Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning(NPTEL)

Course Title
Bioenergy

Lecture -30
Carbonization – Preparation of Graphene Like Molecule

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Welcome back to the lecture series on bio energy so let us catch up where we left in the last class so we talked about the pyrolysis and the pyrolysis technique where we talked about slow pyrolysis /pyrolysis and in the slow pyrolysis we talked about the carbonization process which leads to the formation of solid fuels whereas in the flash pyrolysis we have talked about the liquid fields what we get in the form of by oils and transformation of bio-oil using real lights and hydrogenation processes.

And the third where you do a flash pyrolysis to form gaseous will which we have not gone into the gasification process so in the last class I told you that in terms of that solid fuel formation depending on one highlighting feature which is emerging as we are walking through this whole process of pyrolysis which pretty much is the reason why we have so many carbon-based will which has formed underneath the earth because of high pressure and high temperature over centuries the formation of coal formation of even diamond formation of graphitic carbon formation of patrol formation natural gas.

So if you consider this whole earth as a reactor vessel some in the constants in the surface some insight the ground and deep inside the ground think we had buried so pyrolysis has been happening in a reaction in the absence of oxygen has been happening since the very beginning okay, so based on the level of pyrolysis based on the route of pyrolysis based on the conditions of the pyrolysis the product changes so that is the thematic that is the most beautiful emerging thing what we are observing as you must have seen when we process the same stuff using zealot it has a different fate when you do hydrogenation is a different fate so when you have / pyrolysis we could to get solid sorry we could get liquid as well as gaseous will wear with a slow carbonization what we get are just solid fuels okay.

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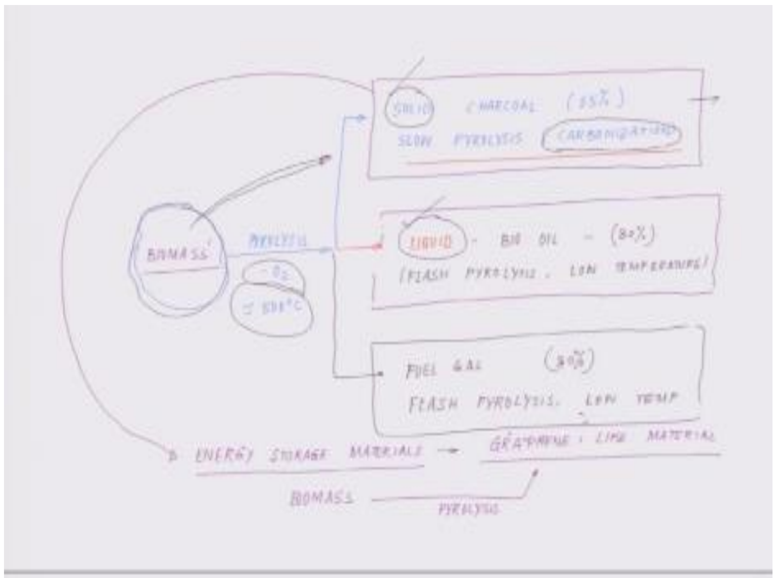

So just coming back to the slide if you remember this is the slide where I ended in the last class so you have the biomass depending on the biomass what we talking about you can paralyze it in the absence of oxygen and at a temperature of 500 degree centigrade what you get is solid charcoal which is the carbonization process as well as highlighting liquid and flick so today what we will do will talk about a very specific kind of biomass which leads to carbonization leading to the formation of graphene like molecules.

