Carbon Materials and Manufacturing

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Lecture – 19
Pyrolysis of Gaseous Hydrocarbons

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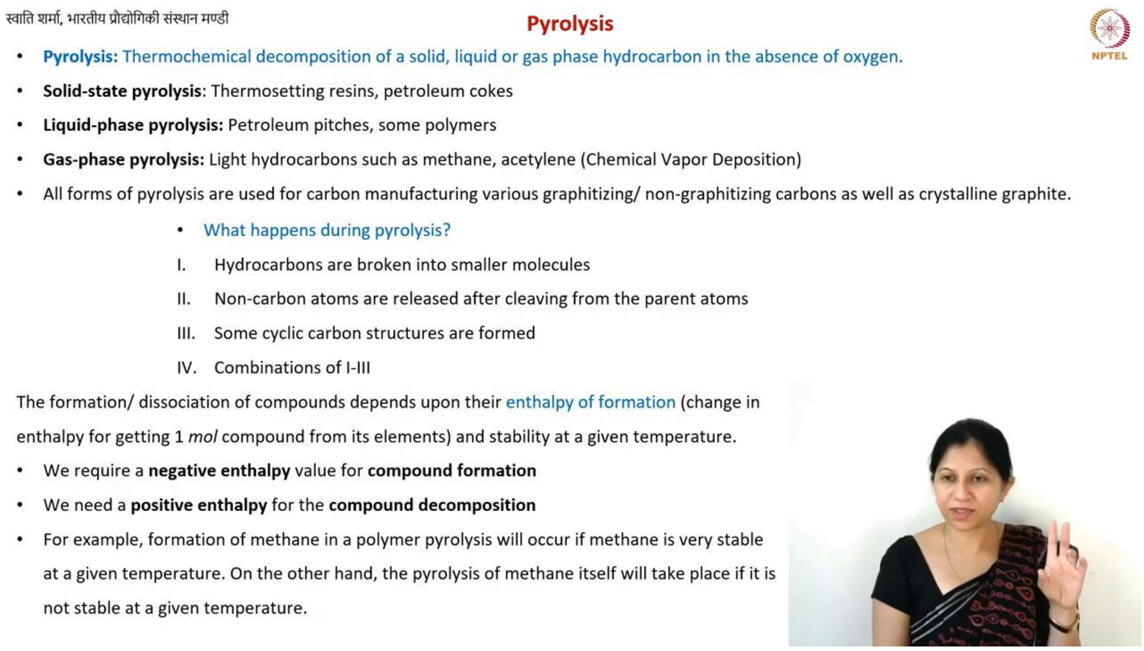

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Pyrolysis

- **Pyrolysis:** Thermochemical decomposition of a solid, liquid or gas phase hydrocarbon in the absence of oxygen.
- **Solid-state pyrolysis**: Thermosetting resins, petroleum cokes
- **Liquid-phase pyrolysis:** Petroleum pitches, some polymers
- **Gas-phase pyrolysis:** Light hydrocarbons such as methane, acetylene (Chemical Vapor Deposition)
- All forms of pyrolysis are used for carbon manufacturing various graphitizing/ non-graphitizing carbons as well as crystalline graphite.
  - What happens during pyrolysis?

I. Hydrocarbons are broken into smaller molecules
II. Non-carbon atoms are released after cleaving from the parent atoms
III. Some cyclic carbon structures are formed
IV. Combinations of I-III

The formation/ dissociation of compounds depends upon their enthalpy of formation (change in enthalpy for getting 1 *mol* compound from its elements) and stability at a given temperature.

- We require a **negative enthalpy** value for **compound formation**
- We need a **positive enthalpy** for the **compound decomposition**
- For example, formation of methane in a polymer pyrolysis will occur if methane is very stable at a given temperature. On the other hand, the pyrolysis of methane itself will take place if it is not stable at a given temperature.

