Mathematical Modelling and Simulation of Chemical Engineering Process

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Lecture 26

Modelling Reaction Systems - Packed Bed Catalytic Reactor

Hello everyone, in this week we are going to talk about reactor problems particularly focusing on catalytic reactions, heterogeneous catalysis, packed bed reactor, enzymatic reaction systems.

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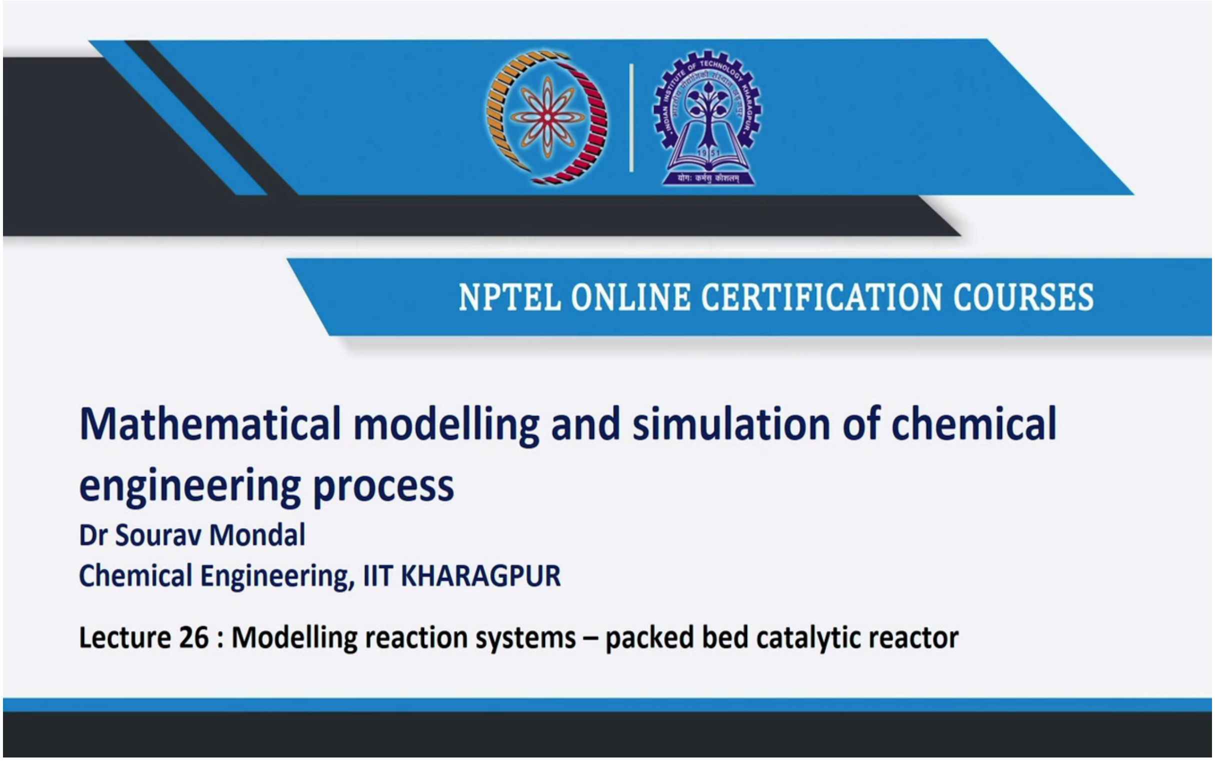

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Mathematical modelling and simulation of chemical engineering process

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Lecture 26 : Modelling reaction systems – packed bed catalytic reactor

CONCEPTS COVERED

- Mass transfer in packed bed column
- Catalytic reactor

So, today the first lecture we are going to focus on general packed bed catalytic reactor, I mean how we can model them, and what are the background of this process. So essentially, we will be talking about heterogeneous catalysis problem in this case, and how the mass transfer in the packed bed column is intricately coupled to this catalytic reactor process.

