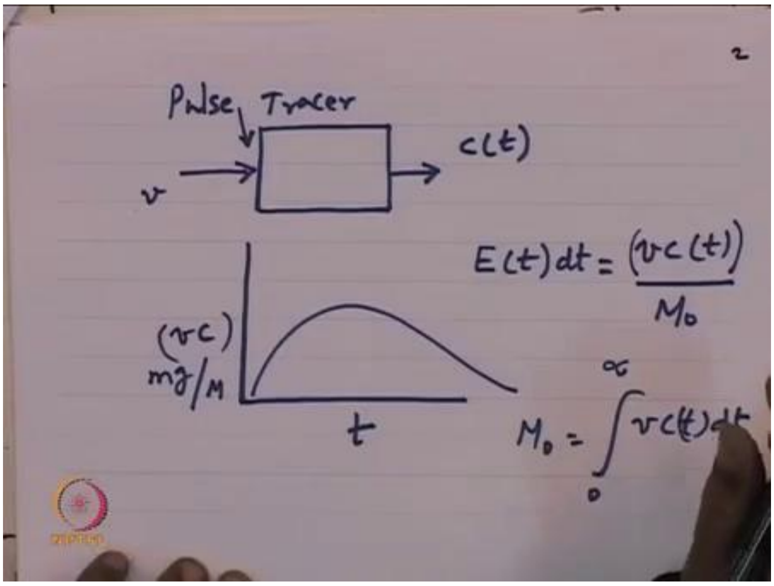
Advanced Chemical Reaction Engineering
Prof. H. S. Shankar
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 27
Residence Time Distribution Models

We go down to Advanced Reaction Engineering. We now look at Residence Time Distribution. Now, why are we interested in look at residence time distribution, of course it comes from common sense that every reaction equipment, the time for which the regency sit inside in the equipment. It determines extent to which the reaction would occur. And that is a prime motivation to understand, is that distributional residence time inside the equipment.

(Refer Slide Time: 01:12)



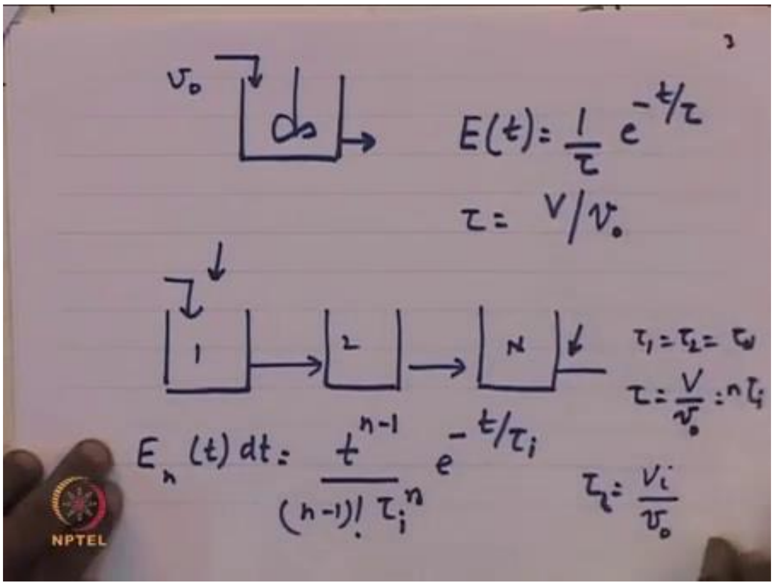
So, typically if we have an equipment like this. And then, we have fluids coming in and fluids going out. And we would like to know, what is the time of residence of different fluid elements inside this equipment? We provide what is called as a tracer. We mentioned earlier, that the tracer can be solid, can be liquid, it can be a gas depending upon the systems, that you are looking at. And only important thing is the traces must be able to mingle with the streams.

And then, should have properties same that is the another stream. And it should be measurable very accurately, so that we can get the information of our interest. So, we said, that if you put a tracer and measure the composition at the exit, with the function of time. We should put a pulse of tracer by pulse you mean is that you put a certain milligrams or grams of tracer very quickly. And that is called the pulse. And we look at the response of the system with respect to time.

So, and then if the flow is v, we can measure this just, we can measure c, we can measure v c. And this will be something like milligrams per sometimes a minute versus. So, we will get a curve like this. We do not know what the curve is, but whatever the curve is. From here we said our E function, our residence time distribution function is given as v time c t divided by M 0 where M 0 is the total amount of tracer. That we have put into this system d t.

So, what is it mean, this term v times c t represents the material. That is leaving this system at time between t and t plus d t; where this M 0 represents total amount of material there where put in. Therefore, this fraction refers to material with time of residence in the equipment, between t and t plus d t. Or shall we say a time of resistance t. And this is v information of our interest. Now, we can do this for any kind of equipments. And we said little earlier, that if you have a stirred tank.

(Refer Slide Time: 03:22)



