Heterogeneous Catalysis and Catalytic Processes
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Lecture - 26

Good morning. So, last time I was talking about reactor design and Fixed bed reactor. Because if you have learnt the reaction in homogenous reaction kinetics; then different kind of reactors maybe used in process industry.

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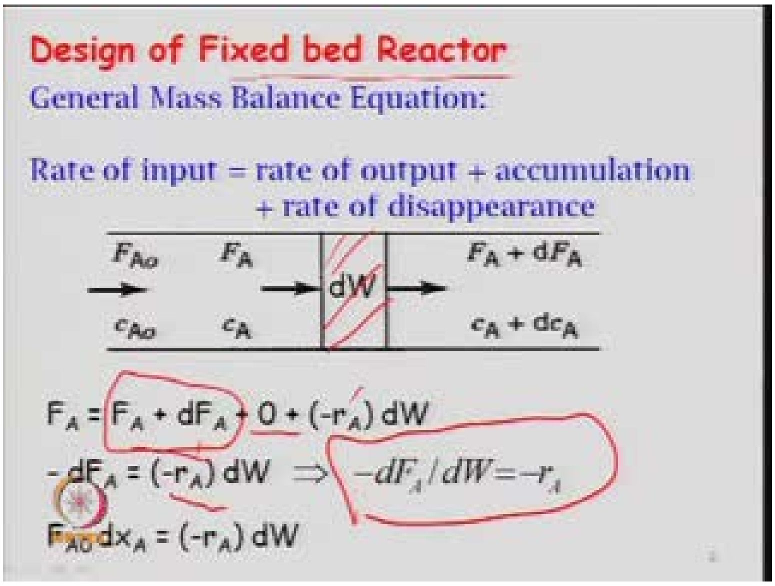

Design of Fixed bed Reactor

General Mass Balance Equation:

Rate of input = rate of output + accumulation + rate of disappearance

$F_A = F_A + dF_A + 0 + (-r_A)\,dW$

$-dF_A = (-r_A)\,dW \Rightarrow -dF_A/dW = -r_A$

$F_{A0}\,dx_A = (-r_A)\,dW$

And, broadly they are classified as batch reactor.

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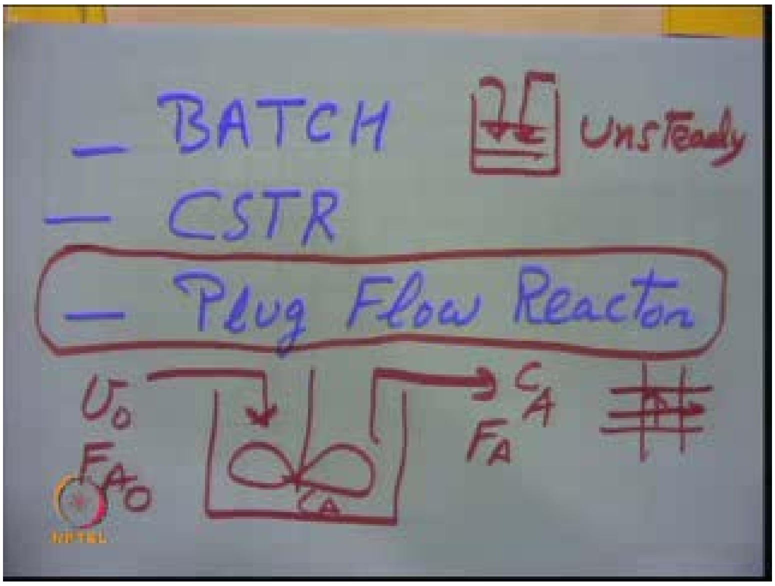

A batch then it can be a CSTR type, flow reactor, tank flow reactor and then thirdly known as plug flow reactor. So, these kind of reactors maybe used in process industry; chemical process industry. So, batch is a kind of unsteady operation; where you have the just to give you the basic idea you have added your reactant mixture here. And, then you wait for certain time depending upon the reaction; it may be slow, it may be fast. So, most of the enzyme type reaction; enzymatic bio fermentation reactions they are generally done in batch reactors, right.

And, small scale industry also uses this kind of reactor. The second one is again a tank type reactor which is known as continuous straight tank reactor. So, you have a tank system where continuously the reactant feed goes inside or the feed go different kind of feed reactant stocks they go inside; and product is continuously taken out. So, it is a continuous type reactor. So here it will be unsteady state operation. So, the conditions inside the reactor will change with time but in the case of this flow reactor CSTR tank type reactor. So, you have a continuous steering here and then product is taken continuously outside.

So, something is continuously flowing here and something is coming out also. So, concentration here inside the reactor and C A here is similar; the moles which are here F A naught inlet and outlet may be F A. So, conversion can be calculated based on input minus output moles of the reactor and the species. And, time is decided based on the reactor design fundamentals; that is the mass of catalyst that is placed here. So, it can be a kind of slurry reactor also; when you have a solid particle. And, mainly in the homogenous reactors or that the heat transfer is a problem; then the CSTR type because the mixing is good in this kind of reaction.

So, in the field stock or the reactant product for them mixing is an issue or heat transfer is a problem; then the CSTR type of reactor can be used. But most of the time when you look at a commercialization a large scale reactor; they are of this type plug flow or fixed bed reactor. So, plug flow is generally an ideal condition of reactor; where the dispersion is neglected excel radial dispersion is neglected. And, basically the ideal electric condition is what the definition says that there is complete mixing in this and no mixing in the direction of flow right or the concentration. If you look at any section it is uniform throughout. So, most ideals to form of reactor, right.

And, the since this can be sized in the form of tubes. So, most of the commercial industry they use this kind of reactor. So, details we will talk later again for the catalytic reactor design and type of reactors which are used in the catalytic process industry. But here just the design of a fixed bed reactor which is a kind of this tubular reactor, right. And, the basic idea what I discussed last time is that the input is equal to output plus accumulation and plus rate of disappearance. So, rate of disappearance generally it is represented in the form of minus r A rate of disappearance of reactant is specie, right.

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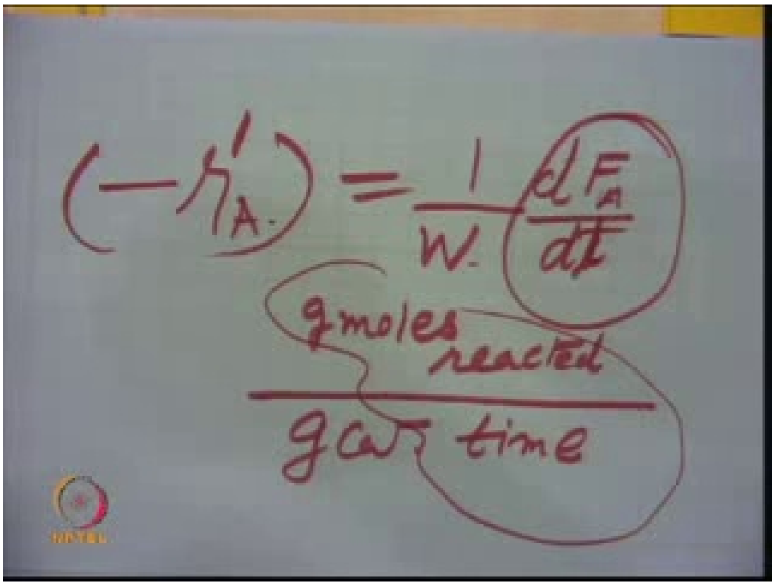

$$(-r'_A) = \frac{1}{W}\frac{dF_A}{dt}$$

$$\frac{\text{g moles reacted}}{\text{g cat } \cdot \text{ time}}$$

So, minus r A dash if I write that will be per unit mass of the catalyst something like this d F A by that is. If I write in this form; so basically this is the moles reacted per unit time per gram of catalyst. So, I am writing in this form. So, d F A per gram of the catalyst per unit time. So, basically here in this time is defined in form of something like this tau; this base time. So, I will write here right now t but I will define it little later. So, basically the definition of this is gram moles reacted per gram catalyst per unit time. So, this is the definition of the rate in the case of heterogeneous catalytic reaction; but this term per gram catalyst per unit time.

So, basically this will depend that what is the field rate per unit time here which I have written here and per gram of catalyst. So, in this case; so this is the just minus r A disappearance of a; and this can be defined per unit surface area of the catalyst also. And, sometimes we can define it per unit volume of the reactor also.

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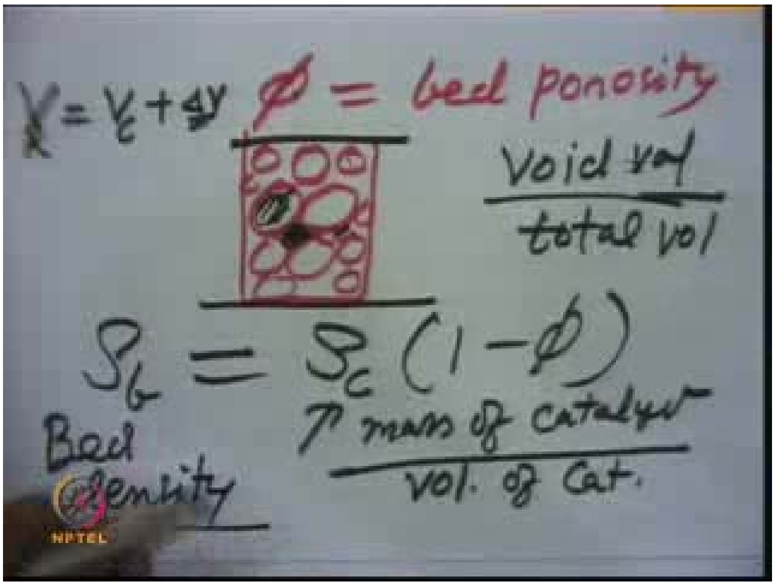

But what I told you last time is that suppose the bed has some porosity phi, right. So, sometimes we write phi as the bed porosity. And, pallet porosity is different that is when you have taken a catalyst pallet; its porosity inside the particle pallet. And, when I am talking bed porosity it is like this the pallets have been placed in a reactor; which is cylindrical form. And, this phi is the fractions of the wide here which are the gaps here; if you look at these gaps. So, just I am just blocking this; so this is a kind of fraction right between the catalysts. So, in between there is no catalytic reaction basically, right. So, catalyst if you have a contribution of some thermal it can happen. But otherwise there is no catalytic reaction in these gaps, voids catalytic reaction will be inside this surface.

