arthrobacter*, *Bacillus* and *Brevbacterium* among some of the various other species. The bacteria *Lactobacillus delbrueckii* can be used for the production of lactic acid via fermentation of glucose.

And *Anaerobiospirillum succiniciproducens* for the production of succinic acid through fermentation of pentoses and hexoses. However, despite the high potential for production of a large amount of chemicals, the slow rate of reaction (that is very important, the kinetic conversion, kinetics part is still very ill understood) and the difficulty in separating final products (the downstream step) can in some cases limit the use of bioprocesses in sugarcane biorefineries for products other than ethanol. Again, for the reason same is that they are energy intensive and costly.

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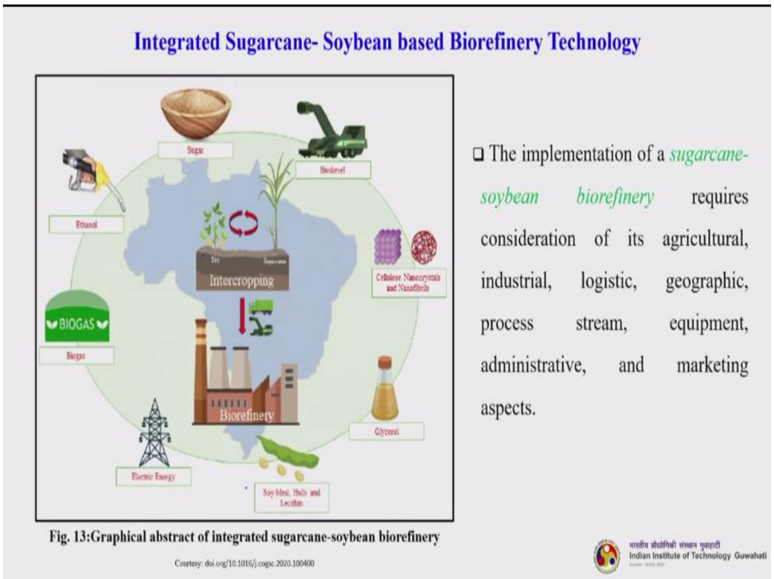

So this is the integrated sugarcane-soybean based biorefinery. Please understand two things here, both sugarcane and soybean are being combined together. So, you can see this is the graphical abstract of the integrated sugarcane-soybean biorefinery process. The implementation of a sugarcane-soybean biorefinery requires consideration of its agricultural, industrial, logistic, geographic, process stream, equipment, administrative and marketing aspects.

So many things has to be taken care of. So, you can see this sugar gets converted to biodiesel, cellulose, nanocrystal, nanofibrils, glycerols, then soymeal, hulls and lecithin, electrical energy, biogas, ethanol. So, this is in combination with various other processes and is a classical integrated refinery in which there are two substrates basically.

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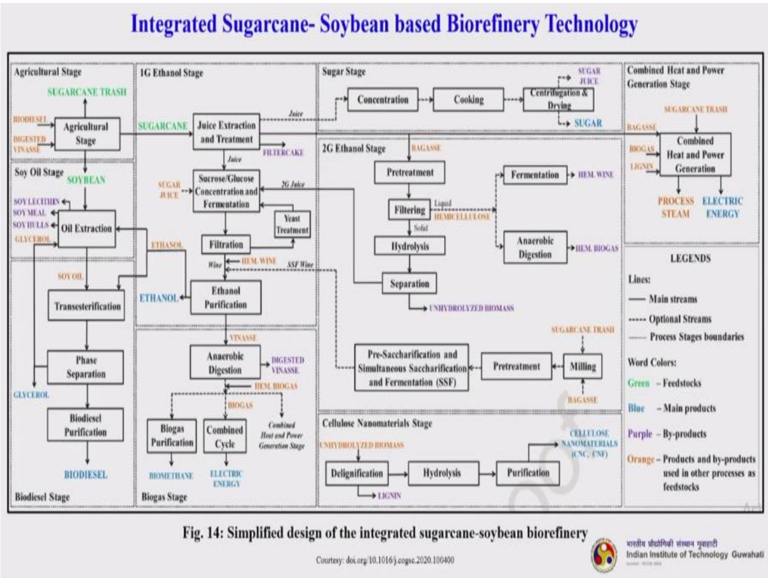

So, this is the simplified design of the integrated sugarcane-soybean refinery. So, this is the agricultural stage. This is 1G ethanol stage. This is the sugar stage and finally is the combined heat and power generation stage - the CHP stage. So, you can see this is the sugarcane being cultivated, it is being taken away. Then soybean you get the oil extracted. Then the sugarcane goes for the ethanol processing. Again here the soy oil also partly can go for the ethanol processing.

