Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture - 10
H 2 Production from Biological Process

Hello my friends. Now, we are going to discuss about the Hydrogen Production from the Biological Process. So, in our past four lectures, we have discussed about the productions of the hydrogen by different process like electrolysis process, by fossil fuels or by some other means. In this particular case, we are going to discuss about the hydrogen production from the biological process itself.

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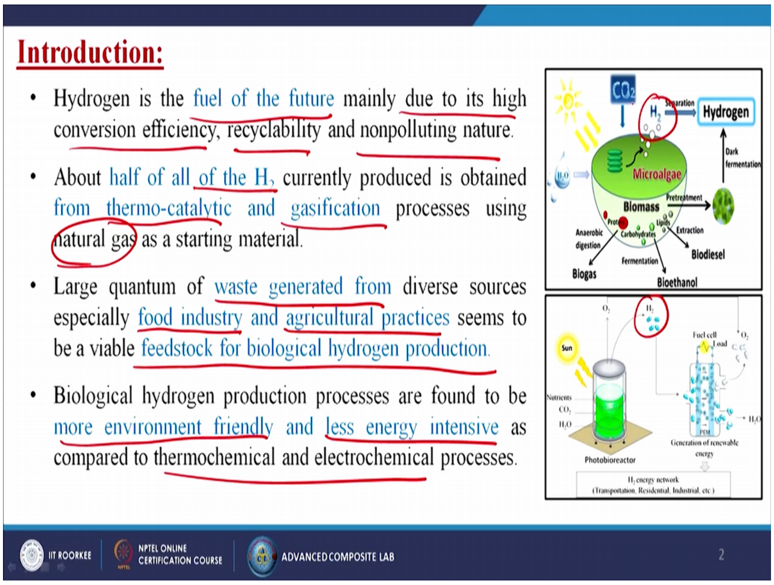

So, in introductions we can say that hydrogen is the fuel of the future because now so many companies like Toyota or maybe in some kind of space shuttles, basically people or maybe scientists are trying to use the hydrogen gas as a fuel. So, this can be used in a future fuel because as the petroleum products or maybe the fossil fuels are going to be finished within some couple of years. So, basically then in that particular case we have to totally depend upon the renewable energy and this kind of renewable energy the hydrogen productions and used hydrogen as a fuel will be the most efficient one.

So, basically hydrogen is the fuel of the future. As I told already mainly due to its high conversion, efficiency, recyclability and non-polluting nature, about half of all the hydrogen currently produced is obtained from thermo catalytic and the gasification process using the natural gas as a starting materials. But in this case also, there is the same problem persist that we are using the natural gas. So, natural gas also the limited one.

So, maybe after certain time we have to work on something like that which can be directly coming from the nature, as a waste product like sunlight or maybe some kind of energy or maybe some kind of electrolysis of the hydrogen. So, electrolysis of the water by which we can produce the hydrogen gas. So, large quantum of waste generated from diverse source especially food industry and agricultural practices seems to be a viable feedstock for biological hydrogen production. Biological hydrogen production process are found to be more environment friendly and less energy intensive as compared to thermochemical and electrochemical process.

So, basically what we are talking about? We are talking about some kind of bacteria some kind of virus, some kind of algae those basically are generating the hydrogen gas. If we are able to capture that hydrogen gas and store it. So, automatically that generation hydrogen generation is the waste one directly it is going into the environment. So, we are not able to collect it. So, now, the scientists are thinking to collect those hydrogen gas as a future fuel.

So, basically, we are having certain kind of bio-reactors or maybe we are having that fuel cells. So, basically by sunlight that photo bioreactor it is producing the hydrogen gas or may be the breaking of the water into the hydrogen and the oxygen we can collect the hydrogen gas. So, they are producing certain kind of hydrogen gas over there. And another beauty of this particular technology is that simultaneously they are absorbing some kind of toxic gases like carbon dioxide carbon monoxide into the systems. So, one way they are reducing the pollutions from the environment, as well as they are giving the hydrogen gas, so what we are trying to store in some for the future applications.

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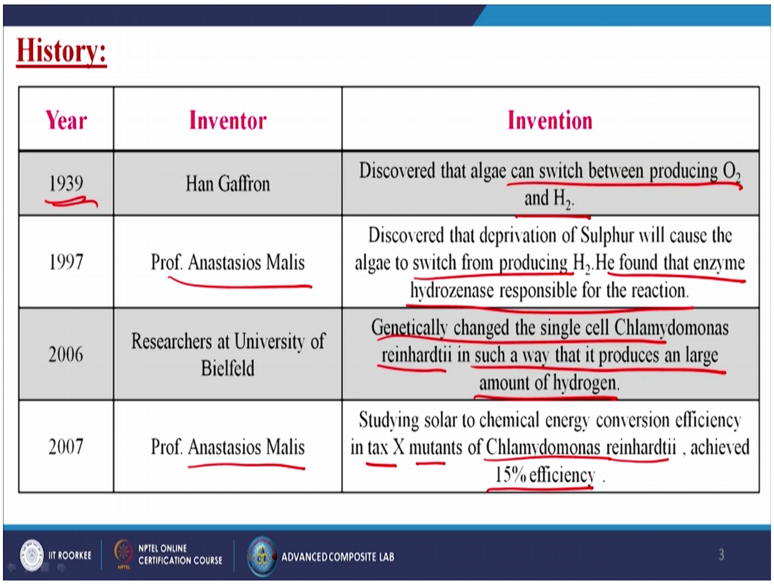

Year	Inventor	Invention
1939	Han Gaffron	Discovered that algae can switch between producing O_2 and H_2.
1997	Prof. Anastasios Malis	Discovered that deprivation of Sulphur will cause the algae to switch from producing H_2.He found that enzyme hydrozenase responsible for the reaction.
2006	Researchers at University of Bielfeld	Genetically changed the single cell Chlamydomonas reinhardtii in such a way that it produces an large amount of hydrogen.
2007	Prof. Anastasios Malis	Studying solar to chemical energy conversion efficiency in tax X mutants of Chlamydomonas reinhardtii , achieved 15% efficiency .

