Carbon Materials and Manufacturing

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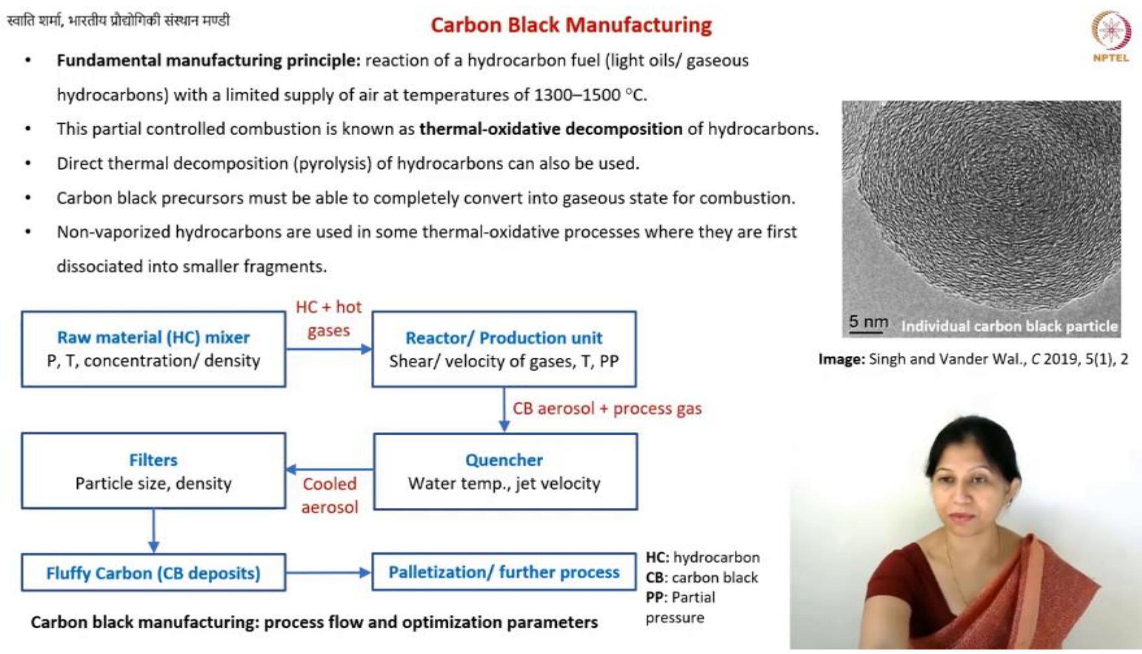
Lecture - 32
Carbon Black: Industrial Manufacturing



Hi. So, let us now talk about the Manufacturing of Carbon Black. So, let me first quickly remind you what is carbon black. Carbon black is nothing, but you have nano-scale carbon particles which are formed by controlled combustion of certain hydrocarbons and these particles are then fused together to form bigger larger clusters which are of the 1 micrometer size range.

And, here you can see one transmission electron micro gap where the scale bar is 5 nanometer. Now you can see how these crystallites are organized inside your carbon black particles. Carbon blacks also contain some impurities, but again in a controlled fashion. So, you may have certain fraction of tars because these are essentially un-burnt carbon particles, but the most important thing is that you need to have these nanoscale particles and a bunch of grape kind of morphology and that is why you call it carbon black; carbon black is not soot. This is something we discussed in the previous lecture.

I think I said that in the previous lecture that what is very interesting for us? This is probably the only carbon material that we are going to study in this course which is formed by combustion and not just pure pyrolysis. So, the process of manufacturing is a combination of combustion and pyrolysis.

And, these two processes in the case of carbon black manufacturing are really difficult to separate. You cannot say this part was pyrolysis and this is combustion. The idea is that here also you take a hydrocarbon as a precursor because for every carbon material hydrocarbons are essentially your precursors.

If you remember in one of the lectures, I think it was HOPG lecture somewhere or when we first talked about the pyrolysis of gaseous hydrocarbons, I had shown this a diffusion flame and premixed flames if you use them in a burner then you will get some kind of carbon.

