Heterogeneous Catalysis and Catalytic Processes

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Lecture - 37
Trickle Bed Reactors

Good morning. In my last lecture, I was talking about multiphase reactor; and I just discussed the basics about these multiphase reactors like bubble column reactors, slurry bubble column reactor; and I was talking a trickle-bed reactor.

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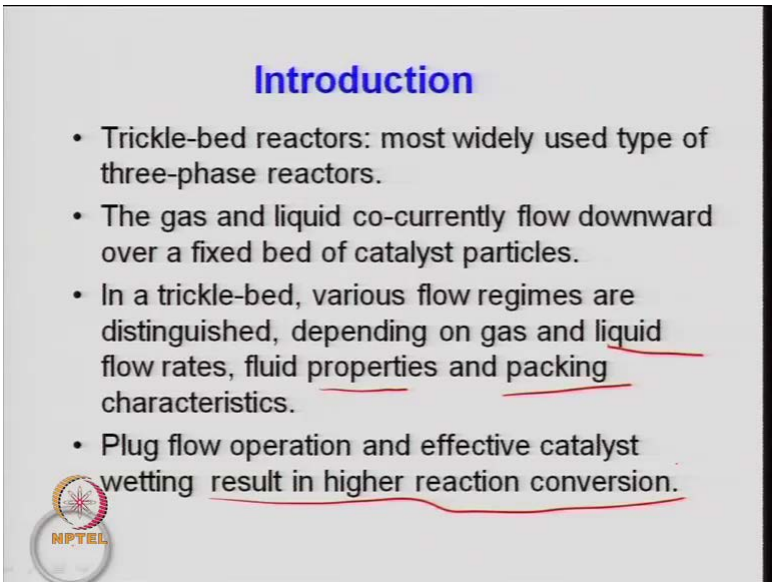

So, let us continue trickle-bed reactor today. Already discussed briefly about the trickle-bed reactor. So, trickle-bed reactors are the type of reactors in which the gas and liquid flow from the top of the reactor that, in co-current or counter current flow. And, the basic idea here in the trickle-bed reactor – if you compare it with the packed bed reactor; in the packed bed reactor, also the similar operation is done. The only thing that, the trickle-bed reactors are mainly governed by mass transfer operation. So, a larger size of catalyst particles are generally used in this kind of reactor. Another thing is that, the flow rate of the liquid is low. So, it trickles on the surface of the solids. So, this is a solid catalyst. It is porous type of material.

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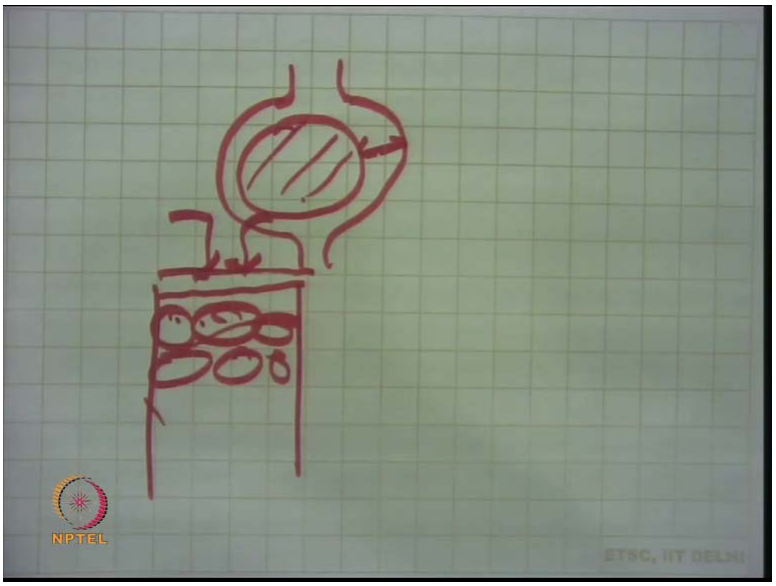

And, over that, the liquid comes like this in the form of droplets or rivulets. And, a thin film is formed across the surface of the solid and then it falls down like this. So, the advantage is, because of this thin film, there is a good contact between the gas, liquid and solid. And, these operations can be done at high pressure. And, the flow rate of the gas and liquid is a decisive factor in this kind of reactor. So, let us continue some design aspects of this trickle-bed reactor also. So, before that, some fundamentals of the trickle-bed reactor, which I discussed last time; I would like to recall that. So, in this trickle-bed reactor, that gas and liquid co-currently flow downward over a fixed bed of catalyst particle. So, already the catalyst is inside the bed just like you do in a packed bed reactor. So, there are the catalysts lying there in the bed.

And, the liquid and gas flow that comes from the surface like this – top of the reactor. So, good kind of distribution is desired here between gas and liquid. So, distributed design in the trickle-bed rector or any multi-phase reactor is very important. Channeling is to be avoided because dead zone channeling – they will affect the performance of the reactor or decrease the conversion inside the reactor. So, RTD or residence time distribution study, which I was talking last time is very important in these kind of multi-phase reactor. And, depending upon the type of solid, the properties of the solid, gas and liquid, temperature, pressure, the residence time distribution and the pressure drop in the reactor may be affected. And, these are very important parameters while considering a

commercial reactor for the definite gas liquid reaction in the presence of a solid catalyst in a trickle-bed reactor.

So, the operation can be co-current; counter current is not very common, but R and D is being done on that area also. But, co-current either upward or downward. So, most of the time, it is downward flow operation at present. So, various flow regimes are formed. When you have a gas, you have a liquid; and then depending upon the gas and liquid flow rate, the flow regime may be also change. So, one needs to control a definite flow regime or control or look at the flow rate of gas and liquid in order to have a trickle-bed or trickle-flow regime. So, that is again important. And, that will depend on the gas and liquid flow rate as I said before, properties of the gas and liquid. So, it will depend on the viscosity; it will depend on the surface tension; and hydrodynamic parameters are very important. So, the pressure drop need to be checked. So, it will depend on the wetting, wetability and holdups, that is, gas holdup and liquid holdup; that is, the volume of liquid, which is inside the reactor per unit volume of the bed. So, that is again important; and the packing characteristics since it is mainly governed by mass transfer operation.

When you have mass transfer operation, you need a definite kind of packing – structural packing. So, just like in a packed towel, you look at different kind of the packing materials, because the surface area per unit volume is very important; and that will depend on the type of the gas, which is to be adsorbed in the liquid. So, packed-bed adsorption column, which is a mass transfer phenomenon. But, in trickle-bed reactor also, the gas and liquid… So, gas is to be adsorbed in liquid. Depending upon the solubility of the gas, the temperature, pressure – these conditions are to be adjusted. That is again important besides the thermodynamics; that is, the reaction condition is actually required. And, simultaneously, since the gas is adsorbed in the liquid; and then it will diffuse and then react at the surface of the solid. So, transfer phenomena or transfer property are very important and one need to check all these properties or control by looking at the resonance time distribution in a trickle-bed reactor. So, trickle-bed reactor parameters need to be studied.

Hydro-dynamic study has to be done and also that, the actual reactor condition performance, or conversion and efficiency is also to be tested. So, plug flow operation can be achieved in the trickle-bed reactor. And, effective wetting of the catalyst results a higher reaction conversion. So, one needs to try the RTD. And, based on the RTD

operation, which is generally you calculate or measure, dispersion number D upon U L or the peclet number; and then you correlate these numbers. You check this peclet number for a plug flow reactor when it is close to that. So, you try to get a closer to a plug flow reactor. And, that can be done by avoiding the maldistribution, by avoiding the channeling and having a good kind of distributer in the reactor. And, of course, when these things are achieved, plug flow condition is achieved; then one can have higher conversion in a trickle-bed reactor.