Hello everyone. By now, you have learned, or you have heard about the term pyrolysis multiple times. Pyrolysis we talked about when we were talking about getting graphite from needle coke or when we were talking about the pyrolysis of hydrocarbon gases for obtaining pyrolytic graphite which can then be converted into highly oriented pyrolytic graphite.

We will also be talking about this particular process multiple times. Because we have an organic material as a precursor whenever we are making synthetic carbons. Now, this organic material can be a solid polymer, it can also be some liquid petroleum material or it can also be a gaseous hydrocarbon.

In all cases, we are getting different types of carbons, but our precursor is a hydrocarbon. And the process of conversion or getting the carbon from this precursor is your pyrolysis. The fundamental process is heat treatment. But the most important part of the heat treatment is when you are getting rid of your non-carbon atoms and then you have the formation of carbon-carbon bonds. This is why pyrolysis is very important to us.

In this particular lecture, I want to tell you what is pyrolysis, what is the region of the heat treatment? Let us say from room temperature until 700-800 degrees, that is the region where you have the breakage of the bonds. You have larger hydrocarbons converting into smaller hydrocarbons, but you also know that this is not the only thing that is happening in your heat treatment.

If you keep on further increasing the temperature, you have carbon-carbon bond formation at some point. If you want to convert your material into graphite, you may have to go to very high temperature.

So, this is your entire heat-treatment process. Pyrolysis is the part where you have the thermochemical decomposition of your organic material. This need to essentially take place in the absence of oxygen. So, this is the definition.

Now, as I already mentioned that your organic material can be a gas phase, liquid, or solid. In the absence of oxygen, this is also very important. If you have any oxygen present, then the chemical reaction will take place. There will be combustion and not pyrolysis.

You will find some examples of when people do waste treatment. They are actually converting a mixture of a lot of materials – mostly organic materials. You know the urban solid waste contains a lot of things. And we do not know the exact composition of these materials. At that time, things are heated. This mixture of materials is heated up to not very high temperatures, but 600-700°C, and then that process is known as pyrolysis.

However, often you may have some oxygen also present in that process. At the end of the day, you have a combination of pyrolysis and combustion. Since your material mixture is very complex, you cannot really separate the pyrolytic and combustive decomposition of the material. So, you end up calling it pyrolysis, but actually this is pyrolysis plus combustion.

Also, in the case of waste management, our primary goal is not to make carbon, but rather to get the byproducts of our current process like the tars and gaseous hydrocarbons. These were the by-products when we are making carbon. Now those byproducts actually become the primary products and the carbon becomes sort of the byproduct. Waste treatment is not something that we are going to discuss in detail in this particular course, because this is a carbon manufacturing course.

In the context of carbon manufacturing, we will take generally very well-known hydrocarbons. And we will optimize the parameters in such a way that the carbon we want to obtain, has a given geometry, given morphology, and given microstructure.

Some examples of solid, liquid and gas-phase pyrolysis; Solid-phase pyrolysis you already know we have talked about needle coke and the conversion of needle coke into graphite. Also, when we were filling the pores of the needle coke if you remember, we filled them with either pitch or some sort of resin. These resins can also be hardened by curing. And in that case, the pyrolysis or carbonization of these resins is also an example of solid-phase pyrolysis.

In fact, we are going to learn about this technique again when we will talk about microfabrication using carbon materials. Because also, in that case, we are taking a phenol-formaldehyde resin then cross-linking it to convert it into a solid form, and then we are carbonizing it. So, these are examples of solid-phase pyrolysis.

How about liquids? You already know that petroleum pitches can be carbonized, they contain up to 95 percent carbon. And we mix them with our needle coke or also use them for pour filling. You will also learn that we make carbon fibers from them. So, these are examples of liquid phase pyrolysis. Some polymers can also be liquid when they are being carbonized.

Gas-phase pyrolysis well you know already. We can use methane, we can use acetylene, we can use benzene, we can even use vapors of certain light alcohols. And at higher temperatures, we can crack these hydrocarbon gases and get carbon out of them. This process is also known as chemical vapor deposition. So, chemical vapor deposition is basically a more general term. You can also for example, make silicon or you can chemically deposit a metal oxide semiconductor that will depend on the precursor that you have.