People realized that hydrocarbons, especially volatile and gaseous hydrocarbons always yield some solid carbon particles when the temperatures are high enough on the decomposition. Now, the question is that the decomposition is just thermal in that case of pyrolysis, or is it thermo oxidative in that case of combustion. The terminology combustion, you will use when you have excess oxygen, but in this particular case we do not have excess oxygen and that is why we do not call it combustion. We rather call it thermo-oxidative decomposition.

This is the experiment where you had the carbon smoke being produced and then we collected the carbon smoke and then we filtered out the particles of that candle experiment or the diffusion flame experiment, that is something that also is very important here.

This is thermo-oxidative decomposition and you can also in extremely few cases, especially when you are using acetylene, then you can use some pyrolytic process as well. So, that is something that we will call thermal oxidation, but the most common technique at least the industrial production, even though the precursor can be acetylene, but the thermo-oxidative decomposition is more common in the case of a carbon black production.

Because now here we are basically taking fuel and we want to burn it and to make sure that the burning is done in a controlled environment, but we want to burn it. So, in that case, what is very very important is that your fuel gets completely mixed or vaporizes completely into the oxygen or whatever gaseous mixture you are using.

That is also very important because only then you are going to get these well-defined nanoscale particles, which ultimately form your larger clusters. So, if you have noticed in the previous class that I had shown this transmission electron micrograph, what is very important to note in that these nanoscale particles which form the entire cluster are very well defined.

If you see that actually, they happen to be almost always approximately 12 nanometer. So, that is like the optimal optimum size. So, in order to get those very highly controlled sizes of nanoparticles, you need to make sure that the process is bottom-up and for it to be a bottom-up process you need to have your fuel completely vaporized inside or hydrocarbon completely vaporized inside your gaseous mixture.

So, this hydrocarbon also I said fuel because often we use the term precursor when we call it pyrolysis, but in the case of combustion we can also call it fuel and you can also use hydrocarbon gases as fuel. So, methane can also be the natural gas that is your fuel.

And, similar to other pyrolysis processes you can use light hydrocarbons as well in fact, sometimes you can even use light oils. So, if you are using these light oils, in that case, you need to make sure that they are disintegrated before they go inside your reaction chamber, where the actual combustion is going to take place. The idea is to have a very uniform distribution of your precursor inside your gaseous mixture.

Now, let us talk about this process flow chart that will make it more clear. The first thing you have is your raw material or whatever is your hydrocarbon. The first step is mixing. So, this is what we are talking about. So, there will be various parameters: how do you mix something inside gaseous fluid? You are basically using the shear forces of your gases and there you will need to control the velocity of your gases. So, that is one option.

Now, it depends, you will need to optimize the concentration of your fuel inside your gas gaseous mixture which by the way definitely contains oxygen or air; it is sometimes also called combustive air. So, the optimization parameter, here I have written in black color. I have written the parameters that need to be optimized at that particular stage or at least the main parameters.

Here you are going to control the pressure, you are definitely going to control the temperature. The temperatures here are often 700 to 800 °C already, and you will definitely control the concentration. If you have oil-like particles as your fuel then the density of that oil or whatever hydrocarbon then the density also needs to be optimized. So, this is step number 1.

Now, what happens? From this mixing chamber now you will have your hydrocarbon mixed inside the hot gases, which then goes into the next chamber, which is your actual reactor or your production unit. These reactors can be of different types and scale.

The carbon black production plants have hundreds of thousands of tons of capacity being produced every year or you will also have a slightly smaller scale carbon black production plant. So, depending upon that and also depending upon what is the process.

So, there are four or five different ways of making carbon black which we are going to discuss in subsequent slides. The point is that based on that, your reactor design can differ. You may have a furnace and not really a reactor, but you can also have a reactor. You can have a fluidized bed reactor similar to what you had in activated carbon.

That is why I am not going to describe individual types of furnaces or reactors because reactors that are similar to activated carbon can also be used here. Now, the optimization parameters: now remember that you do not have pyrolysis here. You have burning, you have combustion taking place in this chamber.