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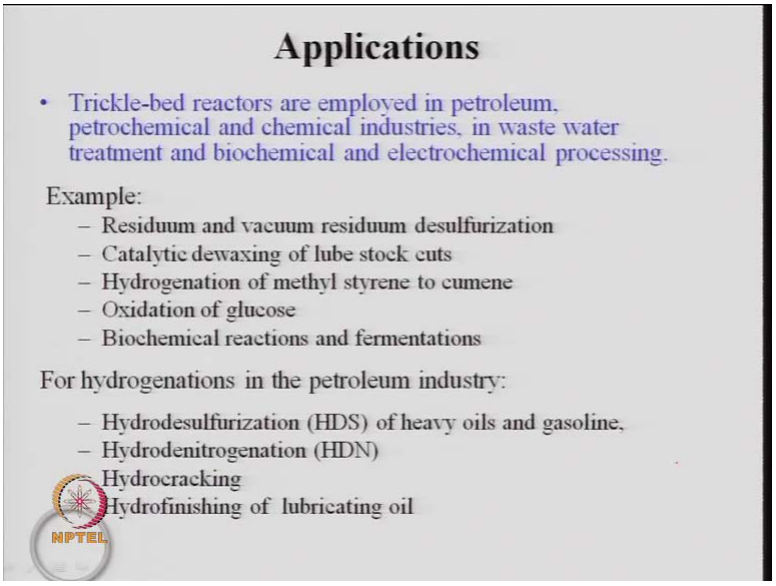

So, application wise, I told these are widely used in the refinery and petrochemical industry as well as in the waste water treatment. So, trickle-bed reactor application is very wide in petroleum, petrochemical and chemical industry and in the waste water treatment. And, they are also used in the biochemical and electrochemical process. So, activated sludge process, which is generally used for the treatment of waste water; that is again a kind of say you have a solid material and on that, some micro organism – they grow and the liquid trickles on the surface of the solid. So, it is a kind of trickle-bed reactor. So, that…

And, advance oxidation process say removal of organic compounds like phenol. So, that is done by wet air oxidation process. And, these are mainly the mass transfer control processes. So, there also the trickle-bed reactor is used. So, some of the examples, which has been mentioned here is the residuum and vacuum residuum desulfurization. So, I told

you the trickle-bed reactors are widely used for the hydro-desulphurization reaction. Now, residuum and vacuum residue – these contain the large amount of sulfur, which is a mercapton benzothioprine and cyclic sulfur compound basically – disulfide. So, these need to be reduced; the sulfur concentration is to be reduced to a certain level before processing it for further say cracking operation, vacuum gasoil cracking or FCC cracking. So, sulfur has to be reduced. So, there again a trickle-bed type of reactors are used. Same thing for catalytic dewaxing of lube stock. So, that is again important when you look at the four point characteristics of the lube oil like. So, wax compounds are to be removed. So, for dewaxing, a trickle-bed reactor is used. Generally, again it is a hydro-dewaxing of these compounds and cracking followed by dewaxing. So, basically, the larger range of paraffin hydrocarbons are to be removed, because paraffins – these are wax compounds. And, when they… In the cold countries, especially when the temperature is low, these may get solidified. So, we need to remove these higher molecular weight paraffin hydrocarbons. So, hydro-isomerization is one way by which it is cracked and isomerized to get a gasoline range of hydrocarbon. So, these kind of treatments can be done and also again in the category of hydro-treatment.

So, same thing for hydrogenation of methyl styrene to cumene. So, basically, a petrochemical process, where cumin is used to produce the isopropyl benzene. And, that is again an important petrochemical process. Oxygenation of glucose material – that is just like a phenol oxidation as an example. So, glucose oxidation is again done in the trickle-bed reactor. Biochemical reaction, fermentation – these are some other examples, where the trickle-bed reactors are commercially used. Similarly, for hydrogenation, which I have already said hydro-desulfurization of heavy oil gas fraction, gasoline – samething – hydro denitrogenation. So, overall, you can call it hydro-treatment for hydro-cracking, where cobalt molybdenum or nickel molybdenum type of catalysts are used. So, trickle-bed reactors are used for this process. And, hydrofinishing of lube oil fraction; which is again similar to what I discussed here in the case of this catalytic dewaxing of lube stock. So, similar things are done by using the trickle-bed reactor.

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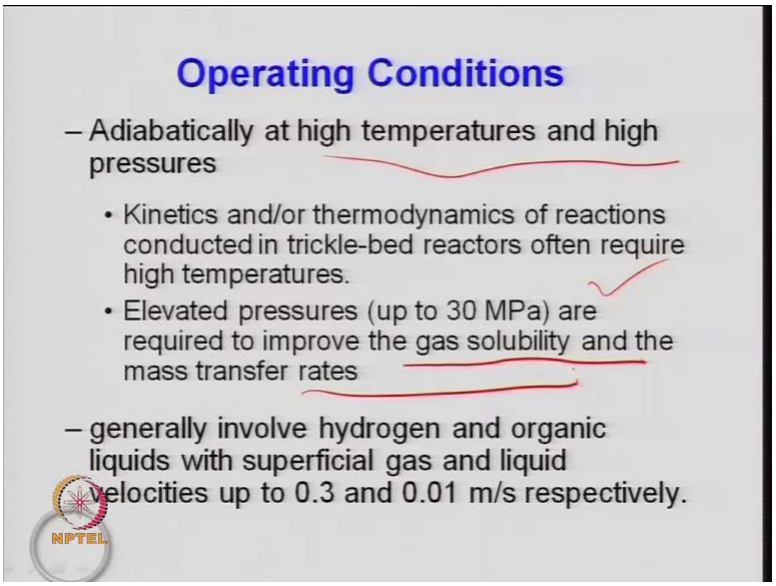

Operating conditions – generally the trickle-bed reactors are operated at high pressure. So, solubility – that is one thing; thermodynamic criterion is another thing; which requires a high pressure for these kind of operations; so, high temperature and high pressure. So, temperature is governed based on the thermodynamics, which is required. And, same thing for pressure; and again pressure is also required to increase a better contact between gas and liquid, so higher the solubility, which is desired because hydrogen is not easily soluble in kerosene.

So, if you have high pressure, then the solubility will increase. So, kinetics in thermodynamics what I said of reaction conducted in trickle-bed reactor often require high temperature. So, generally, all these reactions, which requires hydrogen – they are generally exothermic reaction. And also, they require the high temperature and high pressure, which is governed by the thermodynamics. So, that is one important aspect. Here in trickle-bed reactor, they can be operated up to pressure of say 30 MPa – mega pascal – 300 atmosphere. So, that is the operation, which is there in a trickle-bed reactor. So, 50 atmosphere to 250 or 350.

When you need more and more severity in one way; that is, when you need that, the concentration is to be reduced to a further lower say the… because of the restrictor environmental norms. So, earlier, the sulfur content in the petrol is roughly 50 ppm, but now, it says that it should be 0 ppm or 10 ppm. So, that depends on the… – varies from

countries to countries. So, developing countries have something like 10 ppm. But, already developed countries – they have the 0 ppm; which is further… That is important aspect to look at these kind of severity of operation. So, when you have to reduce the sulfur concentration to a lower level; it means you need to increase the temperature, increase the pressure, and then check whether it is possible or not. So, excessive high pressure may be required; which may not be suitable for the reactor operation. So, one need to check that part also or find out the alternatives or change the catalyst, which is more effective, more active

Or, look at the hydrodynamics what I was talking that, that affects the performance of a trickle-bed reactor. So, that is very important when you commercialize a process. So, you have to select a catalyst for a given reaction and then look at the reactor design also; how the catalyst is placed inside the reactor; how the process conditions or physical conditions are adjusted in terms of the flow patterns like distributed design and how to avoid the channeling, how to avoid the flooding. So, all these dead zones. So, these things need to be checked. So, generally, high pressure up to 300 atmosphere or 30 mega pascal are required to improve the solubility and the mass transfer. So, this is what I was talking that, the mass transfer operation or mass transfer governed operation. So, mass transfer operation is very slow in this trickle-bed reactor. So, if you need to improve that, you have to either increase the solubility of the gas, which is governed by the Henry law.

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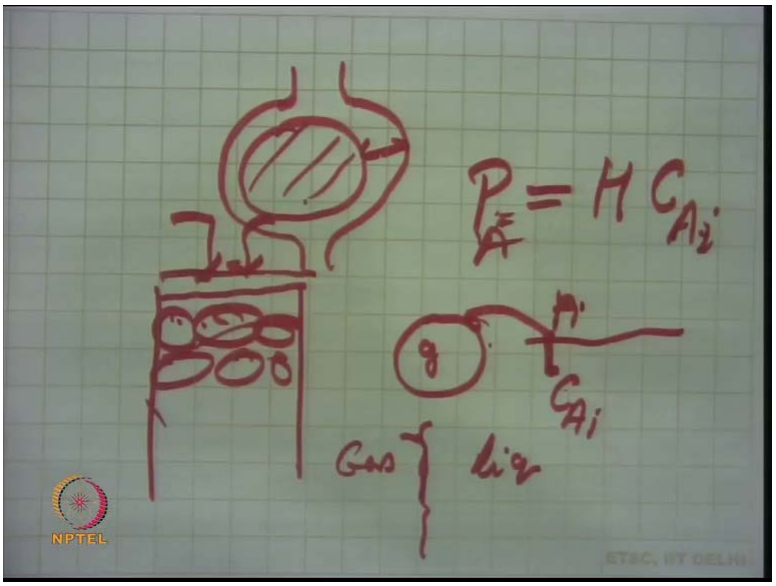

You know the P A is equal to H A times C A i – something like if I say the gas solubility; that is related to partial pressure of A is related to some Henry law constant time the concentration of that gas at the interface or gas liquid interface, because basically, there is a gas bubble. So, gas is g here; and this is the surface interface; and then there is a bulk liquid here; something like that. So, from here the gas will reach to the surface here and then it will be absorbed or whatever the P A i here. And, depending upon this interfacial relation or equilibrium relation, there will be a concentration at the gas-liquid interface; or, from one is the gas film; another is the liquid film. So, from gas film to liquid film. So, I will show a film like this. So, there is a gas and there is a liquid. And, from here to here, there is a kind of transport. So, there is a kind of membrane or a film through which the gas has to diffuse. So, that will depend on the thickness of that film; that will depend on the equilibrium composition or concentration of the gas in liquid. So, that is governed by the Henry law. So, this is one thing.