But when we say pyrolysis, then we are very specifically talking about pyrolysis of a hydrocarbon and then we are talking about carbon deposition. Now the goal of this particular lecture is to tell you what happens during pyrolysis. So, I had briefly told you about the region where you have the cleavage of the bonds.

And cleavage will be of hydrocarbon and non-carbon atoms, heteroatoms. Different bonds break at different temperatures. There are no very well-defined temperatures, but you do know a temperature range where a certain type of bond will break.

However, for gas, solid and liquid phase materials, this mechanism will also differ slightly. If you have larger hydrocarbons, then they will break into smaller hydrocarbons. The smaller ones will further break into you know even smaller.

So, this fragmentation process will go on in the case of heavier hydrocarbon-carbon molecules. However, if you already start with methane or very light hydrocarbon molecule, in that case, you are not going to get lighter hydrocarbon molecules, but the carbon-heteroatom bond will break also in that case. And you may sometimes have non-carbon atoms just being released in the form of some gases. This will also happen in the case of polymer pyrolysis. But when you have this fragmentation process at some point, all the very volatile hydrocarbon or light hydrocarbons will leave your material. These things are happening. What else? So, we talked about this is more like the cleavage process.

But is there some cyclization happening at the time of pyrolysis. Now, what is cyclization? We know what we get out of pyrolysis or our end product is carbon. Now, this carbon often has hexagonal structures, graphitic carbon. You keep on increasing the pyrolysis temperature, you get more and more graphitic content, but to start with you need to have certain hexagons. And these hexagons are being formed at some point.

What is that point? This depends on the precursor material. You may have precursors with a lot of aromatic structures, in that case, you start with some you know hexagonal ring-like structures, cyclic structures. But you also have aliphatic polymers for example, polyacrylonitrile, which is not an aromatic material we are going to discuss that when we talk about carbon fiber fabrication.

What happens if you start with a hydrocarbon like methane? So, in these cases what is happening is at some point there are some cyclic structures being formed. And these the cyclization process often starts at the pyrolysis time. When some molecules are being fragmented, there are also some molecules that have converted into radicals, and these radicals attach to each other. And they form larger cyclic structures which may still contain hydrogen. And the hydrogen may leave at a slightly higher temperature. There is some fraction of cyclization that already takes place at the time of pyrolysis.

It is not just one of these three processes, but all of them are all happening at the same time. In fact, this is what makes pyrolysis a very complex process to understand. I am saying complex because think about a heavy hydrocarbon material. You have this hydrocarbon and then you get smaller hydrocarbon. Now, those are also breaking into smaller pieces. We do not even know a lot of these materials, it is really difficult to characterize all of them because they are not just primary, but also secondary and tertiary reaction reactions that are taking place. We do not know the rate of each reaction, because there are multiple reactions, some may be first-order some may be second order.

Also, these reactions are influencing each other; the byproduct of one reaction might actually influence the reaction conditions for another one. So, this is a very complex chemical process to understand especially when we are talking about heavier hydrocarbon. In the case of smaller hydrocarbons like gaseous ones, it is relatively easy to understand. In fact, I have taken the example of methane, which is also a precursor for getting graphene sheets.

But this is something we are going to talk about in our graphene section, but the fundamental process remains the same. This is the pyrolysis of methane which deposits certain types of carbon layers. These are graphitic carbon layers, but turbostatics, randomly arranged on top of each other. Now, this is what we call graphene. If we further do hot press or annealing of these carbon layers stacked on top of each other, then what we get is pyrolytic graphite. And further heat treatment will yield highly oriented pyrolytic graphite. Right now, our goal is to get graphite, and that is why we are not talking about graphene. But the process and fundamentals remain the same.