So, you definitely need sufficient oxygen or air supply and there you need to ensure that you have the correct partial pressure of gases because you are supplying air and you are forming carbon dioxide, carbon monoxide because when there is any burning taking place and definitely you have a lot of flue gases.

You have a lot of gases that may not participate in the reaction, but you need to ensure that they are removed. So, you have to ensure that the partial pressure of all these gases that are being supplied or being generated, are optimized such that you have the optimum combustion taking place such that you also have some formation of solid carbon particles. Not all carbon is converted into carbon dioxide oxide or carbon monoxide.

Also, you will make sure that the shear forces between the gases and the velocity of gases is optimum. In some cases, when you are using a very small hydrocarbon as your fuel, not oil or anything in that case you cannot have the mixing chamber.

Although in most cases you have the mixing chamber because for example if you use methane, in that case, you will also ensure that there is proper mixing of your fuel in the reactor itself or you can also have the premixed fuel. This is your primary unit where the production is taking place.

Now, from here what goes out? this carbon smoke, this is practically smoke, but the particles in this smoke, unlike soot or anything, are very well defined because you do not just spray the fuel, you make sure that the fuel is very uniformly distributed and that the particles of the fuel are very very small.

So, that is why you have well defined carbon particles formed here, but they are in the form of what is known as the carbon aerosol and this also contains the process gas. Process gas here would also contain some carbon dioxide, carbon monoxide. So, all of these hot process gases and the aerosol of carbon black. Because this entire mixture is still hot, so you now need to quench and with quenching what you are also doing is you are just stopping the process there, no further burning takes place after that. So, you will have a typically water-cooled chamber when you perform the quenching. And there the optimization parameters are the temperature of the entire chamber, temperature of water, and also the velocity of water jets. Sometimes you will spray the water. So, all of these are then your optimization parameters.

Now, you basically have your carbon black, but now this is in the form of a cooled aerosol which then goes inside filters of various types. So, I have only shown one box with a filter, but there may be multiple filters also and in these filters, you obtain a fluffy carbon material, fluffy sponge like carbon deposit. And, in fact, it is also industrially sometimes called fluffy carbon.

So, now you get your fluffy carbon deposits that are essentially your carbon black. Now if you want to sell your carbon black in the form of pellets then you will perform pelletization which could be dry pelletization or wet pelletization. You can also perform further processes for example, in some cases oxidation is performed for these particles because oxidation then further lowers the density.

Because some oxygen will consume your carbon particles, right? You can even get a hallow particle in some case. So, in that case the density is much lower, but that of course, depends on the requirement. Why do you really need low density? That depends, if yes then you can also perform further processes. So, this is the basic idea of the process of carbon black manufacturing.

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Carbon Black Manufacturing

- Carbon black precursors must be able to completely convert into gaseous state for combustion.
- Cluster morphology and particle size can be tuned during manufacturing.
- Carbon blacks can be produced in turbulent (closed furnace) and diffusion (candle-like) flames.
- Based on the reactor and process type, carbon black production is classified into six main categories:
  furnace, lamp, Degussa, channel, thermal and acetylene black.
- Non-vaporized hydrocarbons are used in some thermal-oxidative processes where they are first dissociated into smaller fragments.

Table: Classification of carbon black production methods

Production system type	Process	Precursor
Thermal-oxidative decomposition		
Closed system (turbulent flame)	Furnace black	Aromatic oil, natural gas
Closed system (turbulent flame)	Lampblack	Aromatic oil
Open system (diffusion flame)	Degussa (gas) black	Coal tar distillates
Open system (diffusion flame)	Channel black	Natural gas
Thermal decomposition		
Discontinuous	Thermal black	Natural gas/ oils
Continuous	Acetylene black	Acetylene

Further reading:

Carbon Black : Science and Technology, Jean-Baptiste Donnet (Ed), CRC Press, 1993.