$E(t) = \frac{1}{\tau} e^{-t/\tau}$

$\tau = V/v_0$

$\tau_1 = \tau_2 = \tau_i$

$\tau = \frac{V}{v_0} = n\tau_i$

$E_n(t)\,dt = \frac{t^{n-1}}{(n-1)!\,\tau_i^n} e^{-t/\tau_i}$

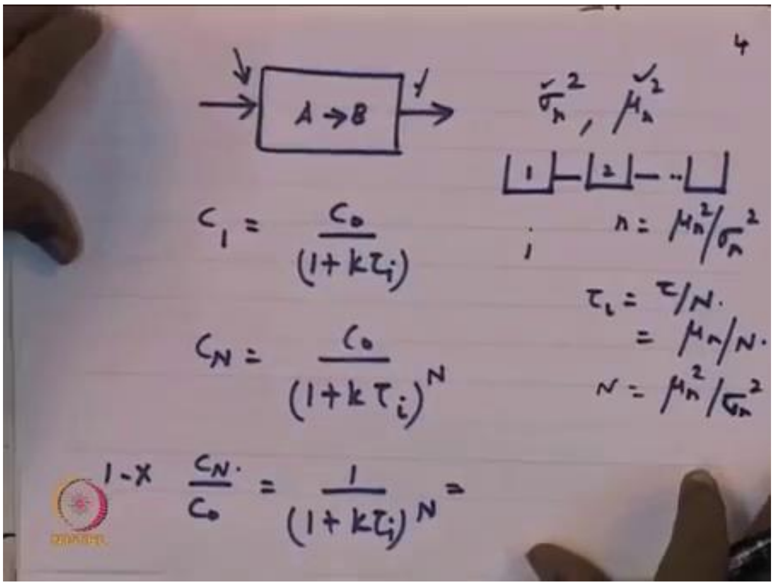
$\tau_i = \frac{V_i}{v_0}$

That means, if you have stirred tank and you have a material coming in and going out. And the residence time distribution function for this stirred tank we said is something like this. We derive this by tau is a residence time, we this given as v divided by v naught, v naught is the flow. Now, we also said, that suppose your sequences stirred tanks. Fluids coming is here going out here out here and this is tank 1, 2 and n.

We derive this and you think first principles to say. That we time of the residence time distribution of the of the n tank, sequence is given as t to the power n minus 1; divided by factorial n minus of 1 tau i to the power of n e rise power minus of t by tau i. Where we said tau i equal to v of any tank divided by v naught. That means, the assumption is that tau 1 equal to tau 2 equal to tau n, that is a assumption. Therefore, the total residence time tau, which is v divided by v naught equal to n times tau i.

Based on this these what we derived. And therefore, this function is a result of the experiment we have done, which means that we take put a tracer here. And then, measure at the end this time is what we will find. If it is a number of stirred tanks of equal volumes. We also said that if you want to understand the performance of a real vessel. You what to understand performance of the real vessels both, we have real vessels.

(Refer Slide Time: 05:11)



σ_n^2, μ_n^2

$c_1 = \frac{c_0}{(1+k\tau_i)}$

$c_N = \frac{c_0}{(1+k\tau_i)^N}$

$1-X \quad \frac{c_N}{c_0} = \frac{1}{(1+k\tau_i)^N} =$

$n = \mu_n^2/\sigma_n^2$

$\tau_i = \tau/N$

$= \mu_n/N$

$N = \mu_n^2/\sigma_n^2$

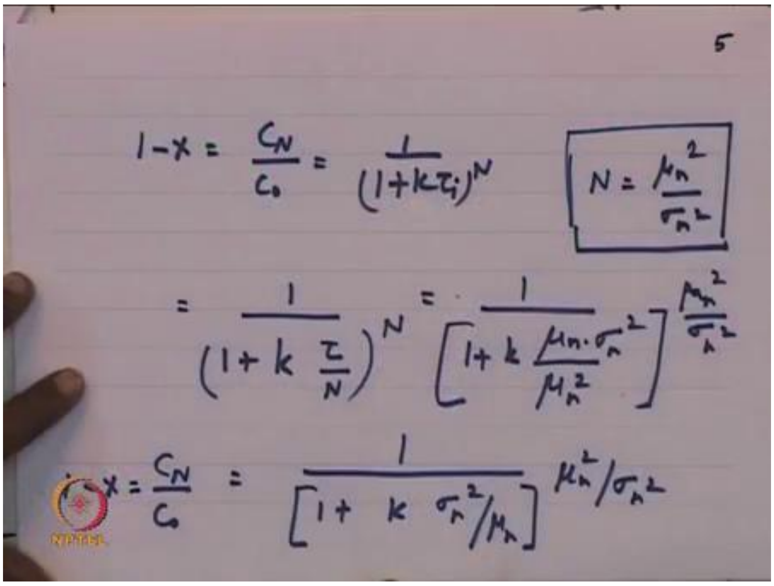
We do not know, how this end this fluids coming in and coming out going out. And we want to see, how this system is performing as a chemical reaction suppose is a reaction of this occurring, what is the expected performance of this equipment. So, this equipments, because of the traces study we have done. We know the sigma squared, we know this mean and variance both mean and variance are known, because we know the residence time distribution.

So, what is our expectation, the way to do this is that let us say, we have this particular system consist of N tanks. As an assumptions both these it e can be approximated, as an n tanks sequence. So, that the first tank this is the first second and so on. First tank will perform like this. Therefore, the Nth tank will perform like this. Therefore, our C N by C naught, which is essentially 1minus of x n this is given by 1 by 1 plus k tau i to the power of n.

And we also said, in our analysis of N tank sequence that this that sigma squared. We mention this, if we recall n equal to mu squared by sigma squared we mention this. So, this is known or in other words, there is to summarize, if you have an arbitrary rest. And we have done the arbitrary test of this vessel for from, which we have found out sigma squared and mu squared. Therefore, this arbitrary vessel can be approximated as a sequences stirred tank, where n is given by mu n squared by sigma n squared.

So, once you know that an arbitrary vessel can be describer in terms of an n time sequence. If it is a first order reaction, we know that 1 minus of x is given by C N by C N 0. Therefore, this is given by 1 by k tau i to the power of N. Now, we can replace this tau i and tau i is tau by N or it is same as mu n by N. Therefore, and this you can replace this n from the fact that N is equal to mu n squared by tau n sigma n squared sorry sigma n squared. Therefore, N everything can be replaced in terms of measured numbers the measured quantities are mu n and sigma n.

