Biomass Conversion and Biorefinery
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Module-08
Lecture-24
Factors Affecting Biooil, Biochar production, Fuel Properties Characterization

Good morning students. Today is lecture 3 under module 8. And in today's lecture we will be discussing 2 main important things. One is the biochar characterization and another is the biochar applications. So, let us begin.

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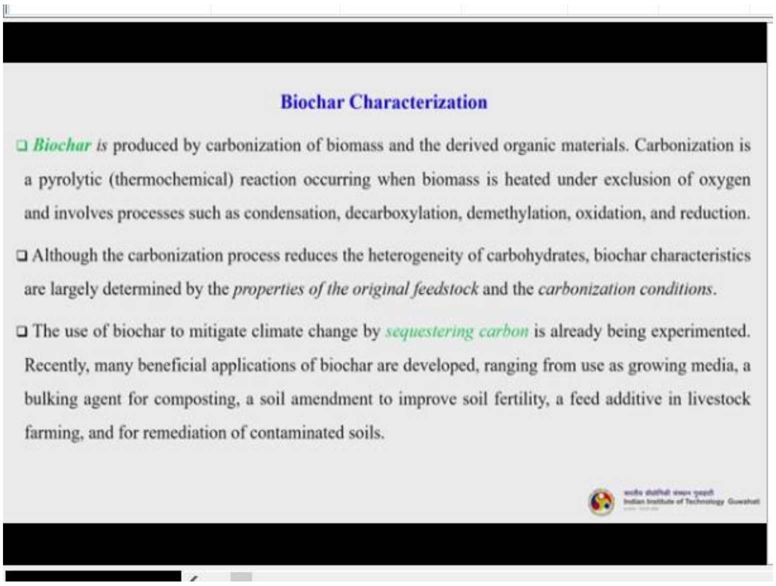

Biochar is produced by carbonization of biomass and the derived organic materials. Carbonization is a pyrolytic reaction occurring when biomass is heated under the exclusion of oxygen and involves processes such as condensation, decarboxylation, demethylation, oxidation and reduction. Although the carbonization process reduces the heterogeneity of carbohydrates, biochar characteristics are largely determined by the properties of the original feedstock and the carbonisation conditions.

The use of biochar to mitigate climate change by sequestering carbon is already being experimented and it is a very interesting topic of research since almost 2 decades, many excellent works have been reported and some are also being implemented. Recently, many beneficial applications of biochar are developed, ranging from use as a growing media, a bulking agent for composting, soil amendment to improve soil fertility (another important class of application of biochar), then as feed additive in livestock farming and for remediation of contaminated soils.

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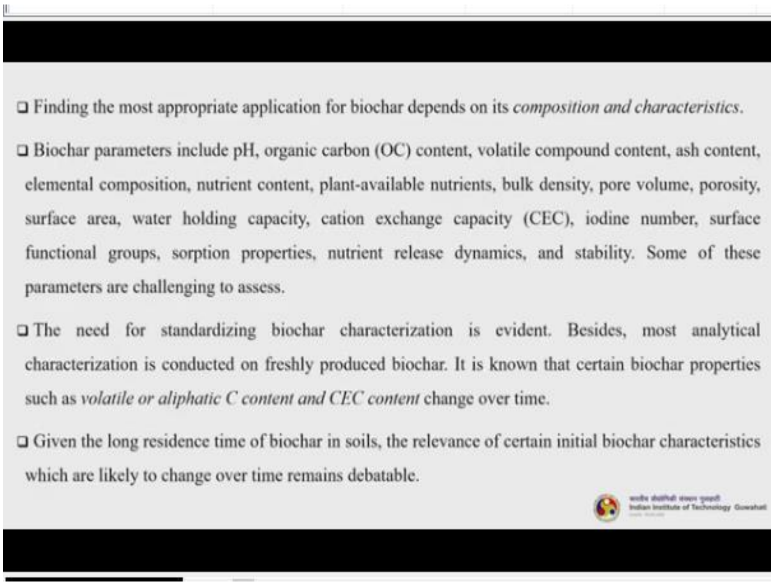

Finding the most appropriate application of biochar depends on its composition and characteristics. Biochar parameters include pH, organic carbon content, volatile compound content, ash content, elemental composition, nutrient content, plant available nutrients, bulk density, pore volume, porosity, surface area, water holding capacity, cation exchange capacity, iodine number, surface functional group, sorption properties, nutrient release dynamics and stability.

Some of these parameters are challenging to assess. Now, the need for standardizing biochar characterization is very evident. Besides most analytical characterization is conducted on freshly produced biochar. It is known that certain biochar properties such as volatile or aliphatic carbon content and CEC content changes over the time. So, that means when you are storing it during its aging this aliphatic carbon content CEC content will change.

Now, given the long residence time of biochar in soils, the relevance of certain initial biochar characteristics which are likely to change over time remains debatable. So, hardly there are any reports on the biochar once it is applied to the soil or some other application and how its properties are changing with respect to time is not much studied.

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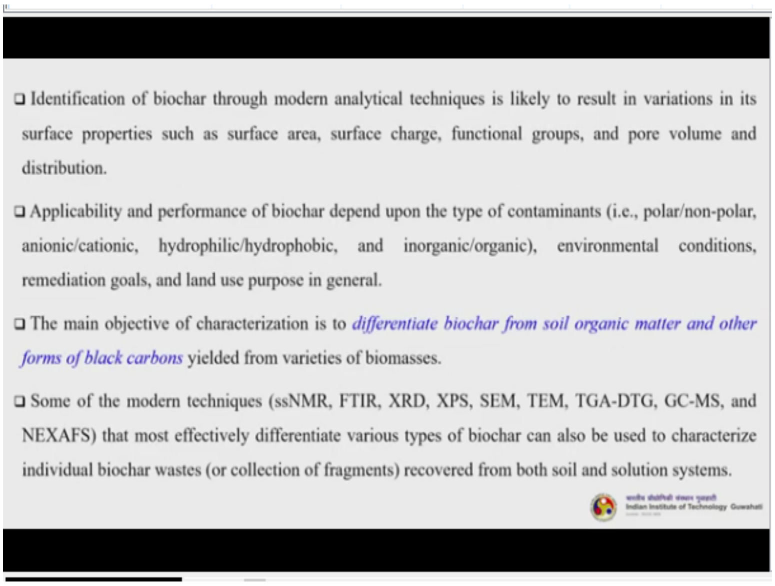

Identification of biochar through modern analytical techniques is likely to result in variation in its surface properties, such as surface area, surface charge, functional groups, pore volume and distribution. Applicability and performance of biochar depend upon the type of contaminants, environmental conditions, remediation goals and land use purpose in general. The main objective of characterization is to differentiate biochar from soil organic matter and other forms of black carbons yielded from various biomasses.

Some of the modern techniques - such as solid state NMR, FTIR, XRD, XPS, SEM, TEM, TGA-DTG, GCMS and NEXAFS - that most effectively differentiate various types of biochar can also be used to characterize individual biochar waste, or you can say the collection of fragments recovered from both soil and solution system. So, we will discuss one by one these things.

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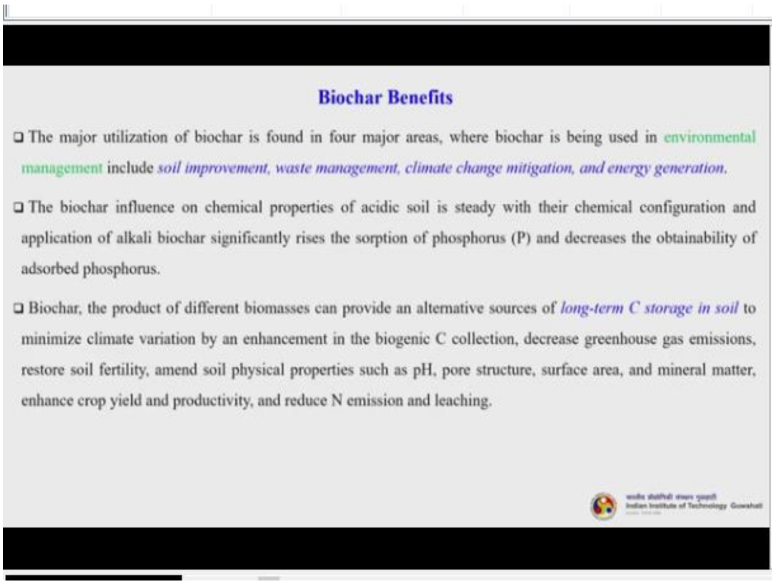

And before that, let us try to understand the biochar benefits. The major utilization of biochar is found in 4 major areas, where biochar is being used in environmental management which includes soil improvement, waste management, climate change mitigation and energy generation. The biochar influence on chemical properties of acidic soil is steady with their chemical configuration and application of alkali biochar significantly raises the sorption of phosphorus and decreases the obtainability of the adsorbed phosphorus.

Biochar, the product of different biomasses can provide an alternative source of long term carbon storage in soil to minimize climate variation by an enhancement in the biogenic carbon collection, decreases the greenhouse gas emissions, restore soil fertility, amend soil physical properties such as pH, pore structure, surface area and mineral matter, enhances the crop yield and productivity and reduces the nitrogen emissions and leaching.

So, these are basically biological and environmental applications or the benefits when we are using a biochar in soil.

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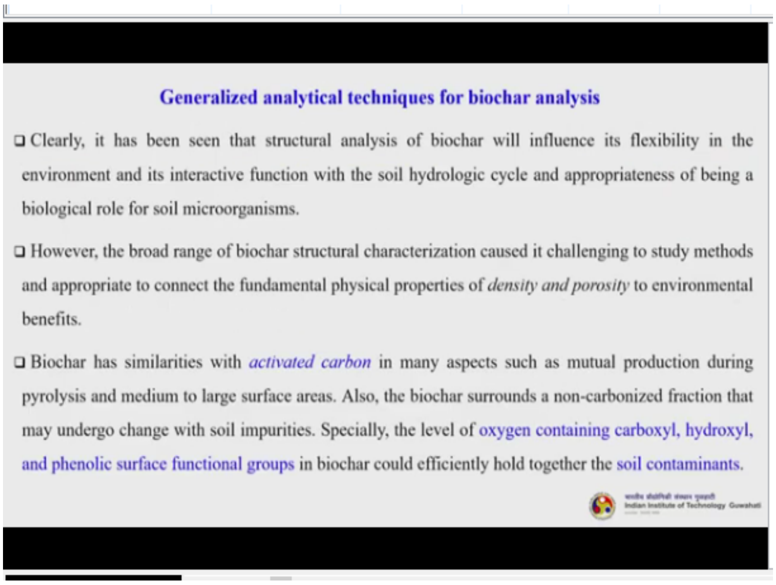

So, let us understand the generalized analytical techniques for the biochar analysis - the characterization techniques. Clearly it has been seen that structural analysis of biochar will influence its flexibility in the environment and its interactive function with the soil hydrologic cycle and appropriateness of being a biological role for soil microorganisms. However, the broad range of biochar structural characterization caused its challenging to study methods and appropriate to connect the fundamental physical properties of density and porosity to environmental benefits.

Biochar has similarities with activated carbon in many aspects, such as mutual production during pyrolysis and medium to large surface areas. Also, the biochar surrounds a non carbonized fraction that may undergo change with soil impurities. Specially, the level of oxygen containing carboxyl, hydroxyl and phenolic surface functional groups in the biosphere could efficiently hold together the soil contaminants.

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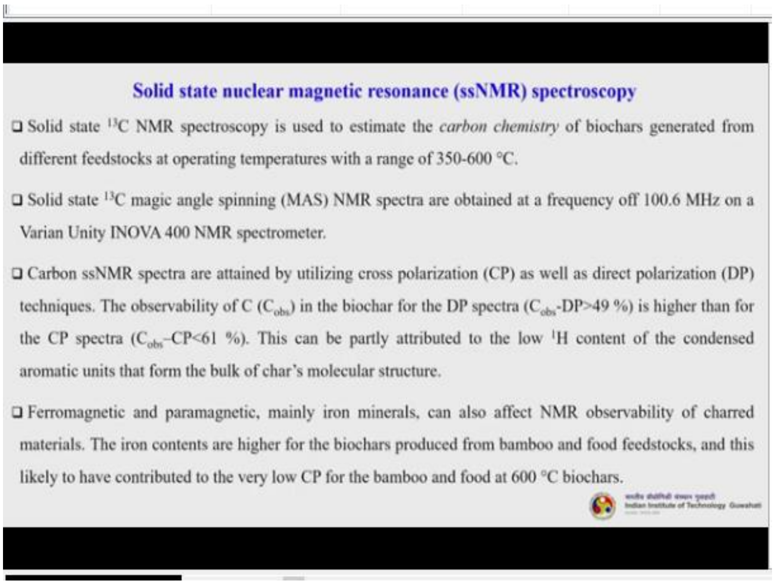

We will see one by one some of the analytical techniques to characterize the biochar. The first is solid state nuclear magnetic resonance (ssNMR) spectroscopy. Solid state C NMR spectroscopy is used to estimate the carbon chemistry of biochars generated from different feedstock at operating temperatures with a range of 350 to 600 degrees centigrade. Now, solid state magic angle spinning the MAS NMR spectra are obtained at a frequency of 100.6 megahertz on a Varian unity INOVA 400 NMR spectrometer.

So, this is one of the spectrometer model please do not understand that only this has to be used there are many. This is just taken from literature. Now carbon solid state NMR spectra are attained by utilizing cross polarization as well as direct polarization techniques. The observability of C in the biochar for the DP spectra is higher than the CP spectra. Now, this can be partly attributed to the low hydrogen content of the condensed aromatic units that form the bulk of chars' molecular structure.

Then ferromagnetic and paramagnetic mainly the iron minerals can also affect NMR observability of the char materials. The iron contents are higher for the biochars produced from bamboo and food feedstock and this likely to have contributed to the very low CP for the bamboo and food at 600 degree biochars. So, the inherent meaning of this entire discussion is that what is the composition of your biochar, mineral composition including that if you have more iron content, then your CP DP value is going to change.

So, this composition also makes effect or impact when you are analyzing the biochar in a particular analytical tool whether it is ssNMR, whether it is XRD, whether it is XPS all such spectroscopic and IR methods.