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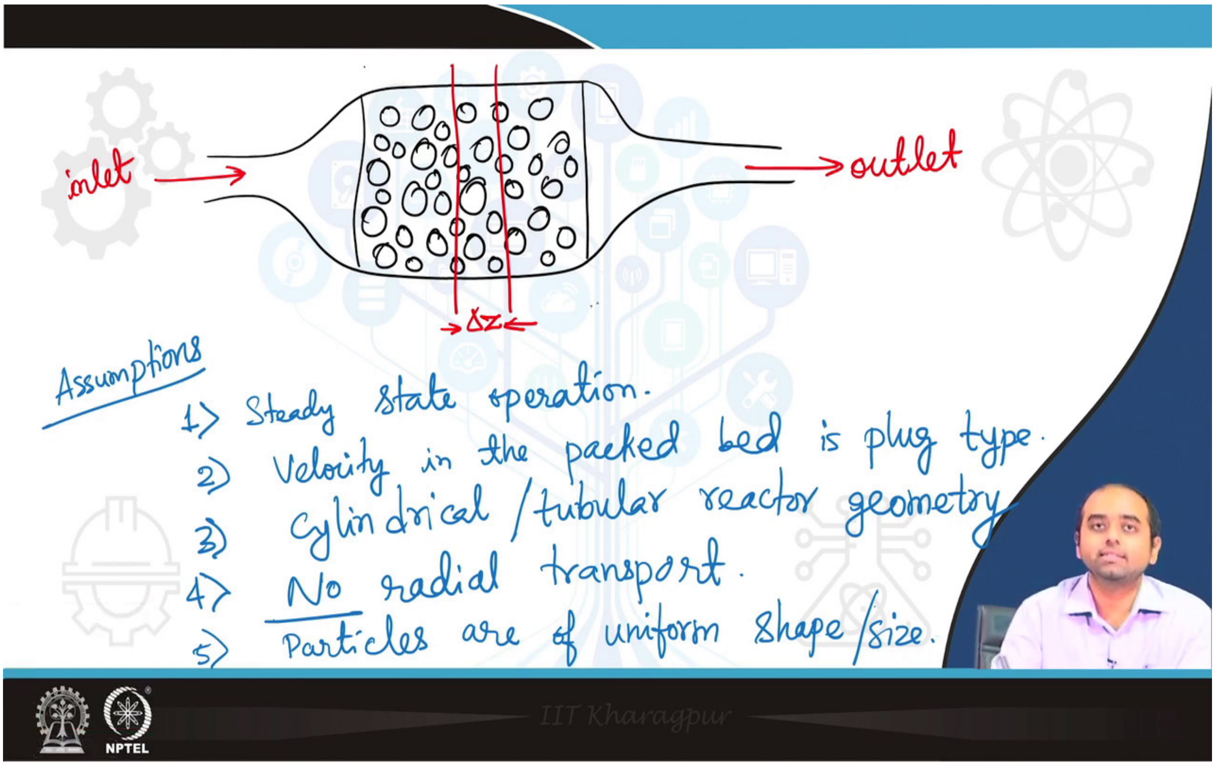

Assumptions

1) Steady state operation.
2) Velocity in the packed bed is plug type.
3) Cylindrical / tubular reactor geometry
4) No radial transport.
5) Particles are of uniform shape/size.

So, let us consider a simple catalytic reactor, and these catalytic reactors are very common in chemical industries whether you go for catalytic cracking, or you go for fluidized bed reactors. So, these are very common. So, let us assume this is my simple packed bed, where I have the catalyst particle, the packings on which the reaction takes place. So, the concept is I mean the configuration is very much similar to the packed bed adsorption except that here we are having catalytic reactions instead of adsorptions. So, this is a packed bed catalytic reactor where you have inlet from this side and this is the outlet.

Let us assume a small cross section of delta Z. But before as we always say that before working or writing out the model equations, it is absolutely important to write down the assumptions. So, what are the assumptions that we are going to consider in this model first? Let us say steady state operation to simplify our lives. Another important assumption we can make is that the velocity in the packed bed is of plug type, cylindrical or tubular reactor geometry, also let us ignore any radial transport.

This is not a practical assumption, but at least for this problem essentially, we can get a very realistic idea of the dynamics, sorry of the process model even without this radial transport mechanism, but this is of course, I must say that this is an assumption that you should relax to get a more practically relevant idea. Mass transfer by convection, I mean this is something which we are also going to look into the case that but let me just spell it out now, that for the time being we can say that the mass transfer by diffusion let us say is not so significant over convection.

But you already know that in case of gas phase systems diffusive effects are very important, for liquid phase systems we can safely ignore any diffusive or actual diffusion can be ignored with respect to actual convection. And the particles are considered to be of uniform shape and size. Particles, catalyst particles of course, are of uniform shape and size.