What property determines which molecule will be formed, which compound will be formed? There is something known as the enthalpy of formation. We also talked about it when we were discussing why does not graphite convert into diamond naturally or diamond converts into graphite naturally. So, at that time also, we learnt about this.

Again just to remind you, this is the change in enthalpy for obtaining one mole of a certain compound from its components when they are infinitely away from each other and you bring them together, make the compound one mole; this is the change in overall enthalpy. But how does that relate to pyrolysis?

When you take a heavy hydrocarbon, now at a certain temperature let us say 500°C, what will happen to it? Some byproducts are going to be formed, some small hydrocarbons are going to be formed. Which hydrocarbons? Will you get benzene or will you get methane? Or will you get some other smaller polymer-like structure?

What is it that you are going to get, will depend on what is the enthalpy of formation of that particular product at that given temperature. This is very important that we are not talking about room temperature enthalpies anymore. We are talking about the enthalpy at 500-600°C temperature.

If any particular compound has a negative enthalpy, then s it is a spontaneous reaction, then there is a probability that it will be formed. So, if at 500°C methane has a more negative value of its enthalpy compared to say benzene, then there is a higher probability that methane will be formed as the byproduct. So, this is one thing.

However, what happens if I take methane itself as my starting material? In that case, if I am talking about the pyrolysis of methane or pyrolysis of the gaseous hydrocarbon, in that case, I will have to figure out the temperature where the enthalpy of methane formation becomes positive.

That means this is not a thermodynamically favorable reaction anymore there is a higher probability that now methane will decompose. So, these are the two important things. Based on the enthalpies, then accordingly that compound is formed or decomposed.

This is basically what we are going to talk about in the next couple of slides. I will take the example of the pyrolysis of methane, in the case of polymer pyrolysis, the process slightly differs.

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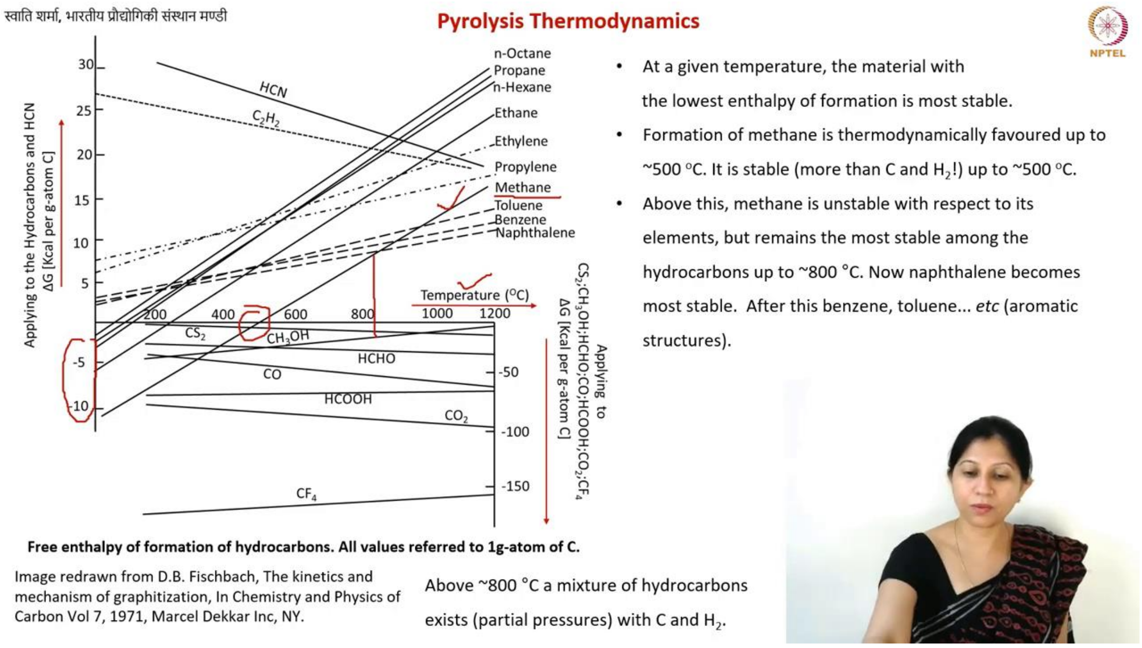

