Carbon Materials and Manufacturing
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Lecture - 30
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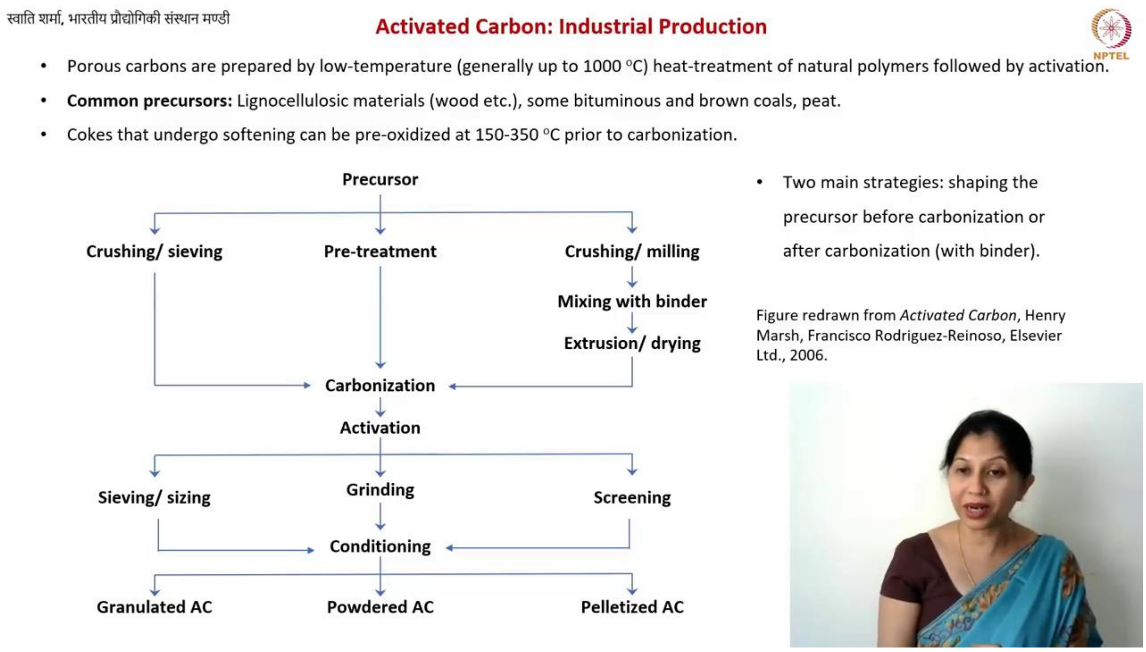

Hello everyone. Now, let us move on to the industrial production of activated carbons. So, You know what are activated carbons. These are porous carbon structures, they have a very good absorbance because of certain physical and chemical activation processes and of course, because of their pored network because they offer a very high surface area.

I told you that these are the carbon materials that are used for making water filtration columns, air purifiers, water purifiers and so on. How do we make these structures? That is actually not too complicated. You can take some shape of activated carbon, you can take granulated activated carbon, you can take the powder, you can also take larger particles or cylindrical particles, all kinds of shapes. And then you can pack them into a column depending upon your requirement, depending upon what kind of impurities are you planning to trap. You can also activate these carbons in different ways, you can also use impregnated activated carbons and there combine these columns with other for example, electrochemical reactions.

The physical manufacturing process of water filtration column would just be to pack a column and have certain filters and sieves, so that your water before going inside the column, gets primary filtration done. And when it comes out of the filter, then it does not contain any carbon in it, you need to make sure. So, this is basically it.

However, what is more important for us is how to make these granular or activated carbons themselves. You buy these cylinders in the market that you see, so how do you manufacture them? That is what we are going to learn. This is what I call the industrial manufacturing of activated carbon not using activated carbon, but of the carbon itself.