And, simultaneously, other process conditions are also equally important if you look at the higher mass transfer rate. So, that is what I told – wetting – wetability. So, all these fundamental things of the solid porosity catalyst, that is, type of catalyst; and that will also be important. Size of that catalyst will change; also change the mass transfer rate at the surface of the solid. So, we will talk on that little later. So, generally, the reaction involves hydrogen; and organic liquids as I said the kerosene. So, you are removing sulfur from kerosene; something like that. Or, this is wet air oxidation; then I was talking of the phenol compounds from the waste water are to be removed.

So, you are oxidizing basically and you get the carbon dioxide something like… So, these kind of reactions are generally done in a trickle-bed reactor. So, when you have these kind, the superficial velocity of gas and liquid is important. So, depending upon the gas to liquid ratio – superficial gas velocity or liquid mass velocity LG divided by the gas mass velocity. So, depending upon these, you will have a change in the flow pattern. So, it may change from bubble flow mist to mist, mist to spray and like that depending upon the velocity of the gas. So, it means when you are working in a trickle-bed reactor or trickle-bed region, also you need to identify first. And, that will depend on the type of gas, type of liquid. So, you try to have a thin film of the liquid on the surface of the solid. So, particle size is relatively higher here in this case; it can be up to 5 millimeter of the particle – catalyst particle.

When you have a packed bed reactor, you try to take a lower particle size. And, that will be decided based on the effectiveness factor of thulium model; which you check that and then try to reduce the particle size in such a way that, this mass transfer into, that is, through the surface of the solid is avoided; or, resistance is to be avoided either. So, mass transfer rate will be very high. So, the rate controlling step when I say; it means it is the slowest step of the process. So, most of the time, the reaction when it is kinetically controlled, we assume that the mass transfer rates are very high. So, it means the external mass transfer rate and diffusion into the pore of a solid. So, all these rates are very high. So, these are not controlling the overall transport for the reaction. So, all the time, your concentration is available at the surface of the solid. But, now, kinetics is controlling. So, kinetics has to be checked in terms of the temperature or the concentration of the reactant species. So, this is the meaning that, how many resistances are available and how to cut down these resistances.

So, this is what – when you look at trickle-bed reactor, you will have more and more mass transfer resistances between the gas-liquid, between liquid-solid, and at the surface of the pore of a catalyst. So, we need to check these things and we need to control in order to have the higher efficiency or higher rate of reaction. So, generally, if you look at the superficial gas velocity in the trickle-bed reactor, is up to 0.3 meter per second. So, this is superficial velocity, which is based on the cross-sectional area of the column. So, this is basically the flow rate of the gas divided by the area cross-section. So, volumetric flow rate divided by the area cross-section. And, that will give you the superficial gas velocity, which is based on empty column. And, for liquid, the superficial gas velocity is roughly 0.01 meter per second.

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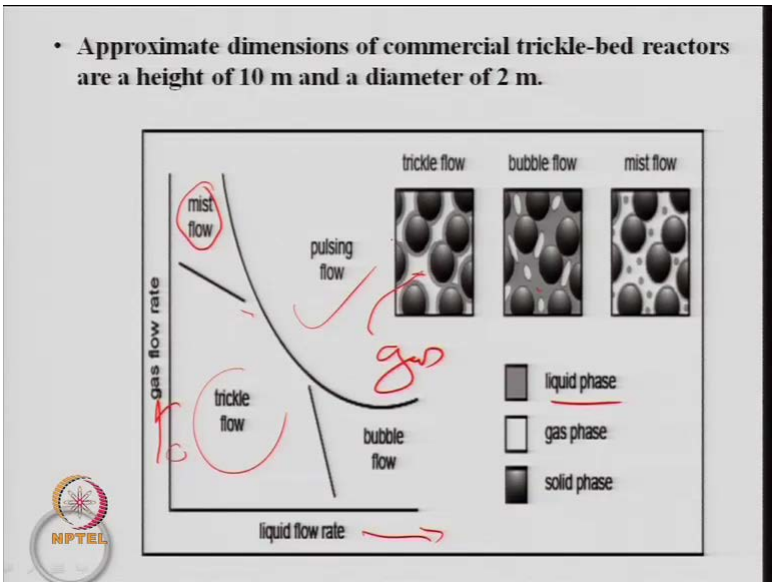

So, I was talking that, depending upon the gas flow rate and liquid flow rate, you can have a trickle flow, you can have a bubble flow, you can have a mist flow also. So, all these types of flow can be possible when you have a reactor or a multiphase reactor, which is something like a trickle-bed reactor. So, in here roughly, the commercial trickle-bed reactor – they have a height say up to 10 meter and diameter 2 meter. So, I told the L by D ratio; D by D catalyst diameter, reactor diameter to particle diameter in order to avoid wall effect. All these things are very important. But, you need to check at simultaneously very large column is also very difficult to handle. So, all these factors need to be checked when you get a size of a reactor for a given productivity; and then take a definite L by D ratio to have a plug flow condition; and simultaneously select the catalytic particle size in order to avoid the wall effect. So, this simply says here a gas flow rate. So, this side, it is a gas flow rate; and this side, it is a liquid flow rate.

So, what I mean to say, either you look at a ratio of gas flow rate to liquid flow rate; or, you just… If you look at the effectively… If you increase the gas flow rate for a given say gas flow rate; if you increase the liquid flow rate for fixing a gas flow rate; and as you increase the gas flow rate, the region changes to bubble flow region. So, this side it is a trickle-bed region, which is something like this. So, liquid on the surface of the solid – it trickles. So, very low flow rate basically – low liquid flow rate. So, low gas, low liquid – that will give you a kind of trickle flow. So, the liquid is just trickling on the surface of the solid. And, when you increase this liquid flow rate, it will start a bubble –

a bubble flow. So, this is a kind of where you can see the bubbles here or you will have something like this white portion if you look at here, this is a gas phase. So, this white portion is a gas phase here. Here the gas is reduced because the liquid flow rate is high now. So, more liquid. So, holdup of liquid is higher in this case. Here the holdup of gas is more relative if you look at. So, more white spot means this is the gas here – the white belt. And, this is the liquid here, which is shown here. So, black or gray portion – that is liquid. And, this is solid. So, when you have this kind of thing, increase the flow rate.

And finally, when you keep on increasing, ultimately you have a bubble flow in this region, which is something like a high liquid flow rate. So, at higher liquid flow rate, you will have a bubble flow; that is, just now, I was talking about bubble column reactor or a kind of slurry bubble column reactor. So, already the liquid is inside the column and... So, you have a large volume of liquid in the column and gas is being bubbled or spurged from the bottom. So, liquid is already there in it. But, in the trickle flow, you do not have liquid inside the reactor; it is trickling from the top; and gas is also coming along with it. So, liquid trickles on the surface of the solid. So, you will have something like a flow; which is where you have more gas and low liquid. But, when you have a higher flow rate, the liquid covers. So, this becomes a kind of bubble flow and so on. So, you can…

And, when the gas flow rate is very high, then liquid will come in the form of just like a droplet – small droplet – mist flow – just like a cloud droplets you see, fog you see. So, it is a kind of mist flow here. So, depending upon the flow regime, you can see here when a gas flow rate is very high and liquid flow rate is low, you get a mist type of flow. So, it is now not covering the surface of the solid, rather the liquid has come in the form of droplets – drop of liquid. And, when you have a region; this is the region, where you have some intermediate gas flow rate, which I told you here something near 0.3 meter per second of the gas superficial velocity; and 0.01 meter per second is the liquid.

So, you always have a trickle flow region. And, if you have high gas, high liquid; you will have kind of pulsing flow. So, pulses form. And, that is a different kind of flow regime, where you have the kind of the gas flow rate is very high, liquid flow rate is relatively high. So, it will be kind of the packed bed reactor type. So, that is again… So, what I mean to say is that, when you have a reactor like trickle-bed, you want to operate it under trickle-bed; you need to have low liquid flow rate. So, low liquid-low gas relatively compared to a packed tower.