(Refer Slide Time: 07:44)



5

$$1-x = \frac{C_N}{C_0} = \frac{1}{(1+k\tau_i)^N} \qquad \boxed{N = \frac{\mu_n^2}{\sigma_n^2}}$$

$$= \frac{1}{\left(1+k\frac{\tau}{N}\right)^N} = \frac{1}{\left[1+k\frac{\mu_n\cdot\sigma_n^2}{\mu_n^2}\right]^{\frac{\mu_n^2}{\sigma_n^2}}}$$

$$x = \frac{C_N}{C_0} = \frac{1}{\left[1+k\,\sigma_n^2/\mu_n\right]^{\mu_n^2/\sigma_n^2}}$$

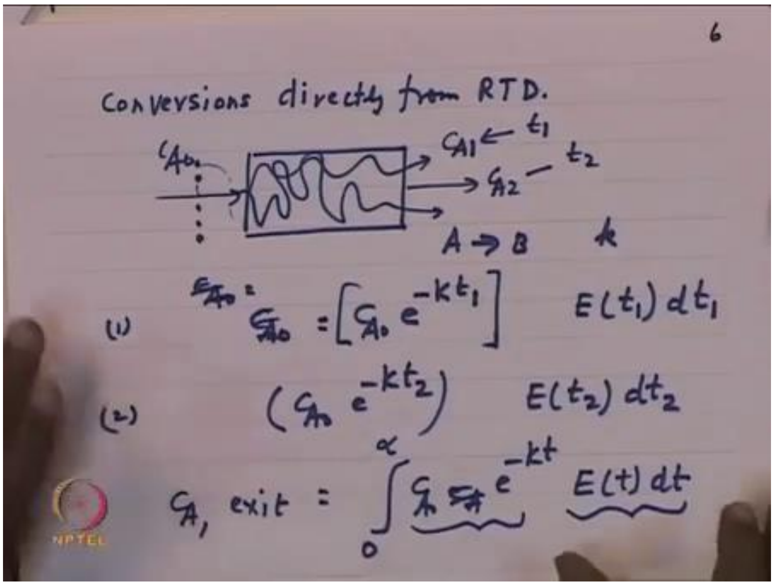
Therefore, 1 minus of x equal to C N by C 0, which is equal to 1 by 1 plus k tau i to the power of N. This is also equal to 1 by 1 plus k. What is tau i, tau by N to the power of N, there is equal to 1 plus 1 by k. What is tau, tau is mu n. And what is this is mu n squared by sigma n squared. And then, what is n, it is mu n squared divided by sigma n squared. Or we simplifying we get this as 1 plus k, sigma n squared by mu n to the power of mu n squared by sigma n squared equal to C N by C 0 is 1 minus of x.

What is it three achieved, what we are saying is that if we have an arbitrary vessel. We do a tracer test on the arbitrary vessel. Then, that tracer test gives you sigma squared n and mu n squared. And once, you know sigma squared n and mu n squared. The number tanks it is given by, number of tanks can be represented as mu n squared divided by sigma n squared. So, in view of this relationship and if it is a first order reaction.

We can now, say that the performance of this N tanks of this arbitrary vessel approximated as an N tank sequence, can be given by this equation 1 minus of x given to the right hand side, where all numbers are known, because rate constants are known. Sigma and mu are come from the experiment. So, this R T D test, now helps you to determine. The performance of an arbitrary system approximated using the parameters of the tanks series model.

So, this is where the advantage of this tanks in series model comes in. We are in a position to tell, what is the likely performance of an arbitrary vessel? We go on further the second type of description, if you want to do.

(Refer Slide Time: 09:56)



Say conversions directly from R T D. What you want to do now, known to directly take the R T D data. And said, what is the likely conversion. Let us, look at this problem again. You have an arbitrary vessel. We have fluids coming in going out. And one fluid element goes like this. Another fluid element does this, does this, does this, does this and goes out like this. And so many fluid elements seems to spent various lengths of time inside the equipment.

We know from our understanding, that the extent to which the fluid elements would react depends upon, how long this spend inside the equipment. Therefore, the time of residency inside the equipment is crucial to the extent to with the reaction occurs. Keeping this in mind let us say, our inlet fluid consist a number of fluid elements. All those elements enter at some concentration C A 0. So, fluid element one enters like this and then goes round comes out. That is I call this is C A 1.

There is another fluid element C A 2 it goes round comes out of C A 2 and so on. So, different fluid elements enter start with the same concentration, but go through the equipment and come out with different concentrations. Why, because they have spend different lengths of time. So, let us say, we have C A 0, which is this element this C A element, element I will call this as C A element. So, C A element 1, which starts at C A 0.

And let us say, the chemical react is a going to B with rate constant k first order. Therefore, this is C A 0 e rise to minus of k t. This is the extent to which, because it is spent time of residence t 1this spends t 1, second this spends t 2 seconds and so on. So, this fluid element 1 starts at C A 0, but emerges as C A e to the minus k t 1. This what we would expect, because it is spent a t 1 second therefore, it reacted and becomes C A 0 e to the minus k 1 t.

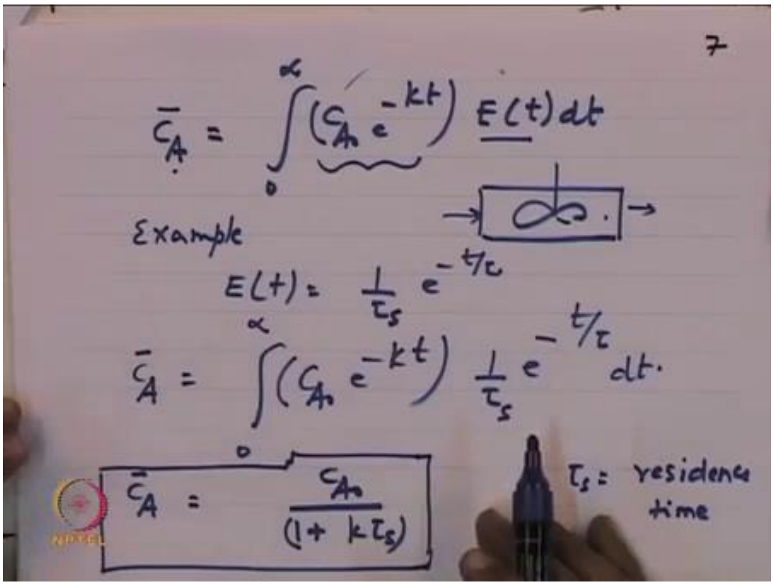
And what is the fraction of material that belongs to this residence time. If we know the e function, we think it is e t 1 d t 1 is the fraction that belongs to time of residence in the equipment, which is t 1 seconds. This is something that comes out of your R T D analysis. They have another fluid element C A 0 which is 2, which starts at C A 0, but reacts for a time of residence t 2. And the fraction of fluid elements in the equipment that belongs to time t 2 is e t 2 d t 2.