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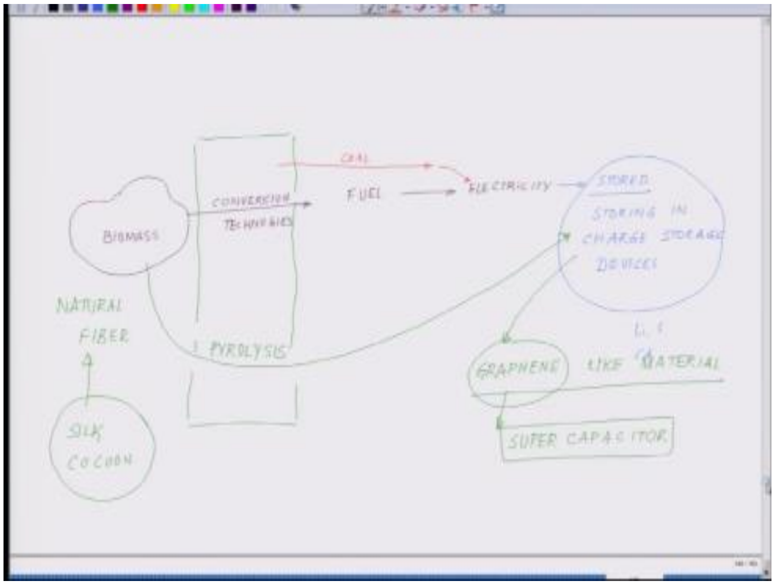

Or a very special kind of graphene which is the need of the hour so what is the philosophy behind this so you have a wide area bio mass on the floor of earth okay, so use different kind of conversion technologies conversion technology of biomass conversion technology to convert it into fuel you are using this wells to generate electricity okay just the same way you use if I parallely look at it you are using natural we have like coal and other things to generate electricity okay.

Now this electricity has to be stored somewhere in the form of charge storage devices or storing in charge storage devices charge storage devices now most of these charge storage devices are either lithium cadmium batteries lithium sulfide lithium cell batteries likewise now think of it this is the philosophical side is B charge storage devices are also obtained from the biomass how the story will be so essentially our life will revolve around biomass technology and the root is the same.

As I told you the thematic is the same the conversion technology what is the conversion technology you are using so today we will talk about a conversion technology of biomass where you can directly convert biomass into graphene like material which is way more efficient than normal graphene and in one of the classes in the later hub will have a video demonstration of how such graphene good which is derived from the biomass sources could be made into a very good functional super capacitor.

So we will have a video demonstration of this process in a later class in the advanced technology so this is part of one such advanced technology were following the thematic that what kind of process conversion technology is being used you can transform the biomass to different kind of materials so here the conversion technology what will be following is pyrolysis okay and the material biomass is a natural fiber one of the very prominent natural fiber which is used for clothing is silk.

So this is one example where silk which is derived from silk cocoon in all of you have fun seen silk some point or other either in the form of clothing or a cheese or any kind of textiles or some military gadgets what happy news so silk is there for a long period of time if those of you are not aware of silk it is clearly simple it is synthesized or it is made by certain group of insects or a huge group of insect.

So just clear your concept there are our supports or the family of insects which q a lot of vegetable vegetative materials and from their mouth they give out a saliva like material and that material is rich in protein and that is what is called as silk okay so there are some 15 to 8000such issues of insect which gives out that exceed 8 from their mouths and that exceed 8 is very rich in protein and other bio molecules.

And they form sometimes they form a complete coating around that insect in order to allow it to go through second couple of stages of their life cycle their dormant phase which lead to the metamorphosis where simple larvae gets converted into a cup which is the doorman fail's to a butterfly sometimes they form very nice thread like structure or called fighter net you all of you have seen this is a common those who have seen spider-man movies they all are aware of the spider net like this.

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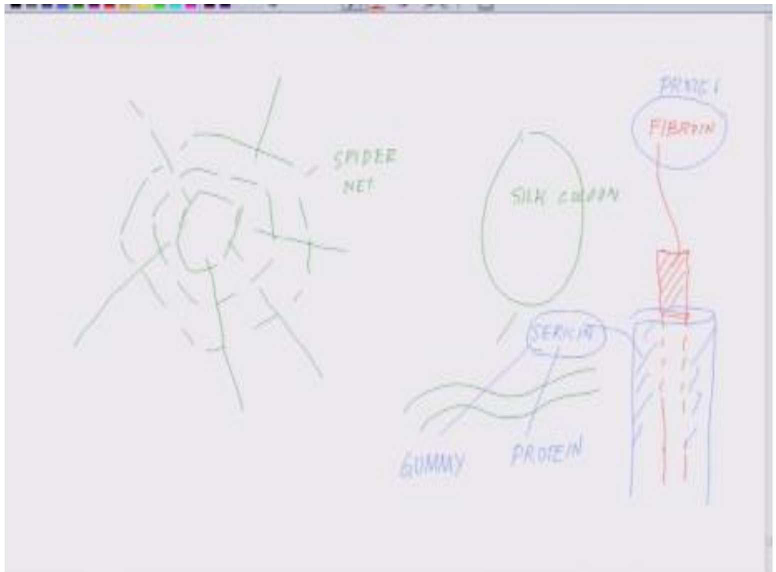