So, now, if we talk about the history, so you can see in the year of 1939, Han Gaffron discovered that algae can switch between producing oxygen and hydrogen. Then in the later in the year of 1997, Professor Anastasios Malis discovered that deprivation of sulphur will cause the algae to switch from producing hydrogen. He found that enzyme hydrozenase responsible for these particular reactions. Then we have come to in the year of 2006, Researchers as University of Bielfeld genetically changed the single cell Chlamydomonas reinhardtii in such a way that it produces an large amount of hydrogen. So, this is a one kind of biological product.

In the 2007, Professor again Professor Anastasios Malis studying solar to chemical energy conversion efficiency in tax X mutants of Chlamydomonas reinhardtii, achieved as 15 percent efficiency. So, now, you can understand that how the scientists are working to produce the hydrogen from the biological product.

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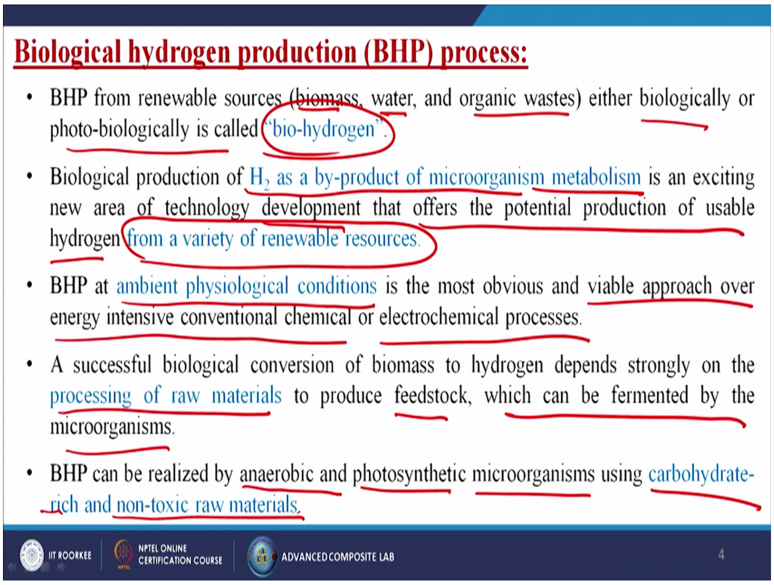

So, biological hydrogen production process in short basically we are calling it as a BHP. So, BHP from renewable source like biomass, water and organic wastes, either biologically or photo biologically is called the bio-hydrogen. Biological production of hydrogen as a by-product of microorganisms metabolism is an exciting new area of technology development that offers the potential production of usable hydrogen from a variety of renewable sources.

BHP at ambient physiological conditions is the most obvious and viable approach over energy intensive conventional chemical or maybe the electrochemical processes. A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock which can be fermented by the microorganisms. BHP can be realized by anaerobic and photosynthetic microorganisms using carbohydrate rich and non-toxic raw materials.

Now, we you are not thinking that we can produce or maybe we can be able to produce the hydrogen from these particular bio-organisms or maybe the from these particular micro organisms. So, now, people are tending their research towards this field. So, basically, they are trying to make certain kind of microorganisms which can produce the hydrogen gas and that hydrogen gassing for future applications we can store.

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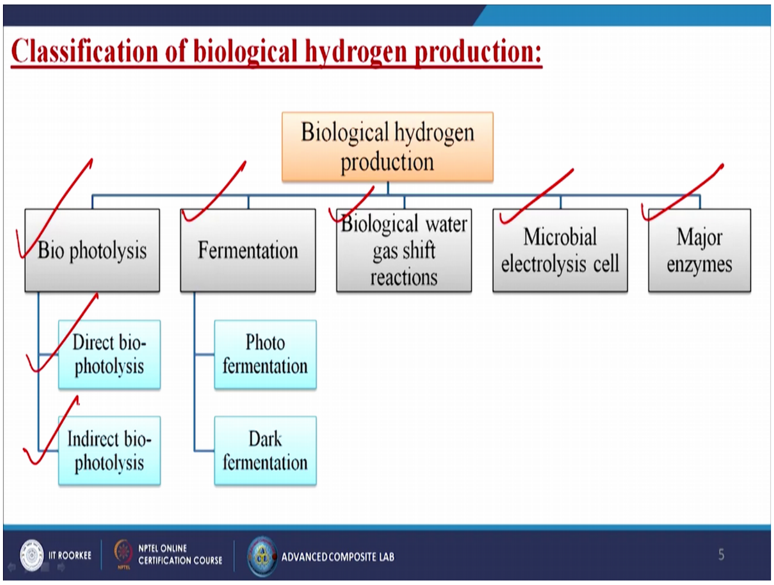

Now, what is the classifications of biological hydrogen productions? So, basically it has been divided into 5 parts, first one is called the bio-photolysis, then second one is called the fermentations, third one is called the biological water gas shift reactions, fourth one is the microbial electrolysis cell, and the fifth one is called the major enzymes.

Then if we go into little bit deeper of the bio-photolysis it has also divided into two parts. So, direct bio-photolysis and another one is called the indirect bio-photolysis. If we talk about the fermentations, it has also been divided into two parts; one is called the photo fermentations, another one is called the dark fermentations. So, this is the whole classifications of the biological hydrogen production. Now, we are going to discuss one by one. So, first is called the bio-photolysis.