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Pyrolysis Thermodynamics

- At a given temperature, the material with the lowest enthalpy of formation is most stable.
- Formation of methane is thermodynamically favoured up to ~500 °C. It is stable (more than C and H_2!) up to ~500 °C.
- Above this, methane is unstable with respect to its elements, but remains the most stable among the hydrocarbons up to ~800 °C. Now naphthalene becomes most stable. After this benzene, toluene... *etc* (aromatic structures).

Free enthalpy of formation of hydrocarbons. All values referred to 1g-atom of C.

Image redrawn from D.B. Fischbach, The kinetics and mechanism of graphitization, In Chemistry and Physics of Carbon Vol 7, 1971, Marcel Dekkar Inc, NY.

Above ~800 °C a mixture of hydrocarbons exists (partial pressures) with C and H_2.

Here in this diagram, you see that I have plotted the enthalpies of formation of various light hydrocarbons with respect to temperature. There is a temperature line here. With respect to temperature, you see how the enthalpies change for every hydrocarbon. This is our methane line. At lower temperatures, the enthalpy of formation of methane is negative.

During pyrolysis, we are increasing the temperature of the process. For any given temperature whatever is the most stable hydrocarbon will have the highest probability of formation. Let us take the example of methane, you see the methane line intersects with your temperature line at around 500°C. What does this mean that?

Below 500°C, methane is very stable; it does not decompose. In fact, it is more stable even compared to carbon and hydrogen, and that is why instead of carbon and hydrogen you will rather have methane. It is not exactly 500°C, it is actually 520°C something like that, but approximately till 500°C methane remains very stable.

What happens above this temperature? Now, methane becomes unstable compared to carbon and hydrogen. If you compare it with other hydrocarbons, it is still the most stable one. Now, there is a possibility that methane will split into carbon and hydrogen.

You see one more interesting thing here that if you go to 800°C somewhere here. Now, after that, other aromatic hydrocarbons such as naphthalene or benzene, their enthalpies are less positive compared to that of methane. So, there is a higher probability that you will have benzene or naphthalene rather than methane at that temperature, now methane is not the most stable. Aromatic hydrocarbons tend to become more and more after 800 degrees.

When we say aromatic, there is some cyclization, that is what I am saying above 800, cyclization is possible or that is more favorable. This is how you are going to decide at what temperature there is a possibility of obtaining carbon solid particles from any hydrocarbon.

You can do for other hydrocarbons like ethane and ethylene and so on. You can also see that some hydrocarbons even at room temperature have a positive enthalpy of formation, and some of them are negative.

As you keep on increasing the temperature, of course, you will also play, play with other parameters. Now, so from here, we understand that at what temperature, it is possible to decompose methane. Now we need to somehow deposit somehow collect our solid carbon from this methane.