Which is also nothing but a form of silk there are some technical differences between the different kind of silks whereas all over you have seen some cocoons from where the silk threads are being they can also this is silk cocoon this is spider net they are all different form of silk the only basic difference between these two silk is if you see this thread this thread is something like this if you see a cross section of this thread to it will look like this.

So as if a tube inside another tube so the inside red tube is called Citroen and the outside blue part what you see is called Saracen this is what regular silk what we use in our clothing concepts on so what they do this Saracen is a protein and Saracen is another protein so this protein is very gummy in nature it is sticks so different see growing threads stick to one another using this service in protein that is why it form a structure like silk cocoon.

It is a very compact structure whereas in the spider net what happens these threads are filling same sibling with the of course different sequence of the protein is a protein but the spider net lacks this particular component the Saracen part so this is minus 13 and that is why you see the spider net to be spread out so they do not adhere to one another thread not adhere to one another in order for the threat to adhere to one another they have to have a gummy like material so then they form a cocoon like structure like this whereas a spider net is more like a spread out because where can we put it is down there but they all are silk and there are at least ten thousand to fifteen thousand or maybe more species of silk threads available but very handful of them has been over the years have been cultivated or are being used for a group purposes so one of the famous one is which is across the world which is used is called BOMBYX MORI which is BOMBYX MORI it is a white color silk cocoon.

The other wild species of this is the domesticated species cocoon there is a wild species which is called which is very common in India which is called a tougher silk successful cocoon and theoria my letter choose a scientific name other cocoons in India which are found in a some so today what will we talk about this one of these wild cocoons which is sucker which is wild and it is found is widely found in several parts of India including Madhya Pradesh, Chhattisgarh power of UP.

And several part of Bihar special mugger food and all that region then down south so but these are all wild silky so now looking at it so this is a form of a biomass so now we are talking about a protein biomass which is.

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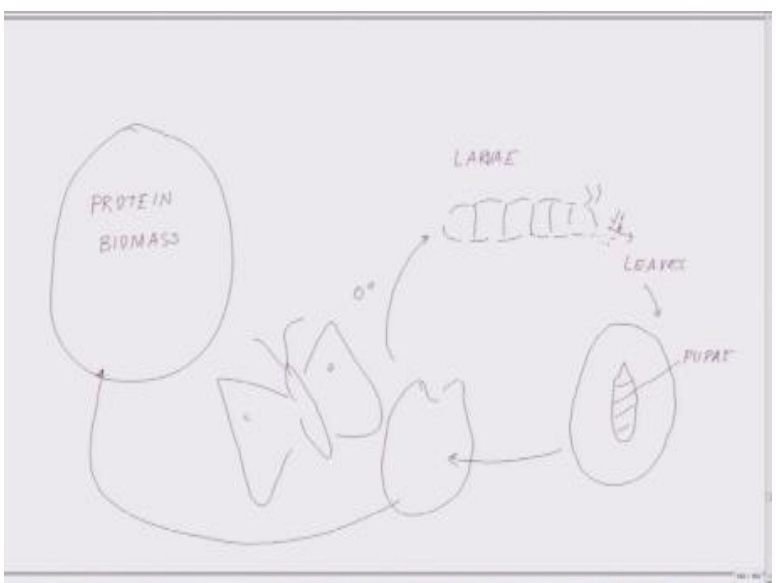

So as of now we are talking about lingo cellulosic carbohydrate biomass so here we are talking about protein biomass in the form of a silk cocoon okay so what happens so as I have already told you so the insect passes through most of these insect pockets of four stage life cycle so you have a large is something like this all of you have seen these larvae you know so these larvae eat on leaves lot of lease and they put on a lot of weight.