And huge amount of biodiesel can be produced after the transesterificatioin and you get so much of glycerol. Glycerol can be converted into various value-added products catalytically. So, then you get, this is the 2G ethanol stage. Then you have also cellulose nanomaterials stage. So, you get unhydrolyzed biomass, delignification, hydrolysis, purification you get cellulose nanocrystals. So, this is a classical example of how soybean and sugarcane can be processed simultaneously in an integrated biorefinery.

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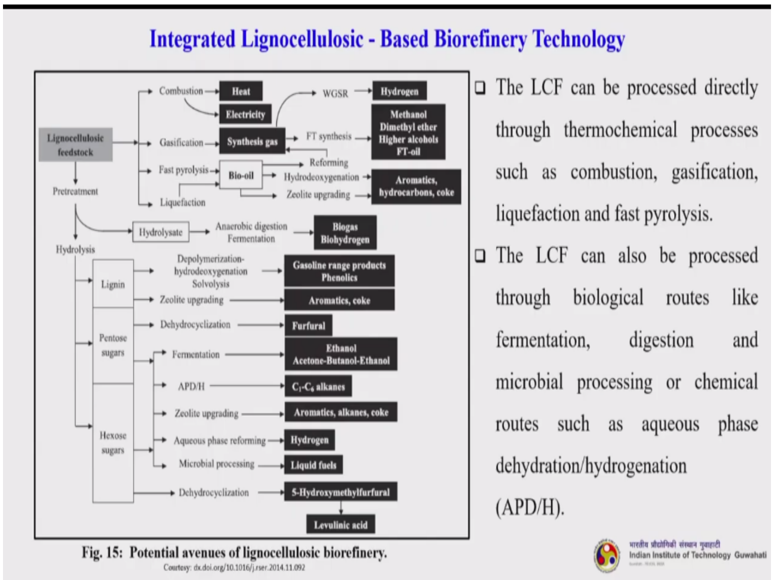

So, this is another classical example which is integrated lignocellulosic based biorefinery technology. The LCF that is the lignocellulosic feedstock can be processed directly through thermochemical processes such as combustion, gasification, liquefaction and fast paralysis or any other pyrolysis slow or medium also. The LCF can also be processed through the biological routes like fermentation, digestion and microbial processing or chemical routes such as aqueous phase dehydration/hydrogenation.

Have a look at this particular figure. This is a potential avenues of lignocellulosic biorefinery. So just see there, so many products. Now lignocellulosic feedstock, pretreatment. You go for hydrolysis. This is the sugar platforms and this is the lignin one. Lignin, then pentose, then hexose. Lignin can get converted to so many things. Gasoline, phenolics, aromatics. Of course then pentose sugars and hexose sugars they can produce the alcohols and other chemicals, furfural.

Then the ABE fermentation - acetone, butanol ethanol. C1 to C6 alkanes, aromatics, coke, then hydrogen, liquid fuels, 5-HMF/hydroxymethylfurfural and levulinic acid. Then the waste part it can go to the combustion, gasification, fast pyrolysis, liquefaction. We get bio-oil, synthesis gas, electricity, heat. Bio-oil can be further refined because they are not suitable for direct use, can be upgraded to aromatics, hydrocarbons, cokes and different types of fuels apart from hydrogen.