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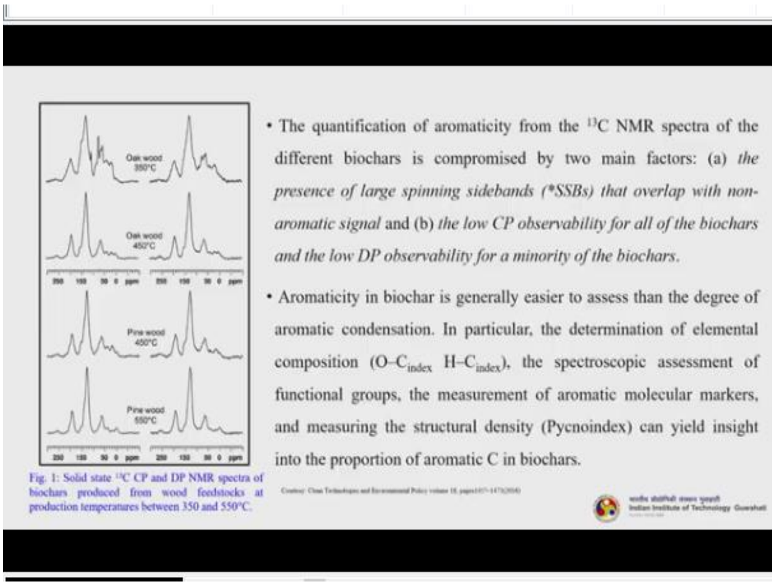

So, this is one typical solid state NMR spectra CP and DP NMR spectra of the biochars produced from the wood feedstocks at production temperatures between 350 and 550 degrees centigrade. So, this is oak wood at 350 and it is 450, you can see that there are changes in peaks. Now, I am, in detail not telling you why the peak has changed and all these things; that actually will take so much of time even out of our discussion with respect to this particular course.

But this is just to make you understand that how actually NMR peaks looks like and what you can infer from it. Similarly, the below one is the pinewood at 450 and 550. So, the peaks at what range actually this is in ppm, you can see the x scale, the peaks are coming. So, from that you have to analyze the peaks; there are standard library available to analyze the peaks. So, you can use that and making use of a software you can analyze it.

So, the quantification of aromaticity from the C NMR spectra of the different biochar is compromised by 2 main factors. The first is the presence of the large spinning sidebands – SSB - that overlap with the non aromatic signal and the second is the low CP observability for all the biochars and the low DP observability of a minority of the biochars.

Now, aromaticity in biochar is generally easier to assess than the degree of the aromatic condensation. In particular, the determination of elemental composition, the spectroscopic assessment of functional groups, the measurement of the aromatic molecular markers and measuring the structural density the Pycnoindex basically, can yield insight into the proportion of the aromatic carbon in biochars.

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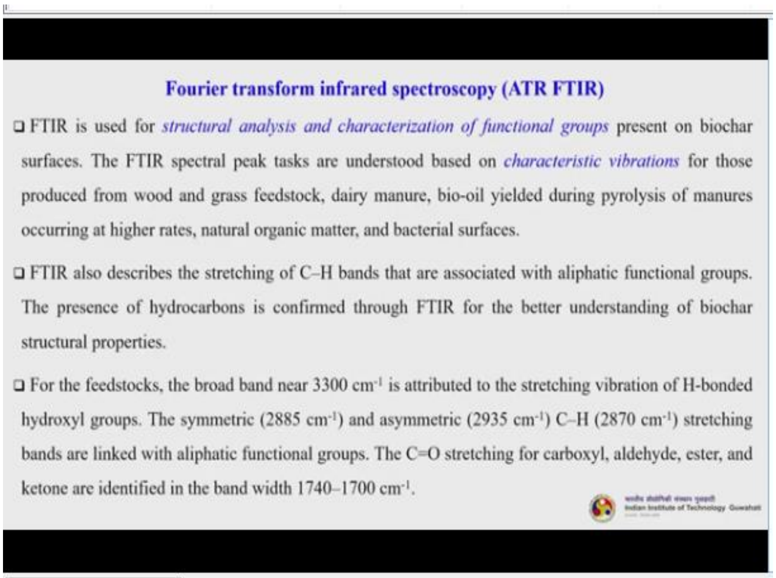

Then, the Fourier transform infrared spectroscopy. So, FTIR is used for the structural analysis and characterization of the functional groups present on the biochar surfaces. The FTIR spectral peak tasks are understood based on characteristic vibrations for those produced from the wood and grass feedstock, dairy manure, biooil yielded during pyrolysis of manures occurring at higher rates, natural organic matter and bacterial surfaces and what not.

You can use any materials to find out the functional groups present on the surface of it, using the FTIR spectroscopy. FTIR also described the stretching of carbon hydrogen bands that are associated with aliphatic functional groups. The presence of hydrocarbons is confirmed through FTIR for the better understanding of biochar structural properties. For the feedstock, the broad band near 3300 centimeter inverse is attributed to the stretching vibration of the hydrogen bonded hydroxyl groups.

The symmetric and asymmetric carbon hydrogen stretching are linked with aliphatic functional groups. The carbon oxygen double bond stretching for carboxyl, aldehyde, ester, and ketone are identified in the bandwidth 1740 to 700 centimeter inverse.

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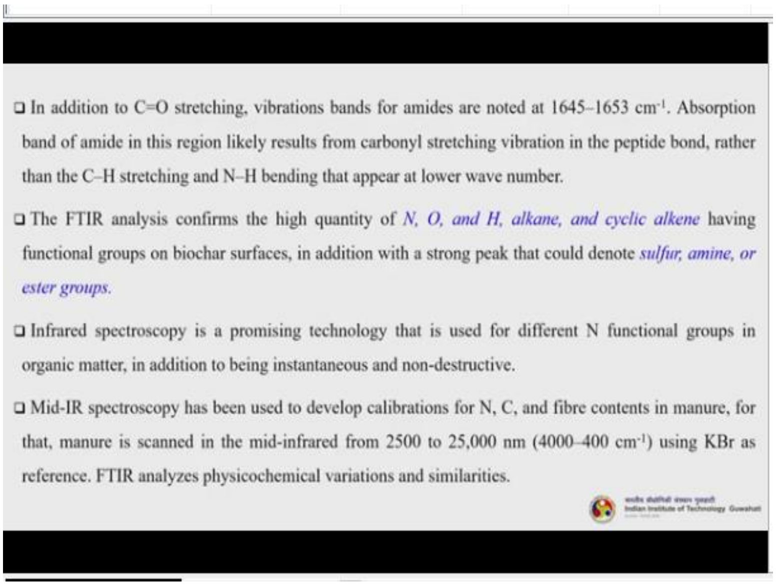

So, in addition to a carbon oxygen double bond stretching vibration bands for amides are noted at 1645 to 1653 centimeter inverse. So, these are wave numbers. So, absorption band of amide in these region likely results from the carbonyl stretching vibration in the peptide bond rather than C-H stretching and N-H bending that appear at lower wave number. The FTIR analysis confirms the high quality of nitrogen, oxygen, hydrogen, alkane and cyclic alkene having functional groups on biochar surfaces in addition with a strong peak that could denote sulfur, amine or ester groups.

Infrared spectroscopy is a promising technology that is used for different nitrogen functional groups in organic matter in addition to being instantaneous and non-destructive. Mid-IR spectroscopy has been used to develop calibrations for nitrogen, carbon and fiber contents in manure. For that manure is scanned in the mid-infrared wavelength from 2500 to 25,000 nanometer. So, that correspond to 4000 to 400 centimeter inverse using KBR as reference. FTIR analyzes physicochemical variations and similarities.

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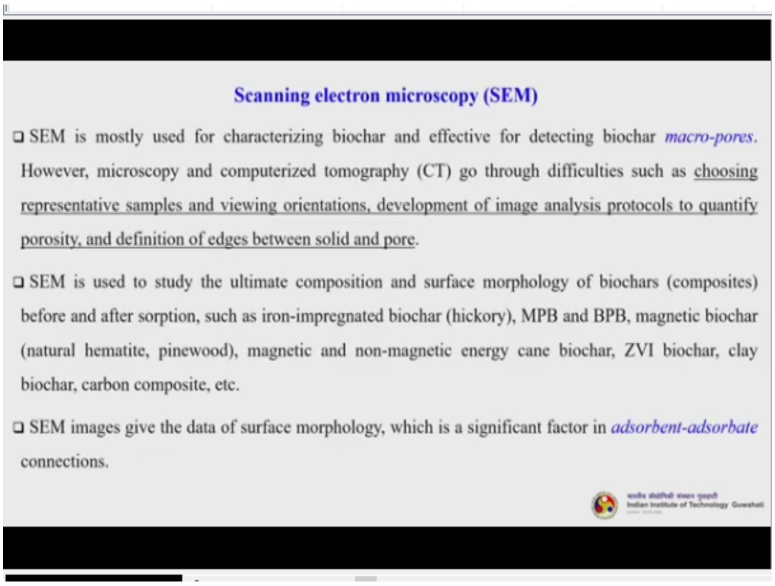

The next is the scanning electron microscope SEM. So the SEM is mostly used for characterizing biochar and effective for detecting biochar macropores, SEM is a surface characterization technique. So, however microscopy and computerized tomography go through a difficulty such as choosing representative samples and viewing orientations, development of image analysis protocols to quantify porosity and definition of edges between solid and pore.

Now, SEM is used to study the ultimate composition and surface morphology of biochars before and after sorption such as iron impregnated biochar, MPB and BPB, magnetic biochar, magnetic and non magnetic energy cane biochar, ZVI biochar, clay biochar, carbon composites etcetera. So, basically biochar, when you produce it and then after its application, you again have to see and see what are the changes in the surface.

So, SEM images give the data of surface morphology, which is a significant factor in adsorbent-adsorbate connection. So, when you are talking about adsorption so, the surface morphology plays a significant role. That is why it is very important to characterize the biochar using SEM.

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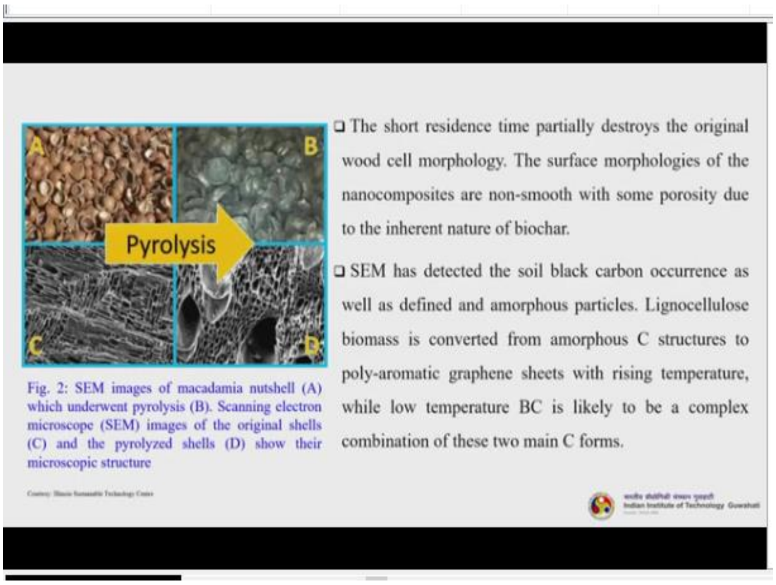

So, this is a typical image of the SEM. So, you can see that this is the original macadamia nut shell, which was used to prepare the biochar. So, then B is actually after the pyrolysis, the biochar is produced, this is the original feedstock, this is after the pyrolysis the biochar is produced, then this is the original cells of the scanning electron microscopy image and this is the inner view.

So, from here you can understand that how actually the scanning electron micrograph of a biochar looks like. So, the short residence time partially destroys the original wood cell morphology. So, that means when we are talking about pyrolysis conditions. The surface morphologies of the nanocomposite are non smooth with some porosity due to the inherent nature of biochar.

SEM has detected the soil black carbon occurrence as well as defined and amorphous particles. Lignocellulose biomass is converted from amorphous C structures to poly-aromatic graphene sheets with rising temperature while at low temperature BC is likely to be a complex combination of these 2 main carbon forms.

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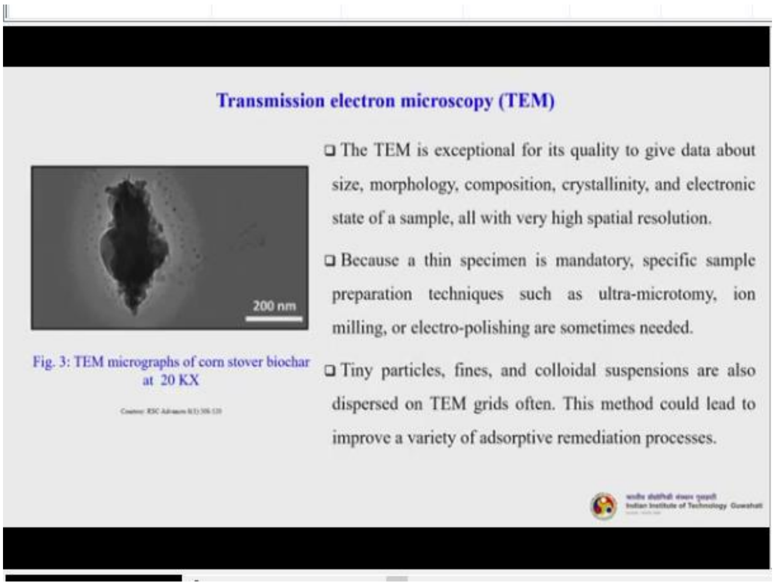

So, next is TEM, transmission electron microscope; So the TEM is exceptional for its quality to give data about size, morphology, composition, crystallinity and electronic state of sample all with a very high spatial resolution. Because a thin specimen is actually required for the TEM analysis specific sample preparation techniques such as ultra-microtomy, iron milling or electro-polishing are sometimes needed.

Tiny particles, fines and colloidal suspensions are also dispersed on TEM grids often, this method could lead to improve a variety of adsorptive remediation processes. So this is a representative image of a TEM micrograph of a corn stover biochar at 200 nanometers.