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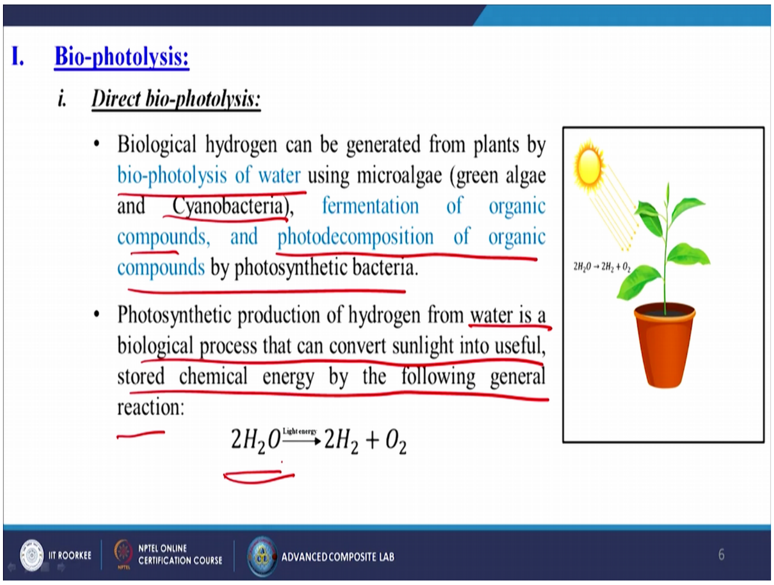

So, first we are going to discuss about that direct bio-photolysis, then second one we are going to discuss about the indirect one. So, biological hydrogen can be generated from plants by bio-photolysis of water using the microalgae green algae and the cyanobacteria, fermentation of organic compounds and photodecomposition of organic compounds by the photosynthetic bacteria itself.

So, photosynthetic production of hydrogen from water is a biological process that can convert sunlight into useful stored chemical energy by the following general reactions. Simple, the water is breaking in the presence of sunlight or maybe the light energy into 2 hydrogen and the oxygen; that means, into the hydrogen gas and oxygen gas. Simple, splitting is taking care by this particular plant or maybe by the plant itself in the presence of sunlight.

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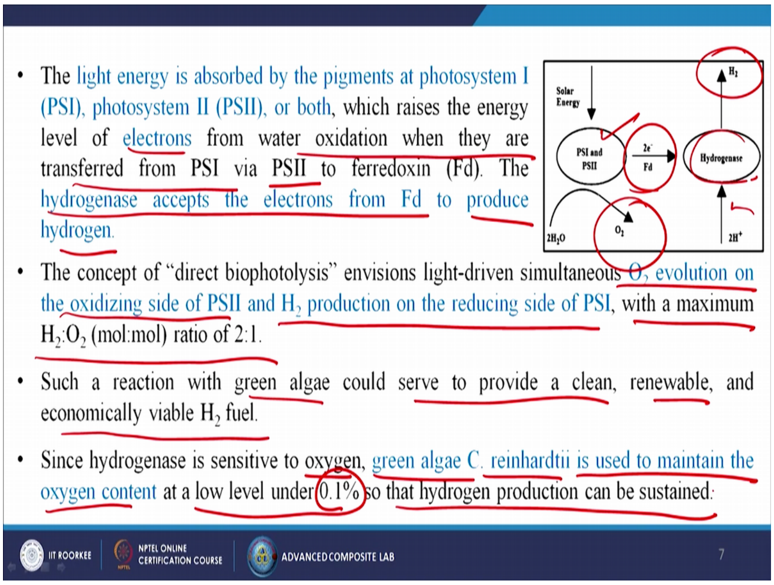

So, the light energy is absorbed by the pigments at photosystem one PS I and photosystem, two PS II or both. So, in this case this is the PS I and PS II both. So, which raises the energy level of electrons from water oxidation when they are transferred from PS I via PS II to ferredoxin Fd. The hydrogenase accepts the electrons from Fd to produce the hydrogen itself. So, in this particular case it is PS I and PS II systems directly solar energy is coming and then we are using this ferredoxins over there or maybe it is already present over there by these hydrogenase is taking place by which we are getting the hydrogen gas and in this particular case the oxygen is coming throughout it.

The concept of direct bio-photolysis envisions, light driven simultaneous oxygen evaluations on the oxidizing side of PS II and hydrogen productions on the reducing side of PS I with a maximum H 2 O 2 ratio of 2 is to 1. Such a reactions with green algae could start to provide a clean, renewable and economically viable hydrogen fuel. Since, hydrogenase is sensitive to oxygen green algae C, reinhardtii is used to maintain the oxygen content at a low level under 0.1 percent. So, that hydrogen production can be sustained for a longer time.

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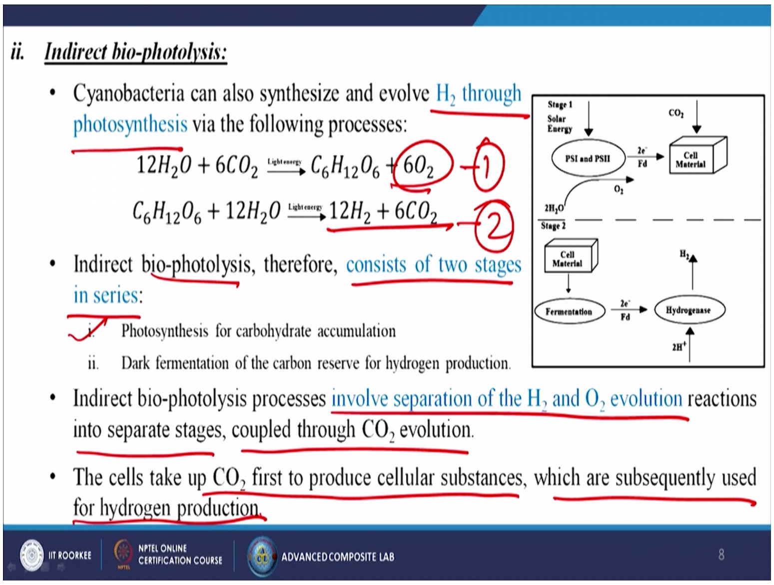

Now, we are going to discuss about the indirect bio-photolysis. So, cyanobacteria can also synthesize and evolve hydrogen through photosynthesis process via the following process. Like, 12 by H 2 O plus 6 CO 2, simple it is preparing the glucose C 6 H 12 O 6 plus oxygen. Then this C 6 H 12 O 6 glucose additions with the water 12 molecule of water, then it at light energy or may be the in presence of sunlight it is producing the hydrogen gas and the carbon monoxide gas.