First of all, when we make any kind of carbon, we need to know what the suitable precursors for it are. As I have mentioned multiple times that activated carbons are derived from natural polymers in most cases, for example, wood which is a lignocellulosic material. Lignocellulosic means the structure itself is made of cellulose, but it also contains a lot of lignins, lignin also is a range of compounds which are these oily compounds and whatever other than cellulose practically. This is the primary material that you have in the wood, natural materials, agricultural waste and also basically plant materials. So, lignocellulosic materials are the primary source of activated carbon.

You can also use certain types of coals. So, if you remember, we use needle coke for making graphite. We also use certain other types of cokes for making glass-like carbons or other non-graphitizing carbons. Now, in the case of activated or char-like carbons, you could also use certain types of coals, not coke. So, coals are these relatively porous structures.

Why do we find all these different petrochemicals? Why do all these different petrochemical precursors give you different types of carbons? Well, they are formed by different precursors. So, if you look at the history or how they were formed, then all of them were ultimately at some point formed by different types of precursors. Whatever was the result of the conversion of natural wood like polymers, it may have converted over time into coal.

Now, coals are also of different purities, different qualities. In fact, in different parts of the world, you find different types of coals. For example, certain types of bituminous coals and also brown coals, are also used as precursors for making activated carbons.

Now, peat is also one more. Peat is something that is sort of organic material which has partially converted into carbon, but not completely yet. So, all of these materials are basically high carbon-containing natural materials that is what you use as precursors for making activated carbons.

You can also utilize certain cokes which do go through softening after heat treatment, but if you pre oxidize them in this range 150 to 350 °C, then you may be able to prevent this softening to some extent. These are rarely used, but they can also be used for the formation of activated carbon.

There are two main strategies so to say. So, if you think about the pallets or cylinders of activated carbon, either you can make the pallets before their carbonization itself or you can make it afterwards. So, what do you think is better? If you think about graphite-related manufacturing or glass like carbon, we are always providing the shape before the final carbonization step. Because once it is carbonized, then it becomes more difficult to give it a shape.

This is precisely what we also do in the case of activated carbon. So, we usually give the shape beforehand. You already take the precursor and make cylinders out of it and then, carbonize them. However, in certain cases, it is very difficult to shape precursor, to form it, in that case you can get the powder of activated carbon and then afterward you can use a binder and then provide a shape.

I have prepared sort of charts, there you can see. You take a polymer precursor, now you want to make palettes. So, for making palettes, what do you need to do let us say I give you a lot of wood. First, you need to crush it, you need to make sure that you will have to dry it first and then, crush it and make uniform sort of particles.

You may also need to do sieving because if you do the crushing of materials such as wood or the seeds of the stones, these are also precursors for making activated carbons. In fact, in India, you often use coconut shells for making activated carbon which actually gives you very good quality activated carbon. So, what you would do is you do crushing and then also sieving to remove like really big particles and to sort of make the size to some extent uniform.

Now, you can either do crushing and then, further milling rather than sieving for removing the bigger particles, you want to make sure that all the particles are utilized. In that case, for bigger particles, you might do milling. These kinds of processes, you will do to reduce the particle size.

In the case of chemical activation of carbons, what we do? We pre-treat them. And in the case of physical activation we do not. But in the case of chemical activation, you would pre-treat your precursor. So, the pre-treatment already degrades your cellulose to some extent which makes it easier to shape it. So, these are the three pathways you will use in the beginning. Now, let us talk about the third one where we do the crushing and milling. So, we have basically a powder of your precursor material.

Now, here at this stage already you will mix it with a binder. Now, this binder again can be resin. In most cases, binders are some sort of resins that may not really give you char like carbon, but you are using reasonably small quantities and you need certain binder to hold to make pallets. You definitely need certain type of binder. So, that is what you will do and then, you might use extrusion techniques.

We also use extrusion in the case of a graphite-related manufacturing for plastic materials. So, plastic extrusion is a very common manufacturing technique. So, you will take this mixture of your cellulosic material and binder. And then, you will perform the extrusion to give it whatever shape is desired and if needed, then you will do drying or even cross-linking depending upon what kind of binder did you use.