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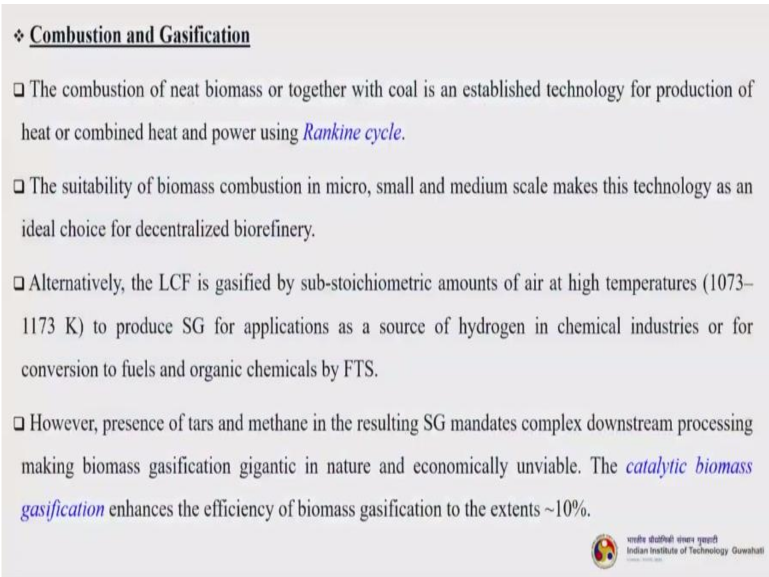

So, first process is the combustion and gasification So, the combustion of neat biomass or together with coal is an established technology for the production of heat or combined heat and power using the Rankine cycle, the CHP. The suitability of biomass combustion in micro, small and medium scale makes this technology is an ideal choice for decentralized biorefinery. Alternatively, the LCF is gasified by sub-stoichimetric amounts of air at higher temperatures (almost 1073-1173 Kelvin) to produce syngas for application as a source of hydrogen in chemical industries or for conversion to fuels and organic chemicals by the Fischer Tropsch synthesis, FTS. However, presence of tars and methane in the resulting syngas mandates complex downstream processing making biomass gasification gigantic in nature and economically unviable. The catalytic biomass gasification enhances the efficiency of biomass gasification to the extent of almost 10% only.

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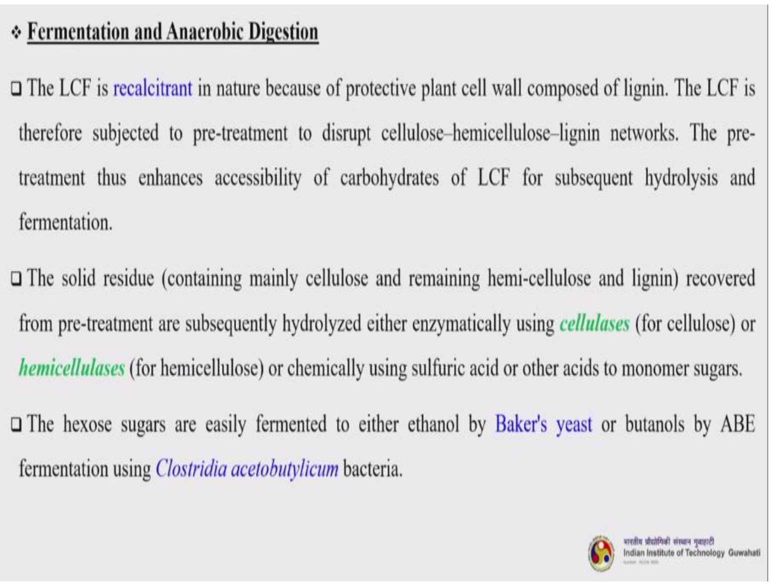

The second is fermentation and anaerobic digestion. The LCF is recalcitrant in nature because of the protective plant cell wall composed of lignin. The LCF is therefore subjected to pretreatment to disrupt the cellulose, hemicellulose, lignin networks. We have studied and understood this earlier. The pretreatment thus enhances accessibility of the carbohydrates of LCF for subsequent hydrolysis and fermentation.

The solid residue containing mainly cellulose and remaining hemicellulose and lignin recovered from pretreatment are subsequently hydrolyzed either enzymatically using cellulases that is for cellulose or hemicellulases, these are the enzymes, for hemicellulose or chemically using sulfuric acid or other acids to monomer sugars. The hexose sugars are easily fermented to either ethanol by the Baker's yeast or butanol by the ABE fermentation using the *Clostridia acetobutylicum* bacterial species.