Indirect bio-photolysis therefore, consists of two stages in series. One is called the photosynthesis for carbohydrate accumulations this is the number 1 and number 2 is the dark fermentations of the carbon reserve for the hydrogen production, that is the number 2. So, basically, indirect bio-photolysis process involves separations of the hydrogen and oxygen evaluation reactions in to separate stages coupled through the carbon dioxide evaluation. The cells take up carbon dioxide first to produce the cellular substances which are subsequently used for hydrogen production. So, this is about the indirect bio-photolysis process.

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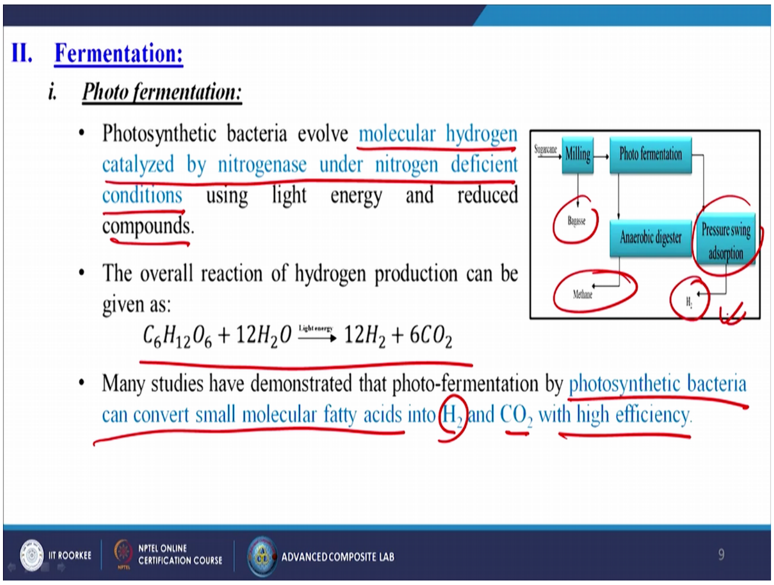

Now, we are going to discuss about the second one that is called the fermentations, that also divided into two parts; one is called the photo fermentations another one is called the dark fermentations. So, in photo fermentations basically the photosynthetic bacteria evolve molecular hydrogen catalyzed by nitrogenase under nitrogen deficient conditions using light energy and reduce the compounds itself.

So, the overall reaction of hydrogen production can be given as same, it is like glucose then we are adding the water and in the presence of sunlight or maybe the light energy, it is producing the hydrogen gas with carbon dioxide gas. Many studies have demonstrated that photo fermentation by photosynthetic bacteria can convert small molecular fatty acids into hydrogen and carbon dioxide with high efficiency.

So, basically, we can do by these methods it is called the sugar cane suppose we can we are taking and then we are doing the milling. So, milling the extract basically it is known as the bagasse or maybe the bagasse fiber then after milling we are doing the photo fermentations. So, in one case we are using the anaerobic digester and we are able to produce the methane gas, in other case we are using the pressure swing adsorption techniques by which we are able to produce the hydrogen gas.

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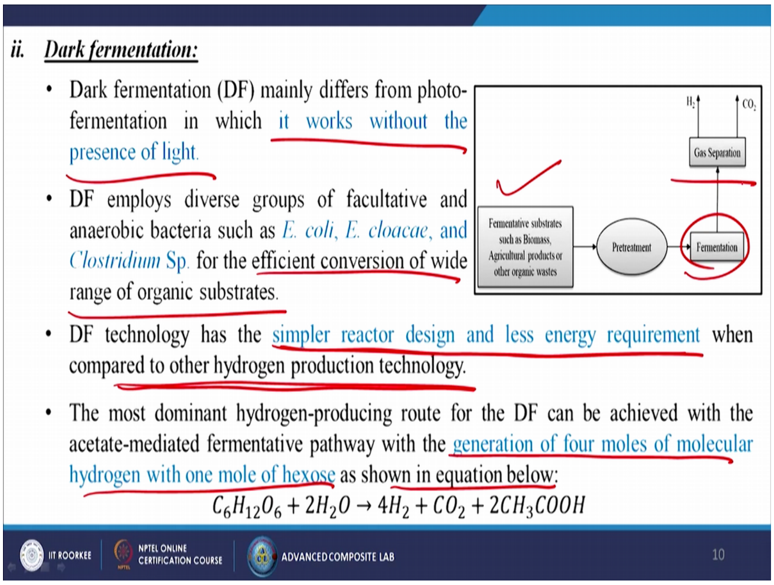

Now, the next one is called the dark fermentations. So, basically the dark fermentations mainly differs from photo fermentations in which it works without the presence of light, so that means, we can do it into the lab or may be the into the inside the room. So, DF employs diverse group of facultative and anaerobic bacteria such as E coli, E cloacae and clostridium Sp for the efficient conversion of wide range of organic substrates.

DF technology has the simpler reactor design and less energy requirement when compared to other hydrogen production technology. So, the most dominant hydrogen producing route for the DF can be achieved with the acetate mediated fermentative pathways with the generation of four moles of molecular hydrogen with one mole of hexose as shown in equation.

So, in this particular case what we are trying to do? So, we are basically trying to do the fermentative substrate such as biomass or maybe the agricultural products or maybe other organic wastes we are collecting. Then we are doing certain kind of pretreatment over there, pretreatment in terms of some kind of cleaning, some kind of pre-heat treatment kind of things then we are doing the fermentations and through fermentations simple we are getting the two gas that is the hydrogen and the carbon dioxide and simple we are separating the hydrogen gas and the carbon dioxide gas by the gas separation process by which we are able to produce the hydrogen gas. So, this is the overall thing about the dark fermentations.