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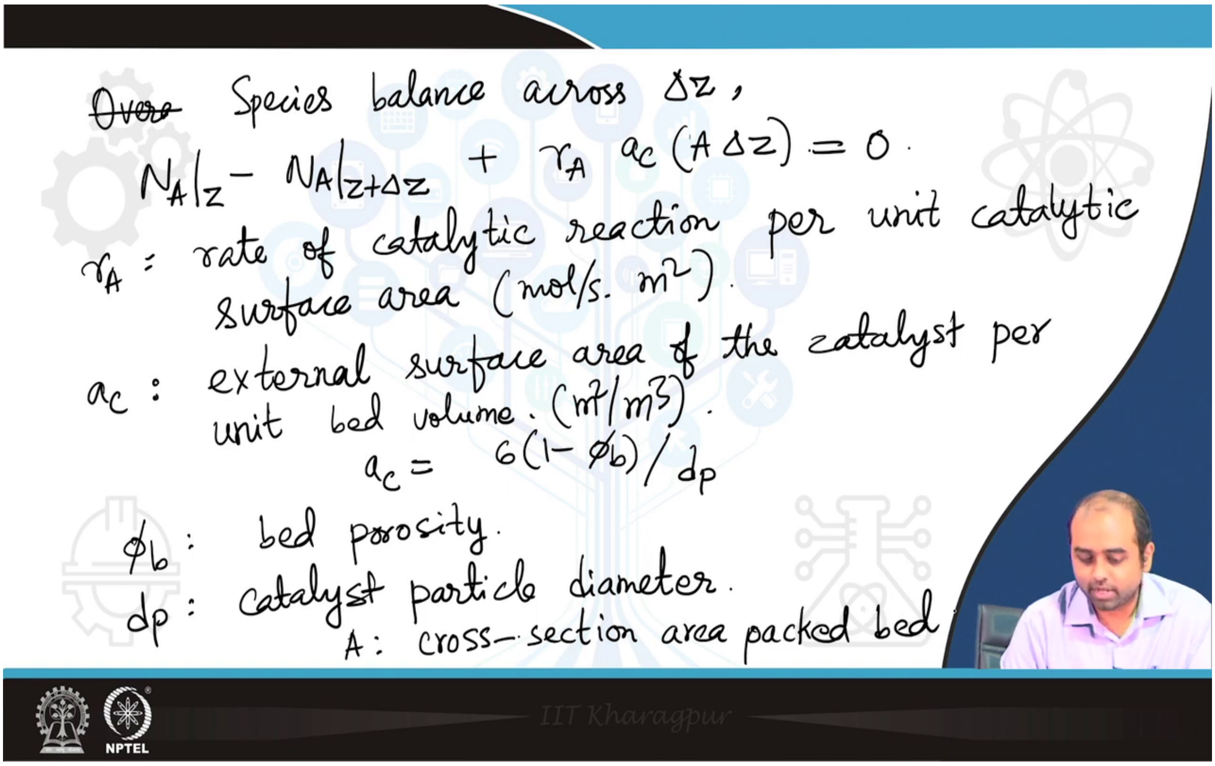

~~Over~~ Species balance across Δz,

$$N_A|_z - N_A|_{z+\Delta z} + r_A a_c (A \Delta z) = 0.$$

r_A : rate of catalytic reaction per unit catalytic surface area (mol/s. m^2).

a_c : external surface area of the catalyst per unit bed volume. (m^2/m^3).

$$a_c = 6(1-\phi_b)/d_p$$

ϕ_b : bed porosity.

d_p : catalyst particle diameter.

A : cross-section area packed bed

Now, let us try to make an overall mass balance over this elemental section of delta Z, or the species balance across delta Z. So, what we get? We are only considering axial fluxes, so, N A at Z minus N A at Z plus Delta Z. So, this is the change in the axial flux can be equated to the, this accumulation which is the reaction in this case, or the consumption r A a C A Delta Z is equal to 0. So, here r A is the rate of chemical reaction, or the rate of catalytic reaction, this is very important per unit catalytic surface area. So, whatever rate you are considering that should be divided by the unit catalytic surface area. So, moles per second per meter square.

a C is the external surface area of the catalyst per unit bed volume because we are multiplying this with the bed volume in that cross sectional, in that elemental section of delta Z, unit bed volume. So, this is meter square plus meter cube, and all of you know this. So, this value of this a C is turns out to be 6 (1 minus phi b) is the bed porosity divided by the particle diameter, this is something which all of you can also work it out, and I leave it to you. So, of course, phi b is the bed porosity here. d p is the catalyst particle diameter, and A is the cross-sectional area of the packed bed.

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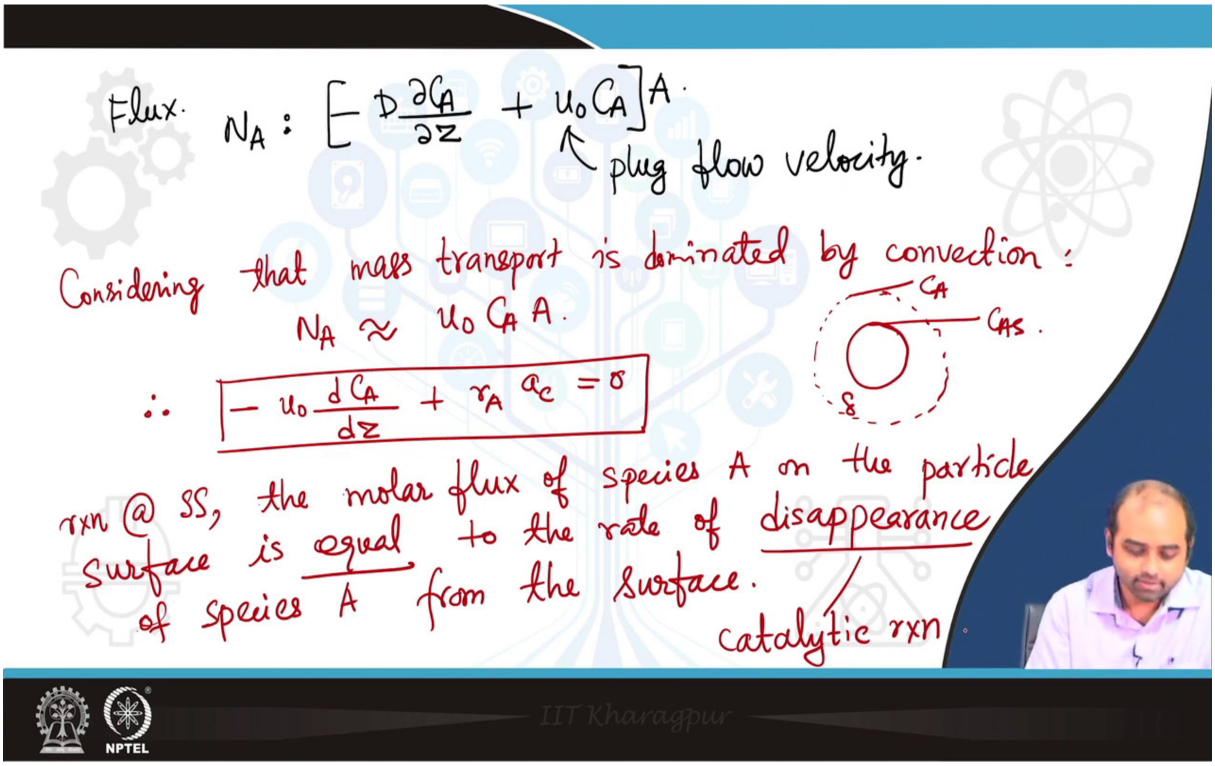

