Heterogeneous Catalysis and Catalytic Processes

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Lecture - 35
Catalytic Reactors

Good morning. In my last lecture, I was talking about different reactors configuration used in the catalytic reactions. And, overall what I discussed was it is a kind of batch CSTR or a tubular reactor. So, batch reactor is generally unsteady state. So, not very commonly used, but the CSTR type, tank type reactors; and, plug flow reactor, which are fixed bed reactor. These are widely used in process industry. And, between these two: CSTR and plug flow type, that is, a pack bed reactor, the pack bed reactor or tubular type reactors are more commonly used, because the production capacity is high with these kind of reactor.

But, there are some limitations related to the transport limitations, which are hydrodynamic conditions, pressure drop problem, selection of the catalyst, deactivation problems. So, we need to look at the configuration or a different type of moving bed reactor, slurry bubble column reactor; which are a combination of some plug flow or a CSTR; that is, there is some kind of degree of back mixing; and, that may be required depending on the mass transfer limitations, which are prevailing during the catalytic reaction especially when you have a gas, liquid and solid reactions. So, we were talking about different reactor configurations; and then, we looked at the design aspects also, a plug flow reactor design equation and a CSTR design equation to find out a mass of a catalyst or a size of a reactor.

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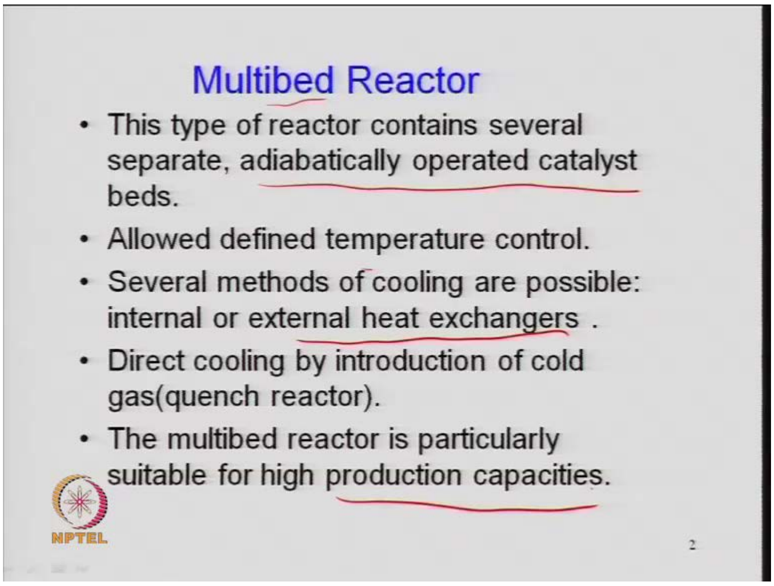

Multibed Reactor

- This type of reactor contains several separate, adiabatically operated catalyst beds.
- Allowed defined temperature control.
- Several methods of cooling are possible: internal or external heat exchangers .
- Direct cooling by introduction of cold gas(quench reactor).
- The multibed reactor is particularly suitable for high production capacities.

So, in the continuation of that, I was talking about a multibed reactor. So, one is the just the fixed bed reactor, where you have in a single tube, a large amount of catalyst mass is placed. So, that is easy to handle in one way. And, that can be used when the reactor is operating under isothermal condition. So, isothermal means there are new temperature gradients prevailing in the reactor. In case of catalyst or when you pack the catalyst with the reactor with solid material, which is a catalyst; then, the hotspot formation when the reaction is exothermic, that is a big issue. So, in that case, we need to look at a different kind of configuration, that is, heat is to be removed at intermediate stages.

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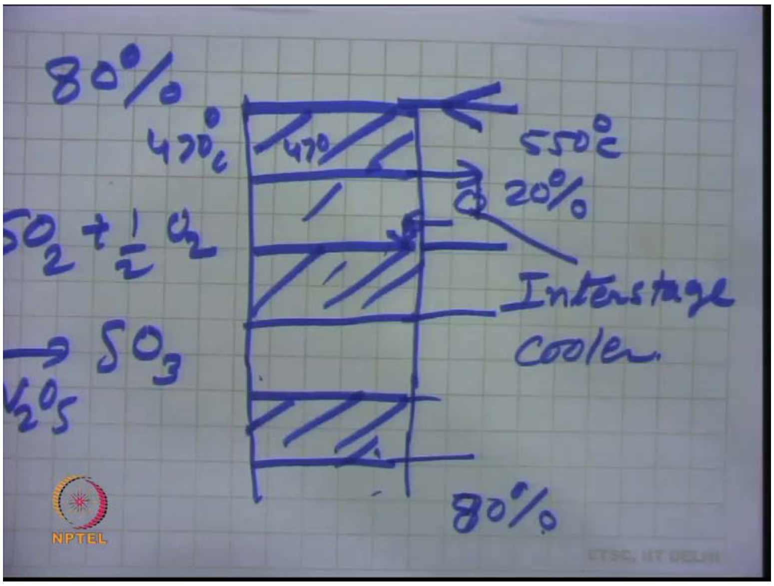

So, in some case like just as an example, if you have a fixed bed reactor with single tube just like in the sulfur dioxide oxidation; so, the reaction is something like this and gives you sulfur trioxide; and, the catalyst used is vanadium pentoxide. So, in this case, since the reaction is highly exothermic; so, what we do we make the different bed of the catalyst like this. So, first stage; then, second bed of the catalyst; and, third bed of the catalyst, like this. And, it can be a four bed of catalyst. The basic idea is that, suppose the overall conversion is 80 percent, then we can control the conversions in this reactor.

So, feed is coming from here; and then, it is coming out: the feed and the product. And then, it is cooled here because in between, the reaction is exothermic. So, suppose the required temperature is around 470 degree centigrade, you would like to have a catalytic bed temperature 470. But, because of the exothermic reaction, heat will generate. So, it can go up to say 500 – 550 degree centigrade. So, if you have a high conversion, then temperature rise will be high. So, we limit the conversion say just 20 percent in the first bed, where catalyst may be highly active in this case. So, it can 30 percent or 40 percent also. So, higher conversion can be kept in the first bed. And then, it is cooled and then again sent back into the second bed of the catalyst. So, you have a cooling system here in between. And then, it goes to the second bed.

Again you have another conversion say may be 10 to 15 percent in the second bed and then in the third bed, so that the overall conversion at the exit may be your desired conversion – 80 percent or 70 percent whatever the required. So, this is what you call interstage cooling here. So, we have the interstage coolers in between. So, in the case of fixed bed reactor, the heat removal may be an issue.

So, just when the reaction is highly exothermic, one cannot use a single bed of the catalyst in the reactor. So, the second option can be we can have multiple tube, because once you have a large number of tubes in this kind of cylinder, then the surface area per unit volume of those tubes will be very high, because it is a small diameter tube. So, the heat removal… The heat transfer coefficient and q, which is hA delta t. So, these will be faster. The heat removal will be faster; that is one thing.

And, same thing in that form of the conversion; so, achievement of the conversion because you can control the temperature in the small tube. So, it can be a kind of multibed or multitubular reactor. So, this is an example of multibed reactor. So, you have

1, 2, 3, 4, like that; where in between, you have the intermediate cooling. So, this type of reactor, which I talked a multibed reactor are generally used in the case of adiabatically operated catalyst bed. So, reaction is exothermic type. So, hot spot formation may be an issue. So, I told you that, when the temperature at a localized point becomes very high because of the exothermic reaction; so, it will damage the catalyst. So, catalyst can be stable only up to a certain temperature. So, that is very important that, how to make the catalyst stable for a longer period of time during a catalytic reaction even. And, that is very important when the reaction is exothermic type of reaction. So, runaway problem may also raise some kind of transient condition, unsteady state condition in the reactor.

So, in this case, when you have a multibed reactor, one is allowed a defined temperature control. So, that is again important that, what I said here that, if the optimum temperature is say 450 or 460 degree centigrade for the reaction, then in that case, one can have a control. So, suppose the temperature is increased to 500 degree centigrade, you cool it and bring the temperature down to 470 or 460 or whatever the optimum condition and get the things turn.

So, several methods of cooling are possible. So, one can have the intermediate heat exchangers in between. And, this is what you call internal and external heat exchanger. So, a cooling device is required and there can be a different kind of heating or cooling media. So, when it is an endothermic reaction, you need a heating media; when it is exothermic reaction, you can have the cooling media. And, direct cooling by introduction of cold gas – that sometime we quench it also. So, some feed, cold feed is added or mixed with this hot feed; and then, it is another way of controlling the temperature at this point. So, multibed reactors – they are mainly suitable for high production capacity. So, when the production capacity requirement is large, we can prefer these kind of reactors – multibed reactor.

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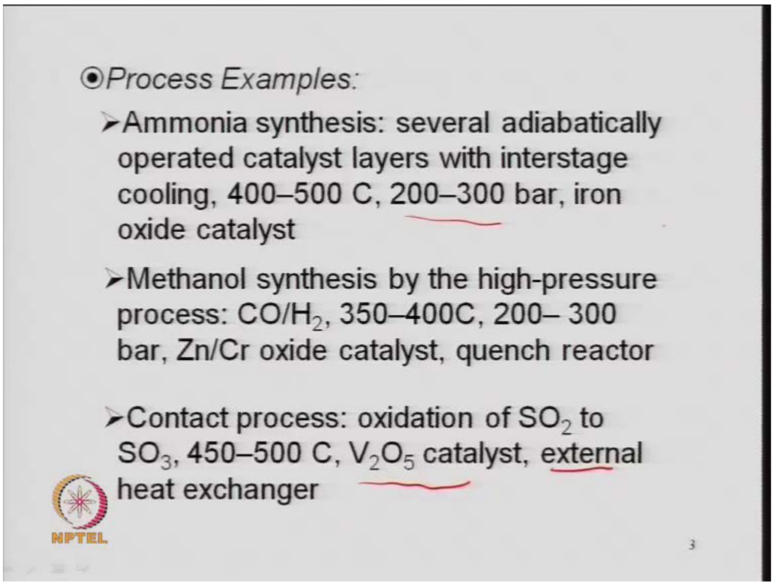

Process Examples:

- Ammonia synthesis: several adiabatically operated catalyst layers with interstage cooling, 400–500 C, 200–300 bar, iron oxide catalyst
- Methanol synthesis by the high-pressure process: CO/H_2, 350–400C, 200– 300 bar, Zn/Cr oxide catalyst, quench reactor
- Contact process: oxidation of SO_2 to SO_3, 450–500 C, V_2O_5 catalyst, external heat exchanger

So, some examples as I discussed here is something like ammonia synthesis. So, it is basically a multi-tubular. Nowadays, we have a large number of tubes in this and you can have the high heat transfer or heat remover, which is possible or controlled because when the tubes are damaged, they can be replaced easily. So, that is another advantage in the case of this multitubular reactor.