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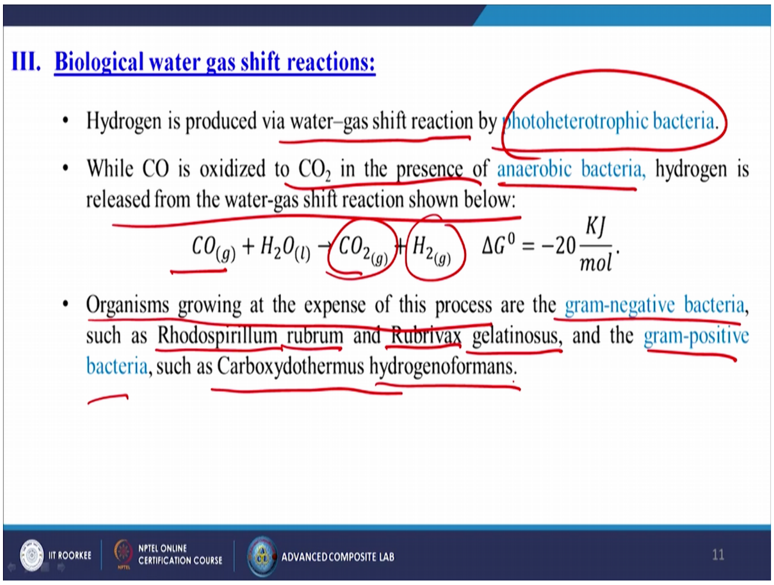

Now, we are going to the third part which is called the biological water gas shift reactions. So, hydrogen is produced via water gas shift reactions by the photo-heterotrophic bacteria. So, while carbon monoxide is oxidized to carbon dioxide in the presence of anaerobic bacteria hydrogen is released from the water gas shift reactions shown in this particular part.

So, carbon monoxide in the gaseous state H 2 O into the liquid form it is forming the carbon dioxide as a gas and hydrogen as a gas. So, in these particular case organisms growing at the expense of this process are the gram-negative bacteria such as Rhodospilillum rubrum and Rubrivax gelatinosus and the gram positive bacteria such as Carboxydothermus hydrogenoformans. So, basically, these all are the names of different bacteria. So, basically bacteria is divided into two parts; one is called the gram positive and gram negative bacteria. So, basically in this case with the help of this kind of bacteria we are trying to develop the hydrogen gas from the biological water gas shift reactions.

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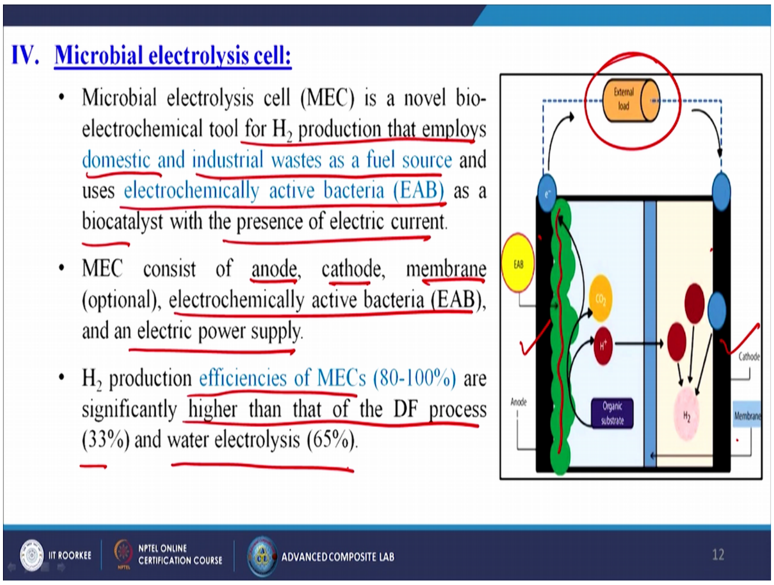

Next the fourth one is called the microbial electrolysis cell. So, in short basically we are calling it as a MEC. So, MEC is a novel bio-electrochemical tool for hydrogen productions that employs domestic and industrial wastes as fuel source and used electrochemically active bacteria EAB as a biocatalyst with the presence of electric current.

So, simple in this particular case what is there? We are having two electrodes; one is known as the anode another one is not known as the cathode. In between that we are using the separator membrane, so basically, we are using some kind of polymeric membrane over there, and one side we are giving the electro chemically active bacteria. So, this is basically the electro chemically active bacteria and it is attaching with the anode materials.

And then after that what is happening? MEC consists of anode, cathode, membrane electrochemically active bacteria as an electric power supply. So, this is the external road that by which we are giving the potential difference in between the two electrode over there.

Now, hydrogen production efficiencies of MECs generally 80 to 100 percent are significantly higher than that of the DF process that is 33 percent and the water electrolysis of 65 percent. Now, you can understand that what is the efficiency we are achieving by this microbial electrolysis cell. So, basically what is happening? We are able to achieve almost 80 to 100 percent efficiency for the hydrogen production.

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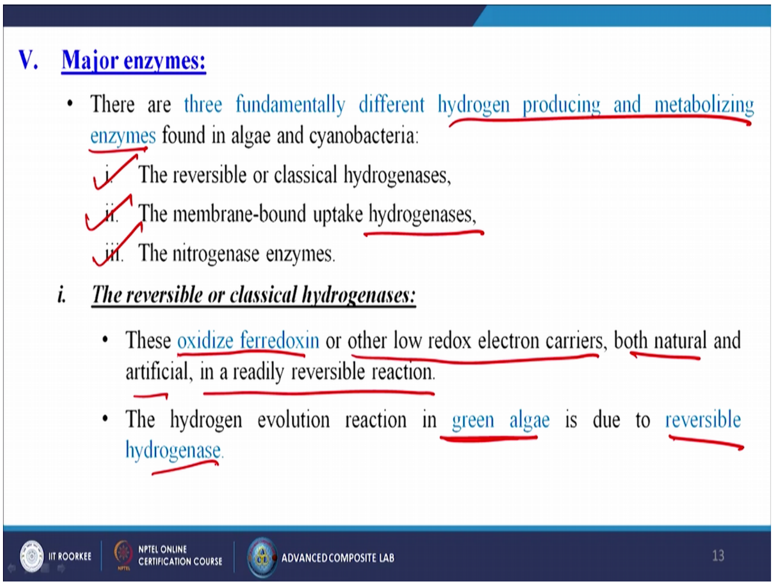