So, it means his bed porosity if I say is the phi it is nothing but the volume, void volume divide by the total volume. And, I am talking in terms of the reactor based on the reactor volume which is now this. But actual if you look at based on mass of the catalyst; suppose, if I crush it if I make a powder catalyst powder then this void will be approximately to 0, right.

So, all the particles are closer together; the pressure drops maybe an issue in that case. So, then this becomes actually if you tap it and that will be two density of this particle, right. So, basically I can write if I define my rho b which is the density based on the bed; that is simply catalyst density rho c times 1 minus phi right; where rho c is the catalyst density; that is the mass of catalyst divide it by the volume of the catalyst which is a powder now. So, this rho c is based on mass of catalyst defined as mass of catalyst divide by volume of catalyst; but since there are voids. So, volume of catalyst it means that will be less; and in the reactor when you put you need a larger size of the reactor because there are gaps right.

So, basically you can write the volume of reactor is equal to nothing but whatever the volume of the solid plus the voids, right. So, if you if you write your volume of reactor v R is nothing but v c right plus the delta which is the because of the void correct; additional volume which has a raised. Because of this and that delta is nothing but this wide volume which is nothing but phi into total volume. So, that is the these are some definitions; because when you put the catalyst in the bed that becomes the bed density. So, this is rho b which is bed density of the catalyst when the catalyst has been placed in the bed; so that will become rho b. So, if you just look at your clear picture in mind; then if you give that picture then rho b will be less than rho c, right. Because still there are more voids now the mass is not there in that gap.

So, rho b will be less than rho c. So, this is what how can we co-relate. So, sometimes we define; if you define this w that can be defined based on the volume of the reactor. So, otherwise this mass of the catalyst is density of the catalyst times the volume of the catalyst right. But when we defined a volume of the bed; then it should be based on this rho b. So, these fundamental things should be clear to you because we have already learnt this surface area of the catalyst, pallet density, particle density, pallet porosity and the one more term which is your bed porosity, right.

So, for any differential system if you write here this differential section of the catalyst bed. Because why we are taking a differential section the concentration is changing down the length. So, most of time when you do the experiment in lab you try to take a small diameter tube. And, small mass of the catalyst; in such a way when you do the kinetics the conversion should be less than 10 percent of your 15 percent, right. The reason is that otherwise the concentration will change. Because you write the concentration equation F A if I write mole that is F A naught into 1 minus x.

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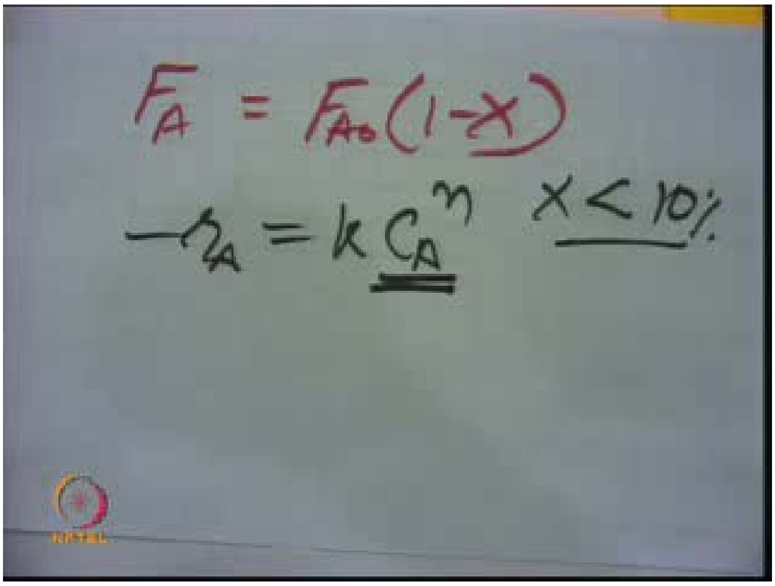

$$F_A = F_{A0}(1-\underline{x})$$

$$-r_A = k\,\underline{\underline{C_A}}^{n} \qquad \underline{x < 10\%}$$

And, suppose your conversation is 90 percent then this means F A is just 0.1 of F A naught, right. And, if you are writing your rate because rate is something like if I write a power law it is k C A to the power n and something like that. So, it means which concentration you are taking right if 0 to 90 percent conversion. Then, this concentration difference is very wide it is changing at z is equal to 0, 0 and z is equal to say L; it will be 0.9 fractional conversion. So, that difference is very high. So, you need to take the average concentration or you divide your reactor into infinitely small reactors. So, we are resembling this a differential reactor and you can call it as a CSTR also right; a differential sort reactor. So, that is because behaving like a CSTR; because in CSTR you assume that concentration is uniform everywhere.

So, in the small zone when x is less than 10 percent which is preferable for the design conditions; you can assume it like a CSTR, right. So, 0 to 10 percent the concentration variation is less; if heat generates the dissipation will be not a problem or temperature gradient will not be too high. So, effect of temperature, effect of concentration variation that can be neglected under these conditions. So, one has to look at these when the kinetic of the reaction is to be studied; a small tube diameter reactor maintains L by d p ratio maintain diameter of the reactor to the diameter of catalyst particle, pressure of condition. So, these should be checked, right.

So, a simple mass balance which is shown here and discussed last time also input is equal to output. So, this is moles of a out and this condition and there is no accumulation inside the system. Because we have assumed steady state condition and this is your rate of disappearance. So, I told you for the mass of the catalyst; so multiplied by the mass of the catalyst. So, this gives you if you just simplify this equation minus d F A is equal to minus r A dash per unit mass of catalyst multiplied by the mass of the catalyst in the differential section. So, one can very easily write a differential form of the equation which is minus d F A by d W is equal to minus r A dash; that is moles reacted per gram of catalyst per unit time. Because F A is the moles per unit time; it is a continuous reactor, right. So, one can write relationship like this also F A naught d x A is equal to minus r A dash into d W which we have already discussed earlier, right.

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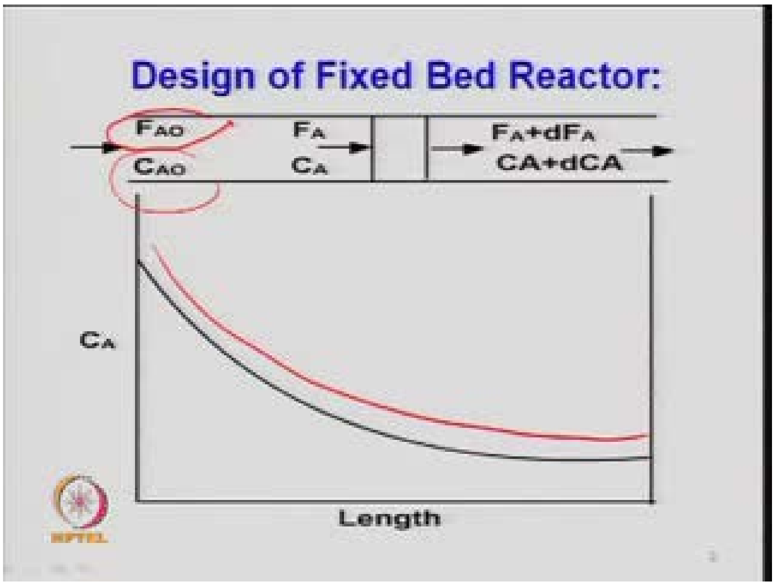

Design of Fixed Bed Reactor:

So what I mean to say that either you write in terms of the molar flow rate; this is F A naught inert molar flow rate moles per unit time. And, this is its concentration which is C A naught right gram mole per liter and there is a relation between F A naught and C A naught all of you know this.

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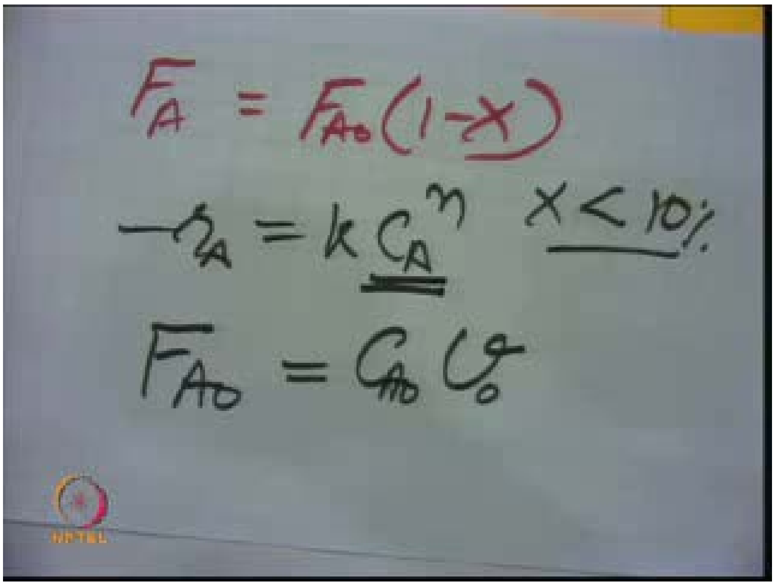

$$F_A = F_{A0}(1-X)$$

$$-r_A = k\,\underline{\underline{C_A}}^{n} \qquad \underline{X < 10\%}$$

$$F_{A0} = C_{A0}\,v_0$$

That F A naught is equal to C A naught concentration multiplied by the volume metric flow rate, right. So, this is the volume metric flow rate not the superficial velocity. And, that can be related by area of the cross section of the reactor multiplied by the superficial gas velocity. So, one can see that when there is a conversion; the concentration of the reactant species goes down, right. And, one can find out the exit concentration or co-relate this concentration with the conversion data.