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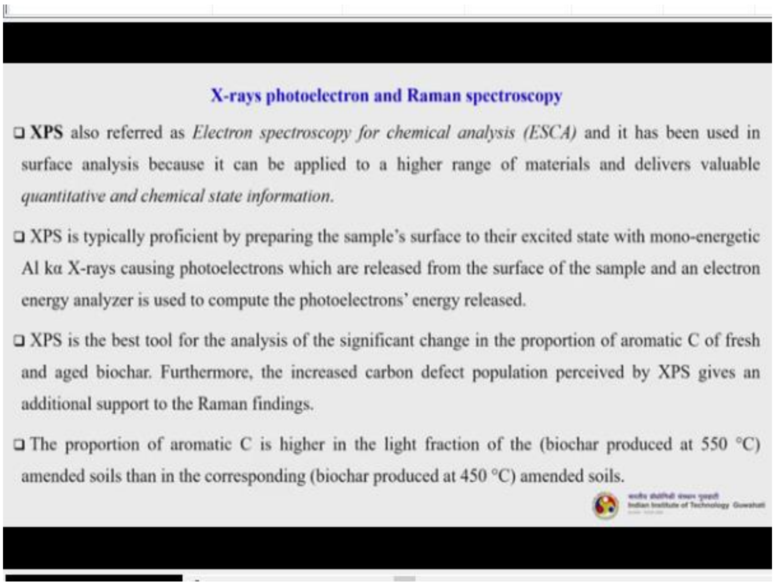

So, then is XPS and Raman spectroscopy. So, XPS also referred to as the electron spectroscopy for chemical analysis ESCA. And it has been used in surface analysis because it can be applied to higher range of materials and delivers valuable quantitative as well as chemical state information. XPS is typically proficient by preparing the sample surface to their excited state with mono energetic Al k alpha X-rays, causing photoelectrons which are released on the surface of the sample and an electron energy analyzer is used to compute the photoelectrons energy released. XPS is the best tool for the analysis of the significant change in the proportion of aromatic carbon of fresh and aged biochar. Furthermore, the increased carbon defect population pursued by XPS gives an additional support to the Raman findings. The proportion of aromatic carbon is higher in the light fraction of the biochar that is produced at 550 degrees centigrade amended soils than in the corresponding biochar that is produced at 450 degrees centigrade amended soils.

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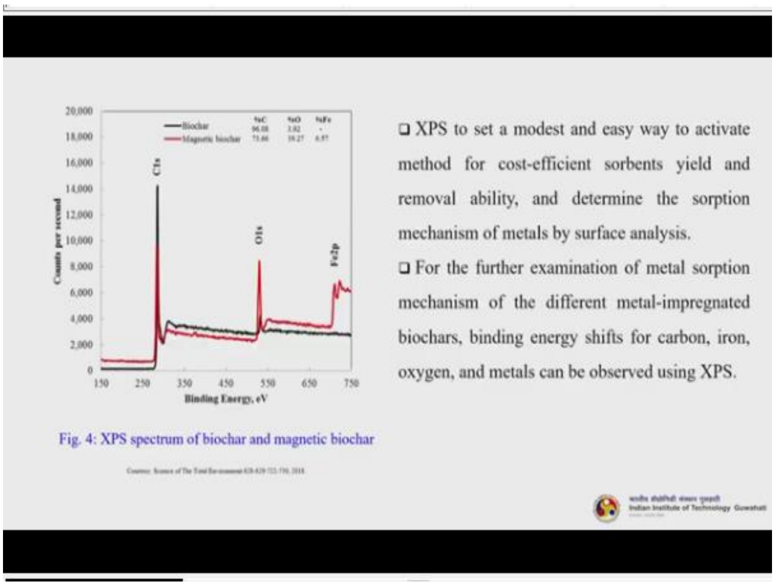

This is a typical spectrum of the biochar XPS spectrum. So, 2 things have been shown here. One is the biochar and other is the magnetic biochar. So, the biochar is denoted by that black curve and the red curve actually denotes the magnetic biochar. So, you can see the magnetic biochar the peak has been reduced here, wherever here it has been broadened or you have a larger peak here.

And in case of here the Fe2p. So, biochar do not have a peak whereas magnetic biochar due to the presence of iron. So, you can see that there is a huge peak. So, XPS to set a modest and easy way to activate method for cost efficient sorbent yield and removal ability and determine the sorption mechanism of metals by surface analysis. For the further examination of metal sorption mechanism of the different metal impregnated biochars. Binding energy shifts for carbon, iron, oxygen and metals and that can be observed using the XPS.

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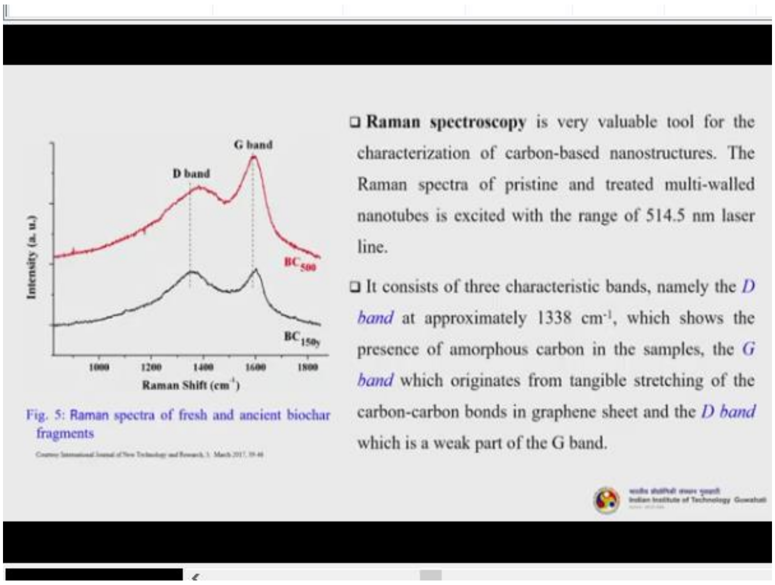

So, then next is Raman spectroscopy. So, Raman spectroscopy is very valuable tool for the characterization of the carbon based nanostructures. The Raman spectra of pristine and treated multi walled nanotubes is excited with the range of 514.5 nanometer laser line. So, Raman usually consists of 3 characteristics bands, the D band at approximately 1338 centimeter inverse, it shows the presence of amorphous carbon in their samples.

Then, the G band which originates from the tangible stretching of the carbon-carbon bonds in graphene sheet and then the D band which is a weak part of the G band again. So, basically 2 D band and G band. So, you can see this is a representative spectra of the fresh and an ancient biochar sample, ancient means the old biochar samples. So, you can see that the D band corresponding to 1338 centimeter inverse here, it is appearing. Then the G band is appearing later on. So, it is also a very good technology especially when you are talking about nanostructures.

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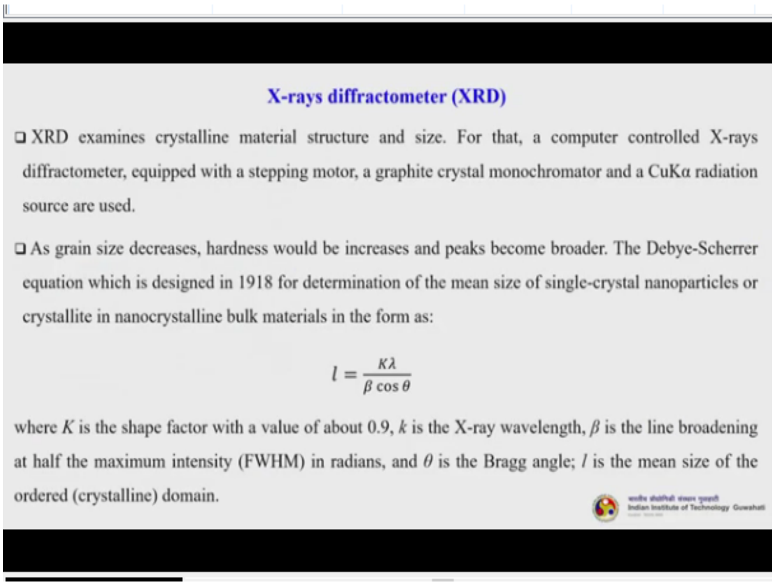

Then XRD, X-ray diffractometer: XRD examines crystalline material structure and size. For that a computer controlled X-ray diffractometer equipped with a stepping motor, a graphite crystal monochromator and a CuK alpha radiation source are used. As grain size decreases hardness would be increased and peaks become broader. The Debye-Scherrer equation which is designed in 1918 for the determination of the mean size of the single crystal nanoparticle or crystallite in nano-crystalline bulk material in the form can be written as l = k alpha beta cos theta.

$$l = \frac{K\lambda}{\beta cos\theta}$$

Where K is the shape factor with a value of about 0.9, small k is the X-ray wavelength, beta is the line broadening at half of the maximum intensity in radians, and theta is the Bragg's angle, l is the mean size of the ordered or crystalline domain.

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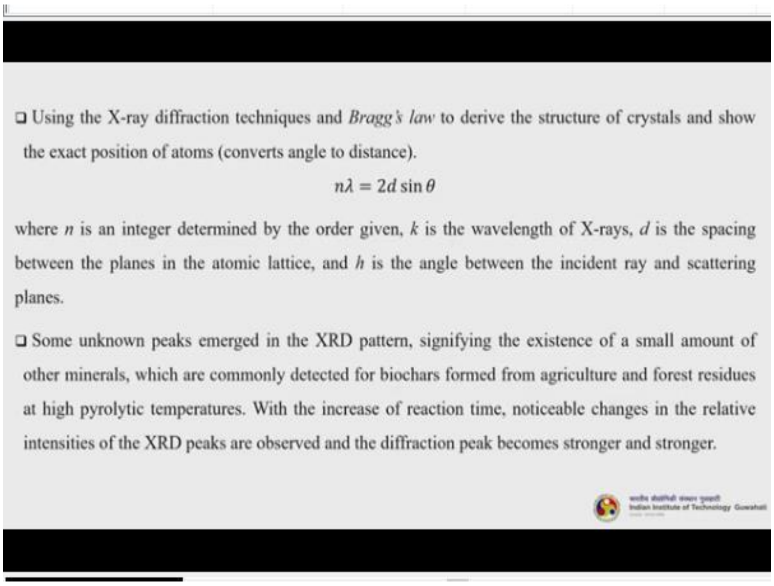

Using the X-ray diffraction techniques and Bragg's law to derive the structure of crystals and show the exact position of atoms, you can use this equation n lambda = 2d sine theta.

$$n\lambda = 2d\ sin\theta$$

Where n is the integer determined by the order given, k is the wavelength of X-ray, d is the spacing between the planes in the atomic lattice and h is the angle between the incident ray and scattering planes.

Some unknown peaks emerged in the XRD pattern signifying the existence of a small amount of other minerals, which are commonly detected for biochars formed from agricultural and forest residues at high pyrolytic temperatures with the increase of reaction time, noticeable changes in the relative intensities of the XRD peaks are observed and the difffraction peak becomes stronger and stronger.

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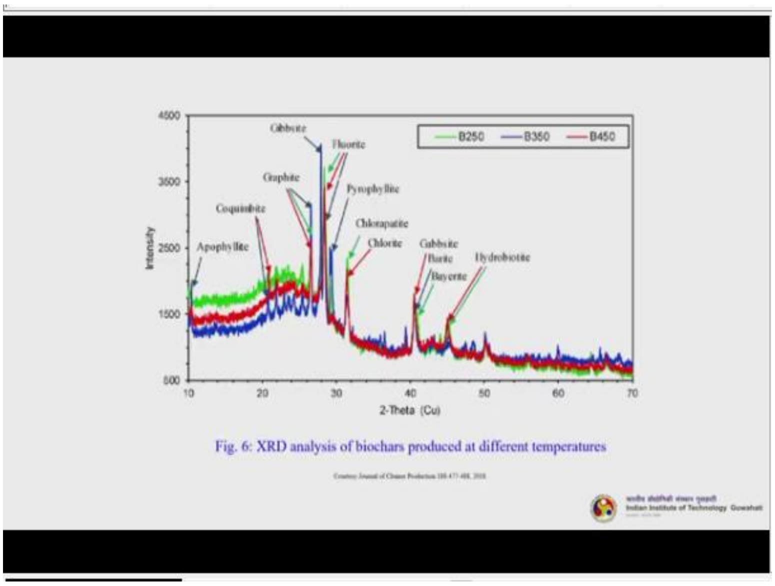

This is one typical representative image of the XRD analysis of the biochars produced at different temperatures. So, 3 different temperature biochars are plotted here you can see that. The green one corresponding to 250 degrees centigrade and the red one corresponding to 450 degrees centigrade and the blue one corresponding to 350 degrees centigrade, 3 different types of biochars.

And you can see that different types of peaks and corresponding this one composition. So, this is a Apophyllite, then you can see that graphite peak here, fluoride peak, then chlorite, then gabbsite, bayerite and all these things. So, XRD is a very important technique to find out the crystallinity index of the biomass or biochar or any such material you can find out whether it is amorphous or crystalline. And you can also find out the molecular structure..

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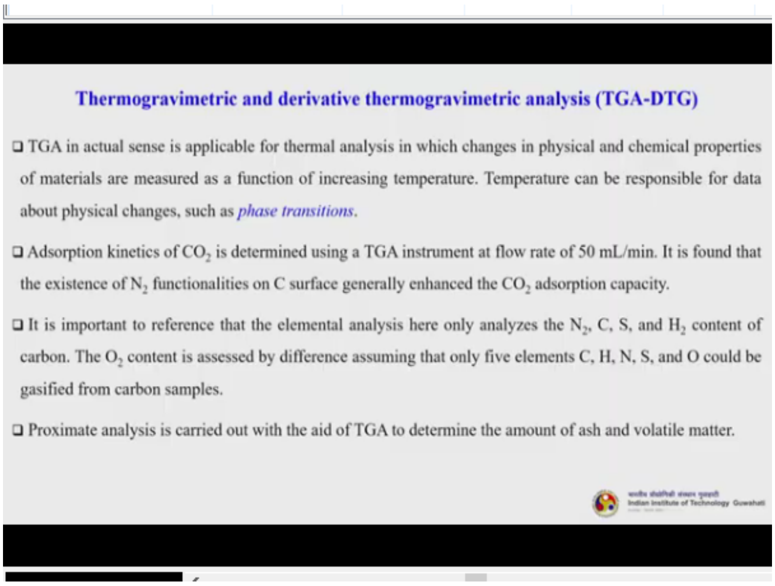

So, then we will talk about TGA and DTG, which is basically thermal analytical technique. So, thermogravimetric and derivative thermogravimetric analysis. TGA in actual sense is applicable for thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. Now, temperature can be responsible for data about physical changes such as phase transition.