And then this lousy from its mount gives out this protein rich fluid by which it forms a coat around its own body and it goes into a dormant phase so this is the doorman this is called a QP okay and then after a certain day that can vary from 20 days to nine months depending on the species we are talking about insect butterfly emerges out leaving behind the open cocoon and the life cycle goes on and this butterfly again lay eggs and likewise the larvae is form this structure is nothing but a protein biomass.

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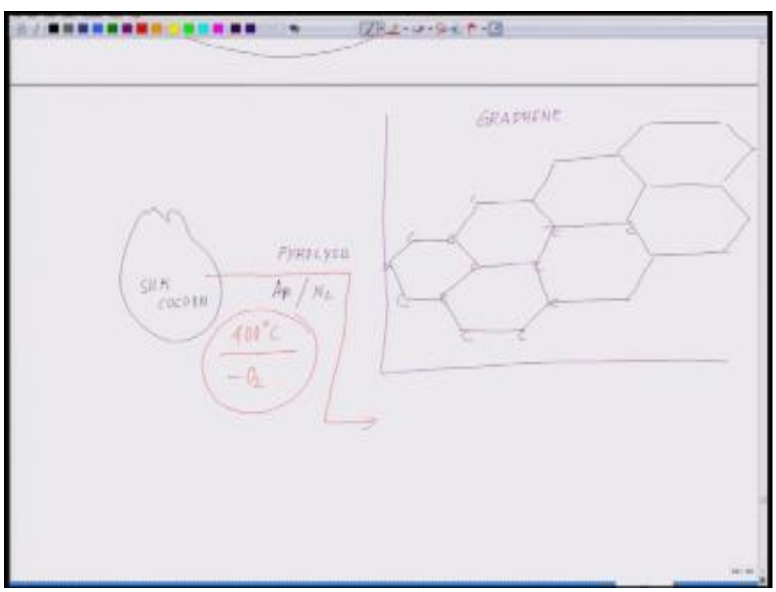

Now if you take this protein biomass and we have silk cocoon and if you pyrolysis it in organ environment AR or nitrogen environment sorry they are argon or nitrogen environment what you get is a very interesting kind of so this is what is a native graphing looks like it is a single layer carbon okay, all these are inputted carbon, carbon, carbon, carbon, carbon, carbon, carbon, carbon, carbon, carbon right. Now this is what you want think in let me just rubit off so this is what is a graphing looks like, now when you burn or pyrolyzed it at the temperature of around 400 degree centigrade minus oxygen again the same carbonization process we are talking about. What you get is very interesting.

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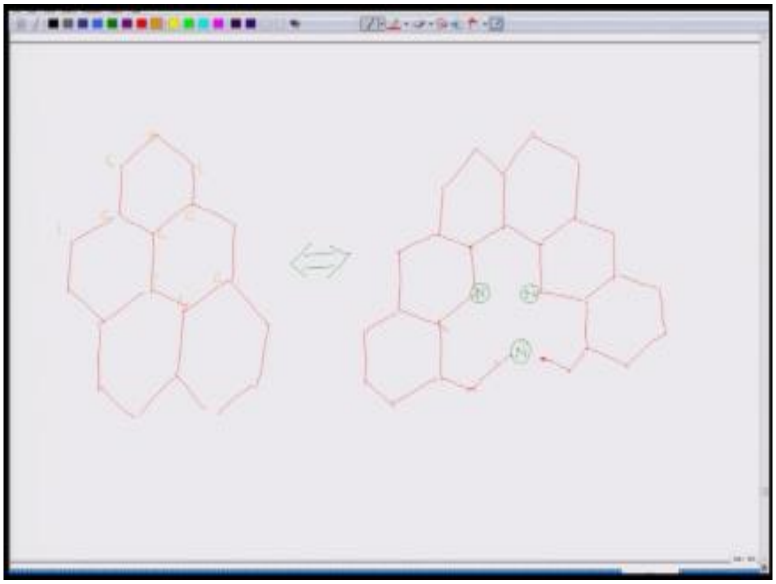

This is your native graphene molecule just for your comfort zone I am redrawing it with all the carbons attached okay, now where is this situation what you are getting is something slightly different from such a uniform structure okay, something like this okay, so you have some of these nitrogen instead of carbon coming in and I will tell you from where they are arriving and okay, and you have put nitrogen here stood nitrogen here

So do you see so if you compare these two structures so here you had nothing but carbon, carbon, carbon, carbon, carbon, carbon, carbon, carbon likewise here you see as if that matrix is now being doped with nitrogen from where the nitrogen is coming so think of the structure of a protein we will come back to this structure again in a second okay, think of the structure of the protein.