Flux. $N_A : \left[D \frac{\partial C_A}{\partial z} + u_0 C_A \right] A .$

plug flow velocity.

Considering that mass transport is dominated by convection :

$N_A \approx u_0 C_A A .$

$$\therefore \boxed{- u_0 \frac{d C_A}{dz} + r_A a_c = 0}$$

rxn @ SS, the molar flux of species A on the particle surface is equal to the rate of disappearance of species A from the surface.

catalytic rxn

So, considering the, and of course, I have to write the flux. So, this flux N A has two components, the diffusive flux and the convective flux. I just multiply with the area here. So, u 0 is the plug flow velocity. So, we do not, I mean the other option is to calculate this based on the pressure distribution either following Ergun equations or Darcy's law, that is something you can also workout or you can also have the Darcy-Brinkman equation to calculate, to estimate precisely how the flow variation or the hydrodynamics inside the packed bed happens.

So, Darcy-Brinkman is a I would say a generalized version of the Darcy's equation which takes into account of the boundary wall considerations. Since Darcy's equation is a, as a first order model, so, you cannot incorporate the boundary conditions effectively, and for that Brinkman equations came into existence where the boundary effects are very important. Now, let us say if you consider, let me write this in red, that if you consider that the diffusion is insignificant or small comparing to convection. So, that the overall mass transport is dominated by convection alone, and this is likely the case in liquid systems.

Because liquid diffusivity is the diffusivity of the species in liquid systems are very small and as a result Peclet number is high. So, mass transport is generally dominated by convection inside beds. So, if the mass transport is dominated by convection. So, this N A is proportional to u 0 C A, A. So, we can write the main equation I mean taking the limits of delta Z tending to 0 as minus u 0 d C A, d Z plus r A, a C is equal to 0. It is a simple first order equation, first order linear equation.

Now, let us try to understand how we can write down this reaction rate here. So, any reaction so, for reactions which is at steady state, reaction happening at steady state the molar flux of A, or the species A on the particle surface, please mark my words, on the particle surface is equal, and has to be equal for mass conservation is equal to the rate of disappearance of of course species A from the surface. So, at steady state the flux or the molar flux of species A on the surface has to be equal to the rate of its disappearance. There cannot be any accumulation at steady state.

So, if there is a particle, or catalyst particle. So, and we say that there is a certain boundary layer, let us say the boundary layer thickness is delta etcetera. So, the particle surface concentration let us say C S and the because of the formation of the boundary layer and the far away boundary condition is C A. So, in this scenario the particle, I mean the whatever this flux that is approaching or incident on the particle surface should be equal to the rate of its disappearance. And how it will disappear? A chemical reaction only.

So, it should disappear from the particle surface and this is essentially I mean this is very much equivalent to the linear driving force model which we have just seen in the previous lecture on adsorption, which tells you that the linear I mean in the linear driving force model, I mean for the mass transfer on the particle surface of the intra. So, inter particle mass transfer affects. We also say the same thing that the molar flux of the species A is equal to the rate of disappearance, and there it was the disappearance was due to adsorption, and here the disappearance is due to chemical reaction. So, this disappearance is due to chemical reaction or catalytic reaction. So, this has to be true.