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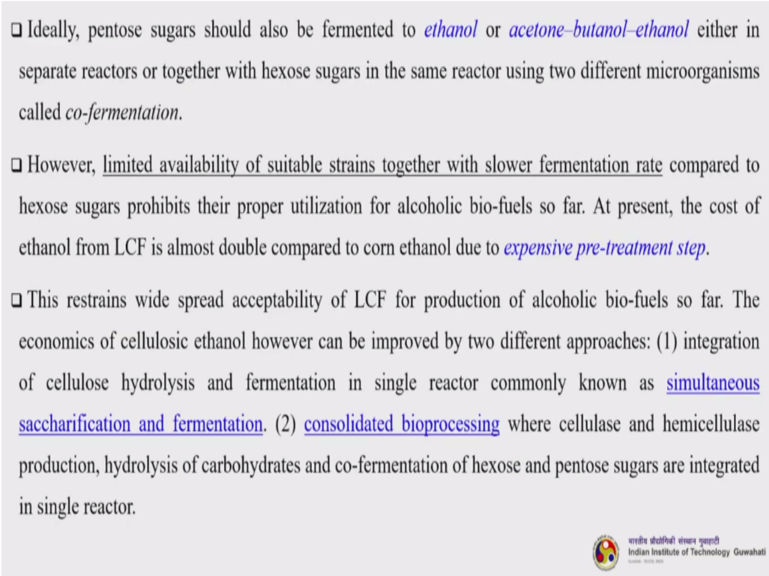

Ideally, pentose sugars should also be fermented to ethanol or acetone-butanol-ethanol either in separate reactors or together with hexose sugars in the same reactor using two different microorganisms called that co-fermentation process. However, limited availability of suitable strains together with slower fermentation rate compared to hexose sugars prohibits their proper utilization for alcoholic bio-fuels so far.

At present, the cost of ethanol from the LCF is almost double compared to that of the corn ethanol due to the expensive pretreatment step. Now, this restrains widespread acceptability of the lignocellulosic feedstock for a production of alcoholic biofuel so far. The economics of cellulosic ethanol however can be improved by two different approaches. First is the integration of cellulose hydrolysis and fermentation in single reactor, commonly known as simultaneous saccharification and fermentation. Second is consolidated bioprocessing where cellulase and hemicellulase production, hydrolysis of carbohydrates and co-fermentation of hexose and pentose sugars are integrated in a single reactor.

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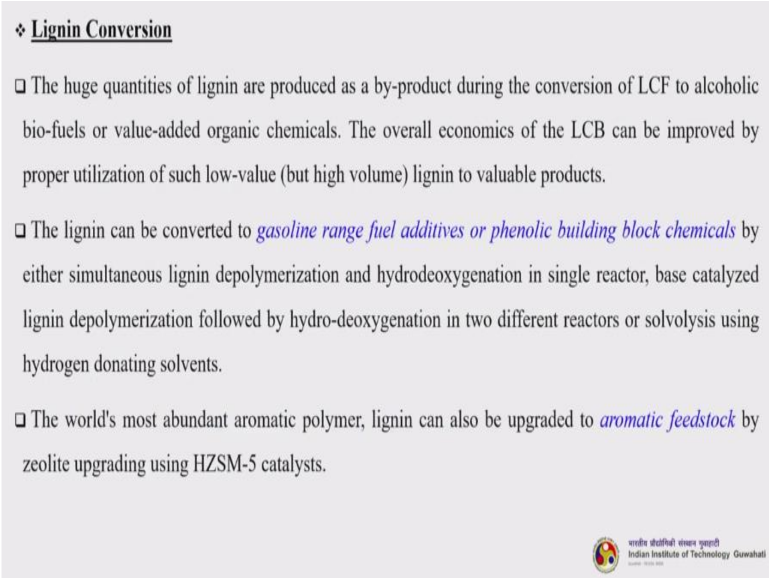

The third one is the lignin conversion. The huge quantities of lignin are produced as a byproduct during the conversion of the LCF to alcholic bio-fuels or value-added organic chemicals. The overall economics of the LCB can be improved by proper utilization of such low value but high volume lignin to valuable products. The lignin can be converted to gasoline range fuel additives or phenolic building block chemicals by either simultaneous lignin depolymerization, or hydrodeoxygenation in a single reactor, base catalyzed lignin depolymerization followed by hydrodeoxygenation in two different reactors or solvolysis using hydrogen donating solvents. The world's most abundant aromatic polymer lignin can also be upgraded to aromatic feedstock by zeolite upgrading using HZSM-5 catalysts.