So, that is a multibed, but there are the reactors, where we have just like in the ammonia synthesis; nowadays, the multitube reactors are used. So, there are thousand tubes, which are placed as small diameter tubes and placed inside. So, several adiabatically operated catalyst layers, which has the interstage cooling in this case like this. So, 400 to 500 degree centigrade is the operating temperature; and, pressure is around 200 to 300 bar. And, the catalyst for ammonia synthesis, nitrogen and hydrogen reacts and make the ammonia. So, the catalyst is the iron oxide type catalyst.

Similarly, in the methanol synthesis also generally, this is a kind of Fischer-Tropsch reaction, where carbon monoxide and hydrogen are reacted and we get the methanol. It is very important process for production of methanol and especially from coal. So, coal converts the syngas; and, one can get this synthesis gas. Here again this copper-zinc based catalysts are used in the system and reaction is exothermic reaction. So, this… So, Fischer-Tropsch reaction is again an exothermic reaction. So, either a slurry type bubble column typed reactors can be used; or, these kind of multi-tubular reactors whenever the reaction is exothermic, because the control is easy in these cases.

So, sulfur dioxide oxidation I have just talked. So, oxidation of sulfur dioxide to sulfur trioxide, where vanadium pentoxide is used as a catalyst; and here the external heat exchanger is used. So, this is the kind of external heat cooling device. So, heat exchangers are used. So, it is a kind of silent tube heat exchanger say.

So, the product gas comes through that and you have some cooling media on the outer side. And then, you get the temperature down to the desired temperature and then it is send to the second bed. And, same thing again here intermediate cooler and comes to the third bed. So, that is a kind of external cooler. Here the quenching is done. So, the cold feed stock, that is, carbon monoxide and hydrogen – that can be mixed with the hot feed stock and you can cool it down.

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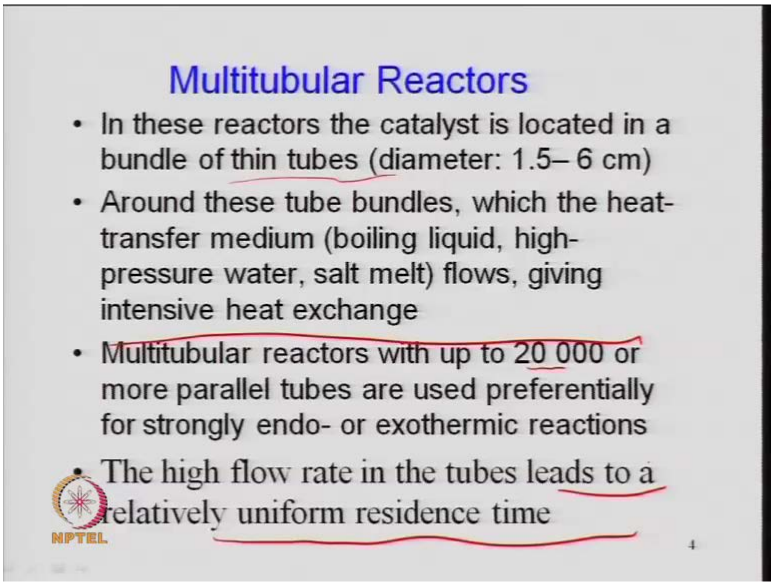

Multitubular Reactors

- In these reactors the catalyst is located in a bundle of thin tubes (diameter: 1.5– 6 cm)
- Around these tube bundles, which the heat-transfer medium (boiling liquid, high-pressure water, salt melt) flows, giving intensive heat exchange
- Multitubular reactors with up to 20 000 or more parallel tubes are used preferentially for strongly endo- or exothermic reactions
- The high flow rate in the tubes leads to a relatively uniform residence time

So, in these kind of reactors, if you look at the tubular reactor; that is same what I talked multibed reactor. And, this is the similar which is a kind of multi-tubular reactor, where you have a large number of tubes or a small diameter tubes. So, these reactors… The catalyst is located in a bundle of thin tubes. So, small tubes; diameter may be roughly between 1.5 or up to 6 centimeter. So, that depends that, what is the amount of catalyst required to be loaded. So, small tube surface area per unit volume will be high in those cases. So, removal will be better. So, the range can be like this. Whereas, if you look at these kind of reactors, the diameter can be 2.5 meter, 3 meter or 5 meter; so, large diameter reactors. So, here the control will be difficult because there will be a gradient when you have a large diameter reactor. But, in the case of a small diameter reactor, the gradient will be less. So, your control is easy. So, here the radial thermal gradient will be minimum; concentration gradients will be minimum. So, these will be better compared to these kind of reactors.

So, around these tube bundles, which the heat transfer medium something like a boiling liquid, high pressure water, salt melt flows, and giving the intensive heat exchange; so, here continuously the cooling or heating is done between the reactor and the outside cell. So, you have a continuously the heat transfer medium, which may be kind of boiling liquid, high pressure water or salt melt that flows; and, that controls the temperature inside the reactor. So, multi-tubular reactors if you can just visualize, that can contain up to 20000 or more parallel tubes. And, that are used preferentially for endothermic or exothermic reaction.

So, when the reaction is highly endothermic or highly exothermic, then one can suggest a kind of multitubular reactor because in those systems, the control will be better. So, catalyst damage; which is a very important issue for the process; so, one needs to control that and need to make a catalyst stable for a longer period. So, you need to besides the design of a catalyst, that is, a stable catalyst, which can resist high temperature, that is one thing.

And simultaneously you have to look at in terms of the process reactors action. So, there also you need to look at a better design and select a suitable catalyst for a given reaction or given process. So, there also, one can control the life of the catalyst; that is one thing. And, simultaneously, the high conversion and high yield, that is, the productivity that is desired; and, one can select a better reactor for a given catalyst. So, high flow rate in the tube leads to a uniform residence time.

So, when the tube size is reduced, the superficial gas velocity will be higher, because there if you look at the diameter is large; so, for the same flow rate if you take, then there is superficial gas velocity in this case will be lower. But, if you have a small diameter, that is, just like as ((Refer Slide Time: 13:50)) tube heat exchanger. So, when you have a small tube, the superficial velocity or velocity in the tube will be high. So, you will have a kind of turbulent condition. So, you get a better heat transfer coefficient. And, the similar for heat transfer, you will have those advantages. And, simultaneously, for mass transfer and hydrodynamic conditions also, you will have a uniform residence time. So, here the mean residence time or what we talk in terms of the plug flow condition; that can be achieved.

So, the radial dispersion will be minimized; axial dispersion will be minimized; and, it will be mainly a dominated convective flow because the velocity is high in this case. So, that is again important when you look at the hydrodynamic conditions in the multitubular reactor. So, we would like to have a uniform residence time; we would like to have the minimum axial and radial dispersion, which is a kind of known ideal flow property. So, we need to control that.

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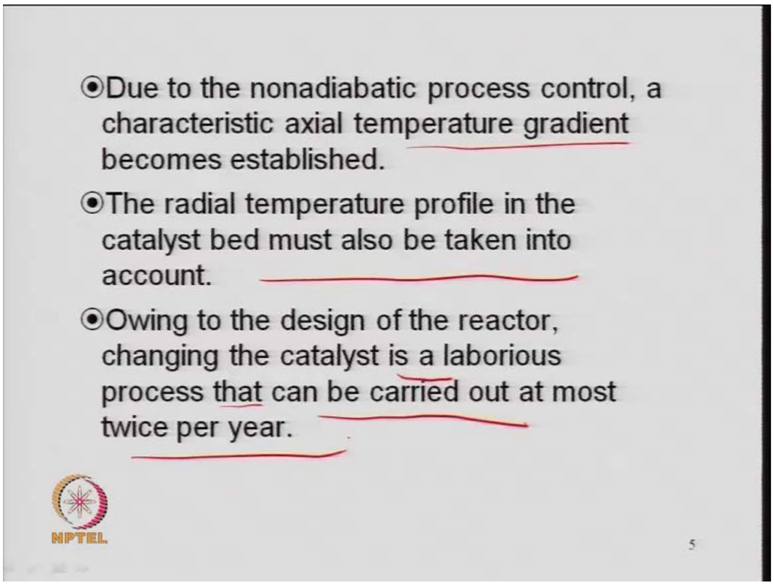

- Due to the nonadiabatic process control, a characteristic axial temperature gradient becomes established.
- The radial temperature profile in the catalyst bed must also be taken into account.
- Owing to the design of the reactor, changing the catalyst is a laborious process that can be carried out at most twice per year.