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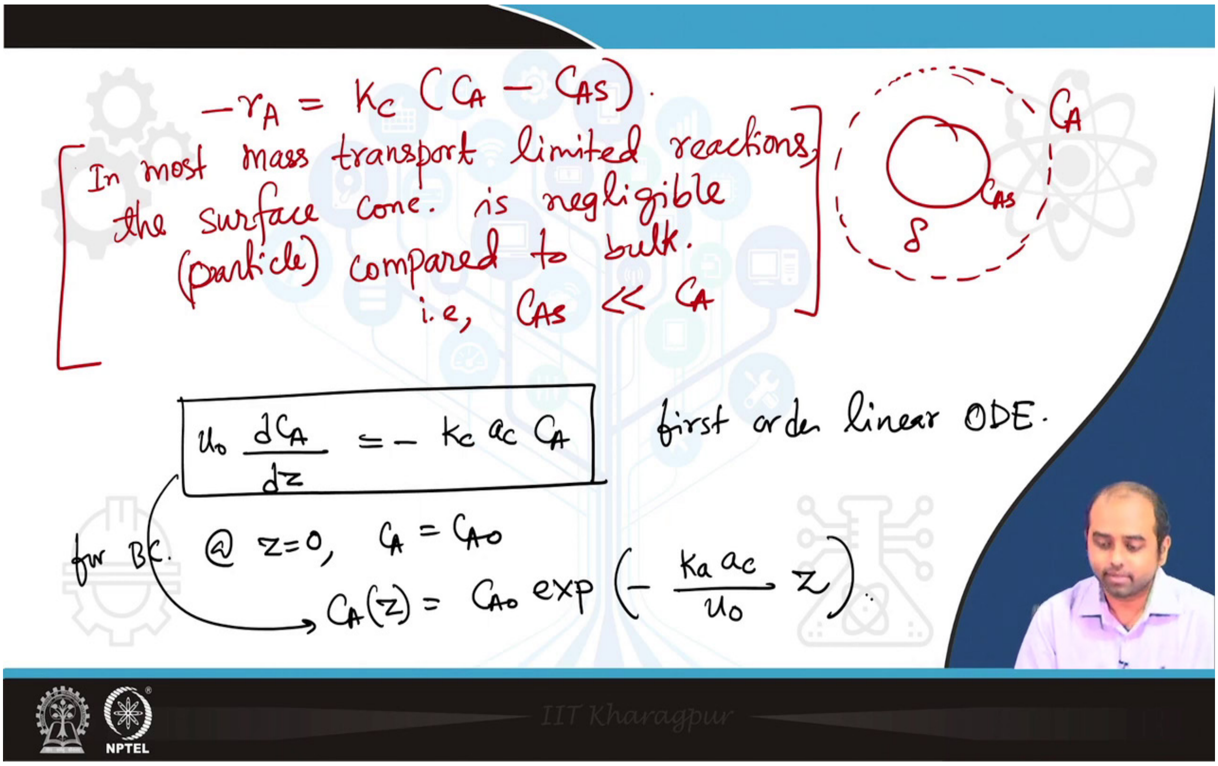

$$-r_A = K_c\,(C_A - C_{AS}).$$

[In most mass transport limited reactions, the surface conc. is negligible (particle) compared to bulk. i.e, $C_{AS} \ll C_A$]

$$\boxed{u_0 \frac{dC_A}{dz} = -k_c a_c C_A}$$ first order linear ODE.

for BC. @ $z=0$, $C_A = C_{A0}$

$$C_A(z) = C_{A0} \exp\left(-\frac{K_a a_c}{u_0} z\right).$$

So, we can, I can write down the chemical reaction rate minus r A is proportional to the mass transfer coefficient into C A minus C AS and of course, I will draw this picture once again here this is C AS is the surface concentration, and C A is the bulk concentration away from the particle surface which is the bulk concentration in this case in the packed bed, and the thickness is delta.

So, you can write this mass transfer coefficient as d by delta based on the thickness of the boundary layer. That is how the flame theory approach actually works. So, in most this mass transfer limited reaction, this is another important point in most mass transport limited reactions which is the case here because we study the, this mass transferring the packed bed.

So, in most mass transfer limited reaction the surface means that the particle surface concentration is negligible compared to bulk. So, which means that C AS is much much smaller than C A. So, you can argue that what happens when it is not a mass transfer limited reaction. So, if it is not a mass transfer limited reaction, its mass transfer is not the slowest step in the process, then the system is dominated by reaction. So, we can just work out the reaction kinetics and that will tell us that how the things change with time. So, there is no point of working out the mass transfer or the mass transport effects.

So, it is only when the mass transfer effects are important in the packed bed reactor, then this question of diffusion, convection all this comes into the picture, but if it is a reaction limited process, or the reaction is the slowest step, it does not matter, what is the rate of mass transfer to the process, then you can just write down the reaction kinetics for the problem, it is just like a kinetics and whatever reaction is happening in the catalyst particles, that will govern the entire system dynamics, because that is the slowest step. But since the timescale of the mass transport is much larger in this scenario and that is what we consider to be mass transport limited reactions.

In this case, the individual reactions happening is quite fast and that is not so important and that is the reason why the catalyst particle surface concentration is much lower than the bulk concentration because whatever is coming to the particle surface is immediately consumed by the reaction, or the reaction rate is much faster compared to the mass transport rate, and that is the reason why this surface concentration is much smaller. So, this is a very practical consideration that we are making here. So, based on this idea, you can easily realize that this r A turns out to be just K C into C A.