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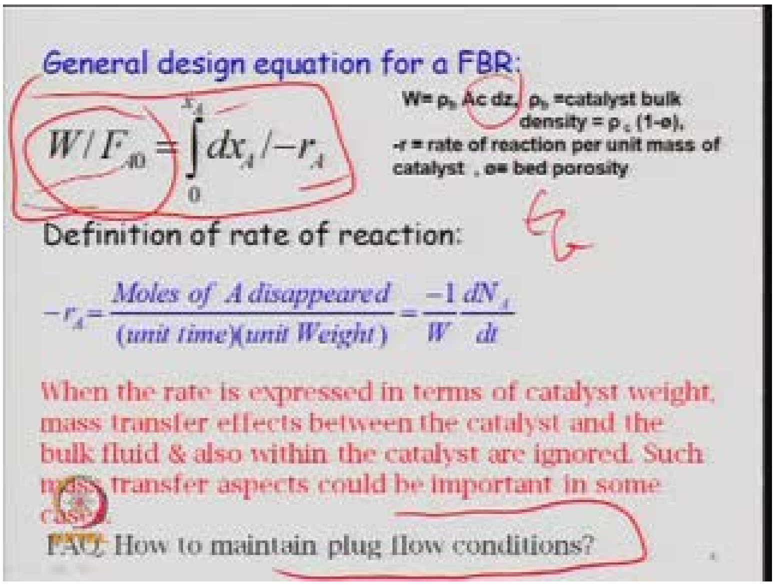

General design equation for a FBR:

$$W/F_{A0} = \int_0^{x_A} dx_A / -r_A$$

$W = \rho_b A_c\, dz$, ρ_b = catalyst bulk density = $\rho_c (1-\varepsilon)$,

$-r$ = rate of reaction per unit mass of catalyst , ε = bed porosity

Definition of rate of reaction:

$$-r_A = \frac{\text{Moles of A disappeared}}{(\text{unit time})(\text{unit Weight})} = \frac{-1}{W}\frac{dN_A}{dt}$$

When the rate is expressed in terms of catalyst weight, mass transfer effects between the catalyst and the bulk fluid & also within the catalyst are ignored. Such mass transfer aspects could be important in some cases.

FAQ: How to maintain plug flow conditions?

So, now you have seen that this is the equation in the differential form. If you have a larger size of the reactor you can very easily integrate it for a commercial reactor. So, W by F A naught because if you have that seeing that. So, integrate this equation where your F A is a function of W and r A dash is an intrinsic property in the small reactor. And, when your commercializing it so for large reactor we have integrated the expression, right. So, W by F A naught is equal to 0 to x A d x A upon minus r A same equation which was earlier in differential form of reactor. Now, has been defined for the sizing a reactor for a given conversion value. Suppose, the in the large scale you have achieved some 90 percent conversion right based on the kinetics. And, now you want to use a commercialize this data or commercialize a reactor design then you have to use this kind of equation with some hydrodynamic study.

So, it is the effect of pressure drop, effect of particle size, effect of reactor, id internal diameter of the reactor, height of the reactor. So, in total there will be other several parameters also but from kinetics one can very easily find out the mass of catalyst required for a given conversion. Because if you in the lab scale you have started with 1 gram catalyst and you got 90 percent conversion; the same 90 percent conversion if you have 1000 gram of the catalyst which you have placed; then this is a parameter which is known as a space time. So, in the larger reactor also you will have the same value of W by F A naught. So, it means now you can have a larger mass of the field stock; that can be passed through the reactor.

So, W by F A naught which in homogenous kinetics; you define as V by v naught tau space time. So, this is also a type of space time; and sometimes we call it weight hourly space time.

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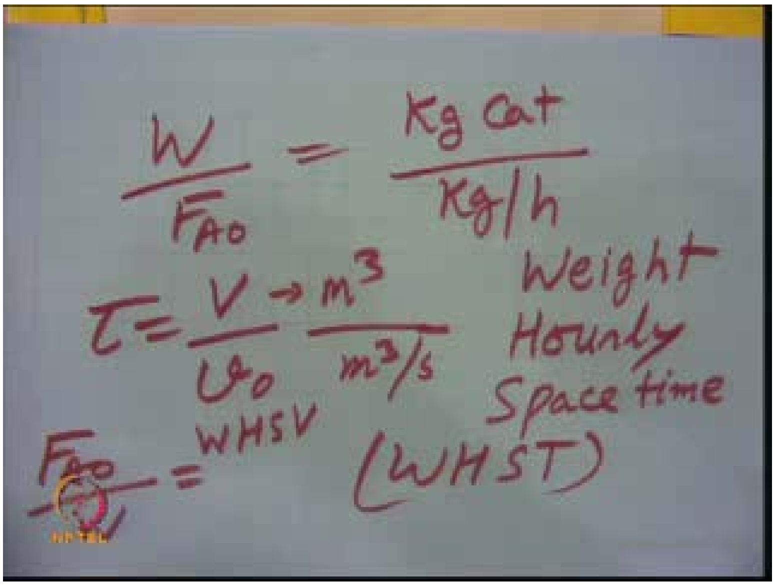

$$\frac{W}{F_{A0}} = \frac{\text{Kg Cat}}{\text{Kg/h}}$$

$$\tau = \frac{V \rightarrow m^3}{\upsilon_0 \quad m^3/s}$$

Weight Hourly Space time (WHST)

$$\frac{F_{A0}}{W} = \text{WHSV}$$

So, this is another very important parameter which is used in reactor design known as W by F A naught which is a kind of tau V by v naught in the homogenous reactor, right. So, volume of the reactor divides by the volumetric field rate. And, it has the volume of reactor something like a meter cube unit, volumetric field rate something like meter cube per second and this as the unit of time. So, that is why this is known as space time. So, and when you have this; so here it is the k g of the catalyst gram catalyst or k g of the catalyst and field rate the molar field rate or mass field rate. So, k g per hour; so k g of the field; so time unit is similar.

So, basically this is known as weight hourly space time WHST here. And, if you define it inverse of this F A naught by W that is known as space velocity, weight hourly space velocity WHSV. So, that F A naught by W is WHSV weight hourly space velocity, right. Again, a very important parameter like W by F A naught because you know if you have a larger residence time inside a reactor for a reactant field; then the conversion may be high. So, conversion will increase if you increase your W for like same F A naught right same field rate or if you have reduced your W and reduce your F A naught in the same ratio; so it will not change. So, vertically it will not change because you have seen that conversion is related to this and this. So, for a given kinetics this is defined like this. And, I have already defined here W which is the mass of the catalyst will depend on the area of the reactor times delta z. And, this is here defined in terms of the bulk density of the catalyst and this is which you have defined which is based on rho c into 1 minus phi. And, rate of reaction is defined based on per unit mass of the catalyst.

So, bed porosity is generally represented by phi and sometimes we represent by absolvent b also; that is the bed density; absolvent p is the pallet porosity, absolvent b is bed porosity right. So, definition of reaction rate I have explained the same here moles of a disappeared per unit time per unit mass of the catalyst. So, minus 1 by W d F A by d t or d N A by d t. So, sometimes in a batch we use this N A but in flow reactor we use the term F flow rate. So, when the rate is expressed in terms of the catalyst weight; the mass also effect between the catalyst and the bulk flow and also within the catalyst are generally neglected. That is the very important thing what I told you that the gas velocity. So I will come to this point later again.

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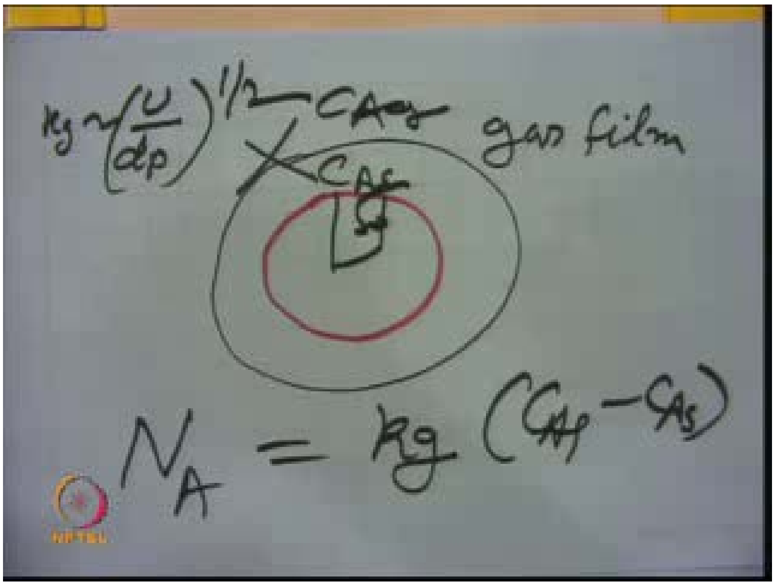

But initially if you remember we were talking about a solid catalyst particle; which is surrounded by a film of gas like this. So, there is a gas film. So, when you do the kinetics you have to make sure that there is no resistance offered because of this gas. Because you write this mass transfer N A is equal to something like mass of coefficient times CAG minus CAS. So, that is the mass which is transferred per unit area if I define of this film. So, this is your CAG basically and this is your CAS here at the surface. So, if there is a gradient then this resistance is important; that is mass of the coefficient is important. And, when you do the kinetics this may hamper your overall rate of reaction.

Same thing their second parameter is your diffusion into the pore and then we are talking third part. So, when you do the kinetics you have to decide the condition in such a way that this mass transfer should not affect the overall kinetics of the reaction. And, that can be studied from hydrodynamics you can confirm it from hydrodynamics. And, there are some physical or studies of effect of mass trans coefficient on its physical property of this gas and solid, velocity of the gas. So, basically these depends on that and one can control it; just like simple example if you remember I told you k g is simply u by d p to the power half. In most of cases we use this thing right; where u is the superficial gas velocity.

So, it means if you increase your superficial gas velocity your mass transfer coefficient will increase. And, it will reach to a value when this will not affect the rate; the second thing is that you reduce your size of the catalyst. So, these things can be checked experimentally and one can measure the rate as a function of velocity or as a function of diameter of the particle. And, you can see that it will increase initially but after that there is no change on the rate of reaction. So, it means the mass transfers is not controlling but remember this u by d p that should be at same W by F A and all. It means the superficial velocity if you increase molar flow rate is also increased, increase the mass of the catalyst also accordingly. So, that your W by F A naught will not change because this should be at the constant W by F A naught.

For catalytic reaction when you change W by F A naught your rate will increase. So, this is very important that the external mass transfer and equation effect should be neglected. So, how to maintain plus flow condition this is very important when you do the reactor design or when you study the kinetic. So, I told you that there are some guidelines; because you know a number which is known as peclet number basically.