This is something we already talked about that whatever precursors you take even if they are light hydrocarbons, alcohols, whatever or oils they should be able to completely convert into this gaseous phase and we are saying gaseous phase means you should have small enough particles that are a uniformly distributed through your gaseous phase.

This will actually determine the morphology of your individual particles and your cluster. So, by changing the hydrocarbon precursor or by also changing its distribution the concentration of your hydrocarbon precursors inside your gases is what determines the size of the cluster because cluster size is important.

The smaller particles that make the cluster, their size is often already defined because this is a bottom process and there is a certain optimum size 10 – 12 manometer that is where those particles will stop growing. So, that is already well defined.

The larger particle size and the morphology can be slightly tuned but not very much, but slightly tuned by optimizing these parameters especially the concentration and distribution of your hydrocarbon inside the gaseous mixture. Now, what is important? So, I said that you can have different types of furnaces or reactors.

Often when we talk about activated carbon, any other form of carbon and later on we will talk about carbon nanomaterials and we will talk about CVD reactors. All kinds of reactors, have certain features that then define them. Either they are closed systems or open system, that is one feature which can always be used for differentiating between your reactors. What you can also have is now in this particular case, you have flames because you are performing, burning, right. So, you have flames.

Now, you can have either turbulent flames or you can have diffusion flames. So, what are turbulent? As the name suggests turbulent flames have a sort of turbulent flow of gases and the species that are produced, but you will typically have these kinds of flames in a closed system.

f you have flames in a closed furnace-like system, then you will have turbulent flames and the open flames which have enough oxygen will typically be diffusion-type flames. Now, again if you remember from this lecture on HOPG when we talked about diffusion and premixed flames, please go over that one more time. That will tell you the difference between premix and mixed and diffusion.

Basically, you are either supplying the fuel in the beginning itself, you are already mixing it with your carrier gases or you are supplying the fuel afterward. So, that also basically is the optimization process for your quantity of fuel. So, in both cases, you can get carbon black, but this is one of the criteria of classification.

Based on all of these factors you have these six main types of carbon black production reactors. You have furnace black, lamp black; lamp black is something that is a very common term you might have heard. Then you have Degussa black; this is named after scientist who developed this process Degussa black. And then Channel black; channel black process nowadays is obsolete, but this is still one of the first processes of making carbon black. Then there is thermal black process also, there is acetylene black processor. So, these are the primary processes that are still used.

Furnace black and also acetylene black in my opinion is the most common one. Now, we are going to also learn about the further classification of these or what is the process, why do we give this name to a particular reactor.

So, I told you before that there is thermo-oxidative process and then there is just thermal deomposition. So, pyrolytic and combustive both types of processes we have. But, in most cases t we are going to use thermo-oxidative. We do not call it pure combustion because we do not supply oxygen in access.

Here is a chart, you can see these different types of processes that I have just mentioned furnace black, lamp black, Degussa black and so on. What are the precursors for each individual process and what is the type of system, whether you have turbulent or diffusion flame and whether you have closed system or open system.

The last two thermal black and acetylene black, you see that these two are actually thermal decomposition processes. There is very little to no oxygen in the case of these decomposition. Mainly thermal, oxidative part is much lower to none.

There you can have either a discontinuous or a continuous process and in that case you can also use different types of precursors. Acetylene black which is a common process for making carbon black, also industrially used a lot. This process as the name itself suggests that the precursor is going to be acetylene.

You can find a lot of publications where people have used other precursors. So, whatever I have written here, some of them are more general in nature anyway. When I say aromatic oil? There can be a lot of different types of aromatic oils. Nowadays, there is also a lot of attention to making carbon black from the waste pyrolysis oil.

So, when you perform partial combustion or pyrolysis of urban solid waste then there are some oils produced and these oils do not have very high a calorific value. They are a mixture of a lot of hydrocarbons. They are very tarry products, but one application of these oils is also for the production of carbon black. So, these are basically all the methods of carbon black production.