Or in other words, you have various fluid elements entry, but is going through the equipment for different lengths of time in emerging. Therefore, this C A exit or what comes out must be a some average of whatever, goes in multiplied by the E function. So, what are we saying is that, if you have a first order reaction. And if you have an equipment, in which fluid elements go through and then come out at different lengths of time. And each those fluid elements react as per a first order law.

Then the fraction that belongs to t 1 is e t 1 d t 1, fraction that belongs to t 2, which spends time t 2 seconds in the equipment d t 2 d t 2. Similarly, so many other fluid elements. Therefore, the average concentration of material that emerges on this equipment will be what happens to each fluid element, multiplied by the fraction of material that belongs that time of residence inside the equipment. So, this will be the average concentration that comes out at the exit.

So, or in other words, what we are saying is that R T D theory directly helps. You to tell you what is the likely concentration of fluid elements in the exit. If you can tell, what happens to each element and what is the fraction of time each of those elements spend inside the equipment. So, this general theory, help us to tell what happens to the chemical reaction taking place. So, let us take an example.

(Refer Slide Time: 14:29)



7

$$\bar{C}_A = \int_0^\infty (C_{A0} e^{-kt})\, E(t)\, dt$$

Example

$$E(t) = \frac{1}{\tau_s} e^{-t/\tau}$$

$$\bar{C}_A = \int_0^\infty (C_{A0} e^{-kt}) \frac{1}{\tau_s} e^{-t/\tau}\, dt.$$

$$\boxed{\bar{C}_A = \frac{C_{A0}}{(1+k\tau_s)}}$$

τ_s : residence time

So, what we are saying is that as per R T D (Refer Time: 14:30) average concentration that comes out is C A 0 e to the power of minus k t multiplied by the fraction that belongs to this time of residence. Example, let us take an example, that this reactor which we are trying to understand is a stirred tank. Let us say, it is a stirred tank, which means, the E function for this tank is 1 by tau e to the minus t by tau. This we know, because if it is a stirred tank this.

Therefore, let us see, what is the concentration that comes out from this reactor as per the R T D theory. So, it should be what, minus of k tau k t this multiplied by E function, which is 1 by tau e raise to power of minus of t by tau and d t. What are we trying to say is that, if you have a an arbitrary vessel of E function given. In this case, if that arbitrary vessel is a stirred tank, then the E function 1 by tau e to the minus t by tau.

Therefore, if it is a first order reaction each element that enters with emerge with this kind of concentration. Therefore, the average that you will see, at the exit from the equipment is the average of all elements between time of 0 to infinity that goes in and comes out multiplied by the e function of the equipment. So, we can integrate this, I mean is quite common sense, please you can check it yourself. When you integrate this you get the output as C A 0, 1 plus k tau s, while tau is the residence time.

I have not done the integration I am but it is fairly straight forward. So, in that the average concentration of material comes out is C A 0 divided by 1 plus k tau s. Now, this equation is something that, we have seen for a very, very long time. This is the output from stirred tank. Stirred tank gives you this kind of output. What have we now saying then, what we are saying is that, if we know the e function of a system.

If you know, what how the reaction takes place, then we have a way of telling what is the concentration of the exit. And the proof is that, moment you put E t as a, c s t r we get results that we have been using for a long time. Is a way of validating, the way our new procedure of understanding stirred tanks. Is validates the same understanding we already have based on our previous knowledge. Now, let us look at another model called the dispersion model.

We have so for talked about, what we call as the tanks and series model for describing an arbitrary vessel. Then we talked about what is call as the general R T D model, we also call as the completely segregation. Completely this particular model ((Refer Time: 17:48)) directly R T D is also called completely segregated model. What are we saying here, when we says when we says completely segregated model.

What we mean is that every fluid element, that enters goes through the equipment without recognizing the existence of other equipment it is a merges. It is here, that we do an averaging of the concentration and find out what is the exit concentration. That means, as per the model. Each fluid element moves through the equipment without recognizing the existence of other fluid elements in a emerges. That means, it is completely segregated as it goes through the equipment.

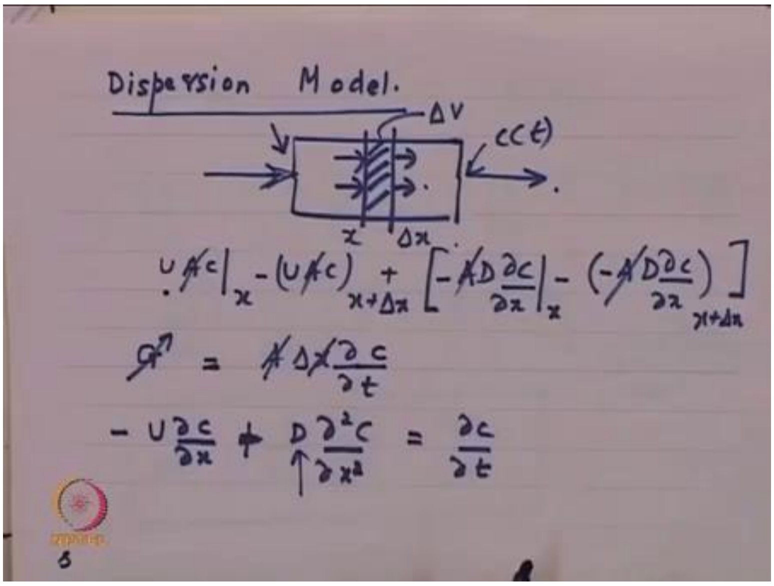
And only at the exit they mix and we measure the concentration. Some people also called this as a late mixing model, late mixing. Why is it called late mixing model. Because, we assume that the mixing occurs after the exit from the reaction equipment. Completely segregate model is also called as late mixing model. What is that model, the models assumes that the fluid elements moved through the equipment without mixing with each other.