Now, you perform the carbonization. Either you perform the carbonization for these particles that are mixed and you use the binder and you made the cylinders. Or you can directly without mixing. if you wanted powdered activated carbon after crushing and sieving, what you had in the first strategy you can already carbonize that. Or if you were doing the chemical activation, then you have the pre-treated material whether or not you made pellets out of it, you could then carbonize it.

After all of these steps, you will now perform your carbonization and this carbonization is not performed at as high temperatures as you would use for graphite. So, relatively lower let us say around 1000 °C carbonization.

After this, now, you have a porous carbon material in whatever shape you wanted it, now you perform the activation. In the case of chemical activation, this process already sort of started when you did the impregnation, but now you will further do some physical activation using for example steam, and this is your activation step.

After the activation, depending upon again what kind of shapes you want. Do you want to do sizing? Sizing typically means that you cut pieces so, if I make a very long cylinder and I want to make small cylinders out of it, that would be sizing. So, this you can perform. If you have powder, you can perform sieving again because you remember that there will be some change in the size during this process of carbonization.

It may not shrink as much as the other polymer shrink or other resin shrink, but some shrinkage will take place. But also because of all of this sort of harsh processing inside your furnace, you may end up losing your material. Some of your material will erode, that some carbon particles will come out, some of these cylinders may break or, some material damage might happen. So, you need to purify again, you need to sort your structures again.

You will perform sieving and sizing these kinds of operations or if you wanted a powdered carbon, then you would perform grinding or in some cases, screening. In the end, you will perform some conditioning. So, this is like a finishing step. So, you will perform certain conditioning and ensure that you have a material with a good purity and uniformity. And then finally, you will have different types of activated carbon, you can have granulated powder or pallets.

The idea is that you will either perform the shaping before in the precursor itself or you will have the material and then, afterward you will have a binder. In the next slide I am going to tell you how we perform the activation step. This is like the overall process you will use, starting from the precursor. But now, we are going to the step where we perform the activation of porous carbons. (Refer Slide Time: 12:09)

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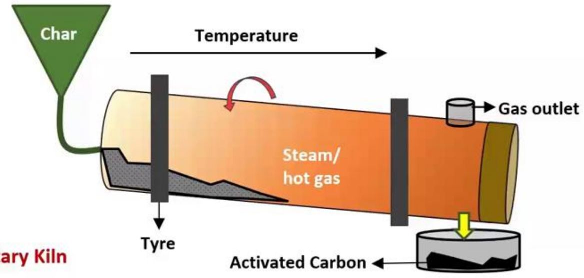
Rotary Kiln

- Types of furnaces/ reactors: (i) rotary kiln, (ii) multiple hearth furnace, (iii) fluidized bed reactor.
- Rotary kiln: Large tube-like set up with char inlet and AC outlet. The tube rotates during the operation. Temperature increases towards the opposite side. They are generally heated using a hydrocarbon fuel gas.
- **Advantages:** Rotation of particles enables larger surface area that comes in contact with heat and steam.
- Particles move towards the other side due to inclined shape.
- Due to large size temperature gradient can be controlled in a precise manner.
- Rate of production depends upon (i) rotation speed, (ii) angle of kiln inclination, (iii) feed rate, (iv) steam injection.
- Rotary kilns can have a capacity of up to several tons. Temperatures can reach up to 2000 K.
- Operating conditions can be determined by simulating (i) mass balance, (ii) energy balance (iii) heat transfer.



A Rotary Kiln

The activation is performed in different types of furnaces, basically you need a furnace for all the carbon related operations. What is very important is high temperature furnace and these furnaces must have a controlled environment. If you do want to supply air in certain cases or you want to supply steam or you want to supply an inert gas or you want to supply a mixture of gases; in all cases what you need is a furnace which has a uniform; which has a very controlled environment. However, the size of these furnaces can vary.