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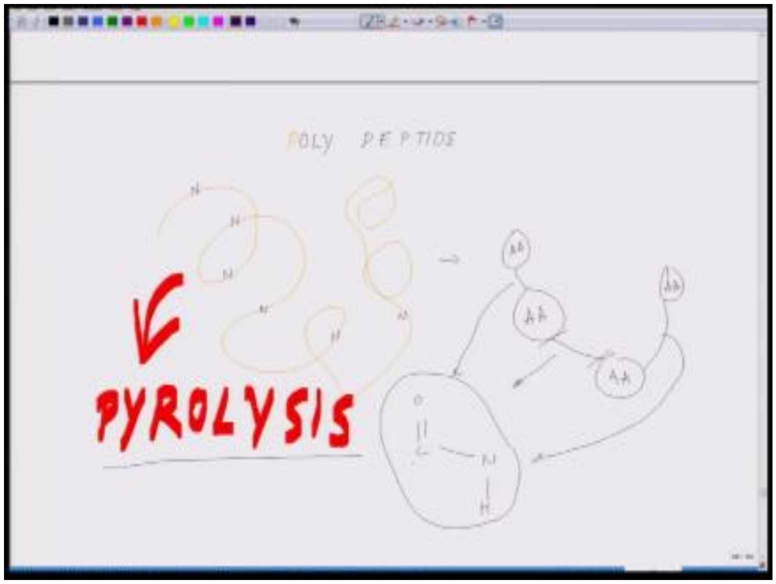

So this protein what we are talking about is essentially if you see a protein chain this is the protein chain okay, so polypeptide ok so the polypeptide is made up of amino acid so of these amino acids AA stands for amino acids, different kind of amino acids and they are attached to each other okay. Now they are attached to each other by a planar bond structure which is peptide bond okay, it is this bonding which is all over the place.

So they are all these amino acids are bound to each other and what you see the protein molecules have bunch of nitrogen in it. Now once you take this stuff and pyrolysis it what is happening after pyrolysis, pyrolysis leads to something similar to this?

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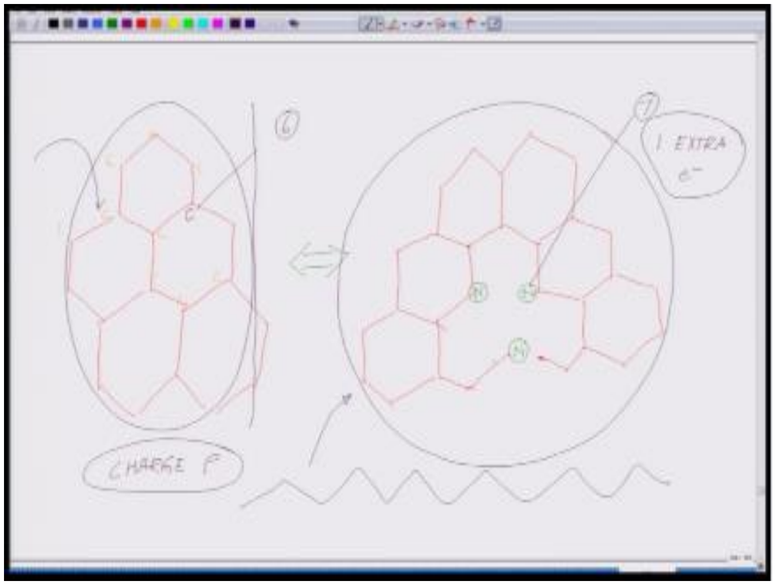

Where this whole structured this linear chain of protein which was something like this gets transformed into it compresses itself into a geometry where the carbon feels much more you know at ease with each other because we work because I told you that there is a structural rearrangement each which is happening and since you are not providing any oxygen so there is no carbon dioxide going through whatever is there and whatever little oxygen makes it will skip through but whatever molecules are there they are already present.