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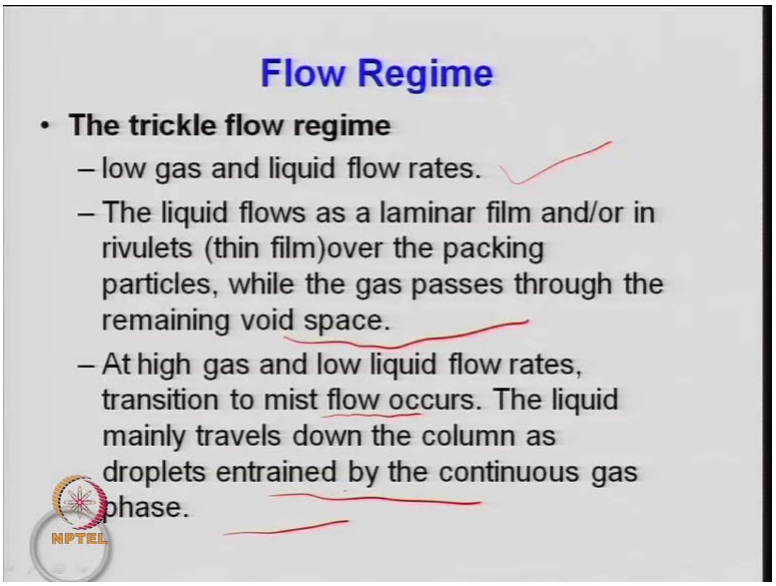

So, when you have a gas liquid flow rate controlled, where the liquid trickles on the surface of the solid and gas passes through that or diffuse through that; basically, I talk a mass transfer control region. We will talk on that little later as I said before. So, here in this case – trickle-bed reactor, the hydrodynamics is very important, which is governed or discussed based on the flow regime, what you get in the trickle-bed reactor depending upon the flow rate of gas and liquid. So, as I said, the trickle flow regime will require low gas and liquid flow rate. So, relatively – relatively low gas and liquid flow rate. Liquid flows as a laminar film.

So, low liquid means we are talking something like a laminar flow. And, this makes a kind of thin film or rivulets, droplets over the surface of the solid. So, it is rivulets on the surface of the solid, which is thin film over the packing particles, while the gas passes through the remaining void space. At high gas and liquid flow rate, when you have a very high gas and high gas flow rate and low liquid; that there is a transition to a mist flow, which I discussed here in this case; so, high gas and low liquid. So, it gives a mist flow. The liquid mainly travels down the column as droplet entrained by the continuous gas phase. So, this we do not want when you have it; you want to have a trickle flow regime.

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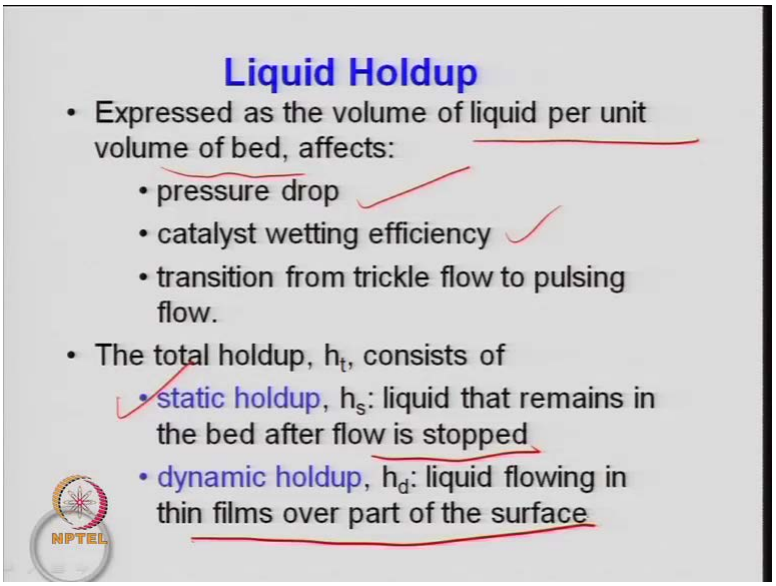

So, that is why a sufficient liquid flow rate is also important. It should not be too low; otherwise, you will have a mist flow. That is important here, because in order to have a high production or high conversion, you need to have a sufficient concentration of gas and liquid on the surface of a solid, because reaction takes place at the surface of a catalyst. So, it means the liquid should be sufficient, gas should be sufficient for the reaction. So, that is calculated or defined in terms of holdup. So, how much liquid is available inside the reactor when it is in operation or when you have just closed the walls.

So, that is known as a dynamic liquid holdup or a static liquid holdup. So, that is something, which is liquid, which remains in the stagnant points – pockets. And, when it is continuously flowing, what is the amount of liquid. So, these are important because the pressure drop will change depending upon the dynamic liquid holdup; pressure drop will change; flow rates are high; it will increase. So, all these parameters are known as hydrodynamic studies in trickle-bed reactor, where you look these flow parameter and correlate it with the performance of the reactor – the RTD study what I was talking, that is, in terms of the plug flow conditions.

So, liquid holdup is expressed as the volume of liquid per unit volume of the bed – very important parameter when we look the hydrodynamic study, which can be done by the computational flow dynamics also by selecting a proper volume of the system. And, one

can just look at the flow visualization or concentration of these and pressure drop at different location – radial, axial, and at different positions. So, that is important. So, the volume of liquid per unit volume of the bed. So, this is known as holdup – liquid holdup. So, this will be affecting the pressure drop, higher liquid holdup, more pressure drop, like that. This will also affect the wetting efficiency. So, wetting efficiency or wetting of a catalyst is again a very important parameter used for the design of a catalyst. So, whether you need a high wetting… So, generally, high wetting means the surface of the solid is completely covered; low wetting means the part of the surface is only covered. So, it means most of the surface of the catalysts is not being used right. So, in that case, you need to look at how to improve the efficiency; or, in some cases, it may need a partial wetting also. So, there you need to coat it with kind of teflon material, but not in all cases.

Most of the cases, you need high wetting efficiency, because that will decide your surface of the catalyst, which is being used or that correlates the surface of the catalyst, which is being used for the catalytic activity. So, transition from trickle flow to a pulsing flow – that will also depend on this holdup, because we have already seen that. At high liquid, high gas, the flow moves towards a pulsing flow regime; there is a transition. So, total holdup – the liquid, which is in the catalyst when you have a catalyst bed; so, liquid which remains there; that depends on the type, that is, static liquid holdup and dynamic liquid holdup. So, static as the name says this is the liquid, which is remained inside the bed or which is left inside the bed when the flow is stopped. So, generally, when you measure this… This can be measured experiment.

You have the flow continuously flowing from the top to bottom; all of a sudden you close both the walls from the top and stop the flow rate. And, now, you drain out; you drain out it; and then check how much volume of the liquid is there. So, that is basically the liquid when it flows continuously, everything is going in, something is going in, something is coming out continuously. But, this is the liquid, which remains in the void spaces between the solids. So, that is known as the static liquid holdup. So, how to measure that? That is the liquid, which remains in the bed after the flow is stopped. So, one can measure it. So, at different liquid flow rates, you will have different holdup till it reaches to some saturation volume.

And same thing here dynamic liquid holdup – it is the liquid, which is flowing in the form of thin film, because when you stop the flow, then all the liquid will fall down in the form of just goes down and goes up and comes out to the surface of the solid like this; trickle comes like this and then falls down. So, when flowing is stopped, then nothing is come; so, there will not be any liquid, only the liquid, which is between the pockets. Something like that zone when you say a CSTR type. So, that will be a static liquid holdup. And, when you have a continuous flow, the liquid is flowing in thin films over the part of the surface. So, at that time, whatever the liquid you have; that is the volume of the liquid, which is inside the bed. That is the dynamic liquid hold. That is a volume of liquid under running condition.