Again due to nonadiabatic process control, the characteristic axial temperature gradient is established. So, whenever the… you have an endothermic or exothermic reaction because the conversion is increasing down the length. So, as you go down, the conversion is increasing. And, because of that, the temperature will rise if you do not control that. So, in the case of adiabatic process or non-adiabatic process, the… In non-adiabatic, see something you are doing that, the adiabatic process when heat is neither added nor given into the system. And, same thing in non-adiabatic, you are controlling the heat, which is either by removing or by adding into the system. So, you are looking something a kind of process. And, there will be a kind of temperature gradient in this non-adiabatic process.

The temperature is increasing down the length suppose the reaction is exothermic. So, that gradient will come and that will affect the performance what I said that, if the reaction is to be carried out at a particular temperature and temperature rise, that may disturb the reversible or disturb the equilibrium. So, reaction may take place in the backward direction. So, that may not be good. So, thermal gradients need to be avoided; same thing for radial temperature profile in the catalyst bed; that should also be considered.

So, in fact, when you are writing this kind of terms, then one needs to write the energy balance equation in the axial direction, which will be a kind of something related to the thermal conductivity term. So, lambda times whatever dT by dz, which you like from the Fourier's law of heat conduction; that will come here. So, one thing is that, you are talking just like a convective heat transfer; but, because of the thermal gradients, there will be a kind of conductive heat transfer also in the radial direction and in the axial direction. So, some term, which is related to the thermal conductivity, that is, k – small k – thermal conductivity of the material times dT by dz or k times dT by dr.

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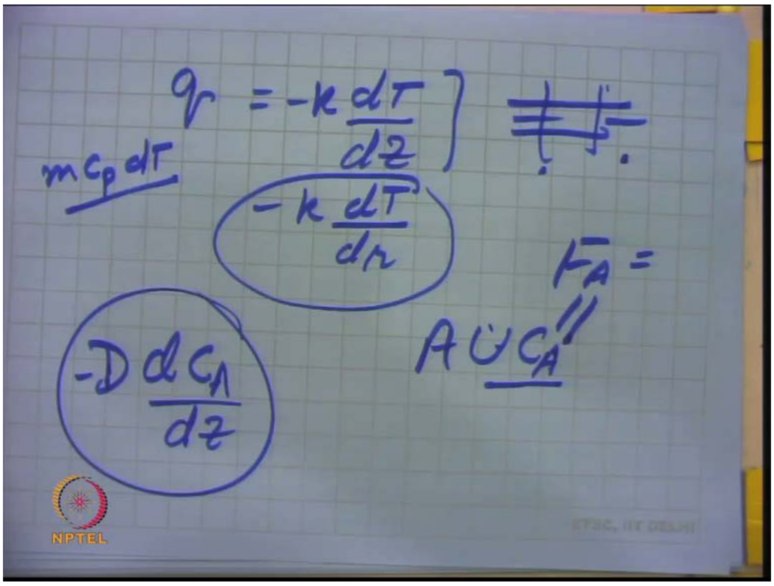

If you remember, the Fourier's law of heat conduction q will be minus k dT by dz in the direction of flow; or, minus k times gradient of T I can write; or, minus k times dT by dr will come for the transfer of heat when I write in this direction something like that. So, heat transfer because of conduction at z; and, heat transfer because of conduction at z plus delta z. So, same thing at z plus delta z. So, this will give you a term like minus k d 2T by dz square.

So, that is the additional term, which will arise and affect the performance of reactor. Same thing just like as I told the axial dispersion term; that time you talk a Fourier's law of heat conduction. So, it means the flow is because of D d C A by dz; something like this in z direction. So, this is related to non-ideal flow parameter, because this is a kind of dispersion; so, dispersion in this direction of flow; so, because this is one flux, which is arising because of the non-ideal or concentration gradient term.

The second is the convective flow term, which you generally write U times C A in terms of flux. So, that is what I am talking or what you write F A – total molar flow rate, which can be written C A naught into volumetric flow rate. So, basically this is area times or cross-section times U times C A. So, that is the convective term. Same thing here in the form of heat transfer; you write it in terms of m c p dT – something like that; which is a convective heat, which flows down the length.

So, m c p dT by dz that ((Refer Slide Time: 18:33)). So, we are not discussing these things in detail; that is separate part. But, I meant to say that, when you look at a actual reactor design and there are the conditions like non-isothermal condition, then the heat is being removed or heat is being added into the system; then, one needs to look into the conditions or material balance, energy balance; and, that should be considered for the reactor design to find out the temperature profile, to find out the concentration profile down the length in a reactor.

So, if you look at owing to the design of reactor, changing the catalyst is a laborious process that can be carried out utmost twice per year. So, it is not easy to replace a catalyst or maintenance of the reactor is not an easy job. So, it means whenever you look at a design or whenever you will select a catalyst for a process along with the reactor, you need to identify a type of reactor system also. So, it means one would like to have the reactor and the catalyst in the system, where the production at least for three years. If the catalyst is deactivating faster, let us have it one year or at the most, let us have it 6 months. If the catalyst deactivation is always that just like I told in the case of cracking reaction, where the hydrocarbon feed stock, they crack and generate the lot of carbon on the catalyst; and, that deactivates the catalyst very fast just like what I was talking of moving bed type of reactor.

So, you need to change the reactor design. Do not go with the reactor like a fixed bed or multitubular reactor if you feel that, the life of catalyst is very low. So, in these type of cases, we expect that, the reactor should operate without any hindrance or disturbance for at least one year. So, that is… Or, it is 6 months; it is a worst to worst case. So, one can control the operations.

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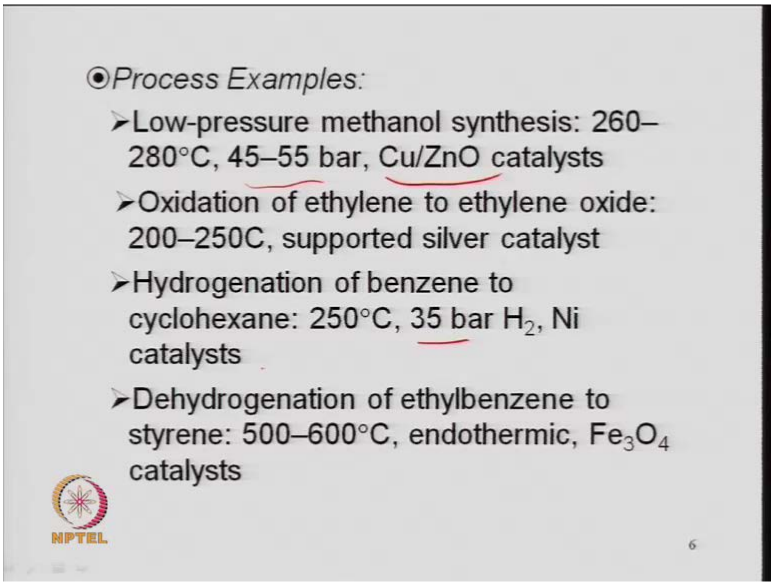

◉*Process Examples:*

- ➢Low-pressure methanol synthesis: 260–280°C, 45–55 bar, Cu/ZnO catalysts
- ➢Oxidation of ethylene to ethylene oxide: 200–250C, supported silver catalyst
- ➢Hydrogenation of benzene to cyclohexane: 250°C, 35 bar H_2, Ni catalysts
- ➢Dehydrogenation of ethylbenzene to styrene: 500–600°C, endothermic, Fe_3O_4 catalysts

There are various process, which have been done and say low pressure methanol synthesis, which is done at 260 to 280 degree centigrade and pressure around 45 to 55 Fischer-Tropsch type of reaction; and, the catalyst are also different kind of catalysts. So, when you need to change the process condition, you need to select a different catalyst, because I told you the catalysts are very active; and, performance is related to some process condition.

So, suppose the… Initially, I was talking a catalyst something like this here for the same reaction – Fischer-Tropsch reaction; if you look at or recall this, a multi-tubular reactor; where, I was talking methanol synthesis over zinc-based catalyst; and, pressure is something like this. So, it means if you rewind the process or if you change; if you want to go for a lower pressure, you need to look at a different catalyst, which is more effective.

So, here the copper-based catalyst, which have been selected in this process, which is a copper-zinc oxide based catalyst; the reaction can be carried out here between 45 to 55 atmosphere bar. So, it means you have saved a lot of energy, because high pressure reactor – they need more energy consumption. So, one can have a catalyst; then, identify the optimum process for that catalyst in terms of temperature pressure, space time or residence time, and look at the hydrodynamic also, because the porosity size, shape, strength of the catalyst – that will also affect the performance in the reactor. When you put the large amount of catalyst in the reactor, does it cramble during the reaction. So, you need to look at the stability or mechanical strength or a kind of attrition resistance in the catalyst. So, this is also equally important. So, you need to look at that.

Similarly, for oxidation of ethylene to ethylene oxide, which is generally used for making epoxy resins, silver-based catalysts are used. So, that is again a very important process in the petrochemical industry. The resins are made from this epoxy resins. Hydrogenation of benzene to cyclohexane is again important in petrochemical and the chemical industry, which is done at 250 degree centigrade and 35 atmosphere of hydrogen pressure; and, catalyst is the nickel catalyst. So, there is some different process, where these kind of multitubular because the reaction is exothermic. So, one need to identify a pressure temperature and the catalyst suitable for the process for these kind of multitubular reactors.