So, we can write down the final equation as minus sorry, u 0, it is u 0 dC A dZ is equal to minus K C a C C A. So, this is a simple first order linear ODE, first order linear ODE. And on integrating you can easily work out the, so for the boundary condition that at Z is equal to 0 you have C A is equal to C A0 which is the inlet concentration, you have the concentration profile I mean the solution to this equation C A as a function of Z is equal to C A naught exponential, sorry. So, even with these assumptions, with so many assumptions and some very practical consideration you can find out that how the reactant, I mean sorry, how this reactant concentration decreases along the length of the packed bed reactor, and this is a very, even though it is very simple it is a very powerful relation in the context that you can actually work out that how the reaction rate varies in the reactor.

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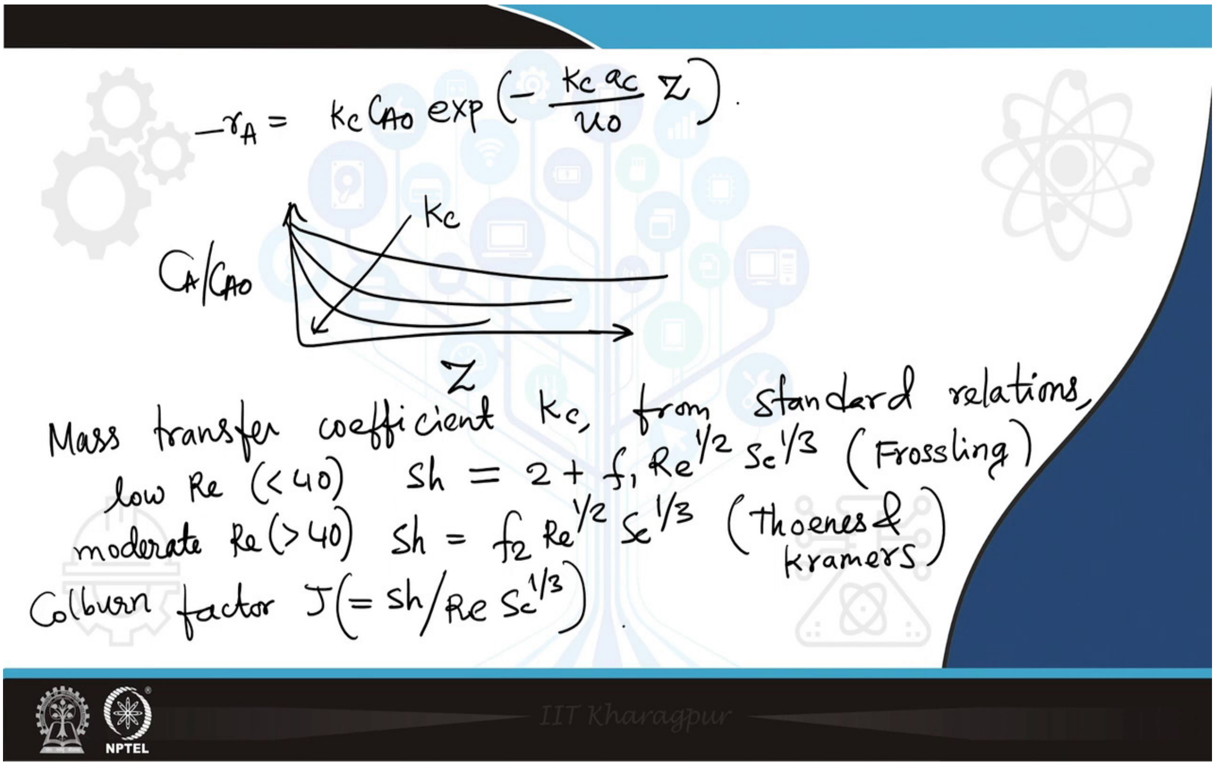

$$-r_A = k_c C_{A0} \exp\left(-\frac{k_c a_c}{u_0} Z\right).$$

Mass transfer coefficient k_c, from standard relations,

low Re (< 40) $Sh = 2 + f_1 Re^{1/2} Sc^{1/3}$ (Frossling)

moderate Re (> 40) $Sh = f_2 Re^{1/2} Sc^{1/3}$ (Thoenes & Kramers)

Colburn factor $J \left(= Sh / Re\, Sc^{1/3}\right)$

So, the minus r A can be written down as like this, let how the reaction rate actually varies along the length of the reactor, and this can also be quite useful for estimating the size of the reactor like what should be the degree of conversion that you want to achieve. So, if I try to make a plot of C A versus C A naught along with Z, so, this will be something like this, and for different mass transfer coefficients, I mean as k C is increasing, these profiles will look something like this. So, with higher mass transfer rate, the effective to have a desired conversion the length will be smaller.

So, this relation provides very useful information in respect to the design of the packed bed reactor of course, making some assumptions that there is no intra particle effects, because we have not considered intra particle effects here, we consider the problem to be in steady state, which is normally the case for industrial practice. We also said that diffusion is the not important for this problem. So, this is the case for liquid phase reactors, and this k C, how do you estimate this mass transfer coefficient k C.