There and if you think of it very carefully so you see carbon when you talk about carbon it has atomic number of six and we talked about nitrogen it has atomic number of 7 so you have one extra electron which is present here so the molecule of graphene as such need some kind of a dopant and introducing a dopant by an artificial technique in terms of say nitrogen which has one additional electron in order to increase say for example I want to increase the charge density, charge density of this molecule okay, charge density of this molecule and just low unchanged for the density charge density of this molecule so in order to increase the charge density I have to increase the number of electrons.

But carbon I cannot do anything so I have to introduce something which is little more than carbon so my nearest neighbor to carbonate the nitrogen but how to introduce the nitrogen I have to do a lot of thermal processes and everything but instead if you follow the age-old technique what nature has done by a simple pyrolysis what will happen these within the protein molecules where there is so much nitrogen present there.

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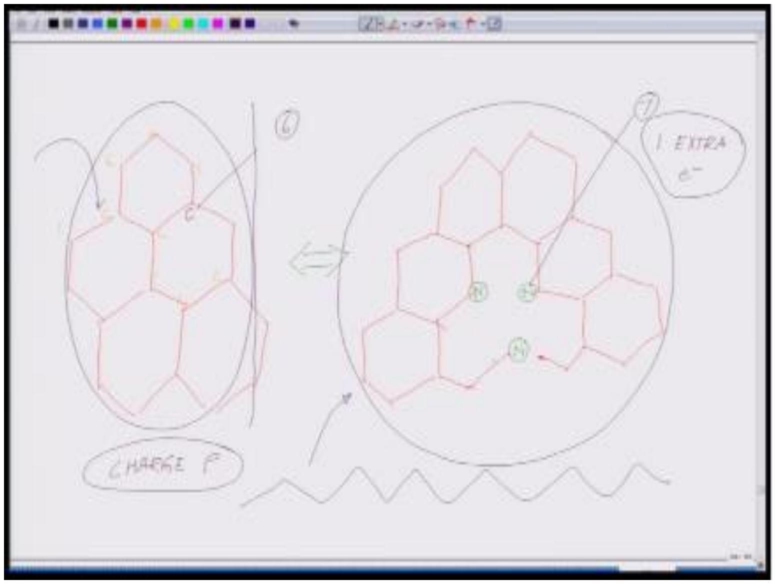

Those nitrogen will rearrange into a very interesting confirmation and the possible confirmation in the next and let me draw the next which will give you an idea about what are the possible confirmation.

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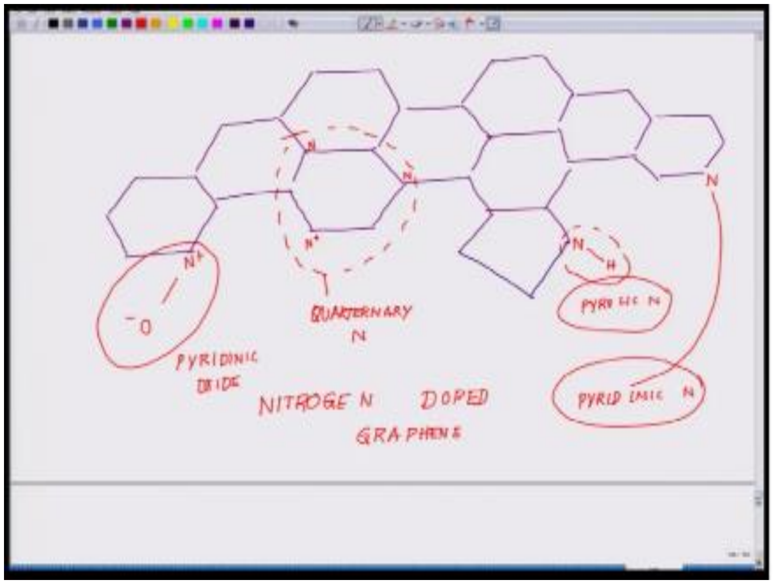

It can go you realize so these are the possible confirmation it can attain okay, so this is a simple standard graphene network which I am drawing and then I will introduce all the different dopant which are getting into the system okay. So out here now I am introducing all that dopants with different colors okay, OH- okay, wherever on positive charge this is one such moiety which will you observe then you will observe something more interesting you will have the nitrogen here nitrogen plus which is the any have another nitrogen out here and I am just circling this I will tell you why I am circling this okay.