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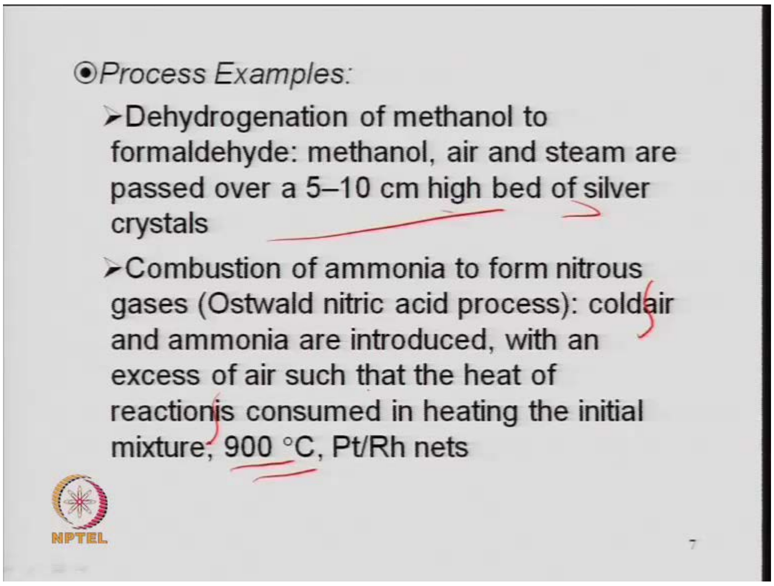

- *Process Examples:*
  - Dehydrogenation of methanol to formaldehyde: methanol, air and steam are passed over a 5–10 cm high bed of silver crystals
  - Combustion of ammonia to form nitrous gases (Ostwald nitric acid process): cold air and ammonia are introduced, with an excess of air such that the heat of reaction is consumed in heating the initial mixture; 900 °C, Pt/Rh nets

So, there are some other examples also, which I have discussed the dehydrogenation of methanol to formaldehyde. There is methanol air and steam, are reacted; and, which is just over a 5 to 10 centimeter high bed of silver catalyst, which is a catalyst – basically a silver catalyst. And, that gives you the dehydrogenation of methanol to formaldehyde. There are other catalysts, which have been used copper-based catalyst also for dehydrogenation; but, that gives a kind of dimethyl ether and ethylene. Same thing – combustion of ammonia to form nitrous oxide gases, which is a kind of Ostwald process for nitric oxide; H-NO 3 production also nitric acid. So, here cold air and ammonia are introduced within excess of air such that the heat of reaction is consumed in the heating of the initial mixture at around 900 degree centigrade. So, here the platinum, rhodium type of catalysts are used for the process.

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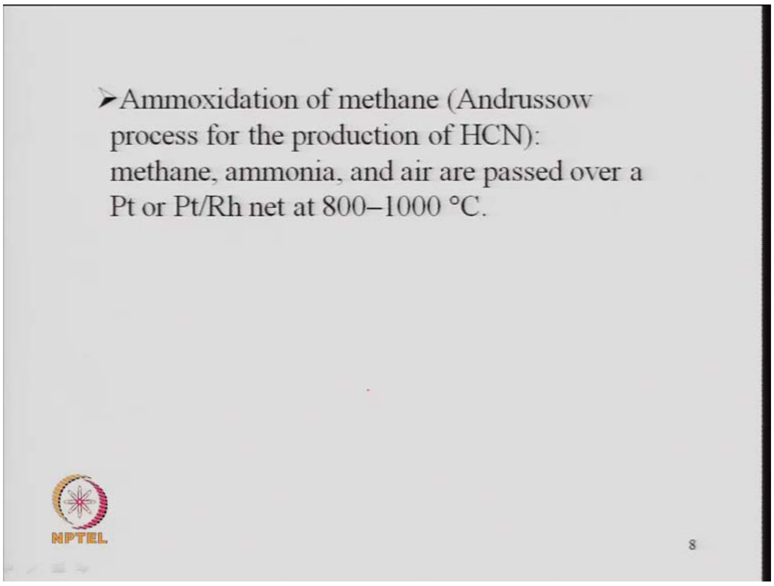

➢Ammoxidation of methane (Andrussow process for the production of HCN): methane, ammonia, and air are passed over a Pt or Pt/Rh net at 800–1000 °C.

So, there are other; I am not going in details of this. But, these are in the… For exothermic reactions, we have different kinds of catalyst and different kind of process. So, methane, ammonia air is passed over a platinum, platinum-rhodium catalyst. And, this is again a kind of temperature 800 to 1000 degree centigrade here.

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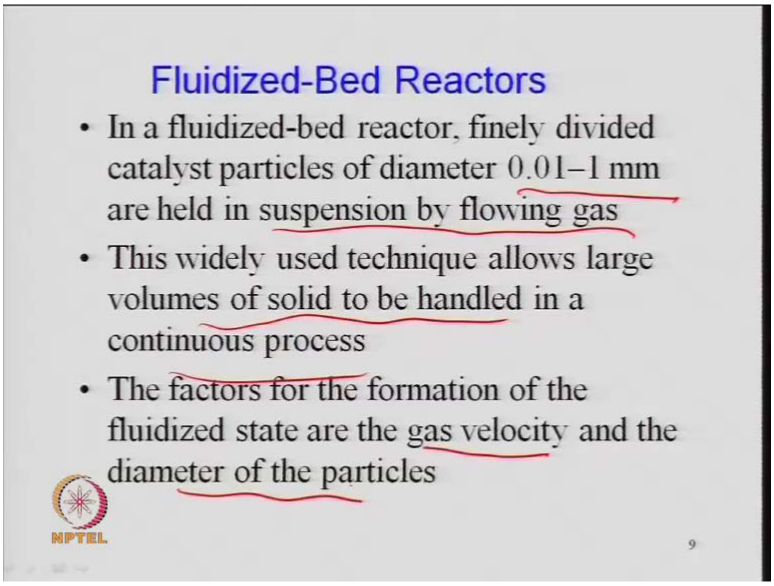

Fluidized-Bed Reactors

- In a fluidized-bed reactor, finely divided catalyst particles of diameter 0.01–1 mm are held in suspension by flowing gas
- This widely used technique allows large volumes of solid to be handled in a continuous process
- The factors for the formation of the fluidized state are the gas velocity and the diameter of the particles

Another kind of reactor, which is used are very commonly used when the catalyst deactivates faster or where the high contact between gas and solid is desired, then it is a fluidized-bed reactor. So, basically, two fixed kind of reactors – system and… If you look at the particle size in the case of the fluidized-bed reactor, that is very important. So, one needs to look at the type of solid material, which is being fluidized, because the fluidization is a different subject; and, entirely if you look at the reactor design is little bit complicated compared to a CSTR design; otherwise, in general, we say that CSTR is a kind of back-mix reactor.

And, when you have fluidized-bed reactor, there is a kind of a solid particle, which moves up; and, then there are different forces like gravity force, buoyant force, viscous force, track force. So, because of that, the particle may come up and down. So, it is a kind of degree of back mixing, which is you get in the fluidized-bed reactor. So, to have a better control or to have a condition like a well-mixed, that is, a condition like a plug flow reactor, you have to re-circulate. So, circulating fluidized bed reactors are also common. So, these kind of reactors are very common in the cracking operation.

And also, when you look at the transportation purpose also, when you have fine powders, they can be fluidized through the bed. So, it is spray type of towers; that is again where you generate the fine powders – milk drying. So, these are the kind of the spray dryers. So, basically, here you have to look at the property of the material.

So, there is a different kind of chart, what you call Geldert chart by which one can identify the velocity superficial loss is required in a column, and then one can see the conditions, which is required for fluidization. So, that will depend on density of solid; it will depend on the viscosity of the media; density of the gas, which is being used. So, so many things will come in picture when you look at the actual fluidization condition. So, hydrodynamic conditions need to be indentified in this case.

But, as I said that, the fine powders are used; small particles will fluidized better. So, generally the particles of the order of micron – 50 micron, 100 micron – they are generally used for this purpose especially when you look at a catalytic cracking. So, the idea is that, the solids are behaving like fluid. So, they are in the condition of fluidized media; they are suspended form in the column or in the bed by a flowing gas.

So, generally, say nitrogen can be a gas; and, sand you are just passing and you increase the velocity of the nitrogen gas. At the end, you will find that the particles are floating in that column. So, initially it is a fixed bed, but there will be a voidage between the particles now; it will increase. And finally, the bed will start fluidizing. But, if you keep on increasing the velocity, these particles will go away from the bed. That is not desired

So, this fluidized-bed reactor technique is widely used in the chemical industry or chemical process industry, because it allows a large volume of solids to be handled in a continuous process. So, one can handle a larger amount of the catalyst in… And, there is a good contact between the gas and the solid. The factors for the formation of the fluidized state are the gas velocity and the diameter of the particles. So, there are several other factors also; but, the fluidization will depend on the gas velocity and the diameter of the particle. But, as I said, it will depend on the density of the gas; it will depend on the density of the solid, viscosity of the media. So, there are many other factors also.

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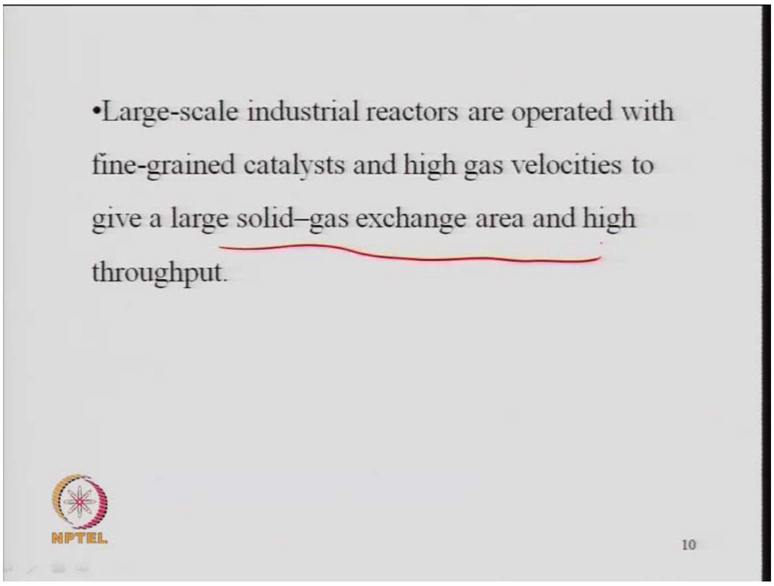

- Large-scale industrial reactors are operated with fine-grained catalysts and high gas velocities to give a large solid–gas exchange area and high throughput.