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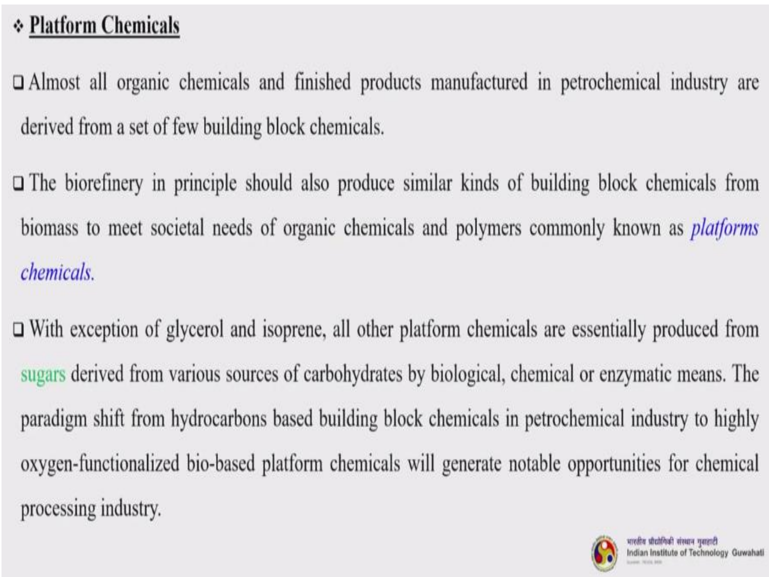

Then is platform chemicals. Almost all organic chemicals and finished products manufactured in petrochemical industry are derived from a set of few building block chemicals. The biorefinery in principle should also produce similar kinds of building block chemicals from biomass to meet societal needs of organic chemicals and polymer commonly known as platform chemicals.

With the exception of glycerol and isoprene, all other platform chemicals are essentially produced from sugars only and that being derived from various sources of carbohydrates by biological, chemical or enzymatic means. The paradigm shift from hydrocarbons based building block chemicals in petrochemical industry to highly oxygen-functionalized bio-based platform chemicals will generate notable opportunities for chemical processing industries.

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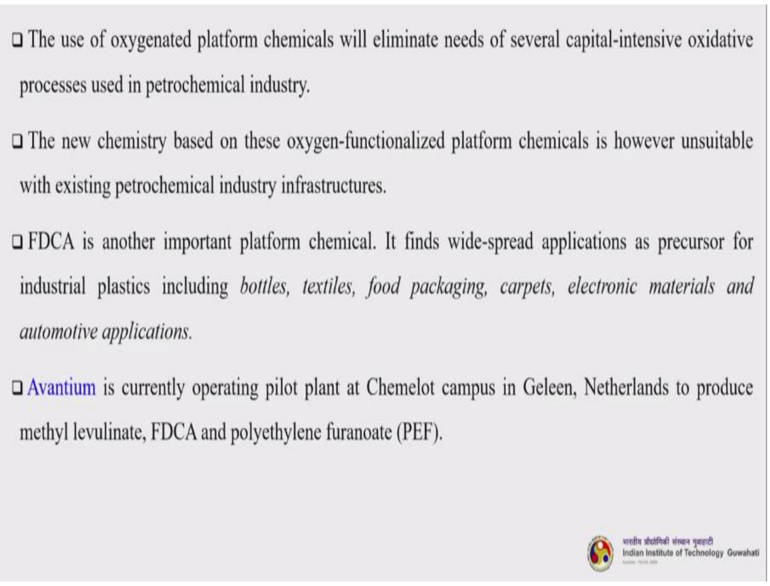

The use of oxygenated platform chemicals will eliminate the need for several capital intensive oxidative processes used in the petrochemical industry. It will reduce the overall cost. The new chemistry based on these oxygen-functionalized platform chemicals is however unsuitable with existing petrochemical industry infrastructures, so this is another problem.