Next is called the major enzymes. There are three fundamentally different hydrogen producing and metabolizing enzymes found in algae and the cyanobacteria. First one is called that the reversible or classical hydrogenases, second one is called the membrane bound uptake hydrogenases, and the third one is called the nitrogenase enzymes. So, first we are going to discuss about the reversible or maybe the classical hydrogenases. These oxides ferredoxin or other low redox electron carriers both natural and artificial in a readily reversible reaction. The hydrogen evolution reaction in green algae is due to the reversible hydrogenase; so that means, they are doing the back reactions over there.

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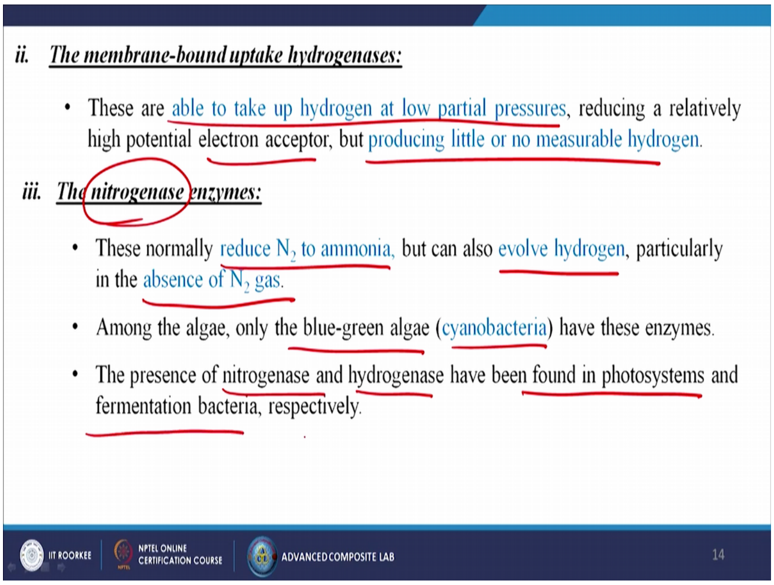

Then second one is called the membrane bound uptake hydrogenases. These are able to take up hydrogen at low partial pressures reducing a relatively high potential electron acceptor, but producing little or maybe no measurable hydrogen. Means, the hydrogen production quantity is very very low in this particular case.

Then the third one is called the nitrogenases enzymes. These normally reduces nitrogen to ammonia, but can also evolve hydrogen particularly in the absence of nitrogen gas. So, reduce reduction of nitrogen to ammonia, that is why it is called the nitrogenase basically. Among the algae only the blue green algae which is known as the cyanobacteria have these enzymes or maybe have being these kind of particular properties. The presence of nitrogenase and hydrogenase have been found in photosystems and the fermentation bacteria respectively.

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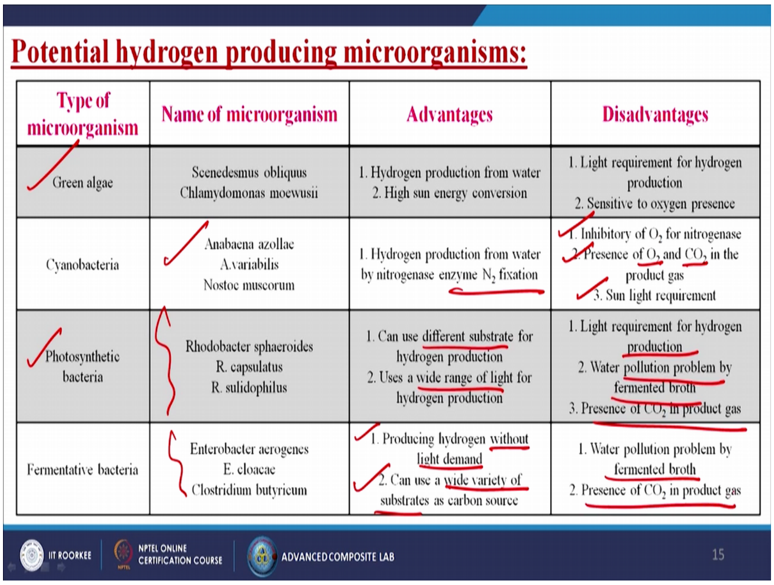

Potential hydrogen producing microorganisms:

Type of microorganism	Name of microorganism	Advantages	Disadvantages
Green algae	Scenedesmus obliquus Chlamydomonas moewusii	1. Hydrogen production from water 2. High sun energy conversion	1. Light requirement for hydrogen production 2. Sensitive to oxygen presence
Cyanobacteria	Anabaena azollae A.variabilis Nostoc muscorum	1. Hydrogen production from water by nitrogenase enzyme N_2 fixation	1. Inhibitory of O_2 for nitrogenase 2. Presence of O_2 and CO_2 in the product gas 3. Sun light requirement
Photosynthetic bacteria	Rhodobacter sphaeroides R. capsulatus R. sulidophilus	1. Can use different substrate for hydrogen production 2. Uses a wide range of light for hydrogen production	1. Light requirement for hydrogen production 2. Water pollution problem by fermented broth 3. Presence of CO_2 in product gas
Fermentative bacteria	Enterobacter aerogenes E. cloacae Clostridium butyricum	1. Producing hydrogen without light demand 2. Can use a wide variety of substrates as carbon source	1. Water pollution problem by fermented broth 2. Presence of CO_2 in product gas

Then this one is called the potential hydrogen producing microorganisms. So, in this particular case we have discussed detailed about the different types of microorganisms, then what are the scientific name of these microorganisms and what are the advantages and disadvantages. So, if we talk about the green algae, so basically the advantage is called the hydrogen production from water and high sun energy conversions.