If you want to read further, so there are many more details of each individual type of reactor. As I said that some of these I had already covered in activated carbon lectures I am not going to repeat them, but if you want to read further details this book Carbon Black: Science and Technology by Jean-Baptiste Donnet is very that is kind of it gives you a complete overview.

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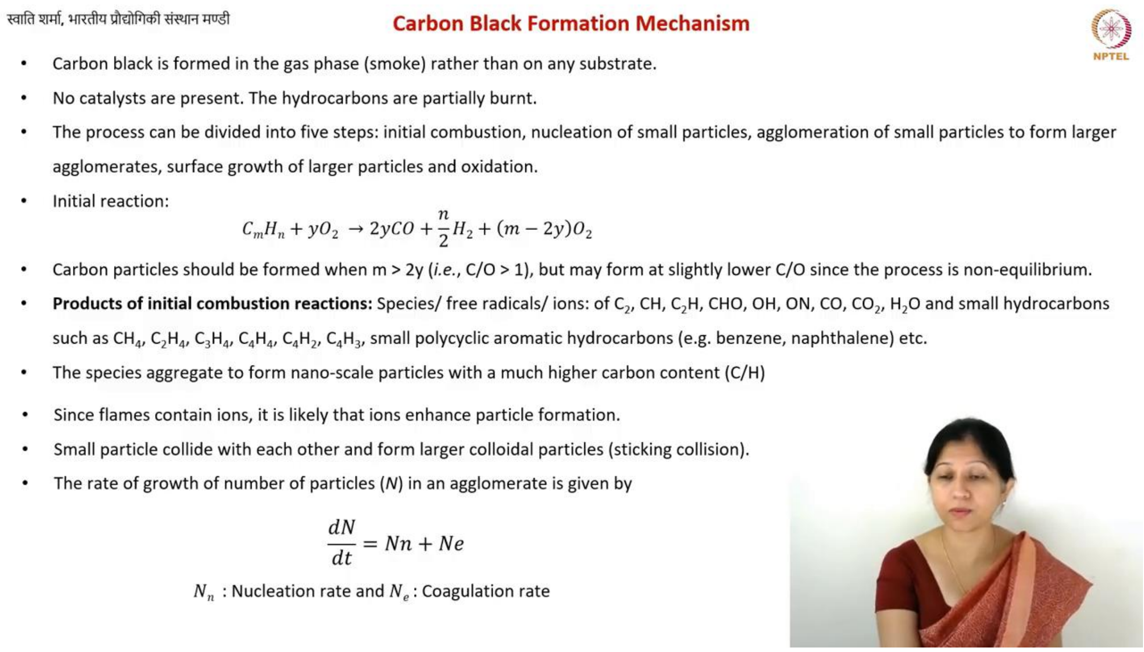

We are now going to discuss the mechanism of the formation of carbon black. This mechanism is very interesting for us. Why? Because it is different, it is not pyrolysis. Whenever we have pyrolysis, we have a hydrocarbon decomposing and then we have small carbon species are formed then they combine together, and then often we are using catalytic substrates.

But, none of those things are taking place here, this is just combustion. How can you have controlled combustion? That is an interesting part. Everything can be burnt and then we know that when something burns, carbon particles are produced then those particles are also sometimes polluting the environment and what not.

But, can we also have this very highly controlled combustion, and if yes, in that case how do we do that? That depends on the mechanism of the formation of carbon smoke. So, let us talk about this a little more. We do not have any substrate. We often have the hot wall type of reaction because the entire process taking place in the entire reactor not just on top of the substrate.

So, this is very important. No catalyst is present in the system because you are just burning something. You do not really have any well-defined growth. It is more a glamorization rather than growth on a substrate or catalysts. So, there are no catalysts typically present and the idea is that the hydrocarbons are unburned or partially burnt and that is why they also contain some tars and so on.

If you want to understand the mechanism we can divide the process into five different steps. These are five main steps. Now, each step can also have certain sub-classification or sub-steps. So, let us see what happens. First thing is that the initial combustion reaction.