FDCA is another important platform chemical. It finds widespread application as precursor for industrial plastics including bottles, textiles, food packaging, carpets, electronic materials and automotive applications. Avantium is currently operating pilot plant at Chemelot campus in Geleen, the Netherlands to produce methyl levulinate, FDCA and polyethylene furanoate.

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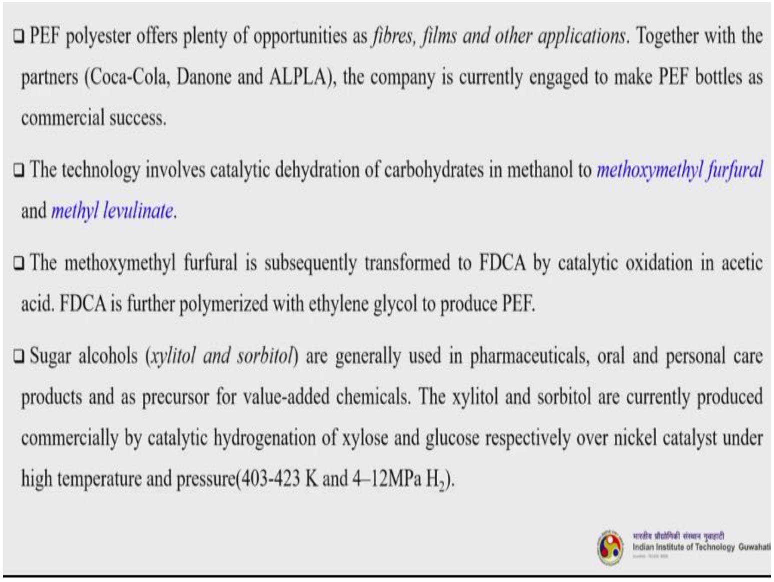

So PEF polyesters offer plenty of opportunities as fibres, films and other applications. Together with the partners that is Coca-Cola, Danone and ALPLA, the company is currently engaged to make PEF bottles as commercial success. The technology involves catalytic dehydration of carbohydrates in methanol to methoxymethyl furfural and methyl levulinate. The methoxymethyl furfural is subsequently transformed to FDCA by catalytic oxidation in acetic acid.

FDCA is further polymerized with ethylene glycol to produce PEF. Sugar alcohols, xylitol and sorbitol, are generally used in pharmaceuticals, oral and personal care products and as a precursor for value-added chemicals. The xylitol and sorbitol are currently produced commercially by catalytic hydrogenation of xylose and glucose respectively over nickel catalyst under high temperature and precursor.

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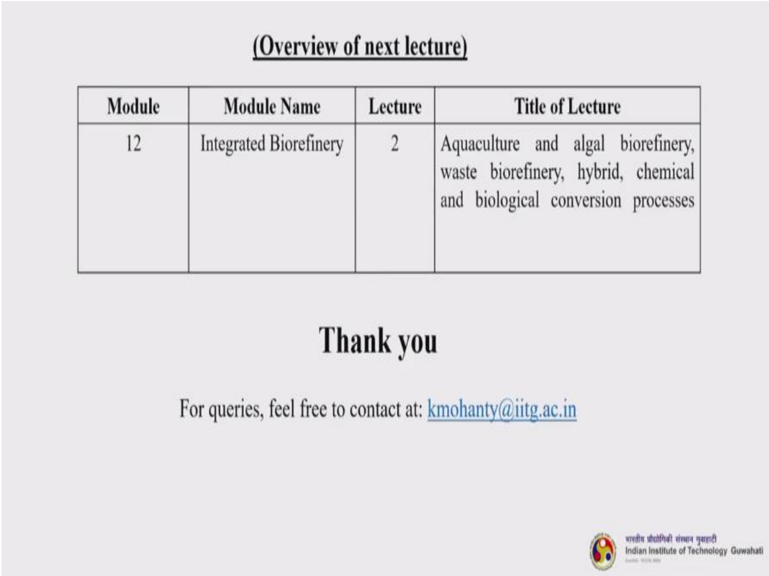

So with this, I conclude today's lecture. In our next class that is under module 12 lecture 2, we will be discussing about aquaculture and algal biorefinery, waste biorefinery, hybrid and chemical and biological conversion processes. Thank you very much. So if you have any query, please register in the Swayam portal or you can always drop a mail to me at kmohanty@iitg.ac.in.