You can actually have these really massive furnaces that have a capacity of several tons of material at the same time. So, you have really massive furnaces for processing, for the industrial process of carbons. At the same time, if you are making a micro nano device, we you will use a lab furnace where you have the tube diameter of just a couple of centimetres. So, the size of the furnaces may vary, but the principle remains the same.

Now, in metallurgy, you would read about several types of furnaces; different materials, different elements, different ores are processed in a certain different type of process because that mainly depends on the by-products that come out of it. Some of these by products can be corrosive or they can be very harmful or sometimes they can also be used as a primary material, as an initial material for some other chemical process. So, depending upon these, you should change the shape and size of the furnace.

The production of activated carbon is typically done at a very large scale. So, these the furnaces that I was talking about with several tons of capacity, those are the kind of things you will potentially use for making large scale activated carbons. That is also the reason you have this material is relatively cheap.

Now, when you use these kinds of massive furnaces, you may not be able to perform joule heating using coils which you would do in a lab furnace. Well you have a coil around your ceramic tube or quartz tube and that is performing the heating, the providing the heat. But in the case of several meters long furnace, you will rather use fuel; you will just use petroleum fuel and you will using these hot gases. In this case it is also not too difficult because the temperatures are not terribly high.

Rotary kiln is the first type of furnace that I am going to talk about. This is the one that is most commonly used for making the activated carbons or for activation of carbons and there are two other types of furnaces or reactors that we are going to talk about that. One is the multiple hearth furnace and other is the fluidized bed furnace or you can also call it a reactor. Reactor is a word typically we use when we have certain chemical reactions going on, here you can also just call it a furnace.

The first one, the rotary kiln. This is a very large tube like structure, several meters long. This is a metallic, typically made of cast iron which you will also make in separate parts and join them together. But this is a very large metallic tube where you have the steam and the hot gas that is produced by your fuel. Now, you can also have carbon dioxide, you can also have other gases, whatever you require for your activation of that type of carbon.

You have a very big tube, but this is where you have the steam flowing or whatever gases you need. You have the starting material here because now we are talking only about activation and not about the carbonization processor. So, starting material is your low purity carbon. Low purity carbons produced by the charring process are simply called chars. You will also hear the term bio-char because often these materials are prepared by biological like plant materials and. In many cases, they are prepared by waste materials. In fact, even if I talk about coconut shell or any fruit stones, these are waste materials. Your waste can be a starting material or useful material for something else. It is just waste for us, but it can be used.

Agricultural and forestry waste of all kind can be used for making chars and these chars now are prepared at lower temperature, so they contain impurities. However, they do contain porosity, so those are our starting materials and now we put them in our tube. Now, one thing you will notice in this tube is that it is an inclined tube, it is not a perfectly horizontal tube, it is slightly inclined and there is a reason for it. If you have the tube that is inclined, then the material can move along due to gravity, it will just move forwards. Now, as the name suggests, this is a rotary kiln, so this entire thing keeps on rotating, your entire cylinder keeps rotating.

If you have seen your concrete making machine on a construction site, you see these rotate for mixing, you use these rotational devices. So, this is also something that the entire thing rotates so, that your material, your char inside that can keep on rotating.

What else do you have here? You have fuel, you have hot gases but often you are putting your source of heat on the other side, opposite side of the feed. Why are you doing that? So that the gases flow this way. You can see the arrow here, the more you go towards the end of the furnace, the temperature increases because the heat source is at the end of the furnace.

Why again? So that your materials slowly heat up. It does not immediately experience a very high temperature; it gradually experiences a higher temperature and the impurities are gradually remove. You can have tar like impurities, you can also have you can have other things, you also want to make sure that you impregnate steam into it.

In initial stages, you will remove your impurities and at some point, you will get the material the impregnated with superheated steam. So, the temperature is increasing along the length of the furnace. At the end, now you also have the material moving due to gravity and you will collect your entire activated carbon.

Here I have drawn only a very basic schematic. Of course, this is not how an industrial plant would look like. As I mentioned, these are massive structures then they will have a lot of different seals, you may have multiple gas outlets, you will also have some steam injection, gas injection.