You have this reactor, with you have the fuel and the mixer, and you already have high enough temperatures. There you have 700-800 °C. So, there is some initial combustion taking place. That initial combustion is already generating a certain type of carbon species. And, those are still hydrocarbon species. They can be hydrocarbon as well as carbon species.

So, this is going to be slightly different from pyrolysis. If you perform pyrolysis of methane and then do certain gas analysis using say mass spectrometry then the kind of species that you are going to find are going to be different compared to what you are going to find here because you have oxygen present.

But, there is some sort of plasma some type, mixture of ions and reactive species that is being formed during the initial combustions that is your step number 1. The second part now, you get these smaller nanoscale particles, they start to form. So, there is nucleation and growth.

Then once you have these large enough particles, although this happens pretty fast within seconds. But once you have large enough particles, now these particles start to agglomerate. And, then agglomeration also is a very important step and if you suddenly quench it or suddenly change the conditions inside your reactor, in that case you can also stop the agglomeration at a certain point.

Now you will have the agglomeration and then you can also say that nucleation of the agglomerates. So, earlier we were talking about nucleation of the nanoscale particles, now we talk about the nucleation and surface growth of the agglomerate, small agglomerate. Then first like few nano scale particles come together and then more start to attach onto the same cluster.

Sometimes the chain of clusters can also be is also possible that is in fact, often happens. There is one more step of oxidation. So, as I mentioned oxidation is inevitable in this process because you have oxygen, but why do not all carbon particles just get oxidized? Well because we have a controlled amount of oxygen.

Sometimes after the agglomeration, you will perform another step essentially to oxidize some of your tar-like materials and some of your carbon also gets consumed in that. So, these are different process steps. What is the initial reaction? So, when we are talking about this initial combustion, so you have a hydrocarbon you have oxygen and then you have the formation of well carbon monoxide and carbon dioxide.

$$C_mH_n + yO_2 \rightarrow 2yCO + \frac{n}{2}H_2 + (m-2y)O_2$$

This is typically what you see and also there may be some hydration that is formed. So, this is the initial reaction and if you carefully observe this reaction, you will see that when the value of m is greater than 2y. You see, where is the m and where is this is C_mH_n type of hydrocarbon and then you have y oxygen O_2.

When the value of m is greater than 2y which if you will calculate, you will see that means the carbon to oxygen ratio is greater than 1. In that case, your carbon particles should be formed, but often in practice, it does not happen. You can have slightly higher or lower rations, but in principle, this ratio of carbon to oxygen should be greater than 1 in order to for this combustion to take place.

One more very important thing here is that this is often a non-equilibrium process. The formation of carbon black altogether is a non-equilibrium process and that is why it makes it very difficult to analyze and to figure out exactly what should be the process parameters. Because this is a non-equilibrium process, most of the thermodynamic and kinetic aspects that we talk about, are valid only for equilibrium conditions, equilibrium reactions.

And, this is a non-equilibrium process especially when we continuously provide oxygen and that is also the reason sometimes you will have the formation of carbon even at 0.5 carbon to oxygen ratio, but in principle, it should be greater than 1 of. For equilibrium conditions, it should be 1.03 or something slight just above 1.

I said that this initial combustion takes place. A lot of carbon species are formed some of them I have mentioned here. So, CH, C_2H, CHO and all of these OH species. Of course, if you have any nitrogen present in your system in your precursor, then you will also have ON species and N so on.

You see that there are so many different species. what is also very important you have C_2 molecules. We did not go into the details of C_2 molecules, but I did mention it somewhere that you can actually have between C_2 to C_8 carbon molecules. So, that have been recognized. Of course, we also know that we have fullerene which is C_{60}, but there we are talking about the larger scale molecule with a well defined geometry.

Here we are just talking about hydrogen H_2 or O_2 can you also have C_2? Yes, but this is an unstable molecule. In fact, during the combustion and pyrolysis of hydrocarbons, this is where you often find these kinds of interesting carbon species.