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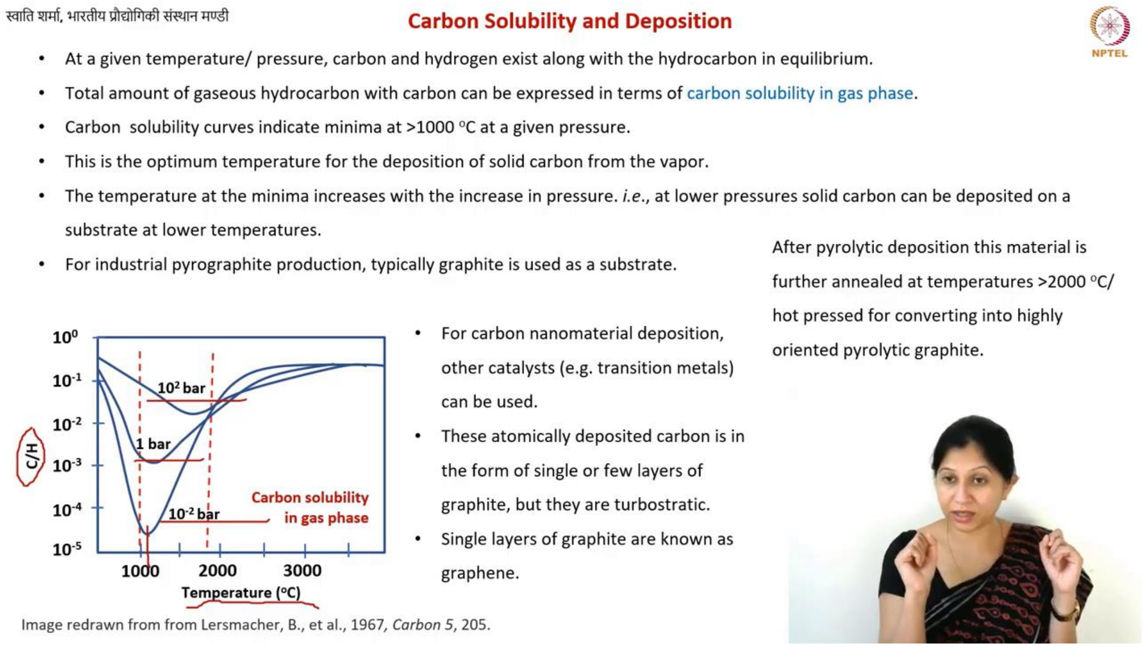

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Carbon Solubility and Deposition

- At a given temperature/ pressure, carbon and hydrogen exist along with the hydrocarbon in equilibrium.
- Total amount of gaseous hydrocarbon with carbon can be expressed in terms of carbon solubility in gas phase.
- Carbon solubility curves indicate minima at >1000 °C at a given pressure.
- This is the optimum temperature for the deposition of solid carbon from the vapor.
- The temperature at the minima increases with the increase in pressure. *i.e.*, at lower pressures solid carbon can be deposited on a substrate at lower temperatures.
- For industrial pyrographite production, typically graphite is used as a substrate.

Image redrawn from from Lersmacher, B., et al., 1967, *Carbon 5*, 205.

- For carbon nanomaterial deposition, other catalysts (e.g. transition metals) can be used.
- These atomically deposited carbon is in the form of single or few layers of graphite, but they are turbostratic.
- Single layers of graphite are known as graphene.

After pyrolytic deposition this material is further annealed at temperatures >2000 °C/ hot pressed for converting into highly oriented pyrolytic graphite.

What do we do next? There is something known as the solubility of carbon-carbon solubility in gas phase, and that now becomes an important parameter. We know that there is a possibility that methane will split into carbon and hydrogen at a certain pressure and at a certain temperature. The optimization of this temperature and pressure condition is important to us.

This is determined by the solubility of carbon in gas phase or carbon solubility. This basically is defined as the total amount of gaseous hydrocarbon which is in equilibrium with the carbon solid carbon that is known as the carbon solubility in that gas phase. There are certain curves that you see in this diagram. You see that this is the fraction of your carbon and this is the heat treatment temperature.

You may or may not call it the pyrolysis region. In the pyrolysis region, we got some carbon and hydrogen from our methane. This is the part when we are going to do the deposition. You see these different curves at different pressure values. And these curves are basically known as the carbon solubility curves in the gas phase. And you will see that all of them show a certain minimum value. They show a certain minima, which is different at different pressures.

At approximately 10^{-2} bar, they minimize at around 1100°C or something like that. What does this mean? This means that this is the optimum temperature for collecting the solid carbon. This is the optimum temperature where you should perform the deposition operation.