Adsorption kinetics of carbon dioxide is determined using a TGA instrument at a flow rate of 50 ml per minute, you can vary the flow rate. So, this is just an example. So, it is found that the existence of nitrogen functionalities on carbon surface generally enhance the carbon dioxide adsorption capacity. It is important to reference that elemental analysis here only analyzes the nitrogen, carbon, sulfur and hydrogen content of the carbon.

The oxygen content is assessed by difference assuming that only 5 element C, H, N, S, O could be gasified from the carbon samples. So, oxygen is always by difference. Proximate analysis is carried out with the aid of TGA to determine the amount of ash and volatile matter.

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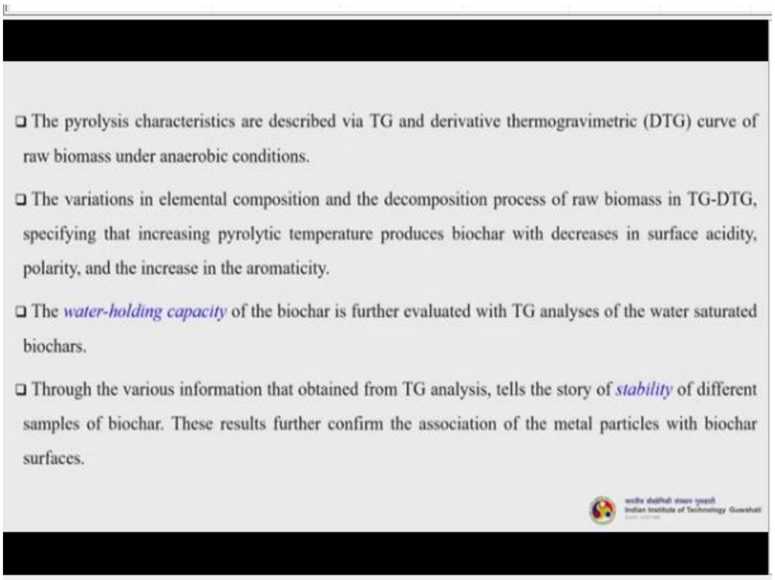

The pyrolysis characteristics are described by TG and derivative thermogravimetric curve of the raw biomass under anaerobic conditions. The variations in elemental composition and decomposition process of raw biomass in TG-DTG, specifying that increasing pyrolytic temperature produces biochar with decreases in surface acidity, polarity and increase in the aromaticity.

The water holding capacity of the biochar is further evaluated with the TG analysis of the water saturated biochars. It is a very important information or let us say the characterization of the biochar especially when you are going to use it in the agricultural purposes, water holding capacity is very important parameter. Though the various information that obtained from TG analysis, tells the story of the stability of different samples of biochar. These results further confirm the association of the metal particles with biochar surfaces.

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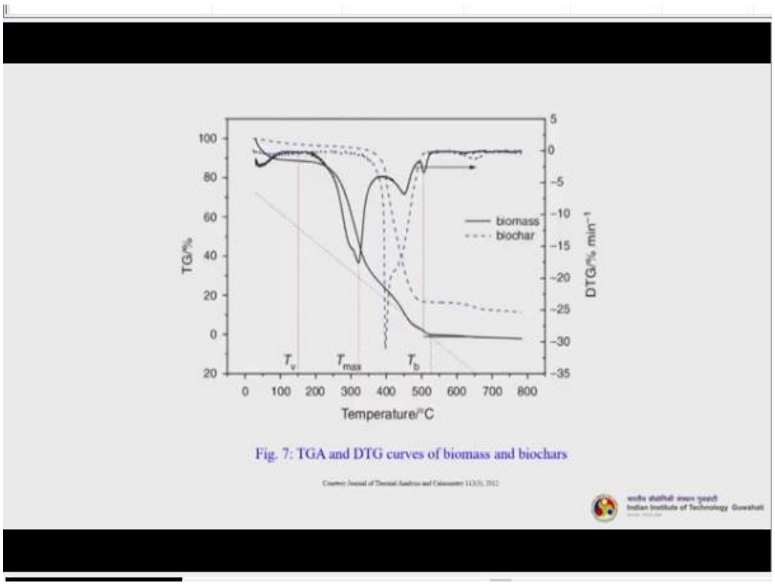

Fig. 7: TGA and DTG curves of biomass and biochars

So, this is one typical representative image of the TG and DTG curves of the biomass and the biochar. So, you can see the solid black line is corresponding to that DTG and TG of the original biomass whereas, the dotted and blue line corresponding to the biochar. So, this curve you can see which is coming like here. So, this is the thermogravimetric analysis curve.

So, initially what we are doing here is that we are measuring the TG percent is basically the weight loss with respect to temperature and time of course. So, we are not plotting time here it is temperature. So, you are increasing temperature of course, the weight loss will increase. So, initially the moisture will be removed then other components like volatile matters and some decomposition started, then slowly you are seeing that we are reaching around 550 close to 550, 530.

So, then it is almost become saturated, so, no more weight loss is being noticed. And DTG is the derivative of the TG plot. So, whatever the TG data you are getting from this instrument, you can plot it by taking the derivative and plot it. So, you get some more information about the phase transition and other things from this plot.

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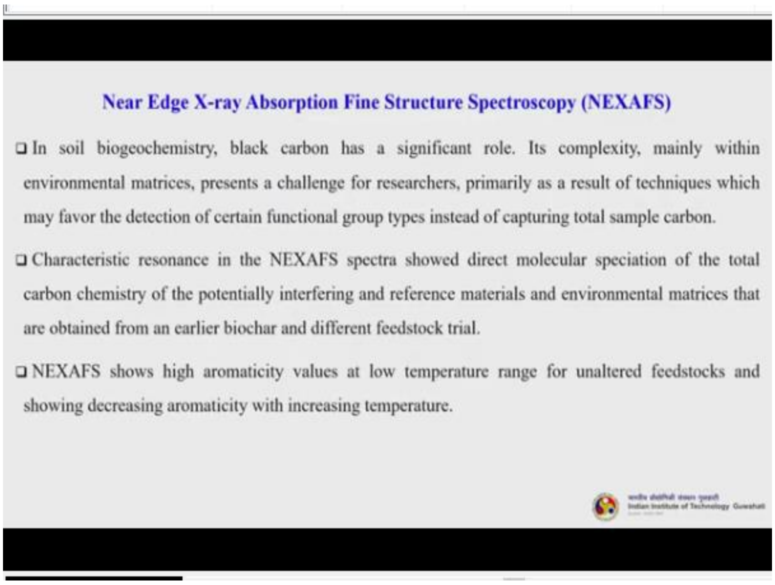

So, the next is near edge X-ray absorption fine structure spectroscopy which is called as NEXAFS. So, in soil biogeochemistry black carbon has a significant role. Its complexity, mainly within environmental matrices presents a challenge for researchers primarily as a result of techniques, which may favour the detection of certain functional group types instead of capturing total sample carbon.

Now, characteristic resonance in the NEXAFS spectra showed direct molecular speciation of the total carbon chemistry of the potentially interfering and reference materials and environmental matrices that are obtained from an earlier biochar and different feedstock trial. NEXAFS shows high aromaticity values at low temperature range for unaltered feedstocks and showing decreasing aromaticity with increasing temperature.

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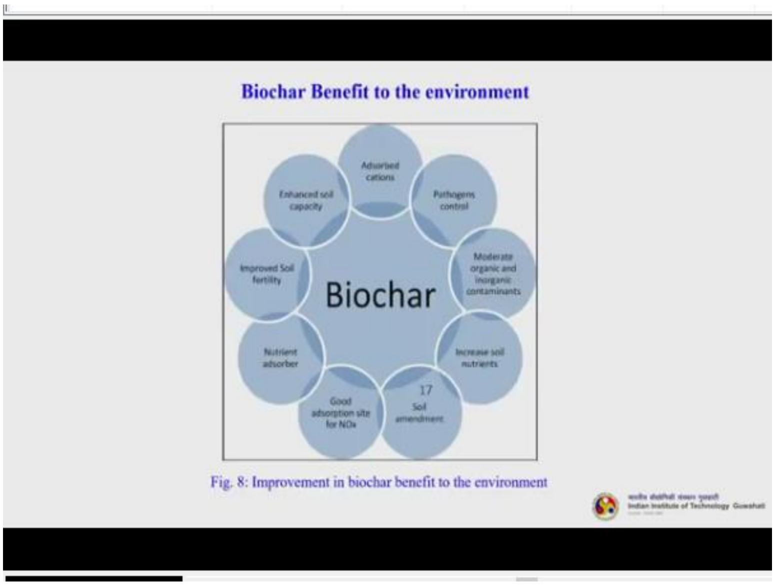

So, next we will discuss about the biochar benefit to the environment. This is a classic slide or representative slide, where you can understand that how biochar can be used in various forms or various applications. So, you can start from the adsorption, then pathogens control, moderate organic and inorganic contaminants removal or again, it is one form of adsorption only, increased soil nutrients, soil amendment purposes.

So, these both are for the agricultural purposes, good absorption site for the NOx, nutrient absorber again agricultural applications, improved soil fertility again agricultural application, then enhance soil capacity again agricultural applications. So, you can understand that biochar has huge application in the agricultural field as well as in environmental applications.

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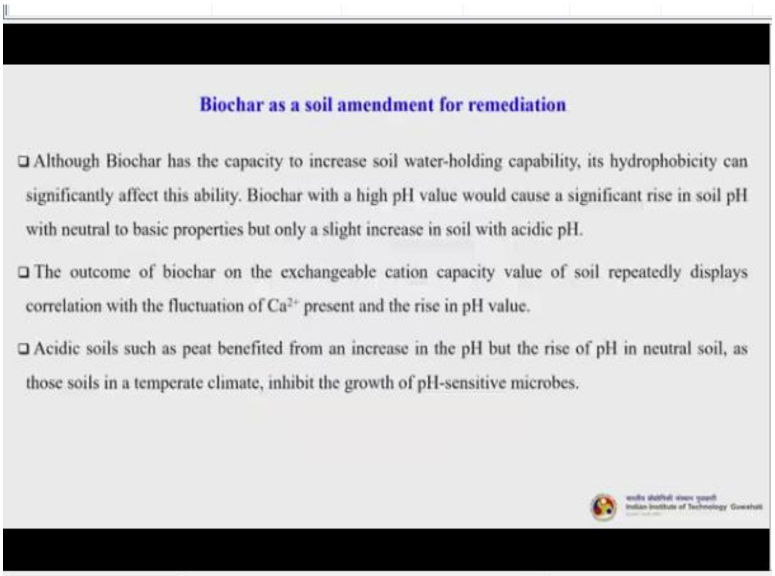

So, a biochar as a soil amendment for remediation. Although biochar has the capacity to increase soil water holding capability, its hydrophobicity can significantly affect this ability. Biochar with a high pH value would cause a significant rise in the soil pH with neutral to basic properties, but only a slight increase in soil with acidic pH. The outcome of the biochar on the exchangeable cation capacity value of the soil repeatedly displays correlation with the fluctuations of the calcium present and the rise in the pH value.

Acidic soil such as peat benefited from an increase in the pH but the rise of pH in neutral soil as those soils in a temperate climate inhibit the growth of pH sensitive microbes.

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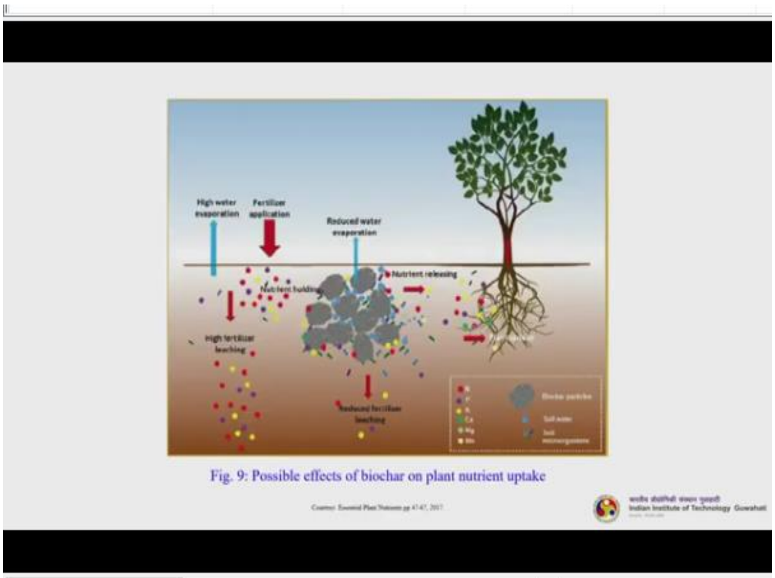

So, this is a slide where you can understand the possible effects of biochar on plant nutrient uptake. So, you can see this is the plant; here the plant roots are taking the nutrients. So, here the biochars which are helping in holding the nutrients in a manner so that they are available in a particular site. Then slowly it is getting released, nutrient holding and nutrient releasing and the plant is taking it up.

So, this can be nitrogen, phosphorus, potassium, calcium, magnesium, manganese and so many things. Apart from this biochars also helps in holding water in a better way than the usual soil. So, when you hold water, when the water holding capacity of the biochar which is applied to the top surface improves. So, it aids in a better plant growth. So, this is the idea.

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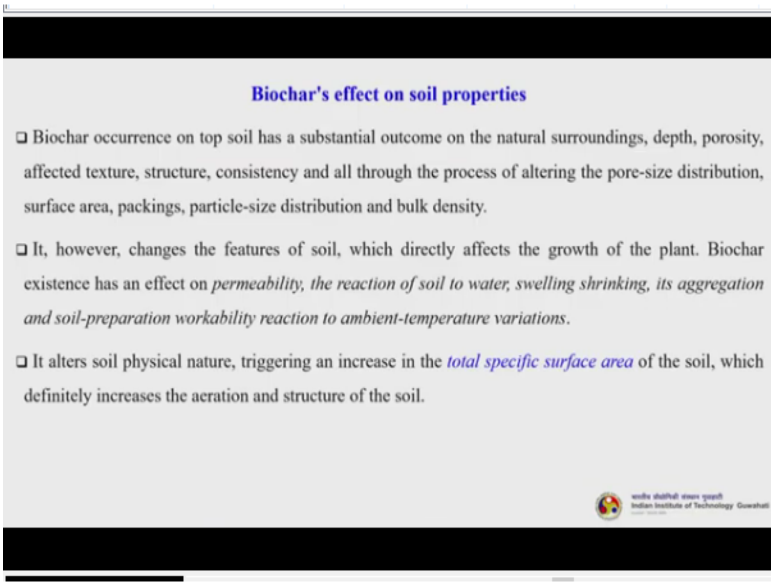

So, let us discuss the biochar's effect on soil properties. So, biochar occurrence on top soil has a substantial outcome on the natural surroundings, depth, porosity, affected texture, structure, consistency and all through the process of altering the pore size distribution, surface area, packings, particle size distribution as well as bulk density. It, however, changes the features of soil which directly affects the growth of the plant.