All sorts you will have, different valves, different seals, also these two big structures, they are like tyres around; they are not rubber tyres, but these are called tyres. So, these are ring like structures around your furnace or kiln. You can even move this entire thing. So, this is the basic diagram, the idea you can understand.

Why are we doing all of this? There must be some advantage of this kind of design right, why are we not using just a standard furnace? We are using this tube like furnace because number 1, in all tube like furnaces, all the by-products can be easily removed relatively. But the scale of manufacturing is so large that our goal is also to make sure that all the particles that we have, all the char particles that we have inside of any size; we want to make sure all of them to experience as much heat as possible. All of them come in contact with the steam for as long as possible.

This time, this duration of your solid material coming in contact with the gases, is known as the residence time. You want to increase the residence time and you want to also make sure that all the surfaces of your particles experience some heat.

If you keep on rotating them, then each surface come in contacts for a long enough duration with the steam or other gases also, this will lead to the heat transfer between the particles. So, heat transfer is not just between the wall of the furnace and particle bed, but now, your heat transfer is also between the particles. So, to ensure all of these things, these are some of the advantages of this design.

One more advantage is that you do not really need to push the particle, you do not need to remove them. Because of their weight, because of the inclination, as they keep getting processed, they will come towards the outlet.

And because these are very large tubes so, you can control the temperature gradient very well because you may have multiple burners to heat your entire structure. So, you can have a good thermal gradient which means your particle is experiencing slow increase in the temperature and that is why the process is more controlled, so these are the advantages.

If you have to decide the rate of production, then what are the things that decide? Number 1, how fast you rotate your kiln. Number 2, what is the angle at which your kiln is tilted because that will determine how fast your particles move and they come out. Of course, depending upon the rate of the feed, how much char you are feeding in and how much activated carbon you are taking out. So, feed in, mass in-mass out that will determine the production speed. And also other factors such as the steam injection because that would determine the residence time. Sometimes you want to increase the residence time, sometimes you want to decrease depending upon what kind of steam it is and also it depends on the particle size and so on.

So, all of these things will determine the rate of your production. As I mentioned already that these furnaces have several tons capacity, in certain cases, you may also use high temperature rotary kilns, so the temperatures can go up to 2000 Kelvin in some cases.

You will first perform certain simulations so, you want to understand how your entire setup is going to function and then accordingly, you will decide on the process parameters or the feed rate and so on. So, typically whenever you want to model something, if I say that you need to model or simulate the operation of a certain rotary kiln, then you need to take care of the mass balance. You need to make sure the mass in and mass out; not just the char and activated carbon, but also the mass of the steam and how much solid is getting converted into vapour and how much vapour is converting into liquid and so on.

So, you need to understand all sorts of mass balance, you also need to understand the energy balance and of course, that is closely related to your heat transfer. So, all sorts of heat transfer whether it is between the inner wall or outer wall.

What is the heat that is being released into the environment and whether it is convective heat, whether it is radiative heat, you need to factor in all of these things and then, maybe come up with some differential equations. And this is how you model your system and then you perform the simulations and figure out what are the parameters that are required for your process.