So, if you look at the large-scale industrial reactors, generally, they are operated with fine-grained catalyst and high gas velocity to give a large solid gas exchange in the reactor. So, that is again important when you look at the high throughput; that the large solid gas exchange area and high throughput. So, that is important. So, you have to design the size of the reactor. And especially, I will just discuss that in the subsequent lectures. But, with the design of the fluidized-bed reactor in terms of the residence time distribution, is very important.

So, it means how the temperature time; or, if it is an exothermic reaction or the concentration down the length in a bed change, that is very important. So, we need to look at a separate hydrodynamic study and a residence time distribution study by using some treasures for the fluidized-bed. And, that we have to include those terms in the reactor design when you look at the average conversion, because in the fluidized bed, it is not a conversion, which is a particular point; it varies down the length; and, there is a kind of back mixing also. So, you have to introduce the residence time distribution and then calculate the average overall conversion in a reactor or conversion down the length or concentration profile.

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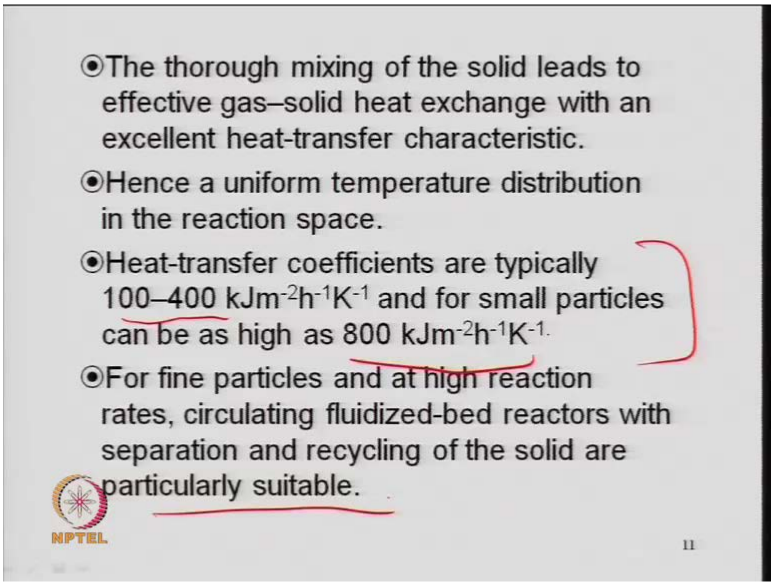

- The thorough mixing of the solid leads to effective gas–solid heat exchange with an excellent heat-transfer characteristic.
- Hence a uniform temperature distribution in the reaction space.
- Heat-transfer coefficients are typically 100–400 $kJm^{-2}h^{-1}K^{-1}$ and for small particles can be as high as 800 $kJm^{-2}h^{-1}K^{-1}$.
- For fine particles and at high reaction rates, circulating fluidized-bed reactors with separation and recycling of the solid are particularly suitable.

So, a thorough mixing – that is very important. And, in the case of fixed bed, generally, the pressure drop is an issue; that is one thing.

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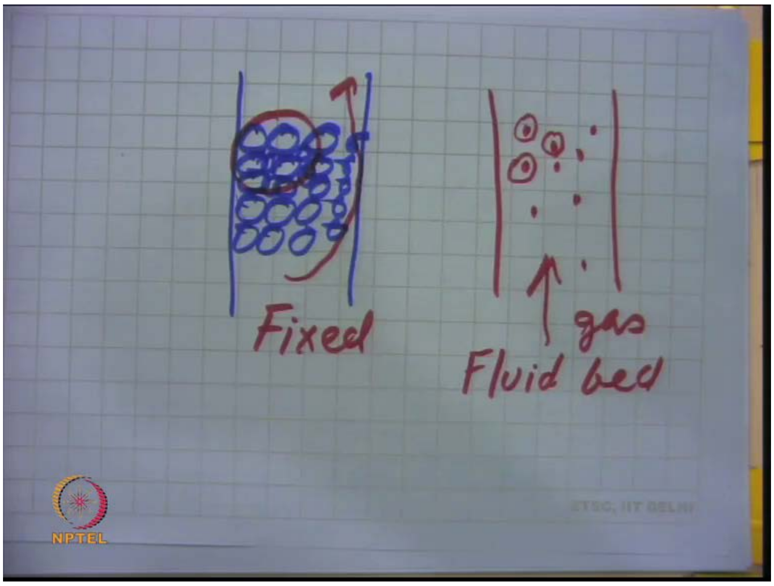

And simultaneously, you see that there are lot of particles placed in the bed; so, depending upon the kind of packing like this. So, the particles are well-packed – suppose densely packed like this. So, the contact between the gas and solid in this zone will be poor, because this is densely packed zone; so, poor contact. So, this is not a good kind of design. So, suppose you have a very fine powder unlike this, where the voidage is very poor; and, you make it tapped compact and try to pass the gas, you will feel that, the gas will not pass through that. So, it means the contact becomes poor and poor or gas will try to have the pass through the channels like this. So, this is a bad kind of design.

If you have in contrast to this, you want a good contact and you make a fine powder like this; and, allow it to pass with the gas from the bottom. So, now, they are suspended from. So, every solid particle is free to contact; just like in a water and you have a some dissolved solid and they are well dispersed throughout. So, something like here – a fluid type condition.

So, this is a kind of fluidized bed here – fluid bed. And, this is a kind of fixed bed. So, in fixed versus fluidized, one can see that, the contact will be better here. So, that is the advantage in this case of fluidized bed. So, a temperature distribution, which you look at here – that through mixing of solid leads the effective gas solid exchange with an excellent heat transfer characteristic; and, a uniform temperature distribution in the reaction space can be obtained. In this case, fixed bed – I told that, there will be a kind of radial gradient; there will be a kind of axial gradient. But, when you have a fluidized bed, then the gradient is minimized, because here the heat is being dissipated simultaneously; same thing – the temperature of concentration will be more or less uniform. So, it is a kind of back mixing just like in a CSTR, you say the temperature distribution will be uniform; concentration distribution will be uniform.

Heat-transfer coefficient will be very high. So, heat-transfer coefficient – if you look at the order of magnitude, 100 to 400 kilo Joule per meter square per hour Kelvin. And, for small particles, it can be as high as 800 because it will depend on the particle size; surface area per unit volume is very important. hA delta T – heat transfer when you write or heat transfer coefficient when you calculate.

So, this will be higher in the case of fluid bed reactor. So, that is the advantage. So, when the reaction is exothermic, the fluid-bed reactor can be preferred, because one can dissipate the heat and the heat transfer, or heat removal is faster. So, for fine particles and high reaction rates, if you have a circulating fluidized-bed reactor, with separation and recycling of the solids are particularly suitable.

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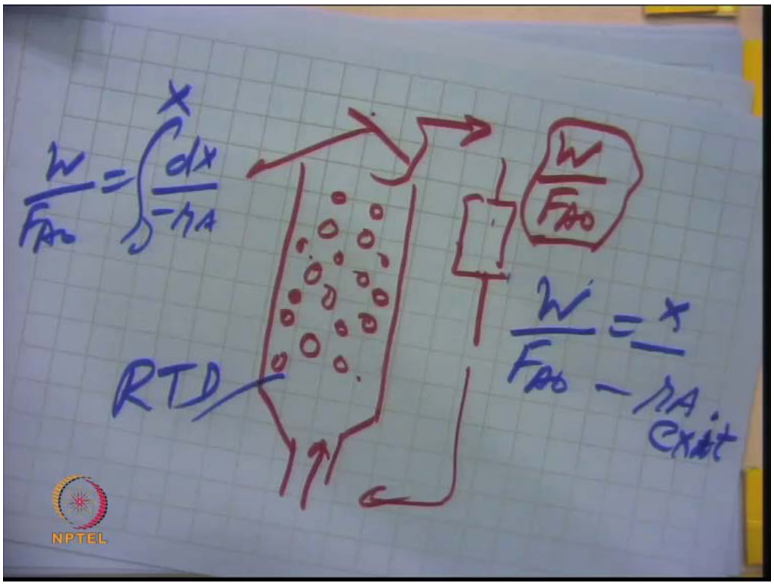

So, as I said, in the case fluidized-bed reactor, you generally have a bed of the solid like this; the particles are in suspended form; and, the reactant gas… So, these particles are something like the catalyst just like simple example of FCC – fluid catalytic cracking. And then, you pass the gas, which is a reactant gas. So, this can be the atmospheric gas oil or naphtha feed stock, hydrocarbon vapors; and then, they pass through the bed. And, you continuously have a product. So, you have a separation here – cyclone separator at the top, and you get the solid separated; and, the goes up like this – that is, the vapors; and then, you pass it through a condenser and you take the product

So, one can have a condenser here and then take the product here. The unreacted gases – they can be sent back if there… That is a different kind of system I am talking. So, then, in order to improve the conversion; if conversion is low just like say coal gasification, it can be done in a circulating fluidized bed. So, then, you circulate the gas again and again or coal particles again and again in the circulating fluidized bed. So, these are circulated like this.

And, the same thing what I was talking is this is a catalyst here; then, they are taken into a second system, where you have a regenerator and then recirculate the catalyst back. But, if it is just like the solid itself is a reactant just like coal combustion, then these coal particles – unbed coal particles are separated and then sent back into the reactor; a kind of circulating fluidized-bed reactor; which is not used in the case of fluid catalytic cracking. But, for coal combustion, it can be done. So, for fine particles at high reaction rates, the circulating fluidized bed reactor with separation and recycling of solid is suitable. So, that can be done. It is not difficult to separate the solid particles or unreacted particles. So, you separate the particle and send it back into the system. So, heat control and everything is possible here.