Then you will see some of the one thing let me just redo it something like this come across nitrogen and hydrogen another form and you have nitrogen here so they have different names so this is called pyridinic oxide this is called quaternary nitrogen this is called hydraulic nitrogen and this is called pyridinic nitrogen so if you observe in a simple structure of graphene following a very low energy technique you just put expose them to 400 degree centigrade and you get to one of the very high quality nitrogen-doped graphene so what is this, this is essentially what you are getting is nitrogen-doped graphene as a matter of fact these kind of making these kind of nitrogen-doped graphene was done in India for the first time.

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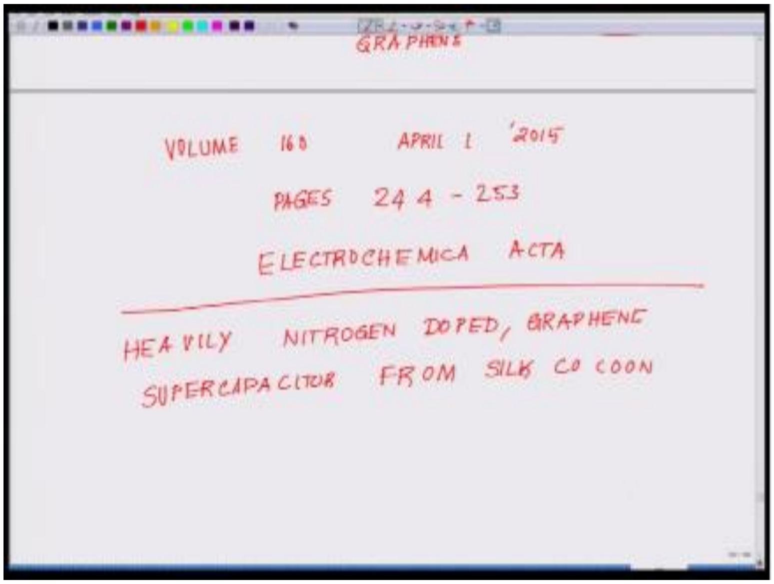

So you can refer to the following paper which will help you to kind of you know no little bit more about it volume 1 0 April 1st, 2015 is published in electrochemical actor okay, please go through it that will kind of give you an idea 253 the journal is electro chemical actor this is the reference where you see heavily so that nice the paper title is heavily nitrogen-doped grapheme, nitrogen graphene super capacitor and this is what we will be demonstrating the class super capacitor from silk cocoon okay.

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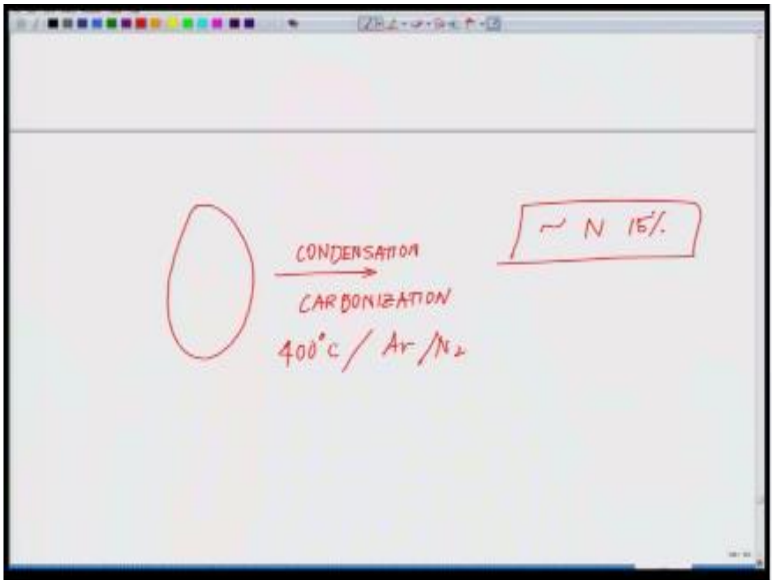