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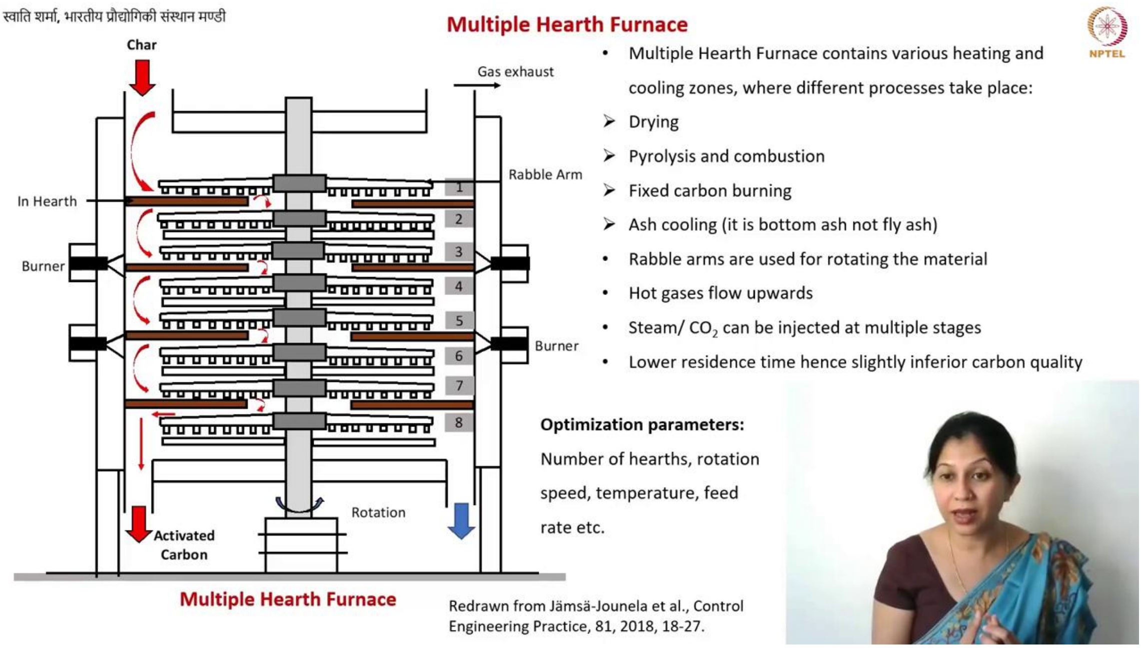

The next type of furnace that is used in the case of activated carbon manufacturing is known as the multiple hearth furnace. So, hearth is basically these furnaces that are made of bricks, more like this fireplace kind of furnace. You have refractory material. This is a schematic diagram of these hearth furnaces. Now, the names itself says multiple hearth furnace. So, here I have shown these 8 stages, you can have multiple stages, you can have less, you can have more.

The idea here is that you have these multiple hearth furnaces connected, this is a vertical system and you have various heating zones, you can have various cooling zones also and you can also have steam injection or any gas injection at multiple stages.

So, what do we have? Here we have this one shaft, you can see in the centre. This shaft is rotating. Now, you have these disc like structures. So, this is a cross-section, here you see disk like structure and you pour your char, your feed from the top. Now, it goes on stage 1 and then, you have what is known as rabble arm. Rabble arm are these structures which are made for rotating or spreading the material. So, they are made for rotation.

Now, the material is rotated on the furnace number 1, after that it goes to number 2, after that it goes to number 3 and so on and then again different processes are taking place at different stages.

In the rotary kiln, you had sort of a continuous operation, but here you do not have continuation of heat, you have these well-defined stages and the number of stages you can determine. Now, what happens at these different stages? Basically, on the first stage, if you have some moisture in your char, so first some drying will take place, second stage there will be some pyrolysis.

If you take the precursor and you want to make the coal, for that also these kinds of furnaces can be used. But when you want to just perform the activation in that case, pyrolysis may take place if you have some organic material left over in it, for example, for very low purity char. So, there may be some pyrolysis, some combustion, if you want to burn away the undesired impurities, so that will take place.

You will also have then some fixed carbon burn. So, fixed carbon is the carbon that you do not want to lose. Now, some gasification burning will take place as well that is what happens at the time of your activation, that you do lose some carbon mass during the activation. Whenever oxygen is present and you have some burning in that case, you will get some ash.

Ash is actually a big problem in furnaces. In all industrial processes, it is the ash formation especially in the case of carbonization pyrolysis based treatment plants it is the ash formation that is a big problem. There are there is certain type of ash which is extremely light, and it flies. So, it basically goes on top and then, there is certain type of ash which is relatively heavy, or the particle size is large enough or the process is done in such a way that the ash can be collected in the bottom.