So, this mass transfer coefficient k C can be estimated from standard Sherwood relations, and you will find several such relation in textbooks, in handbooks, in research publications, I mean, these are some of the popular ones. For low Reynolds number, typically less than 40 you have this relation of Sherwood number as 2 plus some factor which depends on the shape and size of the catalyst particles, or the packed bed particles. So, this is known as the very popular Frossling relation for estimating mass transfer coefficients in packed bed.

For moderate Reynolds number, generally you do not obtain a situation of very high Reynolds number in packed bed. Sherwood number is f 2 Reynolds to the power half, Schmidt to the power half, sorry one third. So, this is known as Thoenes and Kramers relation. You can also use the Colburn's factor J. So, based on the Colburn factor J. So, which is equal to Sherwood by Reynolds Schmidt, I am if I am not wrong, this is Reynolds Schmidt to the power one third. Or maybe Reynolds one half.

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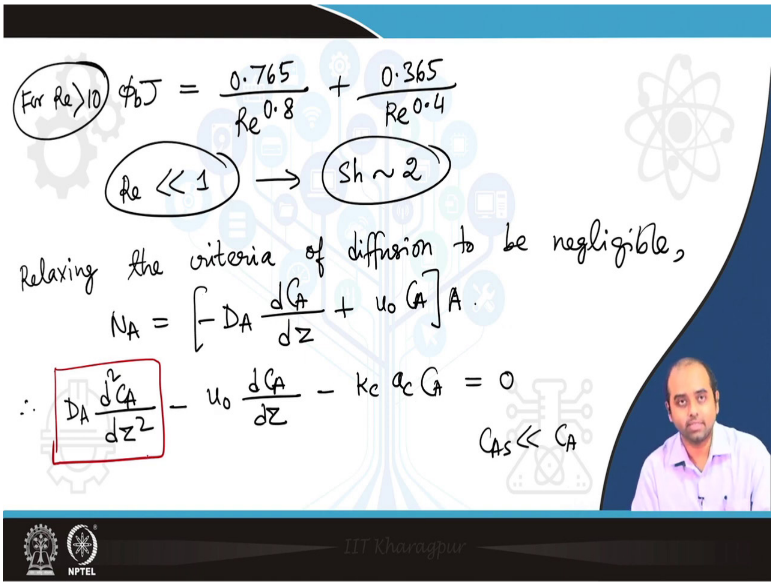

$$\boxed{\text{For } Re > 10} \quad \phi_b J = \frac{0.765}{Re^{0.8}} + \frac{0.365}{Re^{0.4}}$$

$$\boxed{Re \ll 1} \longrightarrow \boxed{Sh \sim 2}$$

Relaxing the criteria of diffusion to be negligible,

$$N_A = \left[-D_A \frac{dC_A}{dz} + u_0 C_A\right] A.$$

$$\therefore \boxed{D_A \frac{d^2C_A}{dz^2}} - u_0 \frac{dC_A}{dz} - k_c a_c C_A = 0$$

$$C_{As} \ll C_A$$

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So, this factor you get phi J, of course phi means phi b 0.765 divided by Reynolds to the power 0.8, plus 0.365. There are some Colburn charts also available and which you can also refer. So, this is for the case of Reynolds number greater than 10. For ultra-low systems, for very low systems, while Reynolds number is much much less than 1. For Reynolds number much much less than 1, it is very reasonable to approximate Sherwood number as 2. Because that is the lowest Sherwood number that is possible flow past a sphere, there is a very classical textbook problem in that you will find in any transport phenomena book.

That for very, I mean the minimum possible Sherwood number, or Nusselt number is generally equal to 2, and based on the assumption that it is a flow past a sphere, which will give you the minimum Sherwood number. So, in case of very low flow rate which may be possible for liquid flows in porous mediums, highly impermeable, or low permeability porous mediums, say the Sherwood number can be easily approximated as 2. Now, let us revisit the condition, or relax the criteria, relaxing the criteria, that criteria of diffusion to be negligible, it is something which you have already made before.

So, we will get N A is equal to, I mean we have to use this full, the diffusive flux into consideration, we have to take the diffusive flux into consideration. So, from here we can get considering that flux has the components of the diffusion along with convection and as I have said, this is for the case of gas phase systems this is very important.

So, what we get is that so, we have an additional term in this problem of course, the reaction part that same thing is done here we consider that reaction surface concentration is much much less than on the particle far away from the particle. So, now, this is an additional term, this double derivative term is an additional term in this case, which is due to the diffusion. Now, just also to give you a mathematical perspective, if you try to non-dimensionalise this equation, just bear with me.