One more interesting thing that you see from these curves is that as you keep on increasing the pressure; the minimum value keeps shifting towards the right. So, for example, it goes all the way to 1900°C and when we are performing pyrolysis we want to actually start collecting our carbon as soon as possible. So, if we want to do it at lower temperatures let us say 800°C or 700°C, what is the option? Well we can keep on reducing the pressure. So, at 10^{-2} already, it can be deposited at 1100°C. And if we go to 10^{-3}, to 10^{-5} and so on, we go in the millibar pressures, in that case, you can slightly shift your curve towards the left. So. you will be able to collect the carbon at 800°C, that is deposited from your methane. This is basically the idea, this is basically the mechanism. And if you understand that and then you can play with these parameters, then you can find the optimum conditions. In fact, that is how modern-day CVD is developed.

In the past, we were only performing pyrolysis of gaseous hydrocarbons for making graphite. But then people realized that by changing these pressure conditions, by changing all the parameters, we can actually get single layer of this graphene-like structure.

And in fact, nowadays we use graphene for a number of applications, but by optimizing these parameters which are shown here, then you can actually get better graphitic carbon or get single layers of carbon or get few layers of carbon, and so on.

One more important thing is that when the solid carbon is formed, and then you also have some hydrogen in the process right. So, your methane splits, you have some solid carbon, you have some hydrogen, and you also have still some methane in your system. And if you are working with not just methane, but slightly larger hydrocarbons, for example, alcohol vapors and so on. You may also have another hydrocarbon present in your system. All of these things will have their partial pressures. It will never happen that at 1000°C inside reaction chamber, you have only solid carbon or you have only methane or you have only hydrogen, you will typically have a mixture.

You will have a partial pressure of each one of them, and that is why it becomes very important that you know the solubility of carbon. It becomes very important that you need to know at what point do you have the highest probability of getting highest partial pressure from your carbon vapors. Now, these are not vapors.

So, this is also one more thing. Is it solid carbon or is it vapor phase carbon? When we were talking about the phase diagram of carbon, we did discuss that is there a possibility of having vapor carbon in the CVD chamber. The answer is yes. In this particular case, you may have some vapor phase carbon when it is forming from methane.

But vapor phase carbon is highly unstable, and it immediately tries to convert into solid phase. And we are collecting carbon on the substrate. But it is not impossible that in this mixture you have certain vapor phase carbon as well.

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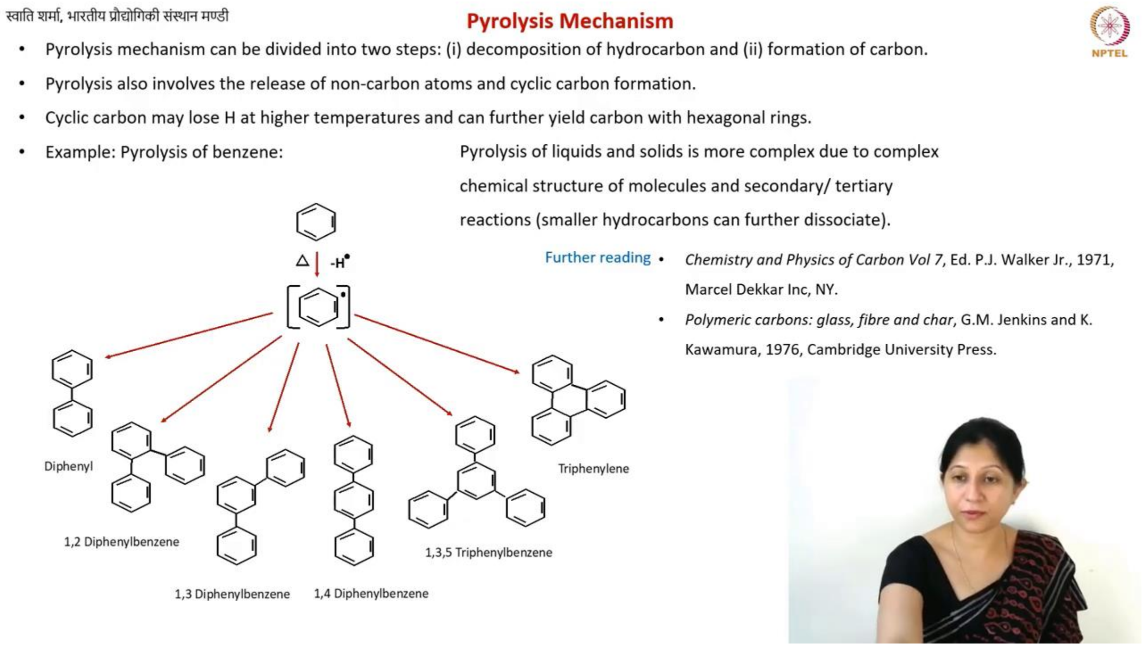