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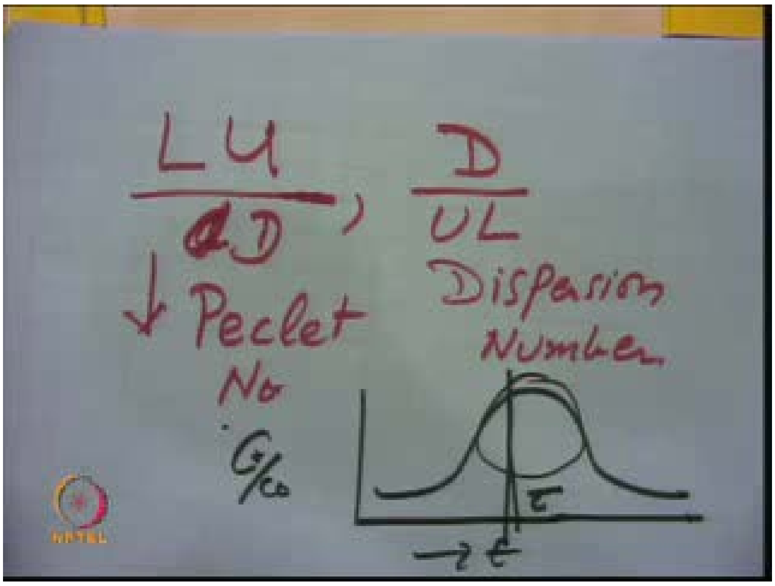

L u upon D; L is the length of bed height, catalyst bed height; u is the velocity right this is the disperse diffusion coefficient or dispersion and the inverse of this is d upon u L this is known as so this is known as peclet number. And, this is known as your dispersion number; peclet number and dispersion number. So, u is the velocity superficial velocity, L is the height of the catalyst bed and D is the dispersion coefficient diffusion like a diffusion coefficient. So, basically it is not a molecular diffusion coefficient but it is because of the flow of condition just as I said that axial dispersion rate, radial dispersion. But unit is similar to centimeter square per second. And, this can be determined from your RTD study by residence and distribution one can see the profile like this something like this that is if I just measure the concentration or dimension as concentration C t by C 0 versus the time here. So, the exit concentration will come at sometime maximum concentration will arrive at sometime which is the mean residence time; which is similar to your W by F A naught, right.

So, now how much is the deviation from the actual plug flow reactor; because if your plug flow reactor everything should come at the same time. So, you will see just a narrow peep and that is your tau basically but I defined space time. But because of the wild distribution, because of the non-ideal condition, because of the dead zone inside the reactor, because of the channeling inside the reactor; you may not get the all particles which have been feed at time t is equal to 0 everything will not come at the time t is equal to t bar which is the average residence time and for plug flow resistance; plug flow reactor it should come at the same time.

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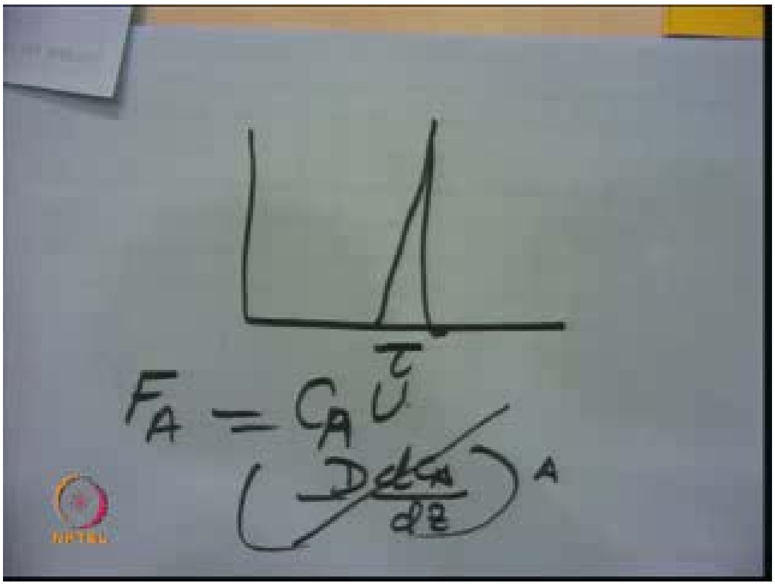

So, what I mean to say if you have a plug flow reactor everything will come like this; all the concentration will appear at the same time tau; that is the meaning. If you inject a dye along with the some say water then everything if you plug flow condition. Then, the dye should the same should come at the same time just like a solid. But this does not happen if you put some Kmno4; it will disperse, it will diffuse. So, depending upon this superficial velocity; so there are 2 terms basically. So, when you talk a flow so flow is because of 2 terms contribution; one is the because of the bulk flow. So, bulk flow is something if I is write F A is equal to C A into velocity the concentration into the volume at the flow rate right that is the flow. And, second term what I said is because of the dispersion and that can be your D time d c A by d z with negative sign multiplied by area.

So, these two are contributing in your actual flow, right. And, when you are looking a plug flow reactor you should neglect this. You should maintain the condition such that the second term has no contribution or zero contribution. So, everything is because of the conductive flow. So, this is the conductive flow, this is your diffusive or dispersive flow. And, when you have a large diameter reactor there may be a radial gradients also. So, that is why I said the small tube when you do the lab reactor. And, same thing it depends on this when you have a excel dispersion term. So, it will depend on the height of the catalyst bed and the tube diameter it will also depend on the size of the catalyst particle. So, all these are important.

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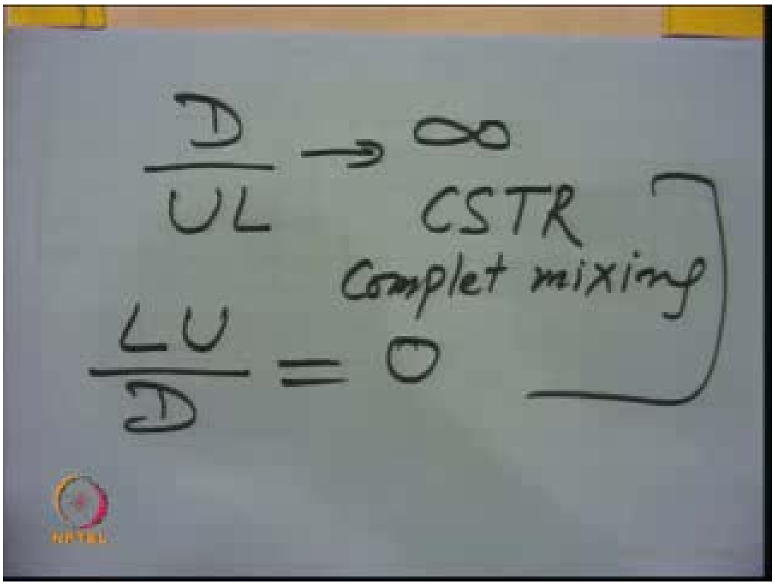

$$\frac{D}{UL} \rightarrow \infty$$

CSTR

Complet mixing

$$\frac{LU}{D} = 0$$

So, what is mentioned here in a form of peclet number which is L u by D or D upon u L which is your dispersion number I said that this number will resemble to infinite approaches to infinite or very high; when you have a tank reactor? That is complete mixing if you have a tank type reactor like CSTR the dispersion number D upon u L is known as dispersion number. And, that will approach to infinite very high value; it means complete mixing we should not look in plug flow reactor.

So, for a ideal plug flow reactor this should be low; if your ideal plug flow reactor then D upon u L should be low or in other words what I said L upon u D which is your peclet number that L u upon D should be high. So, peclet number should be high. So, for a CSTR this number is 0; peclet number is 0. And, if you look at a plug flow reactor then this should approach to 0 right or should be high. How can you maintain this high? It means should have high superficial velocity right; the gas velocity through the bed should be high, height of the bed should be high make larger bed height. So, these are things which need to be checked; when you do the study in a catalytic reactor and looking the kinetics.

So, when you skin out the catalyst we select our reactors of the small tube diameter which small and length large. So, height of the catalyst should be or catalyst should be mixed in fine powder like a smaller particle as I said. But keep in mind that when your very fine powder then it may block right pressure drop problem may arise because the void fraction is 0. So, that you have to check and you have to make sure that there should not be any channeling wall flow. Because the flow may have the tendency to move through the wall without conducting the catalyst powder; it may pass through the gaps, voids, channeling. So, you have to mix it with proper inherit also. So, these things should be checked while doing the experiment.

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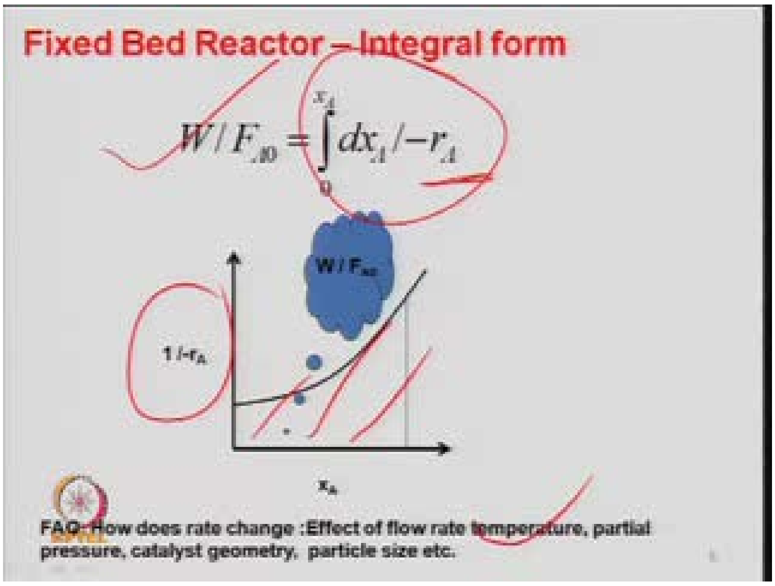

Fixed Bed Reactor – Integral form

$$W/F_{A0} = \int_0^{x_A} dx_A / -r_A$$

FAQ: How does rate change :Effect of flow rate temperature, partial pressure, catalyst geometry, particle size etc.