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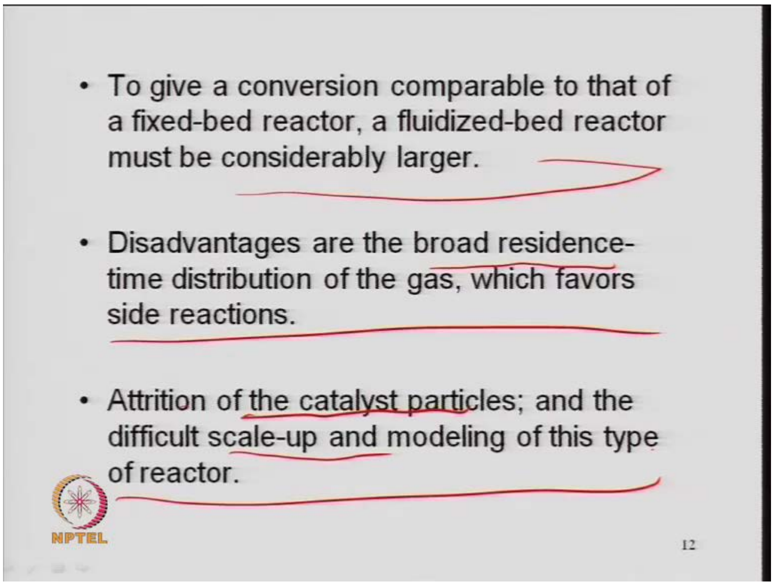

- To give a conversion comparable to that of a fixed-bed reactor, a fluidized-bed reactor must be considerably larger.
- Disadvantages are the broad residence-time distribution of the gas, which favors side reactions.
- Attrition of the catalyst particles; and the difficult scale-up and modeling of this type of reactor.

So, if you need to give a conversion comparable to that of fixed-bed reactor as I said that, the fluidized-bed reactor behaves like a CSTR. If I do not do anything in terms of hydrodynamic, simply one can write a design equation for CSTR here w by F A naught is equal to x upon minus r A. And, this r A is calculated at the exit condition here. So, this is the exit of the reactor. So, as I said, in the case of CSTR, the conversion is less; or, to have the same conversion, the mass of the catalyst desired will be high.

So, it means the size of a fluidized-bed reactor will be higher compared to the size of a fixed-bed reactor, because fixed-bed reactor waste like a plug flow reactor, which we have discussed yesterday like this. So, you are calculating the concentration and that is nothing but infinite number of CSTRs placed in series. So, here in form, in general, when we do the actual fluidized-bed reactor, we have to study the hydrodynamics; we need to find out the RTD here – residence time distribution, because here RTD is nothing but tau. That is what we have discussed that ideal plug flow reactor.

But, in this case, a kind of RTD will be there. So, you need to find that RTD and that should be incorporated when you do the design for a CSTR. So, basically, actually the fluidized-bed reactor is a combination of PFR and CSTR. So, you need to find out the residence time distribution in that exitise of the particles and then calculate mean conversion in the solid. So, it is something like 1 minus x b bar, that is, fraction of the solid, which is not converted in the bed. And, that can be calculated the fraction of the solid, which is not converted at different time intervals. So, basically, it is nothing but the age of the particle is to be find out; that is, in this bed, for how much time the particular lump of a particle remained inside? And, that will decide its future or faith; that is, how much conversion it has achieved will depend for how much time it has stayed inside the reactor, because the different particles will be staying for different amount of time unlike in a plug flow reactor.

So, that is the difference in the case of a plug flow reactor, a CSTR and a fluidized-bed reactor. So, you need to look at the exitise distribution and then calculate the mean conversion by measuring the fraction of the solids their age inside the reactor; and then, accordingly, their conversion as per the formula. And then, take the average for the total number of particles. So, that is important in the case of fluidized-bed reactor.

So, r A – the rate of reaction is not again just a kinetic control; it can be a function of hydrodynamics, that is, the velocity term. So, accordingly, the mass transfer will be there. So, there is a bubble phase; there is a solid phase, vague phase; and, there will be a transport. So, accordingly, there will be the resistances – additional resistances which, may come and the rate may be slowed down. So, that is another issue in the case of fluid bed reactor. So, this is one issue here that, the conversion to get a comparable conversion with respect to a fixed-bed reactor, you need to a get a larger mass of the catalyst in the bed.

So, w will be larger; or, size of the fluidized-bed reactor will be larger; otherwise, the average residence time – we are again calculating by the same number something like v by v naught or w by F A naught. It is the mean what you talk here. So, the mass of the catalyst in the bed is to be find out for a given conversion. And, this mass of the catalyst will be higher compared to a fixed-bed reactor. So, the disadvantage – that is what I talked already, is the broader residence time distribution of the gas, which favors the side reaction. So, that is why the fluidized bed reactors may not be good for those set of operations, where the fixed-bed reactor works.

If the fixed-bed reactors works properly, then one should not consider a fluidized-bed reactor. So, fluidized-bed reactors are preferred only when the catalyst is to be replaced again and again; or, you need a fine powder, which is to be reacted – solid reaction reacted continuously in the bed; and, that time you have to just make it a continuous type of reactor. So, recirculating fluidized-bed reactor in order to enhance just like as I said, the combustion of biomass, combustion of coal material, coal powder. So, that can be done in a kind of circulating fluidized-bed reactor. But, in the case of catalytic reaction, the cracking, which is as I said, the severe coke formation takes place. So, atmospheric gasoil tends to form coke and gasoil or gasoline.

So, gasoline type of product is formed. But, simultaneously, coke also forms… In order to regenerate the coke, you need to have a continuous recirculation of the catalyst – to regenerate the catalyst and send it back or take a moving-bed reactor straight through transport reactor, which are now old type of reactors. But, ((Refer Slide Time: 40:59)) is a kind of a reactor regenerator system for the fluid catalytic cracking. So, this is one issue here in the case of fluid-bed reactor.

Another issue is the attrition of the particles. So, if the… So, when you do the fluid catalytic cracking, you need to look at the mechanical strength of the particles. So, in a pack bed, the problem may not be there, because they are already in the bed and you have given the enough void. So, pressure is not an issue. But, when you have a… In the fluidized-bed reactor, these particles are continuously moving up and up and coming down; and, they are colliding with the other particles also.

So, because of all these type of agitations, they are mechanical strength – if that is poor, then the particle may cramble. If they cramble, they will become a smaller particle; and, if a smaller particle you have at a given velocity, they will leave the bed. So, that is not desired. So, you are losing the catalyst particle, because of their size reduction. So, in that case, it is important that, the catalyst should have enough mechanical strength also.

So, that is again an important issue. When you look at a fluid catalytic cracking, then you need to add some kind of promoters or additives, which enhance the stability of the catalyst in terms of the mechanical resistance or attrition resistance. So, that is also to be checked, because in the case of fluidized-bed reactor, this problem is severe. And, that different scale and modeling of this type of reactor you need to look at this kind of property also. So, these are some other problems or issues with the fluid-bed reactor.

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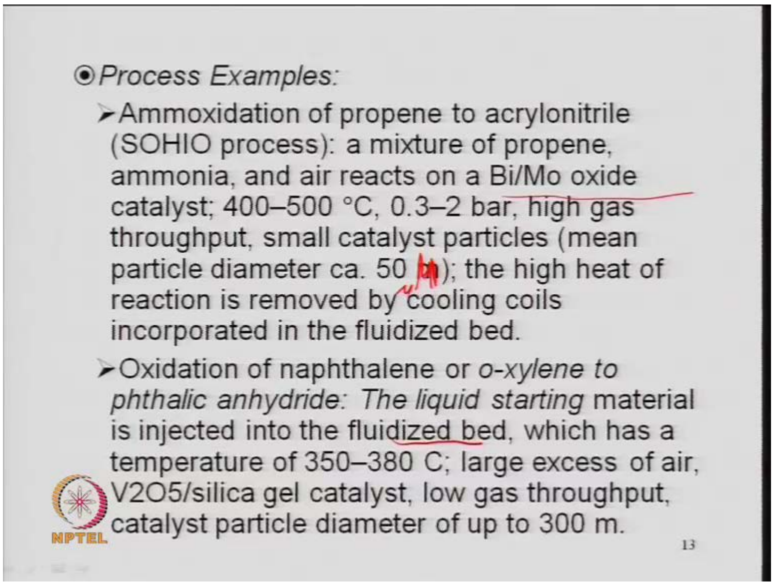

- *Process Examples:*
  - Ammoxidation of propene to acrylonitrile (SOHIO process): a mixture of propene, ammonia, and air reacts on a Bi/Mo oxide catalyst; 400–500 °C, 0.3–2 bar, high gas throughput, small catalyst particles (mean particle diameter ca. 50 µm); the high heat of reaction is removed by cooling coils incorporated in the fluidized bed.
  - Oxidation of naphthalene or *o-xylene to phthalic anhydride: The liquid starting* material is injected into the fluidized bed, which has a temperature of 350–380 C; large excess of air, V2O5/silica gel catalyst, low gas throughput, catalyst particle diameter of up to 300 m.

So, wide applications of the fluidized-bed reactors are when the reaction is exothermic as I said or the catalyst regeneration is an issue. So, these are very commonly used. So, some examples if you look at here, the ammoxidation of propene to acrylonitrile, which is a SOHIO process; and, it is a mixture of propene and ammonia. So, propene – C 3 H 6, ammonia and air reacts over a bismuth molybdenum oxide catalyst.