Biochar existence has an effect on permeability, the reaction of soil to water, swelling shrinking, its aggregation and soil preparation workability to ambient temperature variations. It alters soil physical nature, triggering an increase in the total specific surface area of the soil, which definitely increases the aeration and structure of the soil.

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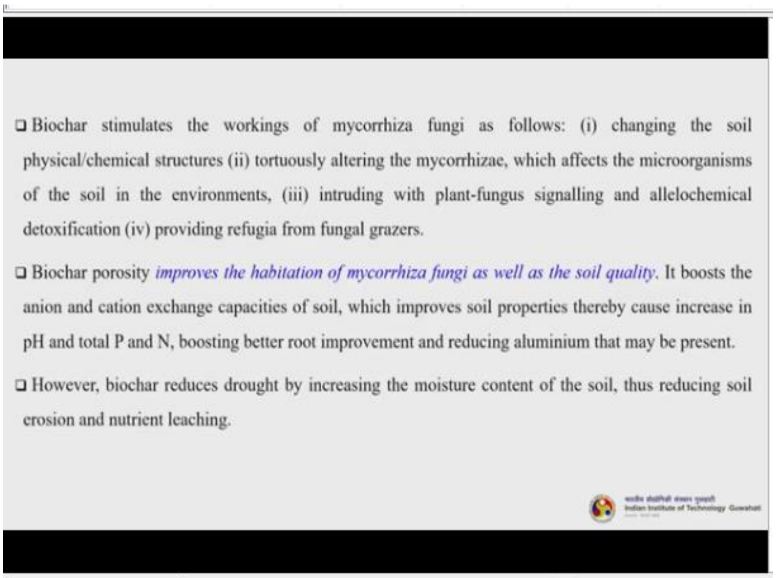

Biochar stimulates the working of mycorrhiza fungi as follows: changing the soil physical and chemical structure, tortuously altering the mycorrhizae, which affects the microorganisms of the soil in the environment, intruding with a plant fungus signalling and a allelochemical detoxification, providing refugia from fungal grazers. Now biochar porosity improves the habitation of mycorrhiza fungi as well as the soil quality.

Now it boosts the anion and cation exchange capacities of the soil, which improved soil properties thereby cause increasing the pH and total P and N, boosting better root improvement and reducing aluminium that may be present. However, biochar reduces drought by increasing the moisture content of the soil, thus reducing soil erosion and nutrient leaching.

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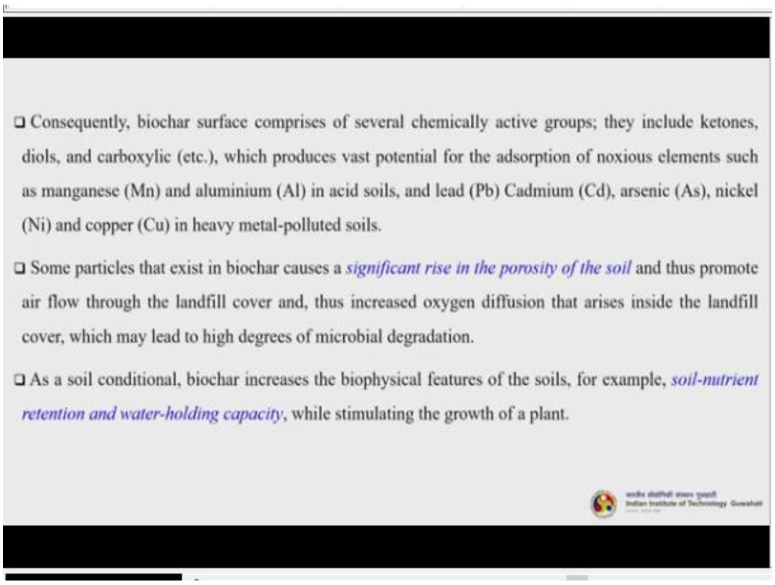

Consequently, biochar surface comprises of several chemically active groups. They include ketones, diols, carboxylic acid etcetera, which produces vast potential for the adsorption of noxious elements, such as manganese, aluminium in acidic soils, lead, cadmium, arsenic, nickel and copper in heavy metal polluted soils. Some particles that exist in biochar causes a significant rise in the porosity of the soil, and thus promote airflow through the landfill cover.

And thus increased oxygen diffusion that arises inside the landfill cover, which may lead to high degrees of microbial degradation. As a soil conditioner, biochar increases the biophysical features of the soil, for example, soil nutrient retention and water holding capacity while stimulating the growth of a plant.

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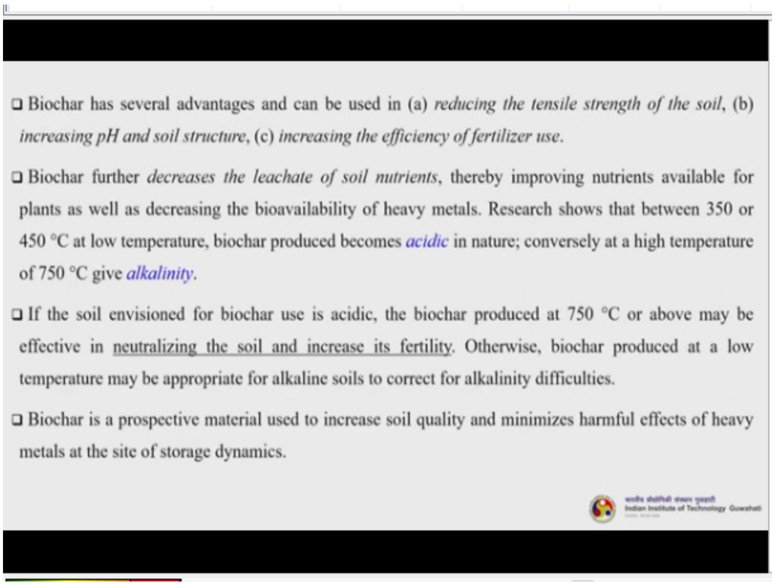

Biochar has several advantages and can be used in reducing the tensile strength of the soil, increasing pH and soil structure, increasing the efficiency of the fertilizer use. Biochar further decreases the leachate of soil nutrients, thereby improving nutrients available for plant as well as decreasing the bioavailability of the heavy metals. Research has shown that between 350 to 450 degrees centigrade at low temperature biochar produced become acidic in nature.

Whereas the biochars that are produced at high temperature of around 750 degrees centigrade gives alkalinity. Now if the soil envisioned for biochar use is acidic, the biochar produced at 750 degrees centigrade or above may be effective in neutralizing the soil and thus increasing its fertility. So, do you get it? From this statement you can understand that biochar can be custom made to suit a particular type of soils amendment or increasing the soil fertility.

So, if you have a acidic soil, you can produce alkaline biochar. If you have alkaline soil, you can produce acidic biochar, vice versa. So, biochar is a prospective material used to increase the soil quality and minimize harmful effects of heavy metals at the site of storage dynamics.

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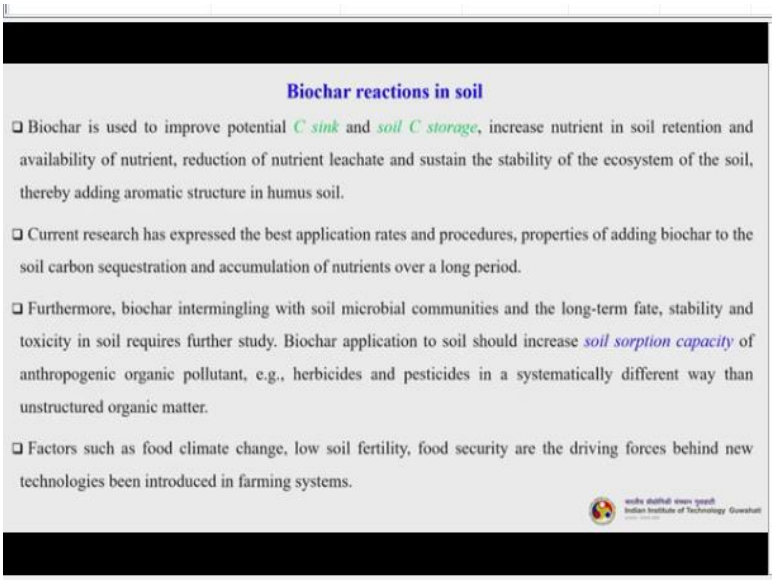

Biochar reactions in soil: Biochar is used to improve potential carbon sink and soil carbon storage, increase nutrient in soil retention and availability of nutrient, reduction of nutrient leachate and sustain the stability of the ecosystem of the soil, thereby adding aromatic structure and humus soil. Current research has expressed the best application rates and procedures, properties of adding biochar to the soil carbon sequestration and accumulation of nutrients over a long period.

Furthermore, biochar intermingling with soil microbial communities and the long term fate, stability and toxicity in soil requires further study. Biochar application to soil should increase soils sorption capacity of the anthropogenic organic pollutants, as for example herbicides and pesticides in a systematically different way, then the unstructured organic matter. Factors such as food, climate change, low soil fertility, food security are the driving forces behind new technologies that are being introduced in the farming sector.

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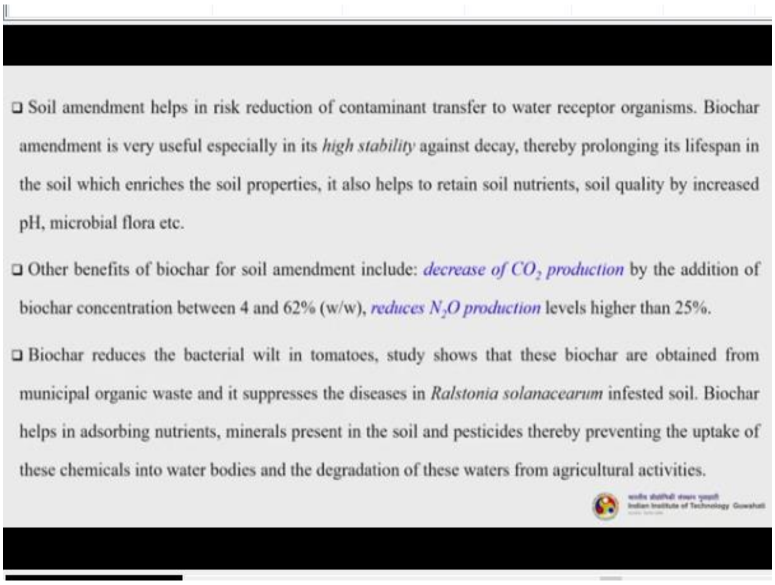

Soil amendment helps in risk reduction of contaminant transfer to water receptor organisms. Biochar amendment is very useful, especially in its high stability against decay, thereby prolonging its lifespan in the soil which enriches the soil properties. It also helps to retain soil nutrients, soil quality by increased pH, microbial flora etcetera. Other benefits of biochar for soil amendment include decrease of carbon dioxide production, by the addition of biochar concentration between 4 and 62%, reduces nitrogen oxide production, levels higher than 25%.

Biochar reduces the bacterial wilt in tomatoes, study shows that these biochar are obtained from municipal organic waste and it suppresses the disease in *Ralstonia solanacearum* infested soil, it is a bacteria. So, biochar helps in adsorbing nutrients, minerals present in the soil and pesticides thereby preventing the uptake of these chemicals into water bodies and the degradation of these waters from agricultural activities.

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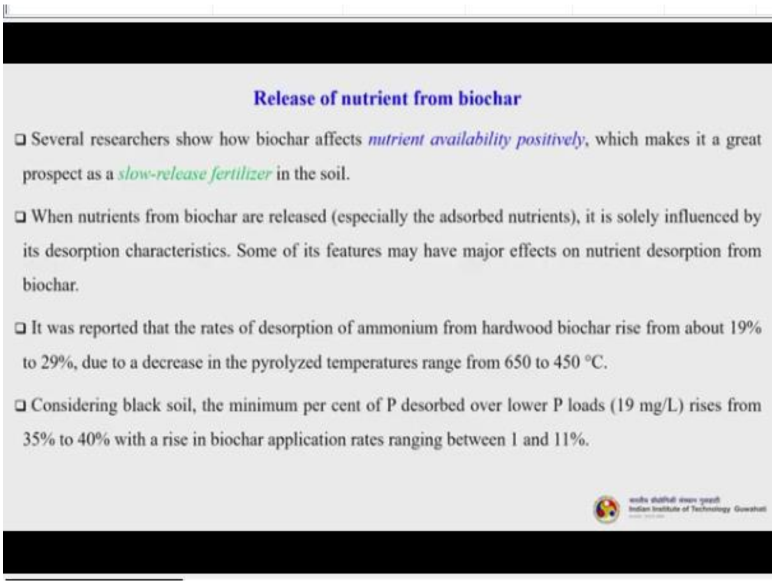

Let us talk about the release of nutrient from biochar. So, several researches show how biochar affects nutrient availability positively, which makes it a great prospect as a slow release fertilizer in the soil. So, it is very important to note that one of the way how the biochar is enhancing the fertility of the soil is this, that it not only store or withhold the nutrients but also helps in slow releasing the nutrients to the soil, so that those can be uptake.

So, if it releases everything and too much of nutrients available, then it is not going to serve the purpose for the plant growth. So, when nutrients from biochar are released especially the adsorbed nutrients, it is solely influenced by its desorption characteristics. So, some of the features may have a major impact on the nutrient desorption from biochar. It was reported that the rates of desorption of ammonia from hardwood biochar rise from about 19 to 29% due to a decrease in the pyrolyzed temperature range from 650 to 450 degrees centigrade.