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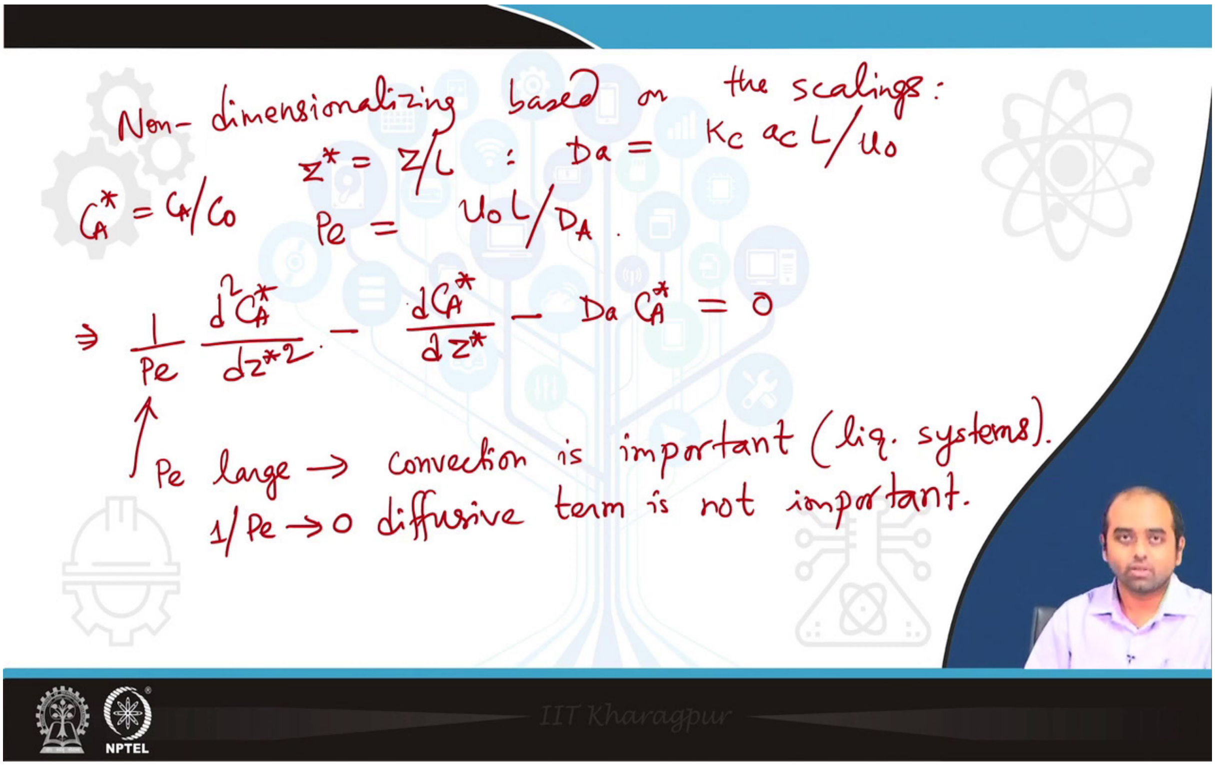

Non- dimensionalizing based on the scalings:

$z^* = z/L$: $Da = k_c a_c L/u_0$

$C_A^* = C_A/C_0$ $\quad Pe = u_0 L/D_A$.

$$\Rightarrow \frac{1}{Pe}\frac{d^2 C_A^*}{dz^{*2}} - \frac{dC_A^*}{dz^*} - Da\, C_A^* = 0$$

$\uparrow$ Pe large → convection is important (liq. systems).

$1/Pe \to 0$ diffusive term is not important.

So, non-dimensionalising this equation based on the scaling. Let us say Z star is equal to Z by L, we define the Damkohler number as, sorry. So, I hope all of you are aware of what do you mean by Damkohler number, the mass transfer rate by the reaction rate, and then you have the Peclet number, which is the convection rate by diffusion rate, D A.

So, the same equation can be modified as 1 by Peclet number of course, C A star is C A by C naught. So, this is the modified equation we get, and here clearly from the criteria of the

Peclet number, we can clearly see that if Peclet number is large, we can say that convection is important for the problem, which is true for liquid systems.

So, diffusive term is not important, because 1 by Peclet number tends to 0. So, diffusive term is not important. And this equation reverts back to the previous case, where we originally made the assumption that to ignore the diffusive term that is something we should also say here based on the criteria of the Peclet number. So, instead of grossly making an assumption that diffusion is unimportant in the problem, you can actually frame the complete equation evaluate the Peclet number, and see that how much of the contribution this diffusive term is making in this problem.

And based on then, you decide and after non-dimensionalising you decide whether to retain that term or to ignore that term. So, if you talk in terms of the perturbation methods, this 1 by Peclet number or essentially the Peclet number can be that epsilon parameter based on which you can also do approximate solution to these ODE, or to this problem, but of course there is a direct solution possible, but if you want, if the problem is slightly complex let us say with the help of if the reaction is second order, or something, it is a slightly complicated to solve out.

So, in that case, you can use this perturbation methods to get approximate analytical solutions over the expansion of 1 by Peclet number. So, that is something that you can of course try out, and looking to the situations when you have diffusion important in the problem. So, when diffusion is important of course, 1 by Peclet number is not a small quantity, and that is likely the case for gaseous systems.

So, with this I think we can close this lecture today, I think all of you found this theory of the packed bed reactor to be quite interesting and exciting. In the next lecture, we are going to talk about more on how the mass transport and the reaction effects takes place inside the particles, or inside the particle pores. Thank you.