So, data analysis or determination of the kinetics related to your knob plug flow reaction which you have seen. So, generally from your experimental data because you have passed some field. And, at the exit you know the moles of those fields out and then based on the limiting reactant one can define the conversion, right. How many moles of a have been reactant per unit time per unit mass of the catalyst can be calculated.

For a given reactant one can calculate that how many mole of species A has been reacted. So, this is your minus r right. So, if you plot for integral approach if you plot a data. So, just what I what you had done you had assumed the differential reactor and for different flow rates different W by F A naught; you calculate the exit conversion or from that you calculate the rate. And, then you can have a graph 1 upon minus r A versus conversion action, right. So this will increase something like this. What is W by F A naught? W by F A naught is mentioned here area under this curve. So, if you take this area under the curve you can do it graphically; one can solve it numerically, numerical integration and you can find out.

So your Simpson’s rule, Trapezoidal rule which are available in any handbook or any book of chemical reaction engineering. So, one can integrate that by using the numerical technique or software’s like metlab has tools, polymath has the tool. So, these can be solved. So, again I have just kept question here that how rate change here? How the rate of reaction change that will change with W by F A naught, that will change the temperature, that will change a partial pressure; and that we have seen in the mechanism of the reaction. So, we need to identify and need to design the experiment accordingly to look at the effect of each process variable.

So, effect of fluoride need to be identified partial pressure, catalyst geometry, particle size everything should be checked; when you commercialize the reactor for a given catalyst.

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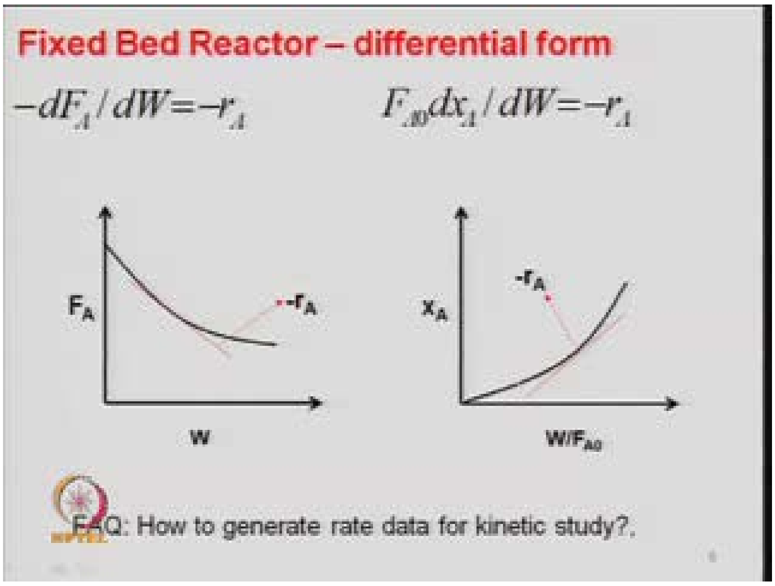

Fixed Bed Reactor – differential form

$-dF_A/dW=-r_A$ $F_{A0}dx_A/dW=-r_A$

FAQ: How to generate rate data for kinetic study?.

So, this is what has been discussed here. If you just plot F A versus W that is F A is F A naught 1 minus x a here, right. So, F A versus W or C A versus W or you can say is a function of time tau right in the case of homogenous reactor; that is v by v naught. So, that is just a drops like this. So, you can have again the forward difference method, backward difference method to calculate the rate. How to calculate rate data that is what here right. So, one can calculate the central difference method, forward, backward difference methods which are again given in any book of chemical engineering or any mathematical book. Because you have to calculate the slope of this line right.

So, one can measure the slope right at different points by doing this tangent right by having a tangent at a one point. And, one can find out the minus r A and if you plot based on x A versus W by F A naught that is another way; conversion versus W by F A naught space time. So, that is that curve and one can measure the slope at the front points and these are the rates.

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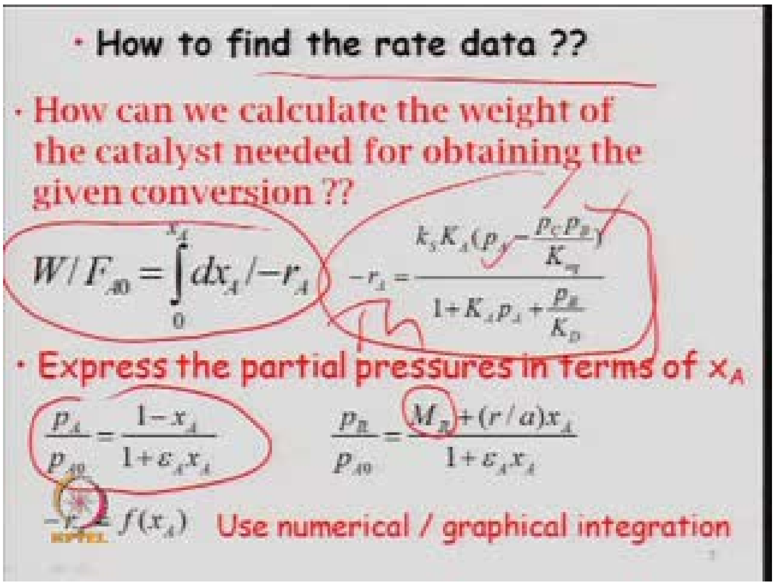

- How to find the rate data ??
- How can we calculate the weight of the catalyst needed for obtaining the given conversion ??

$$W/F_{A0} = \int_0^{x_A} dx_A/-r_A \qquad -r_A = \frac{k_S K_A\left(p_A - \frac{p_C p_B}{K_{eq}}\right)}{1 + K_A p_A + \frac{p_B}{K_D}}$$

- Express the partial pressures in terms of x_A

$$\frac{p_A}{p_{A0}} = \frac{1-x_A}{1+\varepsilon_A x_A} \qquad \frac{p_B}{p_{A0}} = \frac{M_B + (r/a)x_A}{1+\varepsilon_A x_A}$$

$-r_A = f(x_A)$ Use numerical / graphical integration

So, we have done now that how to find out a rate data right versus rate data has been generated then you need to find out the kinetics; but you have to devise the mechanism already. And, now based on that mechanism you have postulated, you have done the experiments and absorbed the rate. And, now you are doing the model discrimination whatever the different models; which have been assumed last time or your last lecture and based on that you have to now validate those models.

So, this is what you have generated data experimentally W by F A naught is equal to 0 to x A d x A upon minus r A. Now, you have a data rate as a function of W by F A naught and rate will be a function of partial pressure, rate will be of temperature, rate is a function of other parameters of this say the inherit is added. So, effect of inherit. So, as I think all whatever the design of experiments you have made; depending upon the mechanic postulation. And, rate theoretically has been co-related something like this.

This is just one co-relation which I had been this theoretical rate basically. Experimentally, this is the data; theoretically you have devised a mechanism and you have valuated the rate. And, now you have to look at the each partial pressure of each species; this is for cumin reaction which we have discussed for benzene and propylene. And, now you can linearize what I discussed last time or you just look at rate data. And, you want to validate this rate for this case as a function of partial pressure. And, partial pressure is related to conversion, correct.

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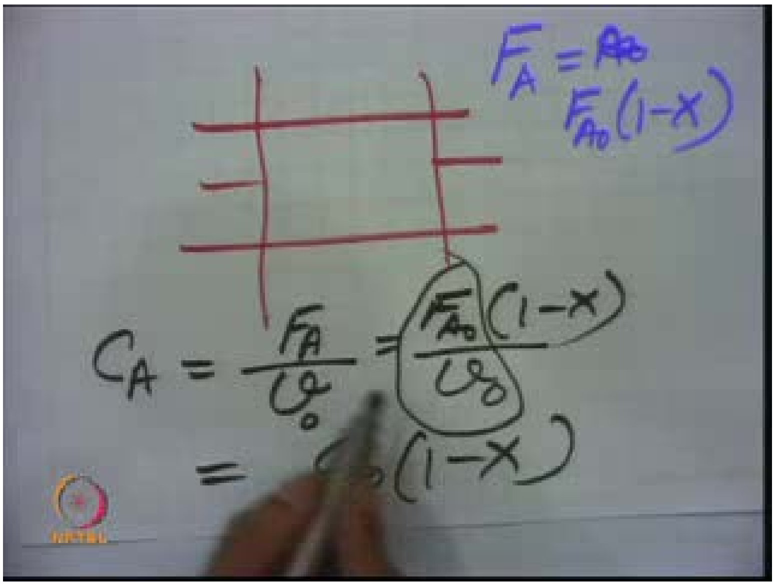

So, in general what I said that partial pressure is changing down the length whether you write in terms of partial pressure or in terms of the concentration. So, F A you know that F A is always given by this F A naught times 1 minus x. Now, how do you define concentration? Concentration is moles per unit volume right. So, F A at any point divide by the volumetric flow rate; if I assume that there is no change in volumetric flow rate then this is throughout v 0 initial. And, that is your basically F A if I write that is in this form. So, this becomes F A 0 1 minus x divide by volumetric field rate. So, F A naught divide by v naught is your initial concentration. So, your C A becomes C A naught 1 minus x right; but this is true only when you have assumed that there is no change in the volumetric field rate. And, volumetric field rate may change during reaction. Why?