If we talk about the disadvantages also it is having light requirement for hydrogen productions because every time it requires the sunlight and then sensitive to the oxygen presence. Then if we talk about the cyanobacteria. So, this is the scientific name or maybe the microorganism names. So, it is also having certain advantages like hydrogen production from water by nitrogenous enzyme, nitrogen fixation.

And of course, there are certain disadvantages too. So, first it is called the inhibitory of oxygen for nitrogenase, second one is the presence of oxygen and carbon dioxide in the product gas and third is that sunlight requirement. If we talk about the photosynthetic bacteria. So, this is the scientific name of that particular microorganisms. It is also having certain advantages like can use different substrate for hydrogen production and second one use a wide range of light for hydrogen productions. Disadvantages, light requirement for hydrogen productions, water pollution problem by fermented broth, presence of carbon dioxide in product gas.

And the fourth one is called the fermentative bacteria that is enterobacter aerogencs or maybe E-cloacae. So, these all are the scientific names. So, it is also having certain advantages producing hydrogen without light demand the that is the biggest advantage over there, second is can use a wide variety of substrates as carbon source. Of course, it is having certain disadvantages too, that water pollution problem by fermented broth and the presence of carbon dioxide in product gas.

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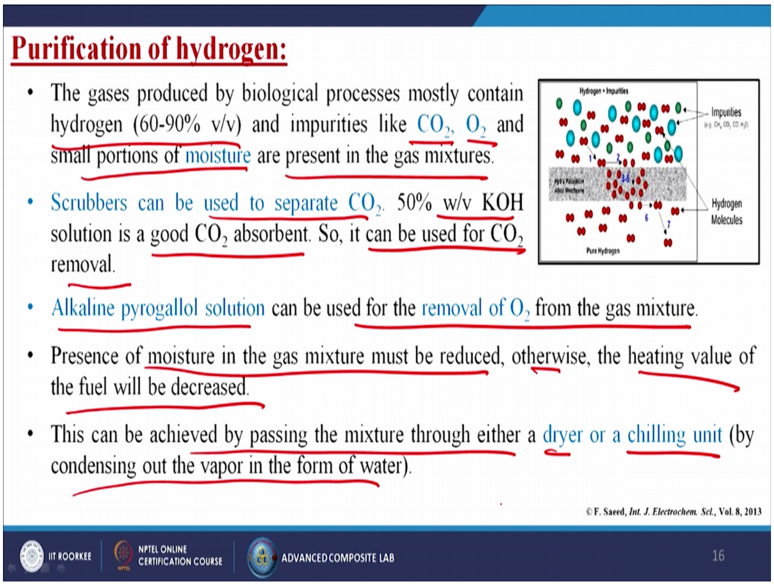

Now, we are going to discuss about the purifications of the hydrogen gas. So, the gas is produced by biological process mostly contain the hydrogen 60 to 90 volume. And impurities like carbon dioxide, oxygen and small portions of moisture are present in the gas mixture. So, there are some kind of byproducts are already added with the hydrogen gas. Now, how we are going to get the 100 percent pure hydrogen gas. Scrubbers can be used to separate carbon dioxide 50 percent w by v.

Student: Weight by.

Weight by volume, potassium hydroxide solutions is a good carbon dioxide absorbent. So, it can be used for carbon dioxide removal. Then alkaline pyrogallol solution can be used for the removal of oxygen from the gas mixture. Presence of moisture in the gas mixture must be reduced otherwise the heating value of the fuel will be decreased. This can be achieved by passing the mixture through either a dryer or a chilling unit by condensing out of the vapor in the form of water. And then after that we are going to get the 100 percent pure hydrogen over there. Now, what are the criteria to choose the nanomaterials for biological hydrogen productions?

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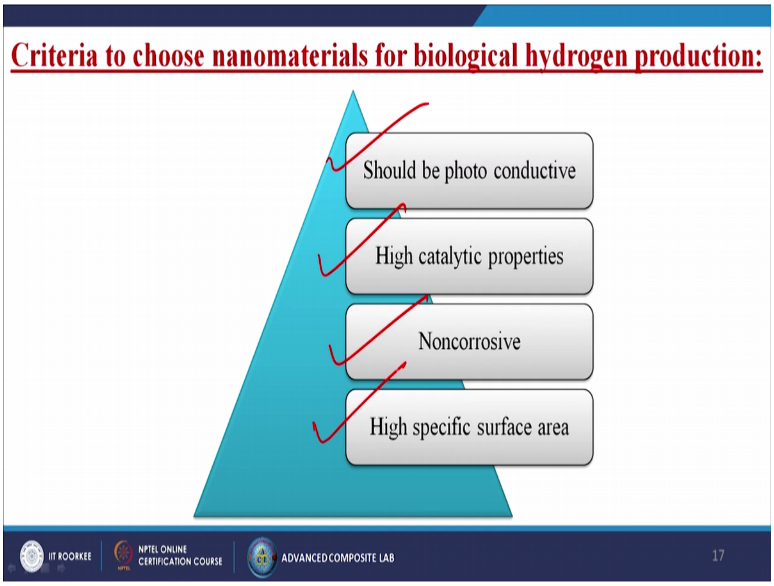

So, it should be photo conductive, it should be high catalytic properties, it should be noncorrosive and it should have high specific surface area.