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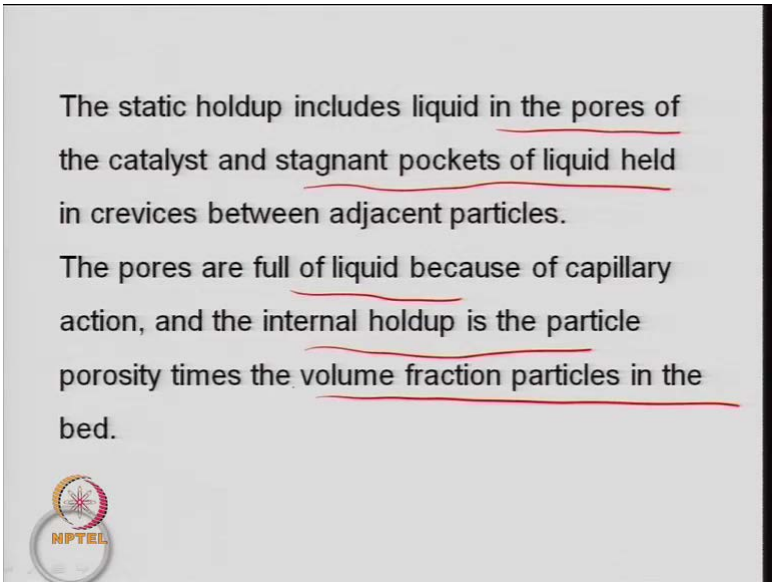

So, the static liquid holdup includes the volume of liquid in the pores of the catalyst and the stagnant pockets of the liquid. So, catalyst is already saturated. This is again important, because when you write a kind of kinetic expression, you write it rate proportional to the concentration of the gas and the concentration of the liquid. And, that will correlate based on the concentration, which is available in the bulk. So, something, which is important here is that, the liquid is or the pore of a solid is already saturated by the liquid; and the gas diffused to that, and then react with that liquid; and then it comes out – product comes out and again the liquid penetrates into the pore. So, all the time, the liquid is saturated. So, one can say that, there is a high concentration of liquid compared to gas. So, that is a design model – reactor design model when you assume that it is a

first order with respect to A. And then you report it pseudo, kinetics; that is, the order with respect to B. If B is the liquid, then it can be written in terms of the rate constant, because C B is a constant – high value of the concentration. So, we will talk on that.

So, the pores of the liquid are full, because of the capillary action. And, the internal holdup is the particle porosity times the volume fraction of the particle in the bed. So, if you know the particle porosity and you know that, what is the mass of the catalyst in the bed; which we are defining here in terms of the porosity of the particle multiplied by the volume fraction of the particle in the bed; that is, the volume of the catalyst divided by the volume of the bed. So, what I mean to say one can very easily calculate this static holdup because it is nothing but the volume of liquid present in the pore. So, porosity is known. So, how much volume will be there inside; the porosity is the pore volume divided by the total volume. So, pore volume of the catalyst divided by the total volume of the catalyst, which is the wide volume plus the solid volume. So, it means if you know the total volume of the catalyst, multiply this; and you can find out the pore volume of the catalyst.

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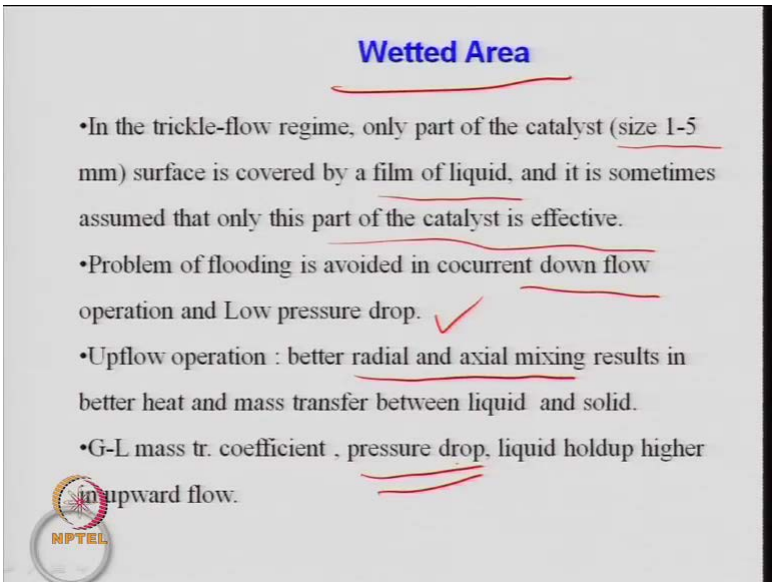

So, wetting is related to wetted area; that is, what fraction of the surface of the solid is covered by liquid. So, this is again important parameter in terms of the design of a trickle-bed reactor or how to improve this wetting if you need a high wetting or a high wetted area. So, again when you are in trickle-bed regime, I told you that, the catalysts

are generally of larger size. So, this is one thing. The surface is covered by a film of liquid as I said earlier also. And, we assume that, this part is the effective for catalytic reaction. So, now, if you have something like what I was talking a solid surface covered by a film of the liquid; the reaction or diffusion in mass transfer will take place through this now, if it is partially covered. So, practically, it is very difficult to measure.

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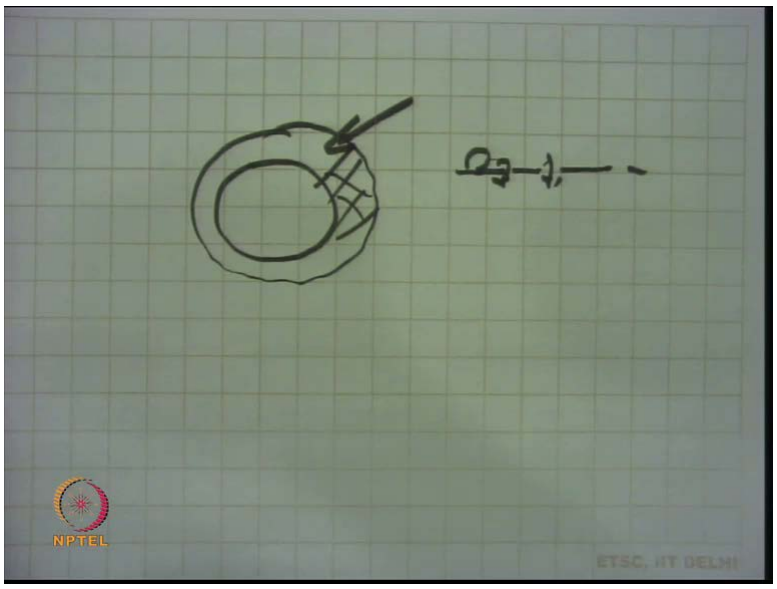

And, we correlated in terms of the wetting, which is related to something like a pining effect also, because liquid will come here; on the dead surface, it will be like this; then it will just diffuse into the pore of a solid. So, these are the pores of the catalyst. So, it is diffusing inside all the time. So, there will always be a kind of concentration difference at the surface of the solid. So, now, how much surface of the solid? Suppose only it is partly covered and this is a bear surface; here it is nothing. So, it means this surface is not being utilized by, because the gas needs some liquid for chemical reaction. And, trickle-bed reactors are mainly the mass transfer control – a kind of channel reactors, which I was talking or net type wire, net type reactor; where, now, monolyst can also be a catalyst for this purpose; where, the simple plates or a wire, which is placed inside say something…

Whereas, non-porous type of material; and then on that, the catalytic material – active metal is being impignated. And, that time, the reaction is only on the external surface. So, this is just a thin film or a small thickness, so that the diffusion resistance should be

capitated to its minimum. And, that is vas-coated type of catalyst, which can be used here in this trickle-bed reactor, because these are mainly mass transfer control process; the kinetics has less role; the kinetics is very fast. So, it means the hydrodynamics and wetting and wetability – both parameters are very important in terms of the design of this catalyst particle size and shape. So, that will decide the external surface area or the surface area per unit volume of the catalyst. Especially for the mass transfer, you need to look at that.

This is very important here. To make the catalyst effective, how the wetting can be improved? The problem of flooding again in the trickle-bed reactor, you may have that kind of problem of flooding. But, if you have a down-flow operation, the flooding problem is minimized. But, if you have up-flow operation, the flooding will be ((Refer Slide Time: 36:02)) that is, again the pressure drop issue will arise. When you have a down flow, then the pressure drop will be relatively low. Up-flow operations are advantageous because trickle-bed reactor has a problem in terms of the axial and radial dispersion, because it is a downward flow. So, there will always be a kind of wall flow. And, there will be a kind of axial gradient; in this direction of flow, there will be a gradient of concentration, there will be a gradient of temperature, because there is no mixer, no stirrer.

And, if you have radial gradient; in terms of concentration temperature, particle is larger in size. So, more thermal gradients will arise, more concentration gradients will arise. So, that will be an issue in the down-flow trickle-bed reactor. If you have the up-flow operation, this problem can be avoided. So, you will have a better radial and axial mixing; gradient will be less. And, when this is less, the heat transfer or mass transfer rates between liquid and solid will be higher. So, this is the advantage. Another advantage is gas-liquid mass transfer coefficient. So, pressure drop, liquid holdup will be higher when you have upward flow. So, these are some advantages, but pressure drop is higher. That is again an undesired property when you have a up-flow operation. So, both methods – both up-flow and down-flow have some advantage and disadvantage. But, most of the time, the trickle-bed reactor operates under the down-flow operation.