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Pyrolysis Mechanism

- Pyrolysis mechanism can be divided into two steps: (i) decomposition of hydrocarbon and (ii) formation of carbon.
- Pyrolysis also involves the release of non-carbon atoms and cyclic carbon formation.
- Cyclic carbon may lose H at higher temperatures and can further yield carbon with hexagonal rings.
- Example: Pyrolysis of benzene:

Pyrolysis of liquids and solids is more complex due to complex chemical structure of molecules and secondary/ tertiary reactions (smaller hydrocarbons can further dissociate).

Further reading
- *Chemistry and Physics of Carbon Vol 7*, Ed. P.J. Walker Jr., 1971, Marcel Dekkar Inc, NY.
- *Polymeric carbons: glass, fibre and char*, G.M. Jenkins and K. Kawamura, 1976, Cambridge University Press.

A little more about this mechanism of carbons and of pyrolysis. We already talked about the pyrolysis of methane. In general, this is also kind of obvious to you that pyrolysis can be divided into two steps. One is the decomposition of hydrocarbon, and two is the formation of carbon.

Formation of carbon continues to take place even after your pyrolysis is over or that range of temperature is over, even at higher temperatures. But the carbon formation is one thing, and the rearrangement of carbon-carbon bonds is another.

So, when we are talking about carbon formation here, we are talking about the formation of carbon from the hydrocarbon. And then whatever happens like carbon-carbon bond formation and rearrangement or reorganization that happens at higher temperatures. In fact, we will also talk about the graphitization, carbonization steps.

But in this particular case, as I mentioned that there is also certain cyclic compounds that are being formed, this is the number 3. On the first slide, we discussed that there are couple of things that happen during pyrolysis. We have already talked about the decomposition aspect. Now, let us talk about this carbon formation aspect. You get certain carbon and there may also have these cyclic compounds being formed.

Now, this will depend very strongly on the precursor and the nature of precursor, but I have just taken a simple example of benzene not very complicated hydrocarbon. Because we you can see how the benzene rings split, and then they form a radical. And then this radical can actually lead to a number of different cyclic structures which will then lose their hydrogen at higher temperatures, and then they will yield carbon which has those many rings.

Here you see, you have in the beginning this one benzene molecule which loses one hydrogen at higher temperatures. You will now understand from this enthalpy diagram at which temperature will benzene decompose.

Now, you do not have one radical, but you have multiple such radicals which can attach to each other which can organize themselves to give you so many different organic compounds. These are still hydrocarbons; they still contain hydrogen. So, this does not happen at very high temperatures but at 300-400°C, these are very initial stages of benzene pyrolysis, but you already have cyclic compounds being formed.

There are actually many examples, if you take naphthalene, if you can take any of these simpler aromatic hydrocarbons, and then you will immediately see that they lead to cyclization. However, aliphatic hydrocarbons also may lead to cyclization, we are going to learn about that in the carbon fiber for poly acrylic nitrile is a good example for that.

As I already mentioned, basically pyrolysis of liquid and solids is a little more complex and that we are going to learn about them in some other lectures. What is important is the further reading, so there are these two books that I have mentioned here. I have tried to collect some information also from these books and presented it here, but these are for further reading.