So, we have C_2 also present. When you do the gas analysis mass spectrometry also you have CH in all of these species that I have mentioned here. You can see that you will also have some methane present. So, of course, this will depend upon what is your hydrocarbon precursor. But these are the possible species or these are the species that have been experimentally validated in such systems.

And, you will also have some polycyclic aromatic hydrocarbons. You will also have some benzene formations, some naphthalene formation, or sometimes the larger hydrocarbons will dissociate and form benzene and naphthalene. Sometimes the very small hydro-carbons like ethane above 500 °C may even form carbon species which will then cyclize at around 800 °C.

You can even have the bottom of formation of benzene and naphthalene, but these are the species that you will find in after the first step of your mixing and heating. Now, let us go to the next part. You have all these carbon species formed and now these species although they are not carbon species, they are still hydrocarbon species and they also contain oxygen or however, these species will then start an agglomerating and they will now form nano-scale particles.

And, these particles compared to the initial species, of course, they have much higher carbon content; so, much higher carbon to hydrogen ratio now after the agglomeration. So, this is the nucleation of your nanoscale particles, nucleation of the small units that ultimately form the carbon black.

One more important thing is that all flames contain ions and ions are very high energy particles. That is what you call plasma when you have highly ionized systems. This is not completely plasma, but all flames do contain certain amount of plasma and this plasma is always high-energy system.

And the interaction between two molecules and the interaction between one ion and one molecule if you compare their energy, there is a higher probability and higher transfer of energy, when there is an ion interacting with the molecule or a species.

So, this plasma is present in the system and most likely the entire process is also plasma enhanced. Basically, these ions enhance the formation of carbon particle, the nucleation and especially during the growth part; if not nucleation definitely during the growth part, plasma is also helpful.

Now, we already have these small particles. Now, they colloid with each other to form larger particles, and there of course, you have a colloidal force. There you have interactive forces that are very important. There is something known as the sticking collision. So, they stick to each other after the collision and they rather they do not bounce back.

This sticking collation takes place which now has the nucleation of larger particles and the growth of larger particles and that can be represented using this relationship. So, the rate of growth of the number of larger agglomerates particles is the term that I have used here that N. N is the number of particles.

And how what is the rate of the increase in the number of particles, then there is this formula

$$\frac{dN}{dt} = N_n + N_e$$

Where N_n is nucleation rate and N_e is the coagulation rate.

Nucleation of larger particles and the growth of larger particles both of these things are happening at the same time. So, both of these aspects need to be factored in and that is how we find out what is the growth of the particles in the system.

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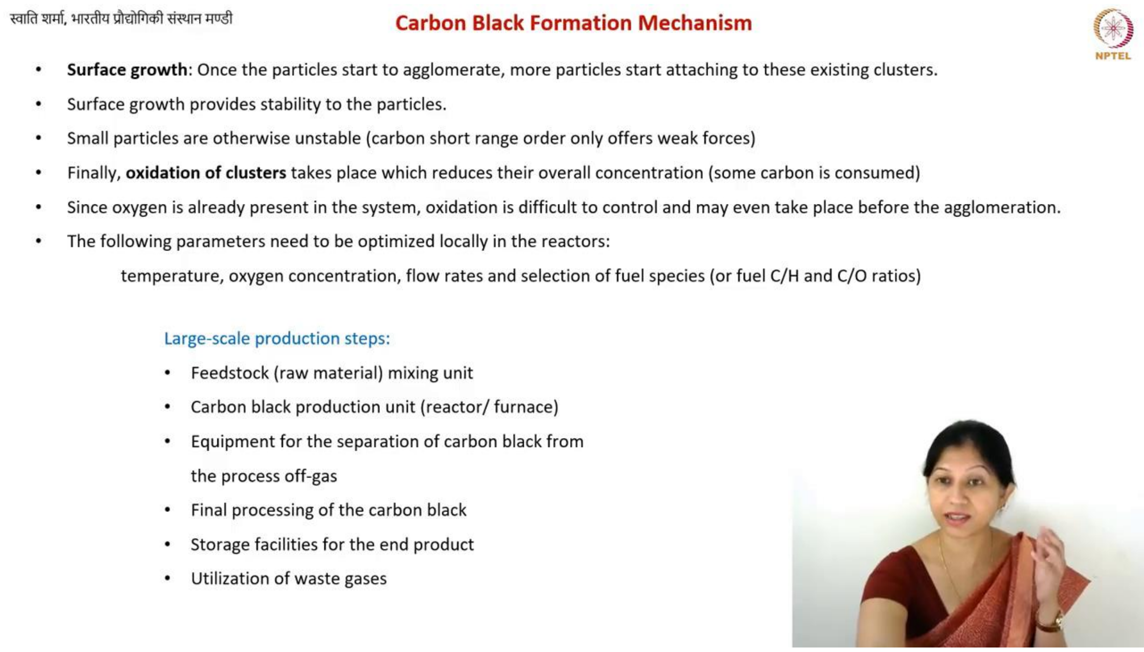