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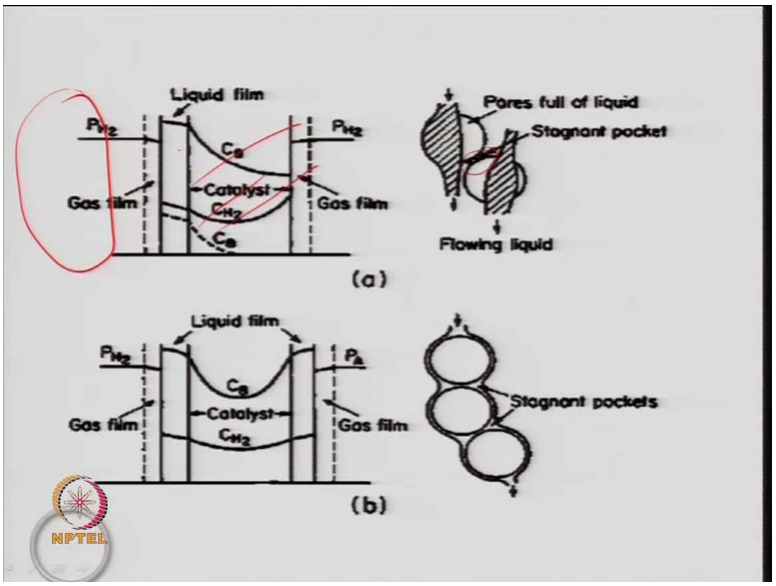

This is what I was talking that, different kind of issues, which arise in the trickle-bed reactor. So, this is just if you look at the flowing liquid here; you have pores full of liquid, which we are assuming; and this is the stagnant pockets of the liquid, where the liquid will remain between these two. And, this is what the solid surface; or, liquid comes in the form of droplets or rivulets like this. And, in between two solid particles, you have the liquid. You can see here; suppose the hydrogen gas; this is the bulk gas here – the hydrogen; and then it is a gas film. So, this will be covered by the liquid; it is covered by a film of gas. So, you will have a gradient from here to here. So, transfer from this gas film to the liquid film. And then from here it will transfer to the surface, that is, from liquid film; and then there is a solid catalysts. So, this is the catalyst here. So, this zone is the catalyst – something like this.

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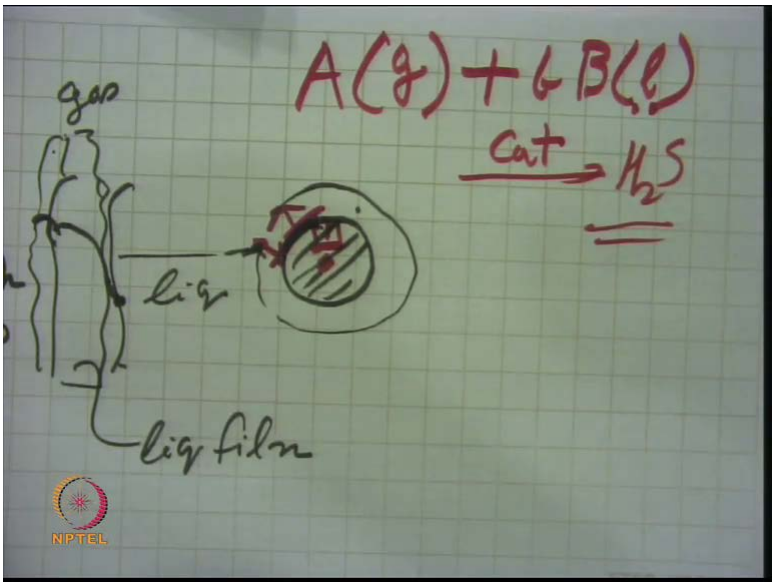

So, here again, from the bulk liquid, if I just make it in a spherical – assuming spherical particle, you have a particle like this – solid particle partly porous; and then there is a film of the liquid. So, solid is covered by a film of liquid. And then you have a bulk liquid here; and then there is a gas. So, here it is a bulk gas something like hydrogen; and then this is a gas film. So, this is basically the interface. So, here it is a gas film here and this is the interface and there is a liquid film here. So, this is the gas film and this is the liquid film. So, one side is the bulk liquid; another side is the bulk gas. So, in between, there is a film. So, depending upon the thickness of that film, you will have the interface. So, this is a kind of interface. So, one side is a gas; another side is the liquid. And now, the gas has to diffuse to that film; so, gas film resistance and then it will come to the liquid side – bulk liquid side.

And then from bulk liquid, when it reach the bulk liquid, then it has come to the external surface of the solid here, because it will come here at this action. So, there is a film again – liquid film. So, there will be another resistance – mass transfer resistance. And, when it reaches here, it will come to the pore of a – diffuse into the pore of a catalyst. So, that… They are again… They have diffusion, surface reaction, chemical reaction. And then the product will form. So, it means from here – this point to this point, the gas has to reach first. And, this is just picturized here that, the gas film, liquid film, and then there is a solid catalyst. So, there will be a concentration difference in the pore and then the product will form. And, this is a symmetry from both side. So, here it is again and this is

the catalyst, which is surrounded by a film of liquid and then there is a gas, because both are coming from the top.

And, stagnant pockets are something like this, which are here; if you look at different particles, you have the pockets of the zones, where there is no reaction basically; white pores if you look at here. And, same picture – gas film, then gas film and then there is a concentration profile. So, b is also diffusing and a is also diffusing. And then they are reacting. So, simple stoichiometrically, one can write A, which is a gas here like hydrogen; and plus some b of moles of the B, which is in liquid, and available at the surface of the catalyst in the presence of catalyst like COMOX, NIMOX as I said for hydrodesulphurization – removal of sulfur. So, this is the sulfur compound.

And then mainly the product will be hydrogen sulfide if it is desulfurized something like this. And, the other liquid kerosene, which has sulfur compound; so, it will get convert to sulfur – hydrogen sulfide. And, other kerosene part of the kerosene, which are mainly hydrocarbon – they will not be converted. So, something like this. So, this will come out from the pore of a catalyst. So, a very complex mechanism. If you look at trickle-bed reactor, gas-liquid reactions or gas-liquid-solid reaction basically; in the presence of solid, the gas-liquid reaction. Alternatives can be a slurry bubble column reactor, but it behaves like a CSTR, what I said earlier. So, conversion will be low. But, the mixing or the mass transfer resistances are minimized when you have a slurry bubble column reactor. The substitute for this trickle-bed reactor can be a slurry bubble column reactor.

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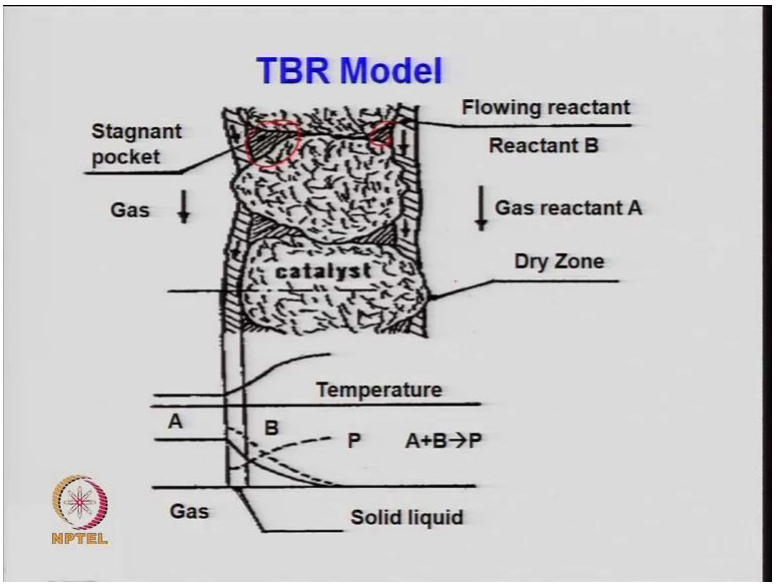

So, when you do the modeling, you have to look at all these properties of these, are solid material; and this is the stagnant pockets here; you can see this portion – red portions – shaded portion. So, this is the stagnant pocket; here is no reaction basically; dead zone just like in a CSTR, gas is coming down from this symmetry; this is solid in the reactor; and catalyst supplies in the reactor, and the gas comes like this.

So, you have a kind of temperature profile depending upon the exothermic and endothermic reaction; you have the kind of concentration profile, which I have showed earlier. So, this is in the gas phase; here is no concentration; but when it reaches to the surface here, here you have a concentration difference. So, concentration of A will decrease like this. And, depending upon the partial pressure and solubility, you can have the concentration at the liquid – concentration of gas A in liquid. And then it comes to the surface of the solid. So, again there is a chemical reaction. So, concentration of gas will continuously drop. And, B is already there, which we are assuming in larger amount. So, that is what the different… This is the dry zone, where there is no liquid. So, catalyst is not being properly utilized here.