Now, what is the meaning of this? The meaning of this is that the pyrolysis condition to produce the biochar finally affects the adsorption and desorption rate of the nutrients to the biochar surface. So, considering black soil the minimum percent of the P desorbed over lower P loads around let us say 19 milligrams per liter, rises from 35 to 40% with the rise in biochar application rates ranging from 1 to 11%.

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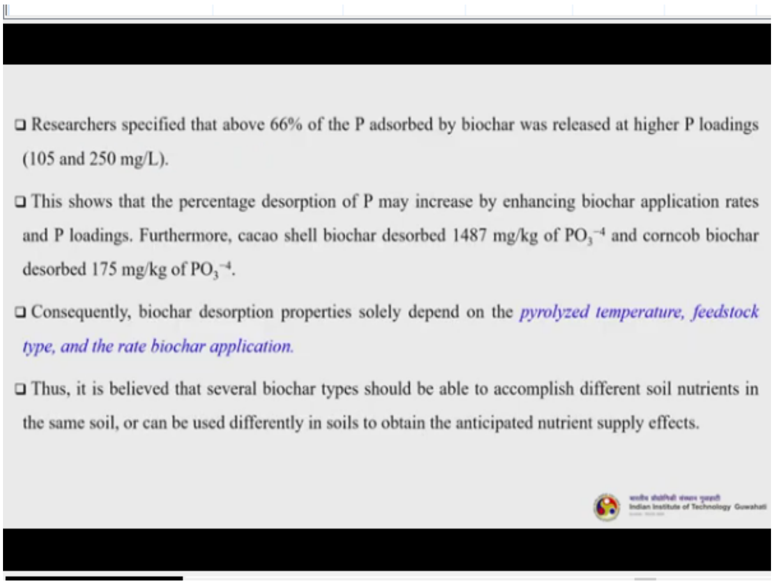

Researchers specified that above 66% of the P adsorbed by biochar was released at a higher P loadings, almost 105 and 250 milligrams. So, that means, when you have more loading, there is the chance of desorption becomes higher. Now, this shows that the percentage of desorption may increase by enhancing biochar application rates and P loadings. Furthermore, cacao shell biochar desorbed 1487 milligrams per kg phosphate and corncob biochar desorbed 175 milligrams per kg of phosphate.

So, consequently, biochar desorption properties solely depend on the pyrolysis temperature, feedstock type and the rate biochar application. Thus, it is believed that several biochar types should be able to accomplish different soil nutrients in the same soil, or can be used differently in the soil to obtain the anticipated nutrient supply effects.

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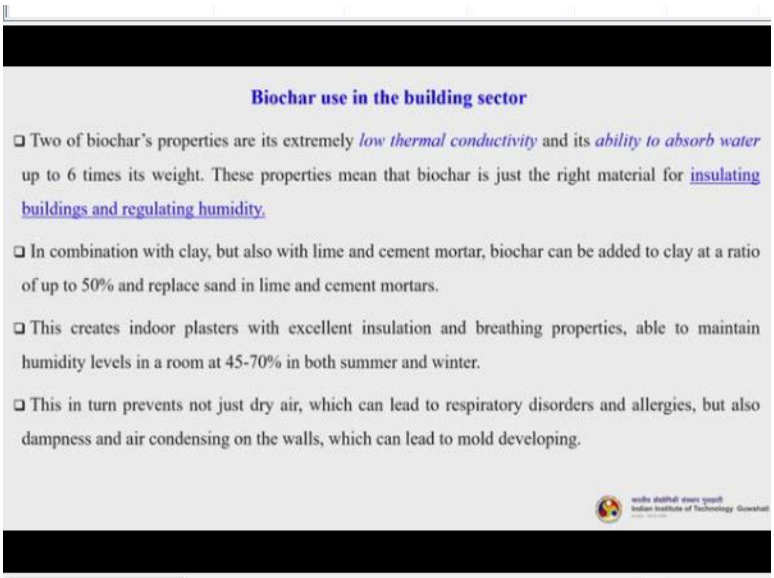

So, we will quickly go through some of the other applications of biochars. So, biochar used in the building sector. So, 2 of the biochar's properties are extremely low thermal conductivity, and its ability to absorb water up to 6 times its weight. Now these properties mean that biochar is just the right material for insulating buildings and regulating humidity in combination with clay, but also with lime and cement mortar biochar can be added to clay at a ratio up to 50% and replace sand in lime and cement mortars.

This creates indoor plasters with excellent insulation and breathing properties able to maintain humidity levels in the room at around 45 to 70% during both summer as well as winter. Thus in turn prevents not just dry air, which can lead to respiratory disorders and allergies but also dampness and air conditioning on the walls, which can lead to mold developing.

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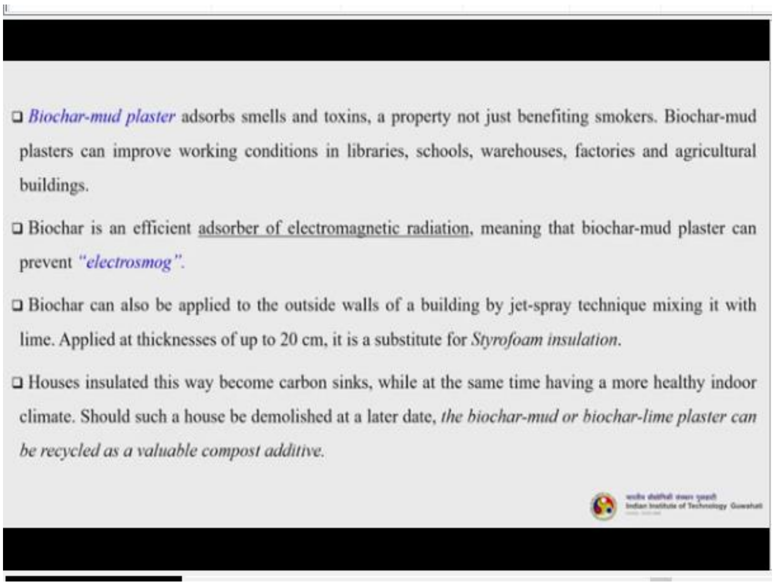

Biochar mud plaster adsorbs smells and toxins, a property not just benefiting smokers. Biochar mud plasters can improve working conditions in libraries, schools, warehouses, factories and agricultural buildings. Biochar is an efficient adsorber of electromagnetic radiation meaning that biochar mud plaster can prevent electrosmog. Biochar can also be applied to the outside walls of a building by jet spray technique. mixing it with line applied at a thickness up to 20 centimeter, it is a substitute for the Styrofoam insulation.

House insulated this way become carbon sinks, while at the same time having a more healthy indoor climate. Should such a house be demolished at a later date, the biochar mud or biochar lime plaster can be recycled as a valuable compost additive. So, this is a win-win situation.

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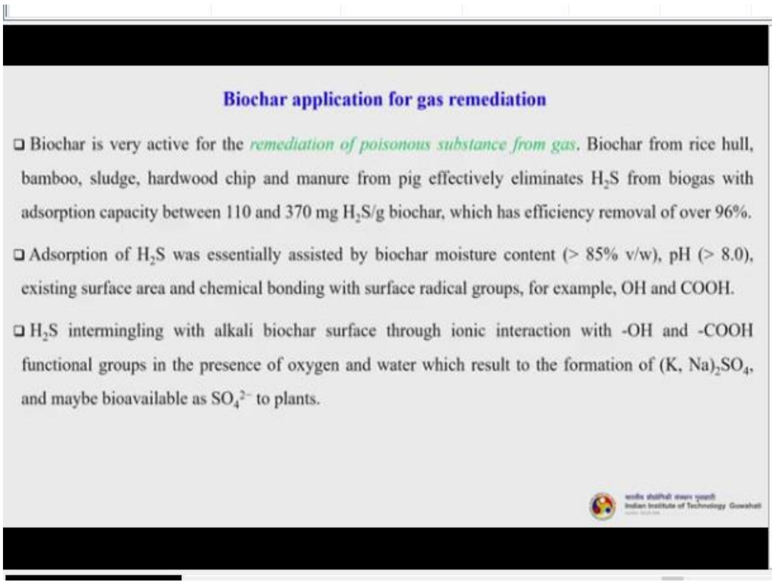

So, biochar application in gas remediation. Biochar is very active for the remediation of the poisonous substances from the gas, biochar from rice hull, bamboos, sludge, hardwood chip, and manure from pig effectively eliminated hydrogen sulfide from biogas with adsorption capacity between 110 to 370 milligram hydrogen sulfide per gram of biochar, which is efficiency removal of about 96%, excellent removal efficiency actually.

So, adsorption of hydrogen sulfide was essentially assisted by the biochar moisture content which is almost greater than 85% volume by weight, pH greater than 8, existing surface area and chemical bonding with surface radical groups. For example, the OH and COOH groups, functional groups. Hydrogen sulfide, intermingling with alkali biochar surface through ionic interaction with OH and COOH functional groups in the presence of oxygen and water which result to the formation of K and sodium sulfate, maybe bioavailable as sulfate to plants.

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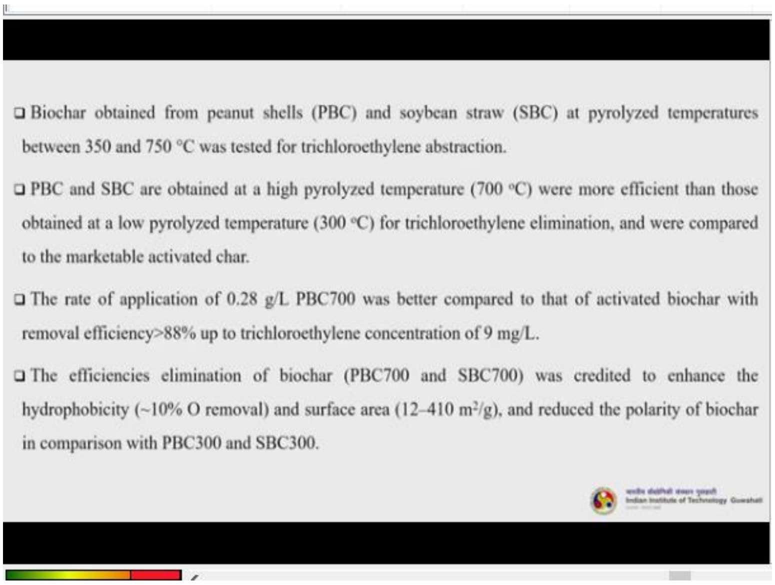

Biochar obtained from peanut shells and soybean straw at pyrolyzed temperatures between 350 to 750 degrees centigrade was tested for trichloroethylene abstraction. This is a typical example which is reported in literature. So, this PBC and SBC are obtained at a high pyrolyzed temperature were more efficient than those obtained at low pyrolyzed temperature for trichloroethylene elimination and were compared to the marketable activated char /activated carbon.

So, the rate of application of 0.28 grams per liter PBC 700 was better compared to that of the activated biochar with removal efficiency greater than 88% up to the trichloroethylene concentration of 9 milligrams per liter. The efficiencies elimination of the biochar was credited to enhance the hydrophobicity and surface area and reduce the polarity of the biochar in comparison of the PBC and SBC that is produced at 300 degrees centigrade.

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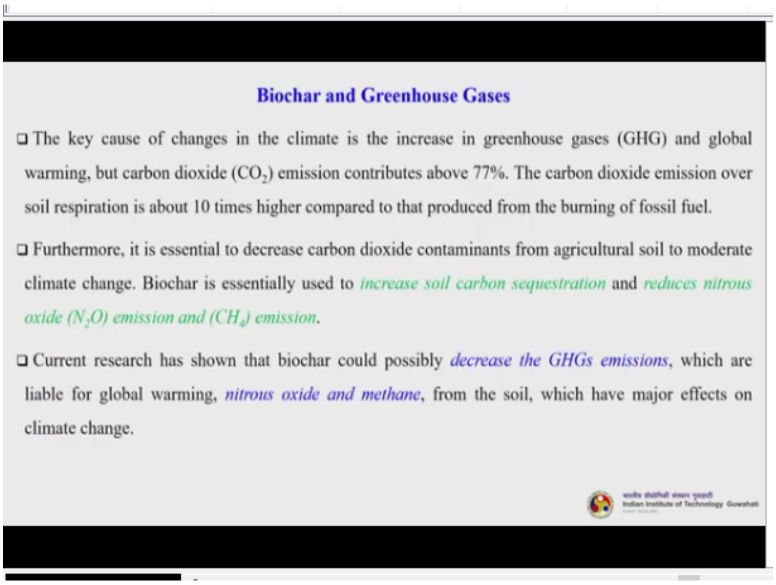

So, biochar and greenhouse gases. The key cause of changes in the climate is the increase in the greenhouse gases and the global warming, but carbon dioxide emissions contribute over almost 77%. The carbon dioxide emission over soil respiration is about 10 times higher compared to that produced from the burning of fossil fuels. Furthermore, it is essential to decrease carbon dioxide contaminants from agricultural soil to moderate climate change.

Biochar is essentially used to increase soil carbon sequestration and reduces nitrous oxide emission as well as methane emission. Current research has shown that biochar could possibly decrease the greenhouse gas emissions which are liable for global warming, nitrous oxide and methane also from the soil, which have major impacts on the climate change.

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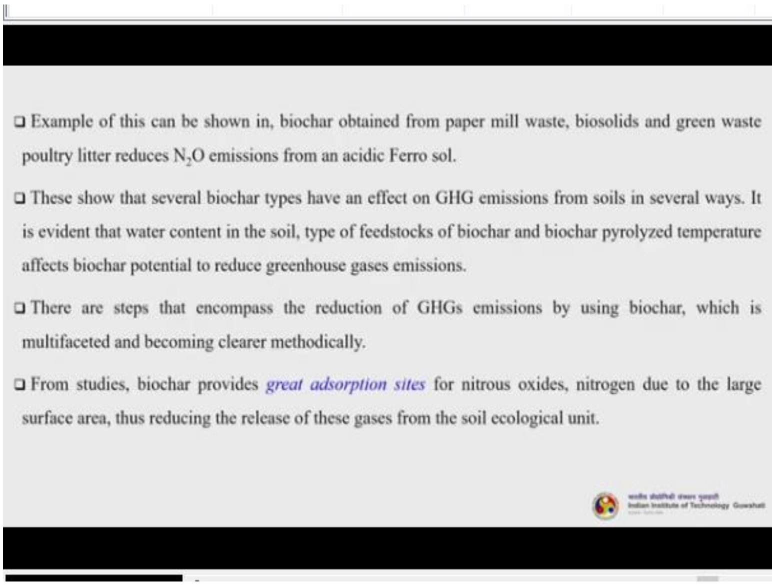

Example of this can be shown in biochar obtained from paper mill waste, bio-solids and green waste poultry litter reduces nitrous oxide emission from an acidic Ferro sol. This shows that several biochar types have an effect on the greenhouse gas emissions from soils in several ways. It is evident that water content in the soil, type of feedstocks of biochar and biochar pyrolyzed temperature affects biochar potential to reduce greenhouses gas emissions.