So by your very simple technique what we are telling using a simple silk cocoon and there are processes which are following condensation carbonization which is basically the pyrolysis 400 degree centigrade in argon or nitrogen environment what you are getting is approximately 15% doping of nitrogen this is in itself is a big record to getting a 15% nitrogen in other word out of 100 you100 carbon molecule you could insert atleast 50 nitrogen-doped molecule so just try to imagine so you have 15 nitrogen means you have 15 extra charge moiety is what you are adding which essentially was not possible with a pure carbon network.

So the charge density and charge storage potential goes up at least 15units more as compared to the native graphene so having said this I will highlight some very interesting aspect of it which will kind of help you to again appreciate that.

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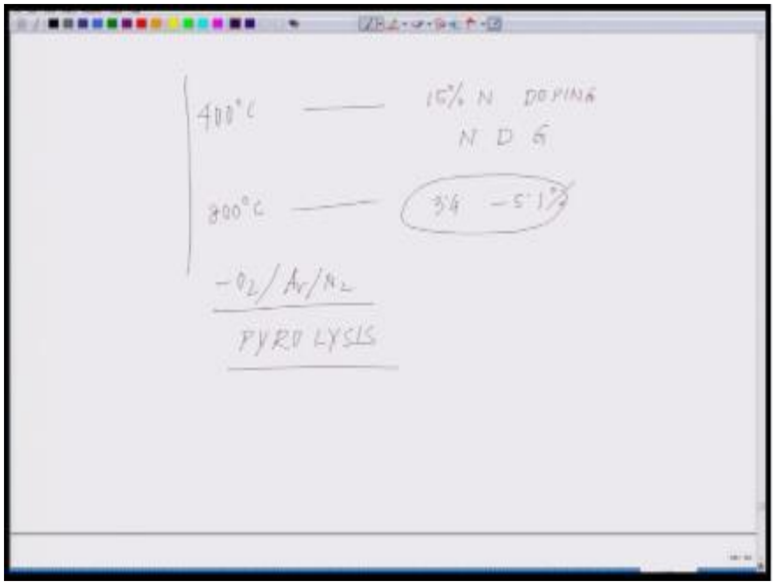

How the pyrolysis can make difference so we talked about that this was done at 400 degree centigrade where one gets 15% nitrogen doping okay, so nitrogen doping in graphene which we call as nitrogen-doped grapheme, okay. Now see for example, you raise the temperature to say 800 degree centigrade of pyrolysis in the surprise the nitrogen person goes down to 3.4 to 5.1 this is the kind of fall and if you go and there are reports which yeah I think this will kind of give you an idea about minus oxygen just showing pyrolysis in the presence of argon or nitrogen okay.

So this will kind of give you an idea that how temperature plays such a critical role and the condition plays such a critical role in pyrolysis that you can change the complete physical properties its whole electrical property changes if you increase it 400 to 800 so these are some of the very interesting technologies which are evolving that biomass is not only for fuel it is could be used for energy storage material and one of the very high profile energy storage material and these are the discoveries which are done in India for the first time it was shown that you know you can use this kind of thing and you really can achieve something which we as Indian of the first one to show that it is possible.

So these are the new dimension and newer and newer technologies which are coming up highlighting the fact that biomass could be converted into versatile product and some day the whole area bio energy will open up to these newer and newer discoveries which will make it a much more compact fine like you know biomass engineering science where biomass converting into fields biomass conversion energy storage devices biomass directly making batteries which would be we will be talking at some point.

So these this is so if you look at it integrating picture features or one common thread is that how what kind of conversion strategies are we following and how that could influence the fate of that particular biomass and what kind of biomass we are picking up for the conversion process, so close in here so next we will move on to gasification and others few advanced technologies thank you.

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