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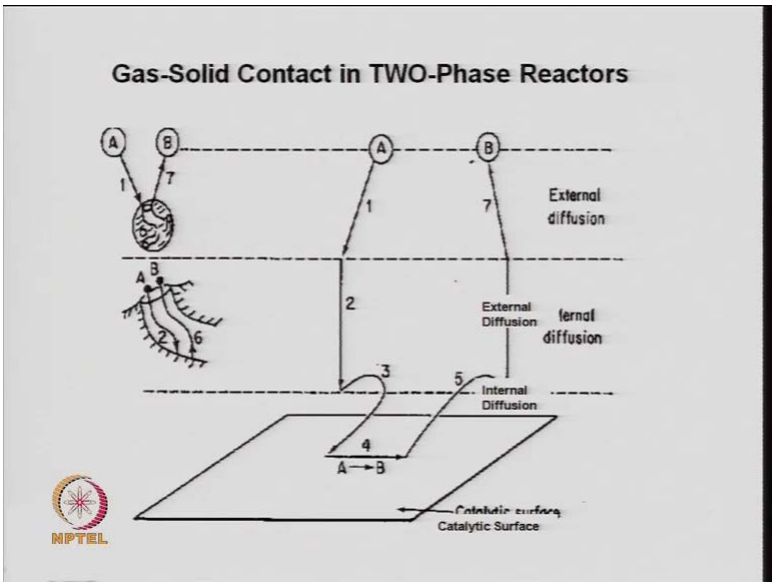

Actual mechanism, which we have already discussed; actually, when you have just a gas and solid in contact. So, basically, a simple example I have taken here before going for the actual in a multi-phase reactor.

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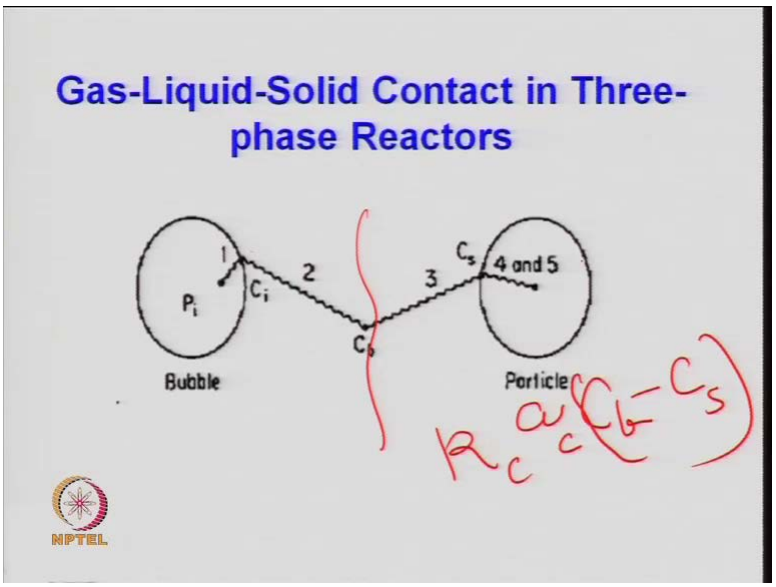

So, this is actual mechanism of transport and reaction; that is, the steps in a three-phase reactor. And, this is the step in a two-phase reactor. So, when you have… Which we have already done in a packed bed reactor; you have just vapors coming hydrocarbon,

vapor on the surface of a catalyst. So, it is a two-phase reactor example. So, there again the reactant A…

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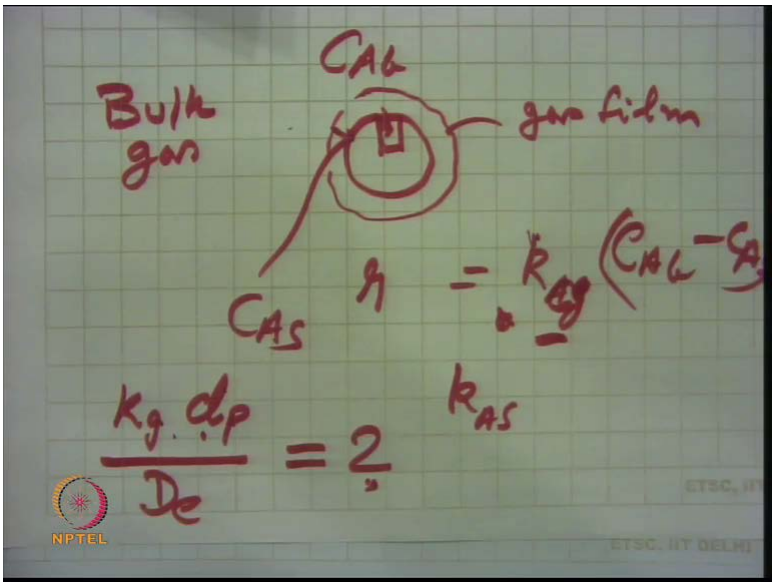

When you have a two-phase reactor, what you saw before; which we have already discussed; you have a porous material here and this is covered by a film of gas. So, earlier in this three-phase, it is liquid; but here it is a gas film. And then there is a bulk gas. So, from bulk gas, the reactant material will diffuse through the film. So, this is a gas film and come to the surface of the solid. So, if the concentration here is C A b; at the surface, it is C A S. So, it means this… Because of this concentration difference – C A B minus C A S and the mass transfer coefficient; which will be something like k A g, that is, the mass transfer coefficient of A at the surface of the solid k A g times C A b minus C A S; that is nothing but the transport; which is external transport. And, because of… This is the rate, which is either rate at per unit surface area or per unit volume of the catalyst depending upon the unit of k g – mass transfer coefficient. So, it means the rate, which is being transported from this bulk gas to the surface of the solid; these are the number of moles transported per unit time per unit volume of a catalyst or surface area of a catalyst.

So, one can very easily write this expression or multiply it by small a. So, k g a; where, small a is surface area of the catalyst per unit volume of the reactor also can be written; per unit volume of the catalyst also. So, it can be correlated. So, that is one thing. So,

when it is reached here, then it will start diffusing into the pore. So, second step will be diffusion into the pore, which we have already discussed by a fixed law of diffusion. And then it will be adsorption, then surface reaction, and then desorption on the surface of the catalyst. So, adsorption, surface reaction and desorption of the product. And finally, the product comes out. And, that is what we had already discussed in the gas-liquid reaction. But, when you have a multi-phase reactor, you have liquid also in between. And, in that case, additional resistances, which are mainly now are the mass transfer resistances – they have come back.

So, this is what a bubble, a gas. So, that is basically a gas – bulk gas; and there is a bubble of that gas. So, it means there is a film of the gas – the bubble. So, there is a film here. And then this is the bulk liquid. So, this is basically… Here it is the bulk liquid, where the concentration of the liquid is constant; but gas will come and diffuse through this film. So, there is first step that is reaching the gas to the interface; and from interface, it is reaching to the liquid. So, that is C i minus C B; the concentration difference similar to that. But… And then from here because the gas has reached to the bulk liquid, now it is uniform concentration of the gas depending upon the solubility and the resistance offered for mass transfer.

And, from here, now, the gas will reach to the surface of the solid. So, reaching to the surface of the solid is again a mass transfer. So, mass transfer coefficient at the surface of the solid times whatever the surface area per unit volume of the catalyst. So, surface area of the catalyst per unit volume of the catalyst; which is just reciprocal to the inversely proportional to the diameter of the solid particle. So, smaller particles, you have large surface area per unit volume. And, multiplied by mass of the catalyst if you are defining it based on the mass and times the concentration, which is here in terms of the difference. So, that is again important that, how to write this expression; whether you write it in terms of per unit volume of the reactor or per unit volume of the catalyst or per unit mass of the catalyst.

So, basically, here again you have the expression, which will be related to some mass transfer coefficient for the solid times the surface area of the solid per unit mass of the catalyst or per unit volume of the catalyst times the concentration difference, which is C b minus C s, which you have already read in mass transfer problem. So, this is the number of moles, which have been transported from here to the surface of the solid. And

then this will diffuse inside; that is, 4 and 5, which are written here; that is, diffusion and chemical reaction. So, again you need an effective factor for this pellet and then kinetics of the reaction. So, we will talk on that.