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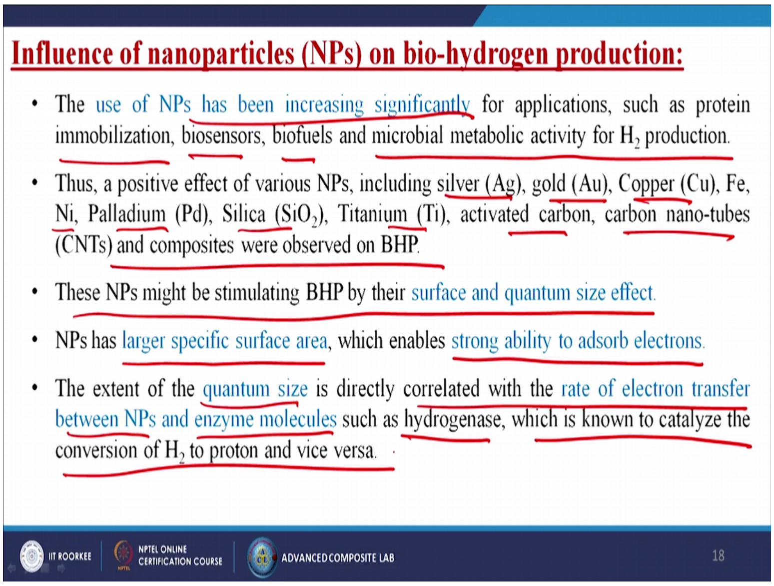

Now, what are the influence of the nanoparticles on bio-hydrogen productions? Till now we are discussing about different types of microorganisms, algae, bacteria kind of things. Now, how the nanoparticle will be able to produce the hydrogen gas or maybe help to produce the hydrogen gas in more volume concentrations or maybe in a lesser time and efficiency of that particular system can be increased.

The use of nanoparticles has been increasing significantly for applications such as protein immobilizations, biosensors, biofuels and microbial metabolic activity for hydrogen production. Thus, a positive effect of various NPs including silver, gold, copper, iron, nickel, palladium, silica, titanium, activated carbon, carbon nano-tubes and composites were absorbed on BHP.

These nanoparticles might be stimulating BHP by their surface and quantum size effect. Nanoparticles has a larger specific surface area which enables strong ability to adsorb the electrons. The extent of the quantum size is directly correlated with the rate of electron transfer between nanoparticles and enzyme molecules such as hydrogenase which is known to catalyze the conversion of hydrogen to proton and vice versa.

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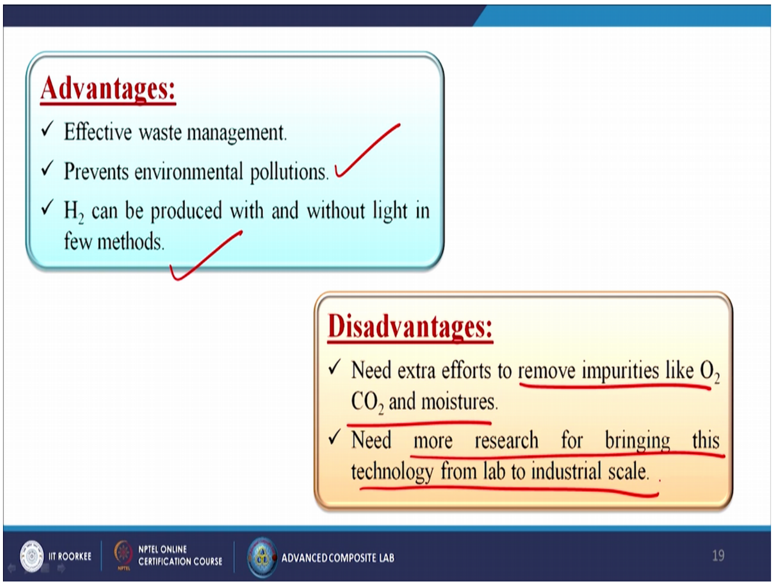

Now, what are the advantages? So, it is the effective waste management system because we are taking all the waste products over there like algae some kind of microorganism, some kind of sunlight, some kind of other energy sources. Prevents the environmental pollutions. Hydrogen can be produced with and without light in few methods. Of course, it is having certain disadvantages. Need extra efforts to remove the impurities like oxygen, carbon dioxide and the moistures from the system.

Need more research for bringing this technology from lab to the industrial scale; that means, the commercialization of this particular technology needs more attention for the future hydrogen production point of view. Now, we have come to the last slide of this particular lecture.

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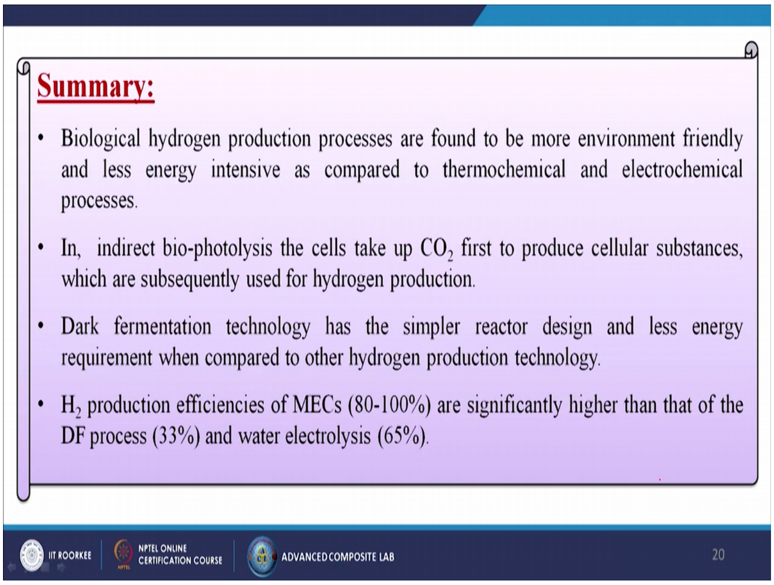

So, in summary we can say that in this particular lecture we have discussed about the biological hydrogen production process, which has been found to be more environment friendly and less energy intensive as compared to thermochemical and electrochemical process. In indirect bio-photolysis the cells take up carbon dioxide fast you produce cellular substances which are subsequently used for hydrogen production.

Dark fermentation technology has the simpler reactor design and less energy requirement when compared to other hydrogen production technology. Hydrogen production efficiencies of MECs is up to 80 to 100 percent are significantly higher than that of the DF process, means dark fermentation process of about 33 percent and water electrolysis process of about 65 percent.

Thank you.