There are steps that encompass the reduction of greenhouse gas emission by using biochar which is multifaceted and becoming clearer methodically. From studies biochar provides great adsorption sites for nitrogen oxides, nitrogen due to the large surface area thus reducing the release of these gases from the soil ecological unit.

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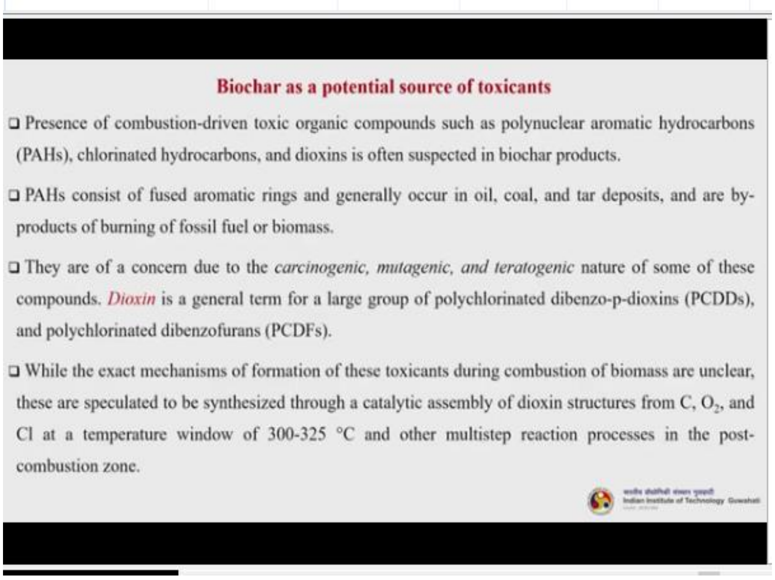

So, let us talk about biochar as a potential source of toxicants. So, presence of combustion driven toxic organic compounds such as polynuclear aromatic hydrocarbon, chlorinated hydrocarbons and dioxins is often suspected in the biochar products. So, PAHs consists of fused aromatic rings and generally occur in coal, oil and tar deposits and are by-products of the burning of fossil fuel or biomass.

They are of a concern due to the carcinogenic, mutagenic and teratogenic nature of some of these compounds. Dioxin is a general term for a large group of polychlorinated dibenzo-p-dioxins PCDDs and polychlorinated dibenzofurans PCDFs. While the exact mechanism of formation of these toxicants during combustion of biomass are unclear, these are speculated to be synthesized through a catalytic assembly of dioxin structures from carbon, oxygen and chlorine at a temperature window of 300 to 325 degrees centigrade and other multi step reaction processes in the post combustion zone.

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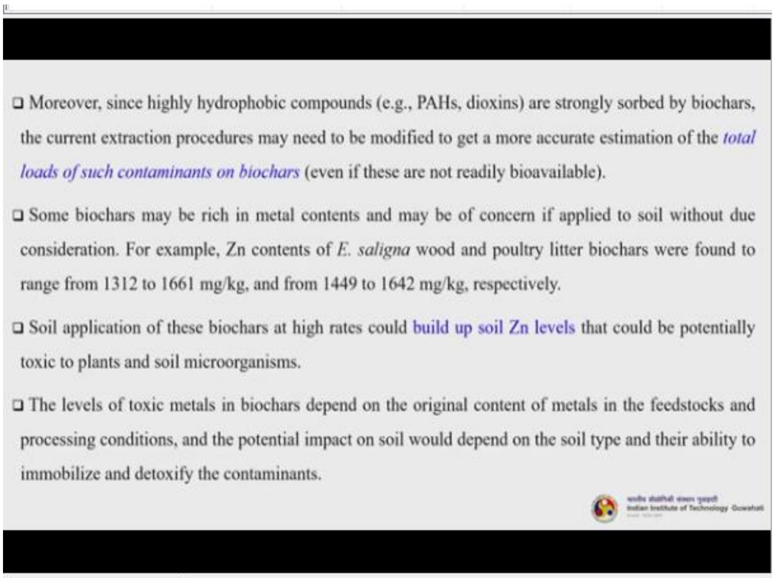

Moreover, since highly hydrophobic compounds are strongly served by the biochars the current extraction procedure may need to be modified to get a more accurate estimation of that total load of such contaminants on biochars. Even if these are not readily actually bioavailable. So, some biochars may be reach in metal contents and may be of concern if applied to soil without due consideration.

For example, zinc contents of the *E. Saligna* wood and poultry litter biochars are found to range from 1312 to 1661 milligrams per kg and from 1449 to 1642 milligrams per kg which is a very huge load actually. Soil application of these biochars are at high rates could build up soil zinc levels that could potentially toxic to plants and soil microorganisms and should be avoided.

Now, the levels of toxic metals in biochars depend on the original content of the metals in the feedstock and processing condition and the potential impact on soil would depend on the soil type and their ability to immobilize and detoxify the contaminants. So, what we understand in a nut shell is that, having said so many good things about biochars, there are certain drawbacks also, just we talked about zinc.

Let us understand that if we are producing biochar, which can inherently contain some toxic compounds. See certain compounds are toxic beyond certain level, it is not that they are always toxic, for example, zinc. Now, zinc is very essential for human growth and any living organism growth, but if you are keep on eating zinc, so, it will not result in our developing immunization, it will rather become toxic to the cell and it will create other problems.

Similarly, the same thing is for the plants also. So, when we are loading the soil with biochar having certain compounds which can be toxic in nature beyond certain range, then we have to be very cautious and to apply such biochars for the agricultural purposes. One example that we have discussed is about zinc. There are similar other examples also.

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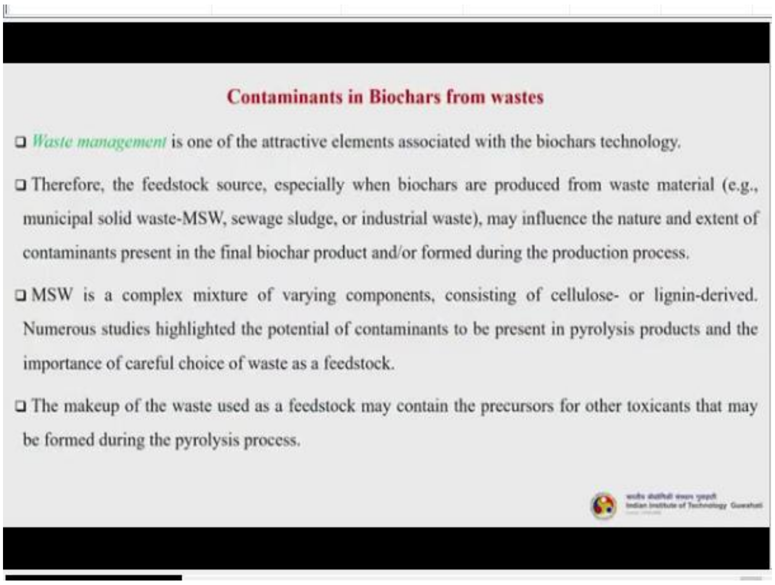

So, waste management is one of the attractive elements associated with the biochars technology. Therefore, the feedstock source especially when biochar are produced from waste material - let us for example, the municipal solid waste, it can be sewage sludge or industrial waste, may influence the nature and extent of contaminants present in the final biochar product and/or formed during the production process.

MSW is a complex mixture of varying components consisting of cellulose or lignin derived. Numerous studies highlighted the potential of contaminants to be present in the pyrolysis products and the importance of careful choice of waste as a feedstock. The makeup of the waste used as a feedstock may content precursors for other toxicants that may be formed during the pyrolysis process.

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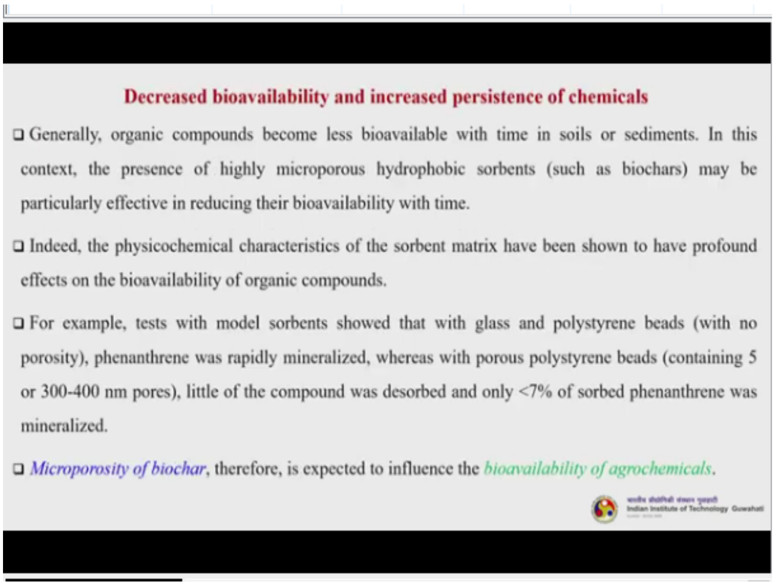

Generally, organic compounds become less bioavailable with time in soils or sediments. In this context, the presence of highly microporous hydrophobic sorbents such as biochars may be particularly effective in reducing their bioavailability with time. Indeed, the physicochemical characteristics of sorbent matrix have been shown to have profound effects on the bioavailability of organic compounds.

For example, tests with model sorbents showed that with glass and polystyrene beads, phenanthrene was rapidly mineralized, whereas with porous polystyrene beads little of the compound was desorbed and only less than 7% of the sorbed phenanthrene was mineralized. Microporosity of biochar, therefore is expected to influence the bioavailability of agrochemicals.

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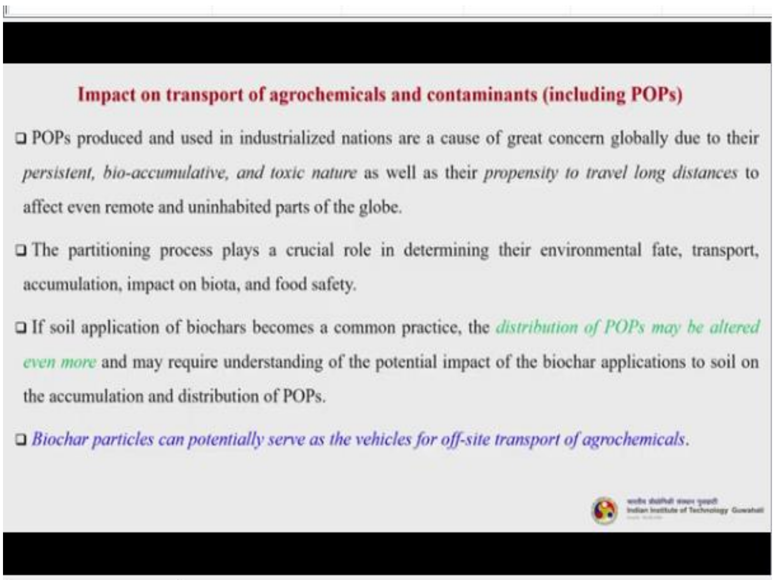

So, let us understand the impact on transport of agrochemicals and contaminants including the persistent organic pollutant POPs. So, POPs produced and used in industrialized nations are a cause of great concern globally due to their persistent, bio-accumulative and toxic nature as well as their propensity to travel long distances to affect even remote and uninhabited parts of the globe.

So, the partitioning process plays a crucial role in determining their environmental fate, transport, accumulation, impact on biota and food safety. If soil application of biochars become a common practice the distribution of POPs may be altered even more and may require an understanding of the potential impact of the biochar applications to soil on the accumulation and distribution of the POPs. Biochar particles can potentially serve as the vehicles for off-site transport of the agrochemicals.

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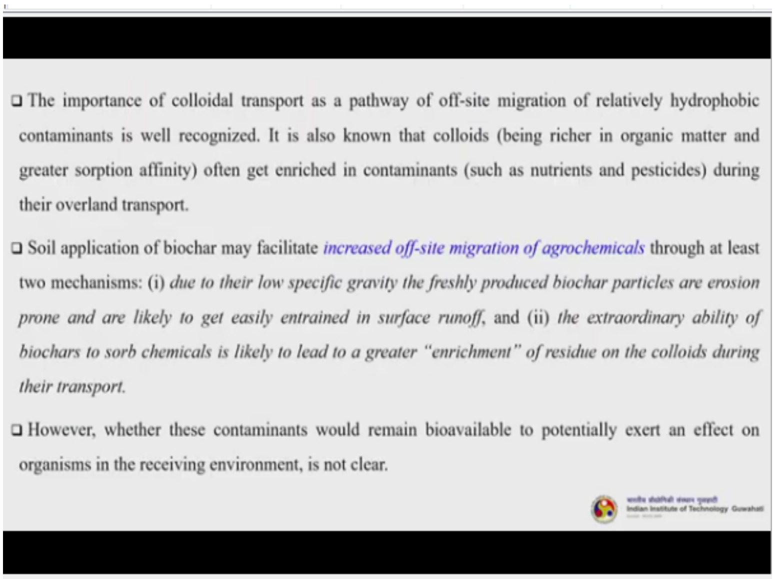

The importance of colloidal transport as a pathway of off-site migration of relatively hydrophobic contaminants is well recognized. It is also known that colloids (being richer in organic matter and greater sorption affinity) often get enriched in contaminants such as nutrients and pesticides during their overland transport. Soil application of biochar may facilitate increased off-site migration of agrochemicals through at least 2 mechanisms.

The first one is that due to the low specific gravity the freshly produced biochar particles are erosion prone and are likely to get easily entrained in the surface runoff. Second the extraordinary ability of the biochar to sorb chemical is likely to lead to a greater enrichment of the residues on the colloids during their transport. However, whether these contaminants would remain bioavailable to potentially exert an effect on the organisms in the receiving environment is not so clear. So, much work is currently going on this particular area.