The emerge outside and mix and we measure that average concentration. So, that is the completely segregated model. Previously, we looked at the tanks in series model. What is the tanks in series model, it is an instance, where as solve as a fluid enters the tank it mixes. So, it is an instance of completely micro mixed model. So, this something that we did earlier, this is the completely micro mixed model, for which we got our answers here.

This is the ((Refer Time: 19:23)) completely micro mixed model, completely micro mixed.

So, the completely micro mixed model, completely segregated model. These two we have used already. And we know roughly what kind of answers they give. Know we have looking at a third model called the dispersion model. Let us understand what this model is.

(Refer Slide Time: 19:50)



Dispersion Model.

$$U\cancel{A}c\Big|_x - (U\cancel{A}c)_{x+\Delta x} + \left[-\cancel{A}D\frac{\partial c}{\partial x}\Big|_x - \left(-\cancel{A}D\frac{\partial c}{\partial x}\right)_{x+\Delta x}\right]$$

$$\cancel{g} = \cancel{A}\cancel{\Delta x}\frac{\partial c}{\partial t}$$

$$-U\frac{\partial c}{\partial x} + \underset{\uparrow}{D}\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

What are we saying here is, we have a reaction equipment to fluid comes in fluid goes out. Now, let us say, what happens at any interface, at any volume what is it that going on here inside an elemental volume. Now, we know from our basic understanding, where is convective flow. And plus there is always a defuse the transport, because of the molecular conditions at that interface.

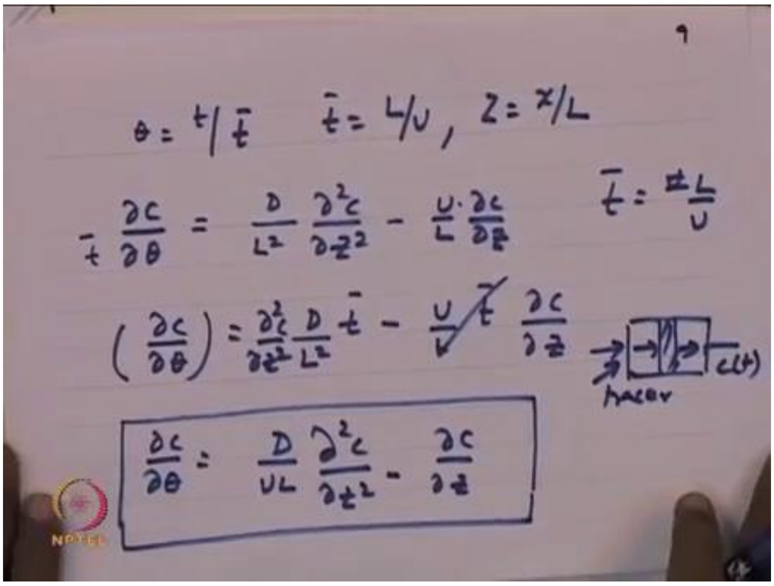
If we take this in to account, we can say, that U A C at some x, U A C at some x plus delta x, plus you have the diffusive transport, which is del c del x at x. And that you have minus of A D del c del x at x plus delta x. What are these, this is convective entry into control this is x and this is x plus delta x. This is the volume delta v. So, this is convective entry, input output diffusive entry input output and then you could have what is called equal to if there is generation reaction.

Then you put a reaction term. If it is not there, we will have accumulation term which is delta x of delta c of delta t. What are we saying, what we saying is that if you look at an elemental volume inside a reaction equipment. We can visualize that there is a convective transport. And as well, there is the diffusive transport a material entering that control volume.

Now, we can divide throughout by a delta x simply and so on. So, that we will get minus of del c del x times minus del c del x. I can cancel of a here, a here, a here and a here and a here, delta x divide throughout. So, you will get U del c del x the minus sign. And here, will get equal to D del squared c by del x squared, plus equal to del c delta let us see, where I have got a right, minus x to the delta x.

So, this minus sign is this is plus. So, this del this fine. So, this is the differentially equation that governs v motion of this fluid inside this. Let us, just make some small simplification make little earlier. So, let a make small simplification.

(Refer Slide Time: 22:38)



$\theta = t/\bar{t} \quad \bar{t} = L/U, \quad Z = x/L$

$$\frac{1}{\bar{t}}\frac{\partial c}{\partial \theta} = \frac{D}{L^2}\frac{\partial^2 c}{\partial z^2} - \frac{U}{L}\cdot\frac{\partial c}{\partial z} \qquad \bar{t} = \frac{L}{U}$$

$$\left(\frac{\partial c}{\partial \theta}\right) = \frac{\partial^2 c}{\partial z^2}\frac{D}{L^2}\bar{t} - \frac{U}{\cancel{L}}\cancel{\bar{t}}\frac{\partial c}{\partial z}$$

$$\boxed{\frac{\partial c}{\partial \theta} = \frac{D}{UL}\frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z}}$$