Temperature is around 400 to 500 degree centigrade; and, pressure is 0.3 to 2 bar; high gas throughput is desired; catalyst particles are kept small. This is 50 micron particles. 1 micron is 10 to the power minus 6 meter; so, 50 micron particles. And, high heat of reaction is removed by cooling coils. So, reaction is highly exothermic. So, in that case, again when you have fluidized-bed reactor as I said, one can have these advantage that, heat can be removed faster. And, that is a kind of cooling coil, which is incorporated in the fluid-bed to remove the heat during the process.

And, another example is the oxidation of naphthalene or ortho-xylene to phthalic anhydride. And, here the liquid starting material is injected into the fluidized bed, which has a temperature around 350 to 380 degree centigrade, and large excess of air is used. The catalyst is vanadium pentoxide on silica gel catalyst support; and, low gas throughput; and, catalyst diameter is here with up to 300 micron. These are given in micron – 300 micron. So, these are some examples.

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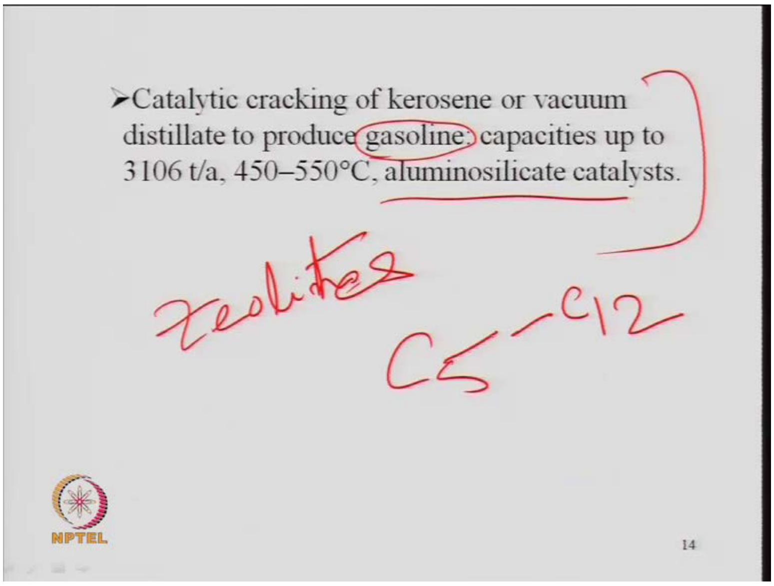

- Catalytic cracking of kerosene or vacuum distillate to produce gasoline; capacities up to 3106 t/a, 450–550°C, aluminosilicate catalysts.

An important example, which I repeatedly said is the catalytic cracking of atmospheric gasoil, vacuum gasoil, kerosene, naphtha to produce the gasoline. So, this is what is called FCC gasoline – fluid catalytic cracking gasoline. And, capacity is up to say 3000 tonnes per annum; temperature is around 450 to 550 degree centigrade. This will depend on the type of feed stock.

So, lighter feed stock will require a lower temperature; heavier feed stock like atmospheric gasoil, vacuum gas oil – there the temperature requirement may be 550. And, the catalysts are generally the aluminum silicate type catalyst; and, which is what I told zeolites. So, these are generally the zeolite materials, which are silica aluminum materials; and, they have the enough resistance at this condition of cracking. So, they can sustain up to 650 or 700 degree centigrade. So, these kind of zeolite materials – they are highly acidic in nature.

So, a good kind of acidity is desired when you look at the cracking of hydrocarbon. So, any hydrocarbon when you crack will turn to a range of gasoline hydrocarbons. So, gasoline, which is something like c 5 to c 12 range of hydrocarbons containing paraffins, naphthenes, isoparaffins and aromatic. So, desired are isoparaffins because they have higher octane number. But, in this case, you get mainly c 5 to c 12 range of the naphthenes and aromatic range of hydrocarbon, which is good for as an additive for the gasoline. So, that can be called FCC gasoline.

But, if you need more isomerization, then isomerization reaction of these kind of straight chain hydrocarbon can be done separately; and, that is isomerization. Or, sometimes the hydro-isomerization, where that olyphenes or double-bonded compounds are for saturated and followed by isomerization. So, that is again a component or used for the additives for the FCC gasoline, because these FCC gasoline may be low octane number. So, one needs to improve the octane number as per the requirement, which may be around 80 or 90; that depends on the rules – environmental regulations and statutory regulations. So, one can control the octane number by controlling the product distribution.

So, in general, the gasoline is a hydrocarbon, which has the carbon numbers from c 5 to c 12 range and contains mainly all paraffins, naphthenes, aromatics, but, isoparaffin and aromatic because they have the high octane number. So, they are preferred. But, aromatic also has certain limitations; aromatic should not exceed more than 35 percent; and, especially benzene is not desired; it should be less than 1 percent because of the environmental regulations. So, one needs to look at the quality and accordingly the alkylated gasoline, polymer gasoline. So, different kind of vacuolar fuels are available in terms of that grades. So, that I am not discussing here.

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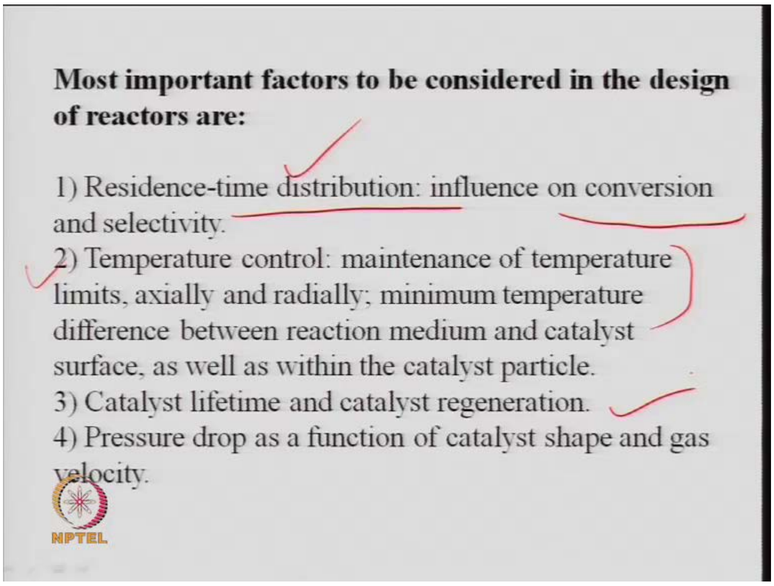

Most important factors to be considered in the design of reactors are:

1) Residence-time distribution: influence on conversion and selectivity.
2) Temperature control: maintenance of temperature limits, axially and radially; minimum temperature difference between reaction medium and catalyst surface, as well as within the catalyst particle.
3) Catalyst lifetime and catalyst regeneration.
4) Pressure drop as a function of catalyst shape and gas velocity.

The important factor if you look at in the reactor design, which I told last time also that, whether it is a fluidized-bed reactor or a CSTR or a plug flow type reactor or pack bed reactor, we need to first look at the hydro dynamic; that is, a residence time distribution inside the reactor. So, as I said, that, this RTD study – that is generally done by tracer concentration. Now, the radioactive methods are, radioactive type of tracer materials are used. And… So, the idea is that, we are trying to find out the concentration down the length of the reactor under the given condition; so, flow conditions for… Just the basic idea is that, how much time the reactant species is spent inside the reactor in the presence of catalyst. And, that will decide the conversion.

So, when you say the plug flow reactor, we assume that, every particle spent same amount of time inside the reactor. But, this is not possible, because I said that, there are not only the convective flow, because when we say that convective flow, we are saying that, fluid motion is only because of its velocity term. So, I write C A concentration and times the velocity times the area of cross section, but this is not true all the time. So, as I said because of the non-ideal parameter, the kind of molecular diffusion – is just like a molecular diffusion when you have a concentration gradient. So, the transport is because of that diffusion. Here it is because of dispersion. What is dispersion? And, that dispersion what I said the last time is the kind of distribution of the molecules in radial as well as in axial direction; that is, in the direction of flow and across the direction of flow.

And, that how much is the deviation that we get or that information we get from RTD, that is, a residence time distribution study. So, we give a pulse tracer or we give some step input of these tracers. They are just like a say you take a dye and then put it in water; and then, at the exit, you see that, when the concentration of that dye becomes 0. So, actually, theoretically, if you add the dye, a small concentration of dye in the water even in a laminar flow; it should come at the same time without mixing, because in laminar flow, you say that, there is less mixing; but, it will not happen. Even in laminar flow, you will see that, there is a kind of a velocity profile in the tube.

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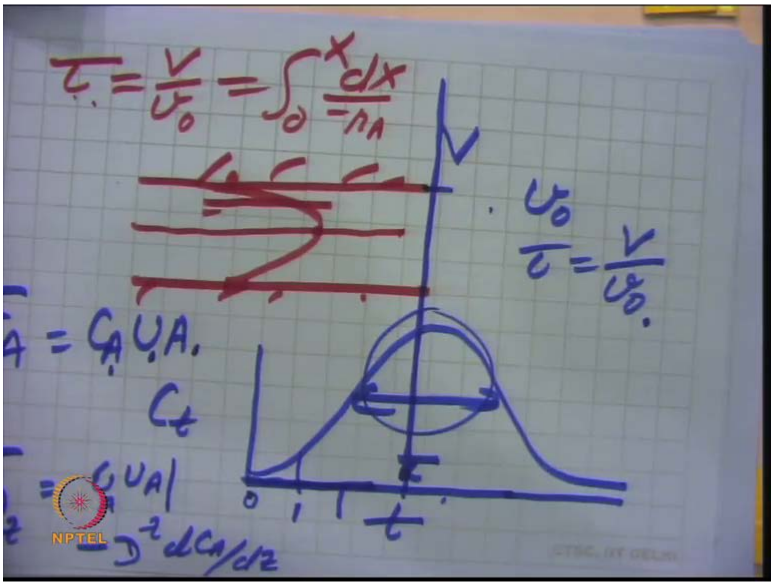

When you have the flow or transport phenomenon, you must have read that, the flow that, it will show a parabola. So, this is the velocity profile. So, if this is the velocity profile, it means the velocity is 0 here, velocity is 0 here. This is the pipe valve. So, there is no velocity here. And, the velocity is maximum at the centre of the tube. So, it means there is a kind of viscosity; because of this viscosity term, you get this kind of profile. So, flow is not ideal. And, because of this velocity profile, there will be a kind of concentration profile also – degree of mixing or what I call back mixing in the reactor. And, it means when this happens, whatever the tracer you inject, will not come at the same time even if you have a plug flow type.