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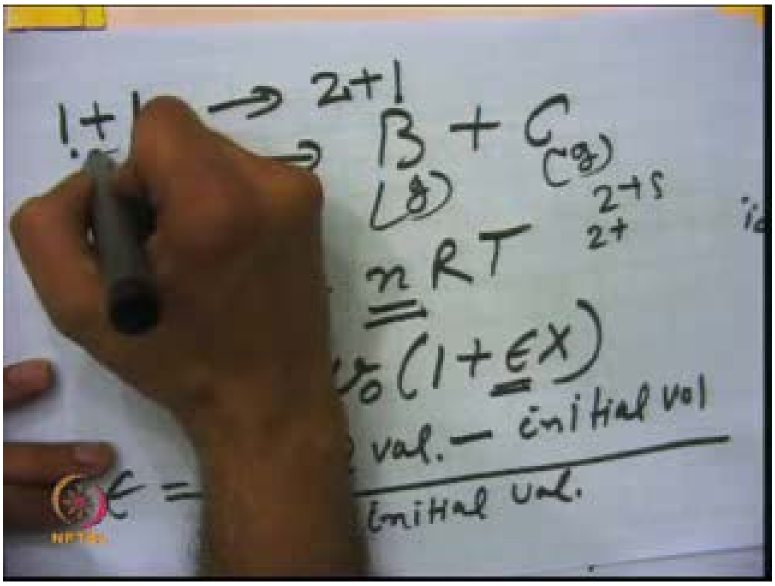

Because suppose your reaction gives you A is equal to B plus C; just like in this case cumin results to benzene and propylene; and this is a gas phase reaction right. So, as per this you can see now that for every moles of this cumin reacted 2 moles of the product will form. So, it means the number of moles in the reactor for a given conversion will increase or if there is complete conversion the final volume will be doubled; number of moles will be 2 times of the original moles; if there is a 100 percent conversion, right.

So, this if the moles are changing. So, volume at the flow rate you know p v is equal to nRT. If these numbers of moles are changing pressure is constant inside the reactor suppose total pressure. Then, this volume at the full flow rate is changing, right. So, how to take care of this change in volume; that will be calculated whatever the volume which is v at anytime will be equal to initial volume plus whatever the Fresnel change in the volume. So, v 0 times if I define a parameter epsilon times x. What is epsilon?

Epsilon is the Fresnel change in volume; that is epsilon what I am saying here are if there is 100 percent conversion possible. Then, for this case the volume change will be 2 times. So, epsilon basically is defined as final volume minus initial volume divide by initial volume right. So, for this case it is 2 minus 1 divide by 1. So, epsilon is 1. So, it means when epsilon is 1 and conversion is 100 percent; so this final volume will be doubled correct. So, it means one can define this epsilon based on this.

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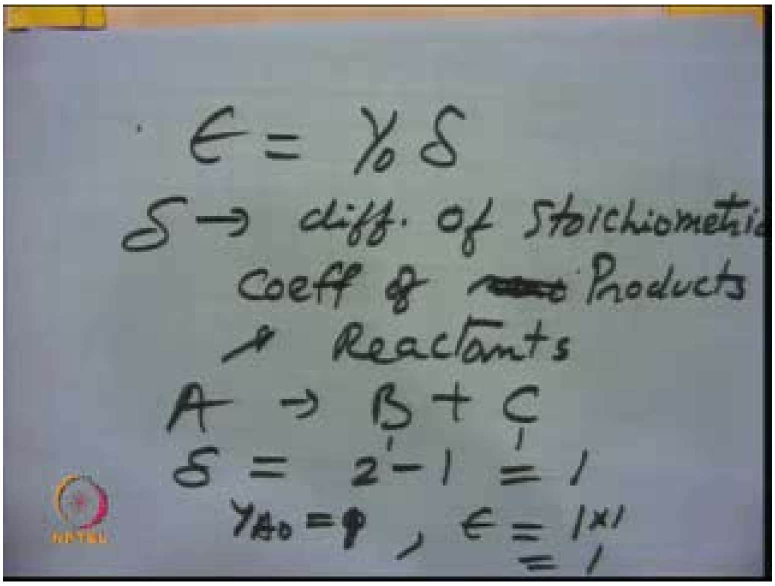

$\epsilon = Y_0 \delta$

$\delta \rightarrow$ diff. of Stoichiometi

coeff of Products

& Reactants

$A \rightarrow \overset{1}{B} + \overset{1}{C}$

$\delta = 2 - 1 = 1$

$Y_{A0} = 1$, $\epsilon = 1 \times 1$

$= 1$

And, also epsilon is defined based on Y A naught times delta; where Y A naught is the mole fraction of the limiting, stack of Y A naught is the mole fraction of the limiting component I am saying now limiting component. So, in this case it is pure cumin suppose field. So, it is1; if it is mixed with some inherit. Because I told you inherit may affect the rate. If you add 50 percent inherit suppose nitrogen along with cumin then Y A naught is 0.5, right. If you add 75 percent inherit then Y A naught is 0.25. What is delta? Delta is the difference of stoichiometric co-efficient, sum of stoichiometric co-efficient of the product minus in the minus the reactant. So, this is the difference of stoichiometric co-efficient of reactants. So, I will write products and reactants, right.

So, in this case suppose A gives you B plus C. So, stoichiometric co-efficient 1 plus 1 minus 1 right. So, delta in this case is 2 minus 1 so that is 1. And, I said that if it is pure cumin so your Y A naught is 1, mole fraction here. So, epsilon in this case is sorry 1; so this becomes 1 into 1, right. So, either you do from this calculation or you do from this result will not change; final volume minus initial volume or you says that in terms of moles right divided by initial.

So, if you have added the suppose 50 percent inherit; so here for 50 percent inherit your Y A naught is 0.5. So, your epsilon will become 0.5 changed now. You can see that epsilon will change depending upon the partial pressure or depending upon the presence of inherit in the phase it may affect the rate. And, if you do from the then final volume whatever you see here; so 1 mole complete conversion gives you 2 moles but there is inherit 50 percent. So, total moles will become 2.5; 2 plus 0 suppose one 1 mole of A has been taken and 0.5 moles of the B has been taken for 50 percent if I am saying. So, either you use your 0.5 of a 0.5 of inherit or 1 of inherit 1 mole of this right.

And, when it completely converts; so 1 mole of this will give you 2 moles, this reactant will convert to complete product 2 moles. But inherit will not convert so it will remain as such right. So, the final mole will become in this case 3; initial 2, 3 minus 2 right divide by 2 is 0.5 right. So, either you do by this or this but one thing is clear it should be defined based on limiting component.

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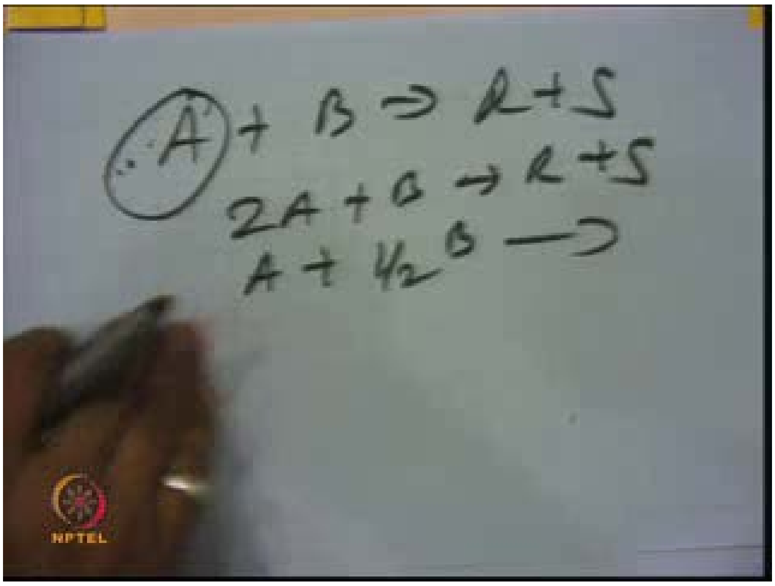

Limiting component means suppose if I have A plus B gives you R plus S and if I say that A is the limiting component. Then, your epsilon will be defined based on A. It means second component is in axis; if they are in stoichiometric then you can define just if it is 2A plus B is equal to R plus S. Then, you just this is limiting component you write the expression in the form like this. And, that you might have read in your homogenous reaction kinetics. So, knowing these things; so this is way once the C A has been defined now.

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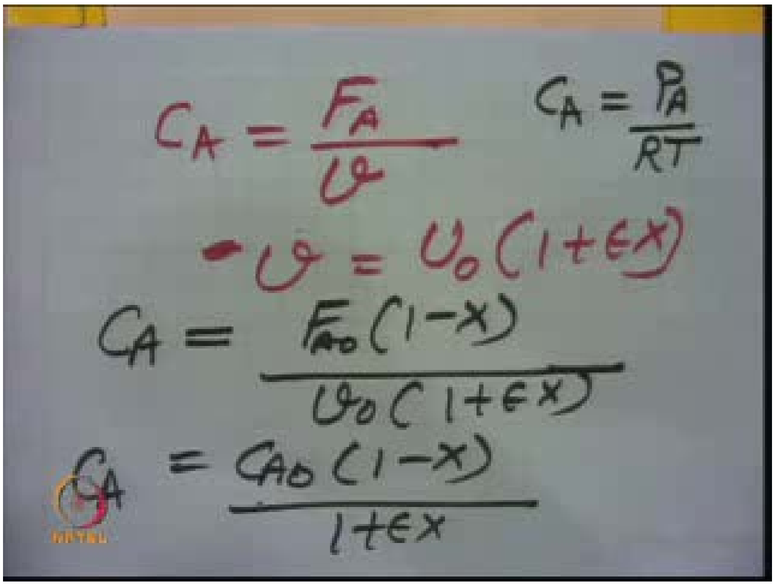

$$C_A = \frac{F_A}{v} \qquad C_A = \frac{P_A}{RT}$$

$$v = v_0(1+\epsilon x)$$

$$C_A = \frac{F_{A0}(1-x)}{v_0(1+\epsilon x)}$$

$$C_A = \frac{C_{A0}(1-x)}{1+\epsilon x}$$

So, C A is now basically F A divide by v; which is the volume metric field rate. But now you know that when there is change in volume; this may change depending upon the epsilon. So, now I will define this v is equal to v 0; 1 plus epsilon x; now once v is defined by this. So, let us see how C A change? So, C A is F A which is F A naught 1 minus x divide by v which is v 0; 1 plus epsilon x fractional change in volume. And, this is now F A 0 over v 0 is your initial concentration C A 0 right. And, this 1 minus x over 1 plus epsilon x; and once you define concentration the pressure can be related to that. So, you know C A is equal to P A upon RT; p v is equal n RT; n by v is your molar concentration. So, C A is equal to P A upon RT and P A partial pressure will change with conversion; partial pressure of the reactant species. Because partial pressure is depending on the moles; so moles of a decrease.