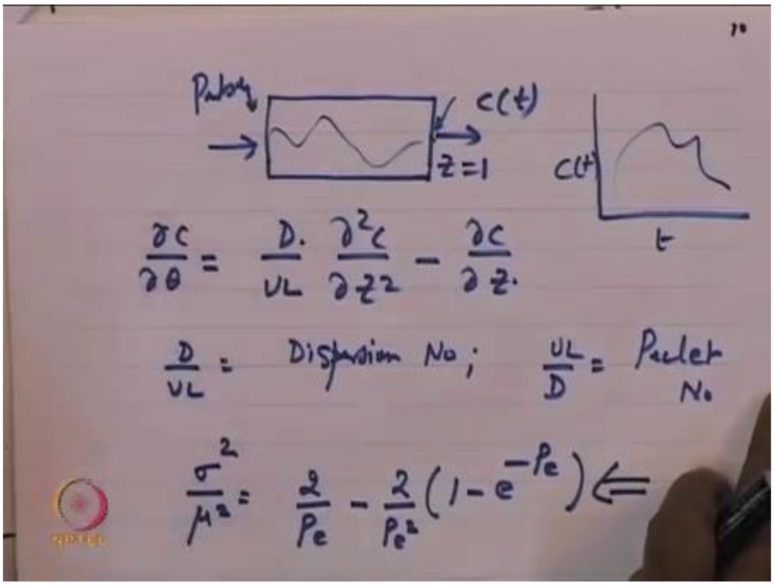
Simplifications I make is that, theta equal to t by t bar, t bar equal to L by U and Z equal to x by L. So, that, this our equation now becomes del c del theta, this left hand side. So, it will become a t bar will come the denominator equal to D by L squared del squared c by del z squared. So, I have taken the second term this. So, this I have taken the second term here ((Refer Time: 23:11)) I replace x in terms of z minus of U by L del c del z. So, ((Refer Time: 23:21)) U del c this x, I have put in terms of z, so L comes here.

So, is I have done nothing new has been done. So, we can simplify this and say this is del c del theta equal to D by L squared t bar minus of U by L t bar del c del z. Now t bar by definition is U L by U sorry is L by U. So, this goes off, so this is becomes L by U. Therefore, these becomes del c del theta equal to D by U L minus sorry del squared c by del z squared I forgot del squared c by del z squared minus of del c del z. So, this is the differential equation that governs.

So, our system is these, this is the system and this is the control and then we have fluids entering a living to which at the here we have putting a tracer. We are trying to see what is the concentration of tracer that exit let me, restate the problem. The problem we are trying to understand and solve is that you have a reactor. There is an ((Refer Time: 24:48)) elemental volume to this whole reactor we have a pulse input going in. We want to know, what is the concentration of the pulse at the exit here.

What is the this concentration. This is the question that we want to solve. Because, moment we know that, we have a better understanding of the effect of this parameter diffusion co efficient, dispersion co efficient on the performance of the system. Now, what we do now.

(Refer Slide Time: 25:23)



$$\frac{\partial c}{\partial \theta} = \frac{D.}{UL}\frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z}.$$

$$\frac{D}{UL} = \text{Dispersion No ;} \quad \frac{UL}{D} = \text{Peclet No.}$$

$$\frac{\sigma^2}{\mu^2} = \frac{2}{P_e} - \frac{2}{P_e^2}\left(1 - e^{-P_e}\right) \Leftarrow$$

So, we recognize, we recognize that our arbitrary vessel, which is described by this equation del c del theta equal to D by U L del squared c by del z squared, minus of del c del z to which we are having a pulse input. And we want to know what is the concentration let me we measure at the exit at z equal to 1. Now, notice here this is the linear problem. There are no non-linear it is involved here D by U L is called as the dispersion number. Some people call U L by D as Peclet number.

This is the more common ((Refer Time: 26:07)) U L by D, which over the way we look at this differential equation has one parameter which is called the Peclet number U L by D. Now, if you have we response to this curve, that to this two an arbitrary vessel going through here. So, you will have data on c t versus t, you will have data at position z equal to 1. So, there is some response. Therefore, once you have this response, in principle you should be able to solve this equation.

And then, adjust the value of the parameter D by U L and fit this data. I am with a which is peclet number, which describes the arbitrary flow inside this equipment. On other words, what we are saying is that, if you are going to describe your system in terms of dispersion model. You require what is called as a Peclet number, which describes this system. To understand the value of Peclet number, you will have to do a pulse tracer test, which you have done and found out the concentration as a function of time.

Having done that, all you are now do is to try and fit. This function to you will have a solution to this. And then adjust the value of D by U L, so there it fits the data. So, that way you can find out, what is the value of D by U L that describes your equipment. So, essentially all we are saying is that, if you know D by U L are U L by D which ever you like, then you know what is the state of mixing inside the system. Now, in the literature solution to this equations are available for various types of boundary conditions.

For a moment, we will try to look at some of these things in our 12th class. For the moment, we can let us assume that we know the solution. And the solution that is available in the literature is of this form. So, what people are saying is that the solution to this differential equation is available in the form of sigma squared or the variants of this of the response divided by the mean value of the response. Second moment divided by the first moment squared, this is given as in terms of Peclet number.

On other words, all that is being said is do a tracer test, find out the variants mean and variants of the response that you will get. Moment you know the mean and variants, the ratio is given by this representation 2 by Peclet number minus of 2 by Peclet number squared into 1 minus of e to the power of minus Peclet number. On other words, if you know mu square sigma squared and mu squared then you can find Peclet number from this equation.

So, you have now, done a tracer test and on that present test you have determine what is the Peclet number there is appropriate for your kind of mixing in your equipment. Now, please refer at a little earlier you said, in this arbitrary vessel can also be thought of as a series of stirred tanks. From sigma squared and mu squared we also determine number of tanks that are required described this flow field. On other words, the number of tanks is a measure of mixing of the equipment.