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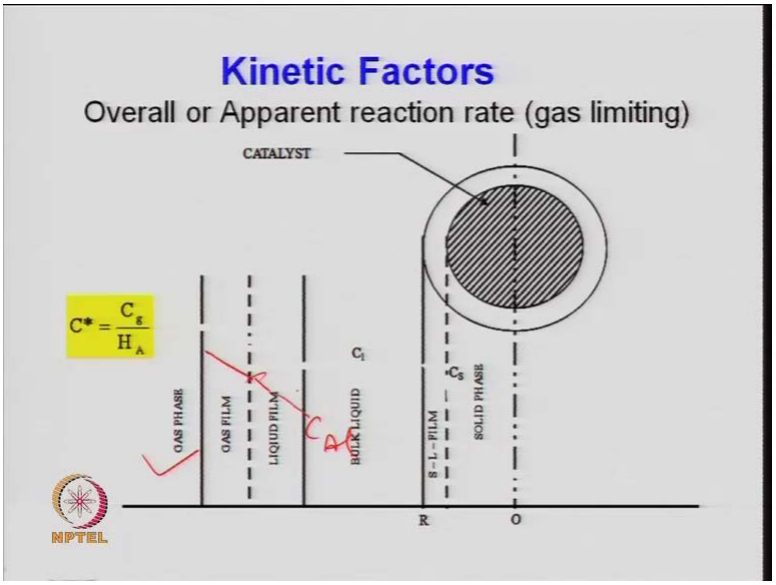

So, the same – that discussion I made has been picturized here. So, you have the system something like this that, there is a gas phase; then the gas phase – that is a bubble – solid bubble, and there is a film of the gas. So, gas film. So, there will be a concentration difference from here to here. And then there is the transfer from here, which is governed by the Henry law given by something like equilibrium relationship by P A is equal to H A times C A i or this is the C s star – equilibrium constant composition; which is gas phase composition divided by the Henry law; either way one can write depending upon the unit of Henry law constant. Then, there is a liquid film. So, there is again a gradient here. And now, it reach to the C A l. So, something like here – a concentration of gas A in the bulk liquid. And then this is reached to the surface of the solid, which is covered by a film of the liquid. So, here again you have a transport relationship, what I discussed. And then there is a diffusion and catalytic reaction. So, all these resistances will affect the performance of a trickle-bed reactor.

So, that is what I said, depending upon the resistances whether it is the k A g or k A l, that is, mass transfer coefficient. So, how to enhance those mass transfer coefficients? The correlations are available, because it will depend on the property of the gas, property

of the liquid; it will also depend on the shape and size of the solid when you look at the k… – this mass transfer coefficient, which I was talking at the surface of the solid. So, when I write this thing, this is basically the mass transfer coefficient in this side; that is, from the liquid to the external surface of the solid. So, sometimes, we write the mass transfer coefficient of A – k A s also. So, that is important, not in the gas way. So, that time it becomes k A s; I will write it like this – k A s – the mass transfer coefficient at the surface of the solid.

So, it will depend on the size of the solid and the other condition, which are related to, because Sherwood number, which is related to the diffusion coefficient and also some factor of the Reynold number if it is the velocity terms, which are related to that. Or, if it is low Reynold number, then this will be just like k g times d p. If you remember this, k g d p, which is the particle size divided by D e, which is effective diffusive due to a diffusion coefficient. And, that is constant generally at low Reynold number. So, it means basically the k g is inversely proportional to d p – diameter of the particle. So, it means smaller the particle, the mass transfer coefficient will be higher. But, to what level, one needs to find out. So, that is what the property, which is related here in terms of the transport coefficients. So, all these factors will affect the performance of a trickle-bed reactor.

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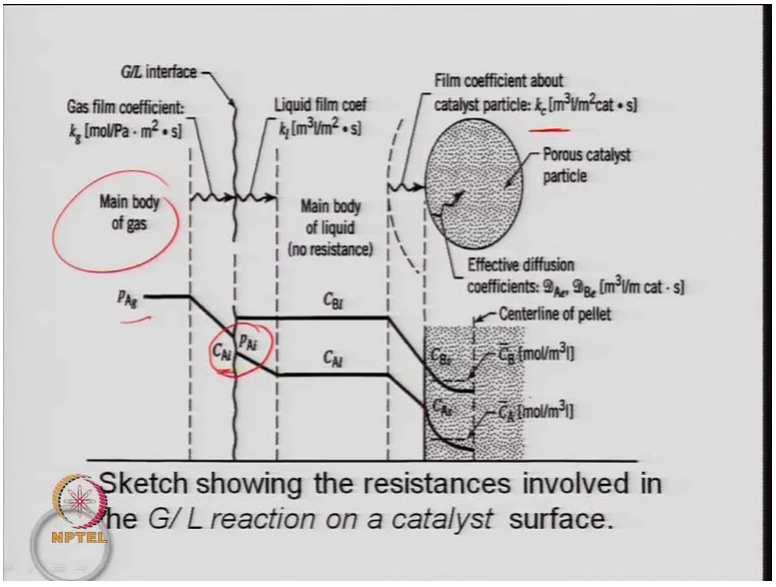

And, this is what the detailed or complicated geometrical picture of the resistances, which have been offered. So, this is the main body of the gas, where the partial pressure of A is in the gas phase is P A g; which can be related to the temperature and concentration. You know P B is equal to N R T. So, this is C A is equal to P A g up on R T; that can be calculated. So, there is a gas film coefficient, which I was talking something like k A g here – gas film coefficient, because this is the interface of the gas just like a bubble. And then this side it is the liquid film, which is k A l. So, this is a liquid film coefficient. So, gas film coefficient, liquid film coefficient. And, these are the P A g; either you write in P A g. And, when it reach to the liquid, we said it C A i – concentration of A at the interface. And, that will be given by Henry law – P A i is equal to H A times C A i. That is the correlation between the gas-liquid solubility, which will depend. So, if you have a highly soluble gas, the Henry law constant will be low; if you have sparingly soluble gas, the Henry law constant will be high. So, something like this.

This C B l is the concentration of liquid B. Since already the liquid is available in large amount and concentration of B we are assuming large, this is unaffected throughout. The concentration of A, which is transport from this to the liquid – bulk liquid; so, that is the mass transfer of A from the gas liquid interface to the bulk liquid. So, bulk liquid means the liquid, then gas-liquid interface and there is a liquid film. And, the gas has to cross this liquid film depending upon the thickness of the liquid film.

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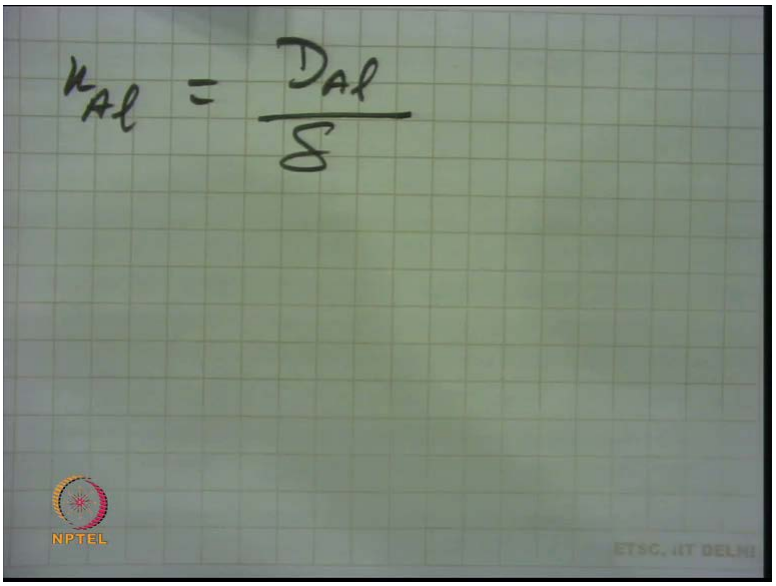

And, thickness of the liquid film is related to the mass transfer coefficient – D A B divided by the delta; where, delta is the thickness of the liquid film, because all the time you write your K A l something like D A l divided by delta; which is similar to… When you write the surface of mass transfer or penetration theory of mass transfer. So, delta is the film thickness. So, just like in a gas liquid reaction, reactor design or gas liquid reaction, smaller the film thickness; some kind of enhancement factors, which is generally used in the gas-liquid reaction. So, smaller the film thickness, you will have larger mass transfer coefficient. So, this is what here.

And, when it reached to this bulk liquid, then there is a transport from here to the surface of the solid. So, this is the catalyst material, which is covered by a film of the liquid; where, the mass transfer coefficient is written in terms of k c, which I was talking k s – something like this same term. So, it is a porous material. So, we need to look at the effective diffusion coefficient also because of the porosity; so, effective diffusion coefficient for A and B concentration in the pellet. So, how the concentration of A and B changes – that will depend on the reaction and the effectiveness factor. So, this is a typical picture of all the resistances, which are involved in the transport in a gas-liquid-solid reaction; that is, multiphase reactant. Whether it is trickle-bed reactor, slurry bubble column reactor; all similar steps will arrive or it will come there also. So, I stop here and we will continue it in my next lecture also.