So, that finally gives you the P A is equal to P A naught 1 minus x A over 1 plus x A. So, C A is equal to P A and P A by RT right C A naught is P A naught by RT; RT, RT cancels. So, finally one can write in this form also; with that you define it on the partial pressure, you define in terms of concentration; no change in the expression only the constant may change depending upon RT units may change. So, this is what the numerically or graphically you can write the expression. And, this is what defined p r upon P A naught that is the product divide by the phase right partial pressure right or you define c r upon C A naught either way right.

And, this is nothing but the molar ratio; that is based on the suppose A gives you 2 r; so it is 2 right. So, that is the ratio of the based on limiting component. So, moles of the product form per mole of reactant reacted something like that. So, thus the but that is the stoichiometric but initially it may happen that if you have defined the field at different ratio then that will be here. Because accordingly you are the total mole field rate or stoichiometric table which you make based on conversion that will change; which you must have learnt earlier also right.

So, you know that a A plus B B is equal to gives you C C plus D C. So, one can vary easily write down the stoichiometric ratio based on that limiting component. So, this is written based on that because a moles of A are reacting and forming r moles of the product. So, per mole of a how many moles of r formed that is what written here. And, that you have just simple stoichiometric make a stoichiometric table and balance it.

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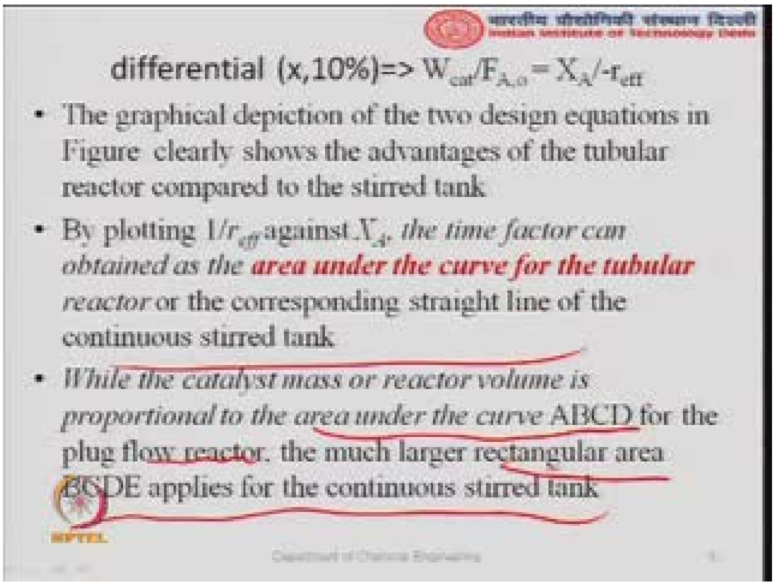

differential (x,10%)=> $W_{cat}/F_{A,o} = X_A/-r_{eff}$

- The graphical depiction of the two design equations in Figure clearly shows the advantages of the tubular reactor compared to the stirred tank
- By plotting $1/r_{eff}$ against X_A, *the time factor can obtained as the* ***area under the curve for the tubular*** *reactor* or the corresponding straight line of the continuous stirred tank
- *While the catalyst mass or reactor volume is proportional to the area under the curve* ABCD for the plug flow reactor, the much larger rectangular area BCDE applies for the continuous stirred tank

So, this is what we have discussed now; that when you do the kinetics in the differential reactor you have to make sure that conversion should not be more than 10 percent right at the most you can go 15 percent. But lower the conversion that is the less the conversion data that will give you better results. Because your assumptions are more valid uniform composition throughout that is very important; when the C A is equal to C A naught 1 minus x A or the expression like this which you are dividing. And, now for CSTR because when you write a differential equation we assume that it is like CSTR a differential ((Refer Time: 46:18)) reactor can be approximated as a CSTR or reverse in I should say that when you have the infinite number of CSTR in series. You make assume that it is a like of ((Refer Time: 46:28)).

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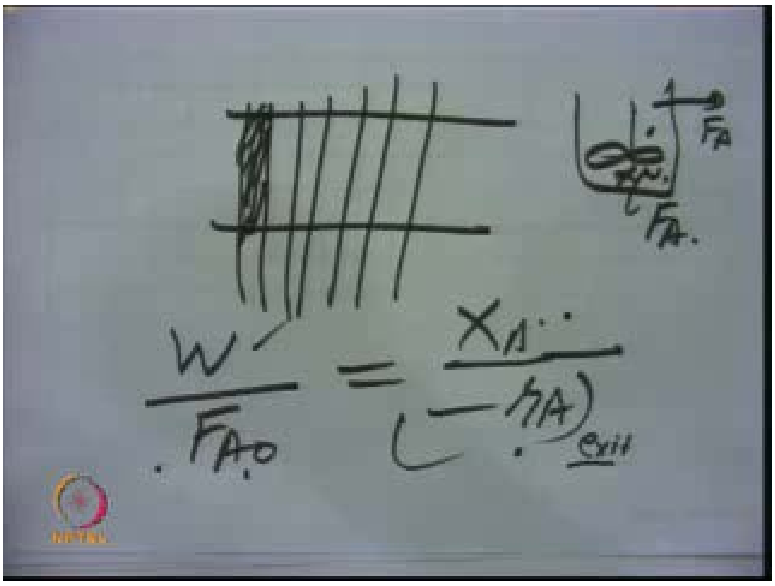

Because in CSTR there is complete mixing in plug flow reactor; you divide your reactor into infinite number of zones. And, every zone is a differential reactor which behaves like a CSTR, right. So, what is the design equation for CSTR that is simply W by F A naught is equal to x A upon minus r A. And, minus r A is evaluated at the exit concentration because I told you in CSTR there is complete mixing no complete back mixing in this; whereas, in plug flow no back mixing at all. So, the concentration here at any point is same and that is equal to the exit. So, this and this is same. If you have this case rights what I have assumed right. Now, for a differential plug flow reactor you have defined it right F A naught d x is equal to minus r A does not to d W right. And, that time this d W becomes W right which is written here; F a naught is FA naught and d x becomes x right. So, because here it is complete mixing conversion can be 80 percent, 90 percent, 70 whatever for that.

So, it means in this case this W by F A naught is equal to x A upon r A; and r A is evaluated at the exit concentration. So, it means whatever the 90 percent conversion; so you directly calculate x is equal to at 0.9; you need not to integrate the expression right. So, because it is a complete well mixed reactor. So, this is what the expression for the

CSTR. So, by plotting this one upon r versus x A which I defined the time factor can be obtained which is your W by F A naught right; that is area under the curve for the tubular reactor or corresponding the straight line of the continuous tank. So, let us see this figure first right.

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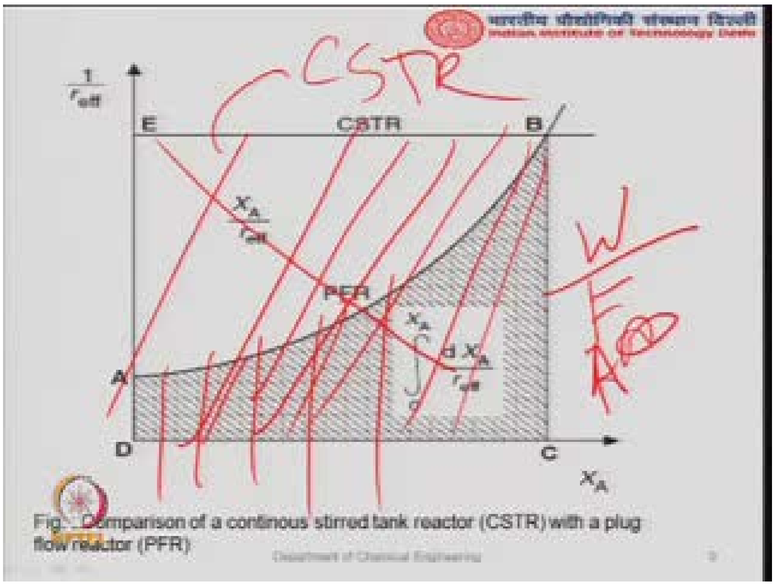

Fig. Comparison of a continous stirred tank reactor (CSTR) with a plug flow reactor (PFR)

So, you know that any reactor you have one upon minus r A versus the conversion data, right. Because the conversion data are experimentally measured; rate has been calculated based on conversion versus W by F A naught data or just whatever the moles reacted per gram catalyst per unit time based on your experimental observation. S, one upon r A versus x A data it appears something like this right; that is conversion versus W by F A naught in all the reactor; most of the case it will increase first.

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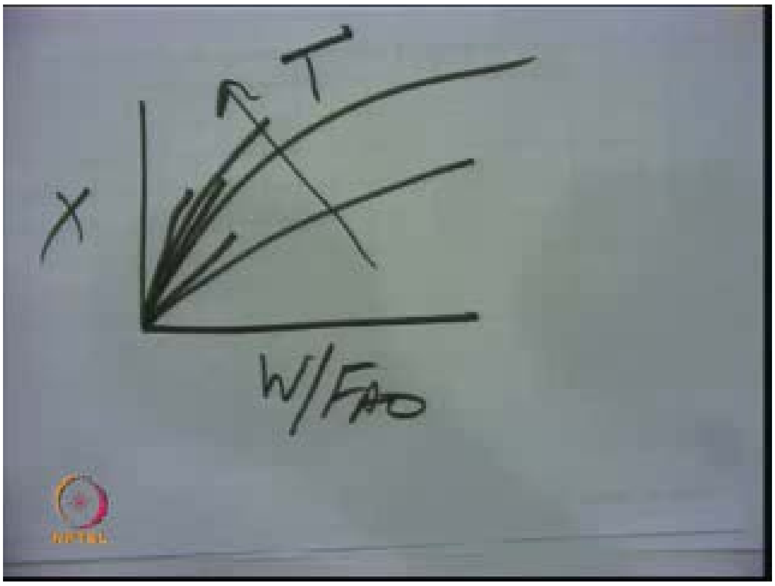

And, then finally come to a flat tube like this. So, this is simple conversion versus W by F A naught data in a plug flow reactor. And, if you do it at different temperatures then rate will increase like this. Because kinetics; the slope of this line at different point is your rate. If I do it at initial rate r A 0 that will be at initial slope, right. So, this is what the conversion versus W by F A naught data. If you plot this one upon r A minus one upon r A versus x A; it will go like this concave upwards, right. So, area under this curve because you know now d x A upon minus r A for any differential section d a say upon minus r A is your W by F A naught, right. So, area under the curve which is 0 to x A d x minus r A and which will be done numerical integration one can find out, right.