A few more things about the growth. We talked about the nucleation and growth of the larger particle which we can also relate directly to the surface growth. When the particles are growing basically their surface area is increasing. So, this is the next step so to say. It is at least studied independently as surface growth. So, more and more particles start to attach. We have a small one and then more and more particles start to attach somehow, they stop at approximately 1 micrometer. So, this is the surface growth. Why is this happening? Because it provides stability to the particles, you can see that these are turbo static particles and even within the turbo static particles the nanoscale particle if you see the microstructure, you do not have a very good order you only have a short range order. So, even the bonds within the carbon sheets and among the carbon atoms are not so strong. You also have a lot of defects. So, altogether these are not very stable systems if you think about each nanoparticle.

In order to gain stability, it tries to attach or stick to another similar particle and these large particles then provide overall structural stability, otherwise, a single individual carbon black particle would be rather unstable. As I said there are weak forces within the carbon within the carbon sheets that are microstructurally present in your carbon black particle.

Now, we have the particles, now we have the clusters and the final step is one more oxidation step. You often perform this step because for two reasons. One – you want to still get rid of some tarry particles because there are impurities Second – you want to decrease the density of your particle.

Some carbon will be consumed and in fact, this needs to be done in a highly controlled fashion otherwise all of the carbon will be consumed. If you are performing it in a control the fraction of oxygen, in that case, your basically just reducing the density a little bit. The overall concentration of the particles inside your chamber will also reduce because some carbon will definitely get consumed at this point.

Oxidation makes your particles more reactive because on the surface, you can also induce certain functional groups this way. However, you need to do it in a very controlled fashion. So, these are the steps in your formation of carbon black in the mechanism.

Now, we can also think of some optimization parameters here. The temperature of course, in all cases anything that is happening at high temperature needs to be a temperature-controlled, but here also it is very important. Each mixing step will also have a certain temperature, then the reactor is between 1300 and 1500 °C in most cases.

So, the temperature needs to be controlled also when you perform the quenching and then collection and so on. Oxygen concentration of course, otherwise it will burn your particles completely. You do not want to do that otherwise then it will become more like soots.

Also, the flow rate; again if the flow rate of gases depend upon your precursor if you have the oils and what is the concentration of your oil inside your chamber? The fuel species basically that also needs to be controlled. Otherwise, if you have too much if your fuel saturates your entire chamber you may end up getting larger fuel particles or larger droplets. In the case of liquid hydrocarbons and those will then form soot rather than a carbon black.

Then you will get these larger particles also attached to your carbon black particles. So, basically both carbon to hydrogen, carbon to oxygen ratio need be very controlled. So, if you perform large-scale production. So, this is kind of a summary again.

First thing is your mixing units; then you have reaction where you perform the carbon black production actually; then you have these various filters and separation equipment and then you will do the final processing where you might perform pelletization and so on. And, then ultimately it will go to your storage facility and end products.

This is more like a supply chain, but not the complete or production line. So, these are the primary steps. And one more important thing is that you might want to utilize the waste gases which is nowadays the big environmental concern. So, the utilization of waste gas gases is also another step.