Here in this particular furnace, you can see this is a vertical furnace. So, whatever products are being generated, they are coming to the bottom. So, the ash can also be collected in the bottom which is a good thing. This type of furnace does not generate much fly ash. So, this is also an advantage of this type of furnace.

Again, why would you choose a rotary kiln or why would you choose this; that would also depend on your precursor. Whatever type of char you have? Whether you have a already high purity char or you are using certain type of coals and trying to activate them or you are just using a very low purity char something that is generated from waste.

Because that will also determine how much ash content you will have. So, how do you want to collect it and based on these things, you can also choose which type of furnace. These are some other things that I have already told you like rabble arms are rotating your material. Here also you are performing the heating by using simple hydrocarbon fuels.

So, these hot gases are flowing upward. Here you also have a counterflow of heat similar to rotary kiln. So, you have feed from one side and heat from the other side. Again, but to ensure the same thing that the material slowly goes towards the higher temperature.

And then of course, you will have several injections where you can inject your steam or carbon dioxide, also you will have some gas exhaust outlet. This gas exhaust by the way is also known as flue gas.

Now, the problem with this kind of furnace is that compared to the rotary kiln, you have relatively lower residence time and that is why sometimes your carbon can be of relatively inferior quality. In fact, these are rather used for reuse of the activated carbons. So, these active all activated carbons can also be reused.

For example, in your house, once water purification column gets saturated with the impurities. Then you can just remove the carbon, you can take the carbon out of the of your column and then reheat it. So, for these kind of recycling purposes or reheating purposes, there these kinds of furnaces are more commonly used.

What will be the optimization parameter for this kind of furnace? Number of hearth; so how many stages do you want that is very important. What type of operations do you perform, if you have too much moisture or you want to gradually increase the temperature?

Then of course, as I said, these rabble arms are rotating your material so, the speed of that rotation would decide your residence time. And the temperature at various stages and feed rate in and out; all of these things are your optimization parameters for these kinds of furnaces.

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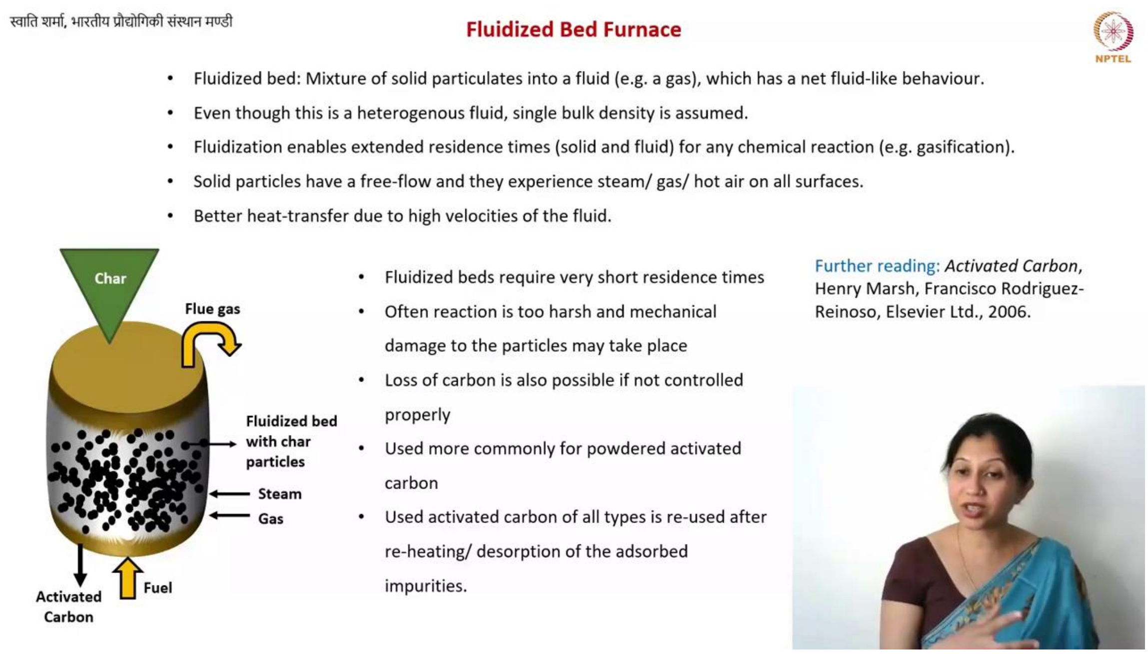