By trapezoidal rule, by Simpson's rule one can calculate this area numerically under the curve or you just divide it into several number of triangles and rectangles also you can find out, right. So, this is your W by F A naught; that is the meaning of time contact time or space time right. And, if you take this area because for CSTR I told you W by F A naught is equal to x A upon minus r A, right. So, area under the curve means this 0 to x A d x upon minus r A but when you have a CSTR W by F A naught is x A upon minus r A. So, what is x?

X is the sole term and r A is this thing. So, this area of this total curve is rectangle that is your W by F A naught; when you have a CSTR. What have you learnt from this? It means because this area is much larger compared to this shaded portion, right. So, it means in the case if you look at same conversion; to achieve if you want to achieve same conversion in any commercial reactor. Then, you need a larger size reactor because F a naught is same W by F A naught; you want same productivity, right. If you are treating thousand, tons of the feed stock then those F A naught is fixed right; and one wants to do in CSTR, another wants to do it in a plug flow reaction.

So, what I mean to say for this kind of curve; concave upwards the area under the curve is something like which is total rectangle area. That is the W by F A naught space time for a CSTR and shaded portion is the space time for a plug flow reactor. So, CSTR will require a larger size compared to a plug flow reactor right for this case or that with the curve with concave upward. So, basically when your orders are positive right. So, this is one can say one say from the graph or interpretation of these kinetic data; this is very important in terms of that reactor design.

So, one should go with the plug flow reactor or one should select a CSTR that becomes important. So, sometimes a combination of the two can be used; recycled type reactor right. So, this fluidized bed reactors, slurry bubble column reactors which are commercially used. Because the mixing is an issue; heat transfer is an issue you cannot use a plug flow reactor right. You need to dissipate the heat time to time. So, either you look at some jacketed or adiabatic reactors you select those accordingly or you use a slurry bubble column reactor ((Refer Time: 52:49)) bed reactor which are nowadays more common; especially when you have a exothermic reaction. When the heat generation is a problem and dissipation of that heat may cause the hot spot formation. So, then these become very important.

So this is important that while that catalyst mass or reactor volume is proportional to the area under the curve for the plug flow reactor. That is integration of 0 to x d x upon minus r A; the much larger rectangular area BCDE applies to a CSTR tank. So, volume is larger of mass of the catalyst which is required for a given conversion is high. So, this is your basically a reactor design; based on your kinetic expression right.

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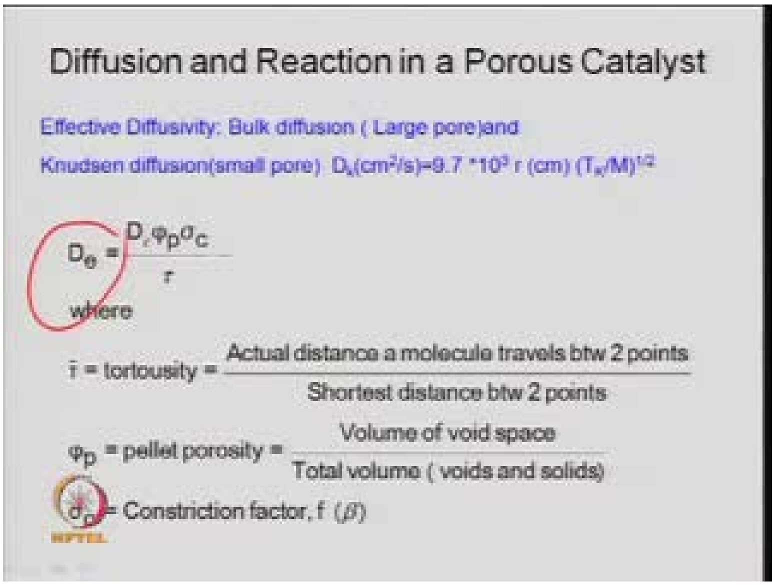

Diffusion and Reaction in a Porous Catalyst

Effective Diffusivity: Bulk diffusion (Large pore)and

Knudsen diffusion(small pore) $D_k(cm^2/s)=9.7 * 10^3\ r\ (cm)\ (T_k/M)^{1/2}$

$$D_e = \frac{D_r \varphi_p \sigma_c}{\tilde{\tau}}$$

where

$\tilde{\tau}$ = tortousity = $\frac{\text{Actual distance a molecule travels btw 2 points}}{\text{Shortest distance btw 2 points}}$

φ_p = pellet porosity = $\frac{\text{Volume of void space}}{\text{Total volume (voids and solids)}}$

σ_c = Constriction factor, f (β)

But if you look at now the first we discussed this kinetics of the reaction.

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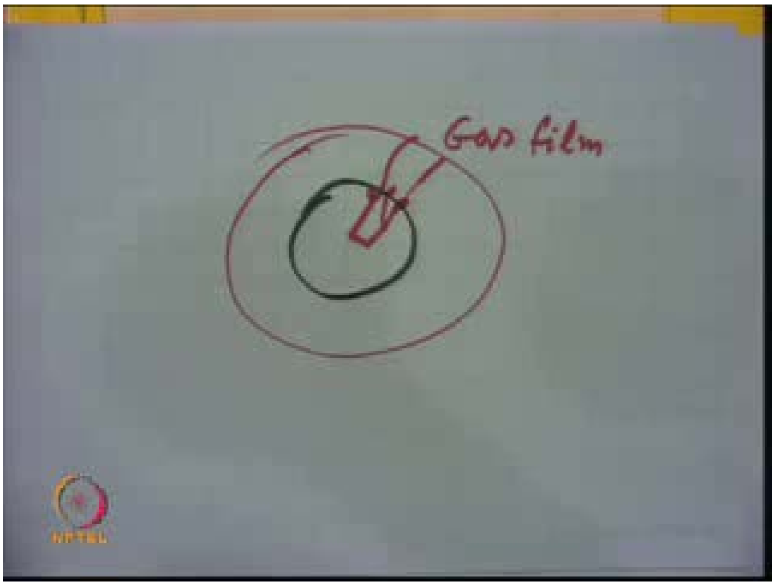

But in total there are several resistances which are here in the film, right. So, there was a gas film resistance which needs to be studied. And, then there is diffusion in that is this the gas film resistance and when it comes to this. And, now the diffusion is a phenomenon in the catalyst pore that what the kinetics or Langmuir Hinshelwood or Raleigh radial type mechanism which has been discussed; that is based on surface reaction. The third step where the two mass transfer stocks have been eliminated. But when you have a catalyst pallet which is porous and kind of porosity, it has ((Refer Time: 54:27)). Then, also important is that to learn about the diffusion resistances right in a pore of a catalyst.

So, this is again when if you remember what we were discussing the diffusion phenomenon; they are 2 types of diffusion in that atlas which is possible right. The bulk diffusion which is the actually depending generally bulk diffusion in a larger pore, right. And, that is just a function of temperature and pressure but if you look at the principle phenomenon of the diffusion that is bulk diffusion is because of the molecules are colliding right among themselves. And, that is will be happen when the molecules are colliding among themselves means; the mean free path of the molecule is smaller than the pore diameter the pores are larger.

So, molecules are colliding among themselves rather than the wall and they are moving inside, right. So, that is the one thing where that is mean prefer. Second case maybe the pores are smaller right. Pores are smaller means, what I mean to say the molecules are colliding more with the wall; it is a narrow channel. So, either pores are smaller or I will say that the mean prefer of the molecule is larger. So, molecules are not colliding between or among themselves but there are colliding more with the wall right. And, that gives you a kind of Metson diffusion right.

So, these 2 kind of diffusion phenomenon maybe dominating in a catalyst pore, right. And, once you have that then you need to define in term which is unit effective, defective. So, metson diffusion is dominating depending on the temperature that is calculated based on 9.7 into 10 to the power 3 r bar under root of t by m right; that is the bulk diffusion there are several coalitions available. Because it will depend on the root mean square velocity based on the kinetic theory of the gases the molecules are colliding among themselves. And, that will be based on kinetic theory it will be a function of temperature, it will function of pressure and one can calculate and check ((Refer Time: 56:43)) formula. Now, if you look at any transport phenomenon book you can find out that the bulk diffusion and metson diffusion right or mainly bulk diffusion. Metson diffusion is mainly dependent on the temperature and the molecular weight of the gas right. So, if you look at here.

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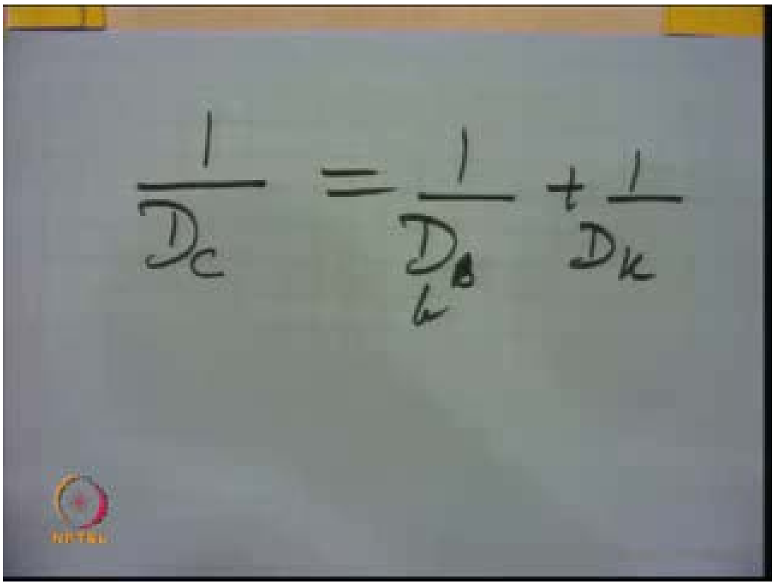

$$\frac{1}{D_c} = \frac{1}{\underset{b}{D_B}} + \frac{1}{D_K}$$

So, your combined diffusivity is which will write D c is related to the bulk diffusion I will write b and the metson diffusion which is k right; that is your combined diffusivity ok. So, I will continue it next time. I stop here.

Thank you.