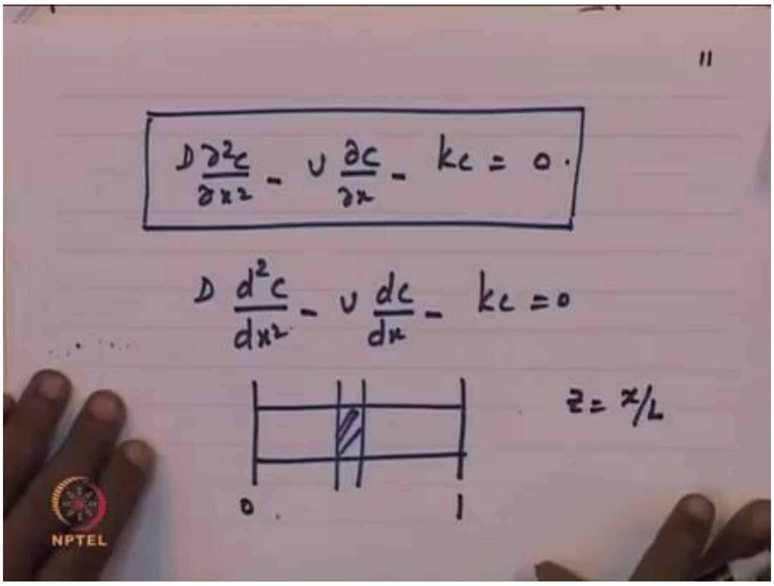
Similarly, Peclet number is also a measure of mixing. On other words, in these two models in one model the parameter is a number of tanks. In another model the parameter is Peclet number. Or number of tanks is a measure of mixing in the equipment. Similarly, Peclet number is the measure of mixing in the equipment. So, different parameters have different way of understanding mixing in the equipment. Now, let we know, the Peclet number in the equipment.

On the other words, which is the state of mixing as captured by Peclet number. Now, we are now in a position used this information to understand. How our reactor as per this model it is call the action dispersion model will performed. Let us, try to do that now. Let us, look at ((Refer Time: 30:05)) the dispersion model once again. What we have said is this is convective flow input, convective flow output and this is the diffusing flow input the diffuse flow output equal to the accumulation.

Generation term we removed, suppose you want to put the generation term is minus of k. And then concentration c times A delta x. Suppose, I put this term as the term of corresponding to the generation. So, in the limit as a tends to 0 remove this here, you will get a term which is minus of k c. What are we saying now, what we saying is that now that we know the Peclet number that describe the state of mixing in the equipment. Now we are in a position to understand how this reactor will perform.

Therefore, we have written the unsteady steady equation take in into account the presence of chemical reaction. We want to understand the performance is a system under steady state. Therefore, we remove the unsteady state term. So, what are we saying now, we want to now look at the performance of this chemical reactor at steady state in the presence of a chemical reactions. The steady state description of our equation is the following.

(Refer Slide Time: 31:17)



$$\boxed{D\frac{\partial^2 c}{\partial x^2} - U\frac{\partial c}{\partial x} - kc = 0.}$$

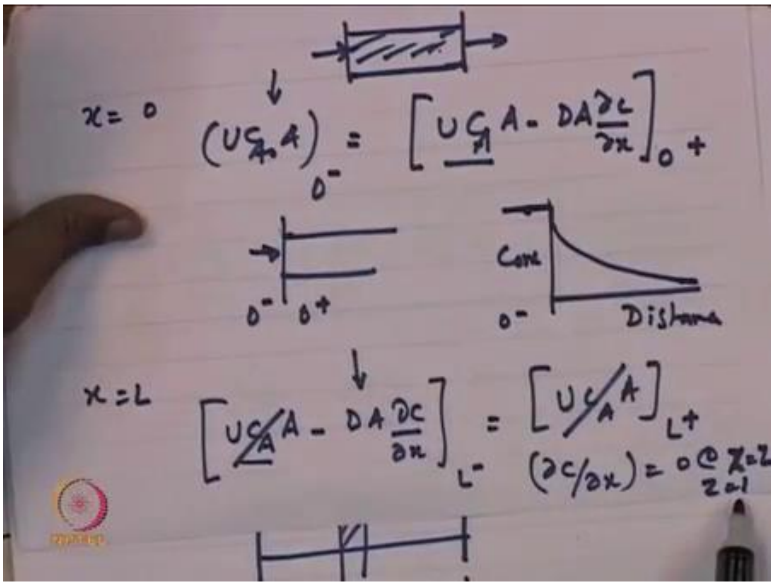
$$D\frac{d^2 c}{dx^2} - U\frac{dc}{dx} - kc = 0$$

$$z = x/L$$

So, we have D del squared c by del x squared minus of U del c del x minus of k c equal to 0. This is what we have to solve to understand the dispersion model behavior of our system. Now, since it is only a first order differential, ((Refer Time: 31:36)) since only a differential equation one variable. So, I will replace this like this D squared c by d x squared minus of U d c d x minus of k c equal to 0. Let us, look at this system once again.

This is our system and we have taken a element. And then we have written our balances and come to this equation. The question is how do we understand the boundary conditions for this problem. So, tremendous amount of literature in this for this situation. But, let us try to understand the boundaries properly. This is boundary 0, boundary 1, z equal to x by L. How do you understand the boundaries? Now, a good way of understanding in the boundary is to see, what happens to flow in and flow out.

(Refer Slide Time: 32:33)



So, what are said here is that, at x equal to 0 minus you have U C A 0 times A at 0 minus must be equal to U C A times A minus D A del c del x at 0 plus do we. What are we saying now, U A C A 0 this is the flux, should be this is the flux at this is 0 minus and this is 0 plus. So, at the boundary whatever, material that is comes in it goes out. It goes out due to convection as well as due to diffusion.

On the other words, what seems to be important to recognize here is that C A 0, if you make a plot this is distance versus concentration. You find that concentration at 0 minus is C A 0 concentration at 0 plus it is not C A 0. Because, of the see del c del x is negative. Therefore, this whole term is positive. Therefore, this whole term U C A would be less than U C A is 0 A. In other words, it starts concentrations are like this suddenly drops and then you does this.

This is the point that we should recognize, the dispersion model explicitly recognizes. The fact that at the boundary 0, there is a certain drop in concentration, because of the effective dispersion. It is this effect, which is not been appropriately accounted for in other models, which makes this model so superior to others. Now, at x equal to L what happens, Let us once again write U C A times A minus of D A del C del x. This is at L minus was v equal to U C A times A at L plus what are we saying.

What we are saying is that our system, which is our tubular reactor the action dispersion problem exists inside. And as soon as emerges outside there is no such dispersion problem. On other words, this term is appropriate to be used only inside the equipment and not outside. Therefore, that term has been deleted. So, this equality of material balance whatever, is coming in at L minus this is convection this is diffusion.