The third one that we will quickly discuss is the fluidized bed type furnace. What is a fluidized bed? It suggests that there is certain fluid in it, but it is not just a fluid, you also have solid particles mixed inside that fluid. So, they are like suspended solid particles in a fluid. The fluid can also be a gas. So, you make this mixture in such a way and you also create so much turbulence in fluid that basically your entire mixture behaves like one single fluid. So, that is the idea of any fluidized-bed reactant.

You can have different chemical reactions. These reactors are used more for different other chemical reactions because there you can have one matrix and then you have the particles. You want these particles to react with the matrix. Or you want to even perform certain types of coating on top of your particles, in that case, this is perfect because if your particles are suspended inside a fluid, then each surface all the time is coming in contact with the fluid. So, if you want to perform certain reaction with the fluid, then that is perfect.

In our case, you can have steam and you can have the char particles suspended in it. And now, if this entire mixture behaves like one single fluid, then we can control flow rate that is how we can treat this entire mixture and you can also call it a heterogeneous fluid.

However, when we think of this heterogeneous fluid, we do consider one single bulk density. So, we do not say that the density of particles is this and the density of the fluid is this. We just think of this entire mixture as one single fluid and then, we consider the bulk density for it. And that is what you would use if you want to model it or if you want to calculate any properties any parameters or simulate anything.

This of course the advantage. So, the operation principle is simple. You see that in the figure, you have the char in, you have activated carbon and there is certain fuel, there is certain gas and steam injection, the flue gas and the exhaust gas can go out from somewhere. So, the idea is that you have this mixture of fluid and solid and there is always almost a continuous turbulence created so all times, the particles are suspended in that fluid.

Here, you can imagine that because the reaction is happening all the time, you actually need smaller residence times. In fact, if you end up having a very long residence time, then you may end up losing your carbon. So, the optimization of residence time here becomes important because the reaction is relatively quick.

I should not say very harsh, but it is a constant reaction so, that is why it is important that you ensure you do not have very long residence times. And your steam or hot gas is always around your coal or your char particle all the time, with very high velocities.

So, heat transfer is also relatively fast. So, because of all these factors, you need to make sure that you do not leave the carbon inside the furnace for too long or you may end up losing the carbon mass, the fixed carbon mass. So, this reaction can also cause mechanical damage because of the velocity of the fluid.

Because these char-like particles activated carbons, they are not mechanically too strong at least as compared to other carbon materials. So, you may also get some erosion from the surface. These are the things that you will need to optimize.

You will use this process rather than for the powder activated carbon for two reasons, one that the damage to the powder surface is less. If you have bigger particles you may end up crushing them and also because the powder is light so, it is easier to have them in the fluidized beds.

These are also used for reusing or reheating the activated carbon. In fact, the one big advantage of activated carbons is that you can always reuse them. So, whenever your activation absorption is exhausted, your material is saturated with it, in that case, you can just heat it again, wash it again with several chemicals and you again have your activated carbon ready. So, this is also one reason that this is a very important industrial material.

If you want to read further on activated carbon, this is in itself a very vast field of research. This is one book that I suggest. There are also several papers, review articles that you can read. This activated carbon is also very important for waste treatment. So, if you carbonize waste polymers often you end up getting either a mixed type of carbon or you get porous carbon. You do not get good quality graphite or glass-like carbon of course, from the waste. So, in that case, conversion of char into activated carbon and utilizing these activated carbons for different processes is very important.