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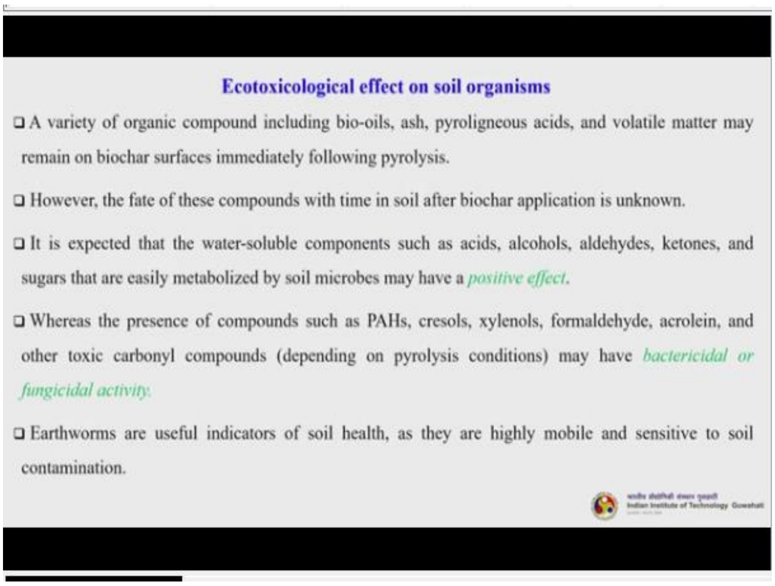

See, if you could talk about the ecotoxicological effect on soil organisms. A variety of organic compounds including the biooils, ash, pyroligneous acids, volatile matter may remain on biochar surfaces immediately following pyrolysis. However, the fate of these compounds with time in soil after biochar application is not known. So, it is expected that the water-soluble components such as acids, alcohol, aldehydes, ketones and sugars that are easily metabolized by soil microbes may have a positive effect.

Whereas, the presence of compounds such as PAHs, cresols, xylenols, formaldehyde, acrolein, and other carbonyl compounds depending on the of course pyrolysis process conditions, may have a bactericidal or fungicidal activity. Earthworms are useful indicators of soil health as they are highly mobile and sensitive to soil contamination.

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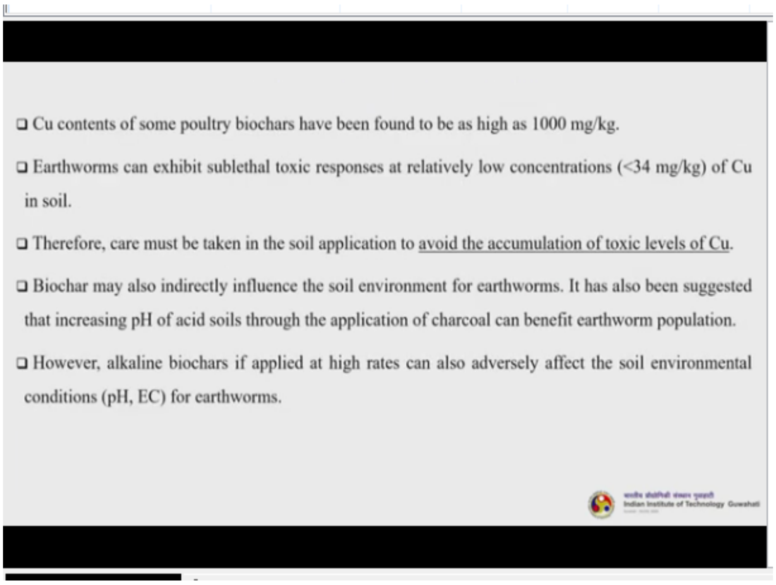

Copper contents of some poultry biochars have been found to be as high as 1000 milligrams per kg. Earthworms can exhibit sublethal toxic response at relatively low concentrations almost less than 30 milligram per kg of copper in soil. Now you can understand that if you have huge copper content in the biochar and you are applying it to the soil for the agricultural purposes than the earthworm will have a toxic response.

So, therefore care must be taken in soil application to avoid the accumulation of toxic levels of the copper. Biochar may also indirectly influence the soil environment for earthworms it has also been suggested that increasing pH of acid soils through the application of charcoal can benefit earthworm population. However, alkaline biochars if applied at high rate can also adversely affect the soil environment conditions for the earthworms.

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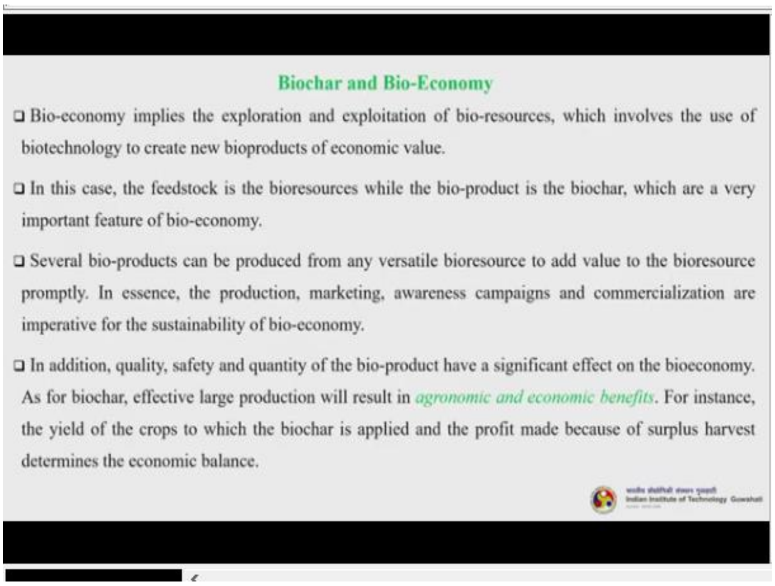

So, will finally conclude by talking little about the biochar and the bio-economy. So, bio-economy implies the exploration and exploitation of the bio-resources which involves the use of biotechnology to create new bioproducts of economic value. In this case the feedstock is the bioresources while the bioproduct is a biochar which is a very important feature of the bio-economy. Several bioproducts can be produced from any versatile bioresource to add value to the bioresource promptly.

In essence the production, marketing, awareness campaigns and commercialization are imperative for the sustainability of the bio-economy. In addition, quality, safety and quantity of the bioproduct have a significant effect on the bio-economy. As for biochar, effective large production will result in agronomic and economic benefits. For instance, the yield of the crops to which the biochar is applied and the profit made because of surplus harvest determines the economic balance.

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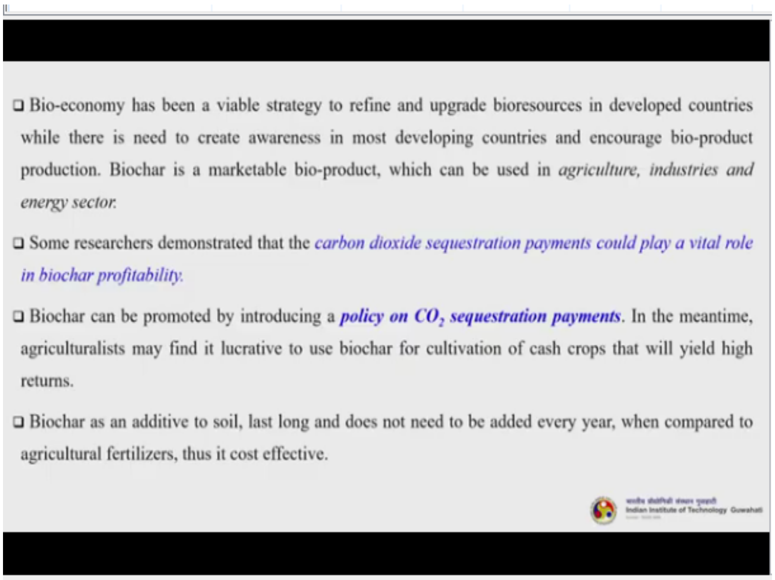

Bio-economy has been a viable strategy to refine and upgrade bioresources in developed countries while there is need to create awareness in most developing countries and encourage bio-product production. Biochar is a marketable bioproduct which can be used in agriculture industry and energy sector. Some researchers demonstrated that the carbon dioxide sequestration payments could play a vital role in biochar profitability.

So, there should be a policy. So biochar can be promoted by introducing a policy on carbon dioxide sequestration payment. In the meantime, agriculturalist may find it lucrative to use biochar for cultivation of cash crops that will yield high returns. So, biochar is an additive to soil last long and does not need to be added every year when compared to agricultural fertilizers, thus it is cost effective.

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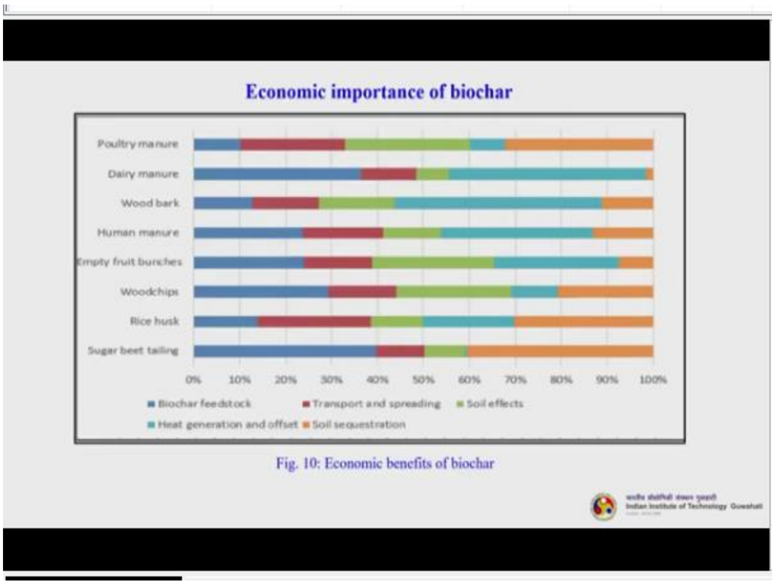

So, if you look at this particular slide you can understand the economic importance of the biochar. These are the different types of materials or feedstocks from which the biochars have been produced and these are the typical things, you can see the colours, the blue one is the biochar feedstocks percentage actually your economic consideration or importance. Red one is the transport and spreading, green one is the soil effect.

Then light blue is the heat generation and offset and the orange one is that of the soil sequestration. So, in a different biochars that is produced from different feedstocks have different economic consideration.

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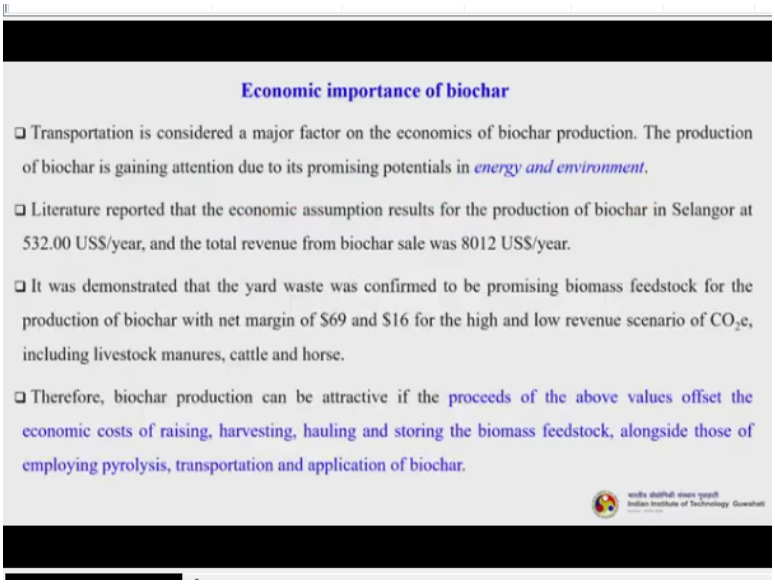

So, transportation is considered a major factor in the economics of biochar production. The production of biochar is gaining attention due to its promising potential in energy and environment. Literature reported that the economic assumption results for the production of biochar in Selangor at 532 US dollar per year and the total revenue from biochar sale was 8012 US dollar per year.

It was demonstrated that yard waste was confirmed to be promising biomass feedstock for the production of biochar with the net margin of 69 dollar and 16 dollar for the high and low revenue scenario of the carbon dioxide equivalent including livestock manures, cattle, and horse. Therefore, biochar production can be attractive if the proceeds of the above values offset the economic cost of raising, harvesting, hauling and storing the biomass feedstock, alongside those of employing pyrolysis, transportation and application of the biochar. So, the entire cost of procuring biomass to the final biochar production.

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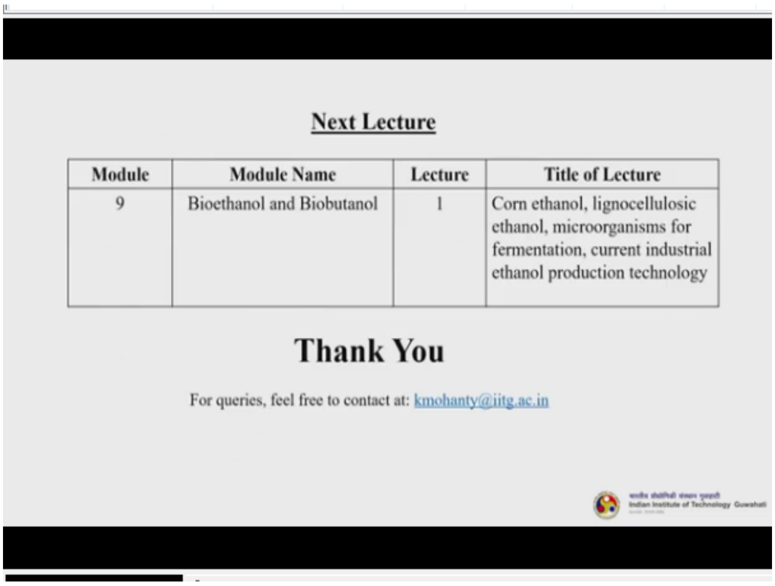

So, with this I conclude today's lecture, in case you have any query please register in the swayam portal or you can also drop a mail to me at kmohanty@iitg.ac.in, thank you very much, in the next module that is module 9 we will start talking and discussing about the bio-ethanol and bio-butanol, 2 of the most important class of products from the fermentation pathway, so thank you.