So, it will disperse. So, at some point, you will have high concentration of tracer; which I was just talking yesterday that, if I just take a concentration versus time profile, I will get a distribution something like this. So, you have injected the tracer at t is equal to 0, but you expect that, sometime suppose the height, length, volume of this reactor is v; volumetric feed rate is v 0. So, the residence time is v by v 0 if it is a plug flow reactor; volume of reactor divided by volumetric feed rate. This is the residence time.

And, if you say plus flow reactor, then I said yesterday also, if this is the tau, then I should get everything at this point. So, a largest pipe should come here; that is, this is equal to a total concentration representing the total concentration. But, this does not happen. So, what will happen? You get some concentration here at time say t is equal to

1 minute; some concentration t is equal to 2 minutes and so on, so on. And of course, the maximum value you are getting at around the mean residence time. So, this time it becomes tau – mean residence time – mean. And, this is the deviation from the mean something like here spread.

So, it is spreaded now. So, that is a kind of diffusion phenomenon. Or, here we call it dispersion, because it is not a molecular property, but it is a flow property; it is a kind of non ideal flow behavior. And, because of this, you need to find out how much is the time, which is spent by each reactant element, because it is not the actual reactant distribution, where you say that, every element is spending same time. So, you define tau is equal to v by v naught and you write it like this in a plug flow reactor. So, this is the plug flow reactor.

Here you say that, every element has spent same time. So, you write the expression like this. But, if this does not happen, we need to look at what is the deviation; why that deviation has arrived. And, that has arrived because there is in this direction some gradient, there is some gradient in this direction.

So, radial and axial gradient exists. And, because of that, the total flow, which you write F A in plug flow something like C A into U times A – concentration times superficial velocity times area of cross section of the tube. And, this is what the volumetric flow rate. But, now, this F A at any point z if I write, this is this term C A time U times A evaluated at z plus another term, which is the dispersion or minus D d C A by dz; something like this.

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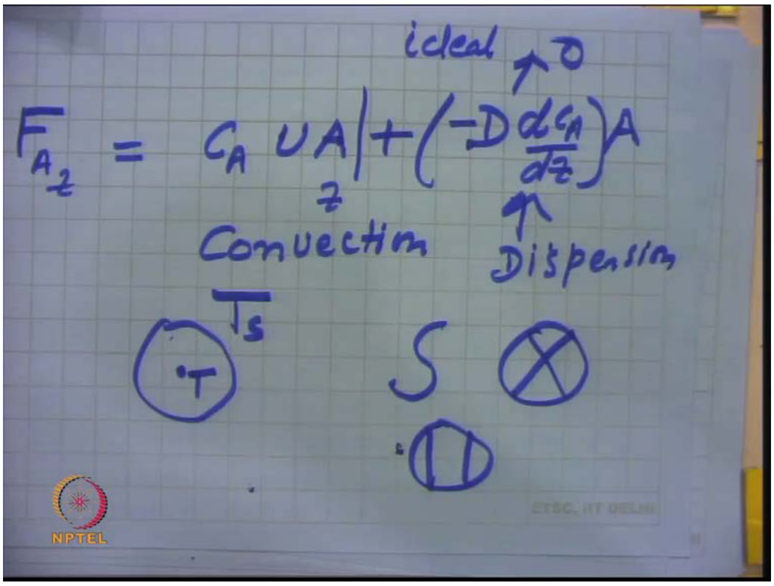

So, just to clarify that, because of this dispersion – non-ideal term, C A into U times area of cross section evaluated at z point if I write here; this is the kind of convective flow plus a dispersive term, which is written from the fixed law of diffusion. So, minus D, which is now dispersion coefficient times d C A by dz, which is the flux. So, multiplied by the area of cross section. So, this is the convection term; and, this is now a dispersion term and a kind of non-ideal parameter. This can happen in the direction of flow; this can happen normal to the direction of flow also.

So, this is what… If you say the reactor is ideal or behaving like a plug flow reactor, this term will be 0 for ideal reactor. You need not to work… In that case, it means the RTD is representing the same time, which is equal to tau. So, you need to find out this D, which is a kind of diffusion coefficient, but not actually diffusion coefficient, because diffusion coefficient is a property of molecule; but, here it is a flow property. So, this is very important to study, because this will affect the performance in terms of conversion, in terms of selectivity.

So, a commercial reactor – when you do it from small scale reactor and you scale up, then the property may not remain same. But, we tried to look at some kind of, that is, dimensionless numbers; as I said, picklet number yesterday; dispersion number, where you talk D upon U L – a kind of a non-ideal parameter. So, we talked these terms and then we scale up. Then, superficial gas velocity, diameter of the reactor, length, height of the reactor, size of the catalyst particle – so, all these factors will become important when you scale up the reactor or commercialize the reactor. And, these need to be checked or need to be studied.

The second is the temperature control. So, that is again important especially when the reactor is operating under non-isothermal condition. So, maintenance of the temperature limit. So, axial temperature gradient, radial temperature gradient, minimum temperature difference between the reaction medium and the catalyst surface; and, this is very important within the catalyst particle, because when you look at a catalyst particle – a solid particle like this, here is some temperature T s and it will be some temperature here T different.

So, because of this temperature, when the reaction is exothermic, temperature at the center of the pellet will be maximum. And, here it is the… Surface temperature may be just the reactor temperature. So, conversion is down the length inside the pore. So, at the centre, you may have maximum temperature. So, this is something like what you call non-isothermal parameter. And, you need to calculate it because this will affect and will be a function of temperature like RNS parameter we discussed – E upon r T. So, all these factors will be important when you look at the temperature or thermal gradient in a pellet. And, that is also to be checked because the maximum stability or temperature required; beyond which the catalyst will become unstable or it will sinter. We have to avoid that temperature. So, hot spot formations – that is to be avoided. And, for that, you need to look at the work on that, the temperature gradient or temperature difference in a pellet.

Then, catalyst life time, catalyst regeneration – these are important. I said that, when you have a fluid catalytic cracking, you ((Refer Slide Time: 58:04)) the catalyst is deactivating faster. So, you looked regeneration. So, regeneration of a catalyst – I told is possible, but not in all cases. So, when the carbon deposits on the catalyst, you can regenerate it just by burning the carbon with oxygen.

So, when you burn the carbon with oxygen, you get carbon dioxide; which is again an exothermic reaction. So, here again when you have a carbon or coke removal from a catalyst, you need to look at simultaneously that, the temperature of the catalyst bed or should not exceed beyond the limit or permissible limit for the catalyst. So, you have to just… Either you add something fresh catalyst or you do the reaction in such a way that, partly it goes to the carbon dioxide and partly converts to carbon monoxide. So, you need to control C O 2, C O 2 ratio in the bed; you need to look at what should be the air flow rate; and, also you need to look at how much coke can be removed.

You cannot remove all the coke if the temperature rise is very high; you have to make it in stages. So, this is again an important issue for design of a reactor and selection of a regenerator – suitable regenerator; and, reactor-cum-regenerator system for a process especially when the catalyst or coke deposition on the catalyst is very high – significant amount of coke. So, 5 percent, 10 percent – this is the amount of coke, which can be deposited on the catalyst just after a day. So, you have to look at that. So, amount of the coke deposited on the catalyst from the lab scale study and then scale up it to a larger scale. So, that is again an important issue. So, life time of catalyst is important.

Pressure drop as a function of catalyst shape and gas velocity – so, as I discussed that, pressure drop… See you know in the fixed-bed reactor, the calculation of pressure drop, fluidized-bed reactor pressure drop. So, this Kozeny-Carman equation, Blake-Plummer equation – you must have read in fluid mechanics. So, you know that, how to calculate these. So, this pressure drop you know in the bed is a function of the porosity of the bed. Simultaneously, it depends on the sphericity of the particle if it is a non-spherical particle.

So, for a spherical particle, one can calculate whatever the Kozeny-Carman correlations. And, same thing for the non-spherical particles. So, what I mean to say that, this pressure drop is also a function of one thing in the superficial gas velocity. So, of course, higher the gas velocity, the pressure drop will increase. But, simultaneously, it is a function of shape of the particle also. So, especially when you have a mass transfer control reaction, you look at the shape of the particle, because you try to enhance the surface area of the catalyst per unit volume of the catalyst. So, you try to have a definite size and shape of the catalyst in the bed.

Also, as I said that, when you have smaller particles, the pressure drop in the bed increase. So, it means we need to look at that, pressure drop should not exceed beyond a certain limit, which is prescribed. So, we need to look at that what size and what shape of the particle. So, shape of the particle may be like this. In a packed bed mass transfer, you know the intellect saddles or different type of ((Refer Slide Time: 1:01:29)) rings like this – this kind of structures – parallel like this kind of structure. They are used. The idea is that, to reduce the pressure drop in the bed. The similar thing is done in the case of catalytic reactors also. So, the catalyst selection is depending on the size of that catalyst also, so that the pressure drop should not be exceeding. But, when you have larger size particles, the mass transfer problem will arise. So, you have to control that, there should not be any mass transfer limitation; and simultaneously, there should not be very high pressure drop. So, the particle should not be very fine also. So, these are some issues, which need to be considered when you select a reactor and the catalyst for the process. So, with this, I stop here and I will continue it in my next lecture. So.

Thank you.