And whatever is going out is by convection only, because there is no diffusion term outside the chemical reactor. That is the way we are understanding the chemical reactor. How do you make this equality, this equality must hold at L minus and L plus. Let us, look d p at this. We notice that del c del x in a chemical reactor is negative, del C is negative. And between L minus and L plus we also know, that this concentration C A cannot have changed, because there is no reaction equipment.

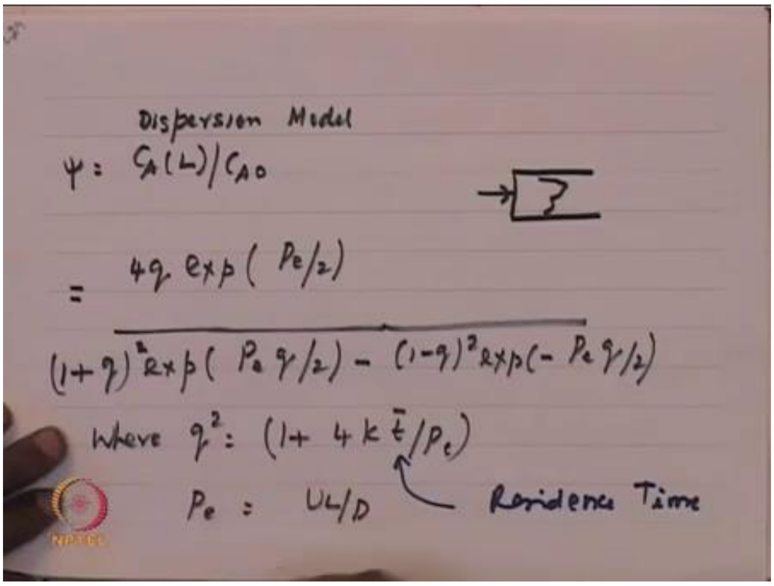
Therefore, we should expect that these two should go away, implying that the del c del x must be equal to 0 at del c del x equal to 0 at z equal to sorry x equal to L or z equal to 1. What we are saying is to understand the boundary conditions for solving this problem of action dispersion, where there is chemical reaction occurring is to recognize the fact that there is convective flow outside at 0 minus inside the equipment there is convective flow as well as diffusion flow. That is why it is 0 plus.

And the other end, there is convective flow and diffusion flow inside the equipment at 0 L minus, but outside the equipment there is no diffusive flow. And therefore, that term has been deleted. In order that this equality wholes and since there is no reaction capering between L minus and L plus, we would expect that C A is the same at L minus and L plus implying that this term del c del x must be 0 at the other boundary.

So, this is this or in other words del c del x equal to 0 at z is equal to 1 is call so called as a celebrated dank ward boundary conditions. This issue was brought out and explain beautifully by dank wards many, many years ago. And this is now very well recognized as we have understanding tubular reactors with action dispersion. So, come to I mean summarizing this whole thing, what we are trying to say is that, our differential equation d squares ((Refer Time: 37:29)) which describes the tubular reactor with the action dispersion.

Now, can we solved with boundary conditions, what are the boundary conditions, the boundary conditions are this is the flux condition U C A 0 at A minus equal to the flux at the other this one condition. Other condition del c del x equal to 0 z is equal to 1. The solution to this equation I mean this from huge amount of literature, which is looked at this and then solve this problem. And we will probably have a time to look at this once again during our tutorial classes. But, as for now what we will do we will take the solution, because it is not necessary to spent too much time.

(Refer Slide Time: 38:15)



Dispersion Model

$$\psi = C_A(L)/C_{A0}$$

$$= \frac{4q \exp(P_e/2)}{(1+q)^2 \exp(P_e q/2) - (1-q)^2 \exp(-P_e q/2)}$$

where $q^2 = (1 + 4k\bar{t}/P_e)$

$P_e = UL/D$

Residence Time

So, I am just writing down the solution. Just so that we can go forward, so our solution looks like this ((Refer Time: 38:48)) q squared equal to that the differential equation ((Refer Time: 39:05)) that describes action dispersion with chemical reaction insert is given by this. And the boundary condition that is appropriate to describe the problem is ((Refer Time: 39:14)) the flux equality condition at 0, 0 minus and 0 plus. And then the no flow del c del x equal to 0 condition at x equal to L.

This is the two boundary conditions with these two kind of boundary conditions the solution looks like this. There is a lot of speak literature in this available. So, we will not do this once again. You will do it in our tutorial classes. What does it that it is saying. What it is saying is, now if we did not have dispersion. On other words, if dispersion was nil, which means what it is flux flow reactor we know to solve the problem. Because, the differential equations are much, much simpler.

One term disappears ((Refer Time: 39:57)), this term disappears, so you can solve these two straight way. That is what we have been doing for a long time. What we are now added this term and try to understand the importance of this term, these deferential equations solutions are available in terms of two parameters. One is q, which involves was called the dam polar number. Otherwise is a Peclet number. So, solution to the action dispersion problem it is available to us in terms of two parameters.

One is called as the action dispersion coefficient or Peclet number U L by D inverse of dispersion number. Other is called dam polar number, which is essentially k times t prime. Now, what is that we expect, what we expect is that when the dispersions are large or then our performance approaches c s t r when desperations are small our performance approach is a flux flow. On other words that real equipments, either perform between flux flow and mixed flow.

So, we will have great variations of performance between flux flow and mixed flow. And our real reactors lies somewhere, in between and to be able capture the performance of real reactors. We need to have an understanding of the flow field or understanding of mixing. And to be able to understand mixing we should have a model which quantities mixing. First we had one model, which is called as the tanks in series model, and where number of tanks was the way of understanding mixing.

Then we had what is called as the dispersion model, where dispersion number U L by D is Peclet number is a measure of mixing. So, depending upon the model the parameters vary, but they all describe mixing in their own way. So, we have looked at three models. One is the completely segregated model based on R T D, where there is no other modeling parameter excepting the raw data directly plugged on with the reaction kinetics.

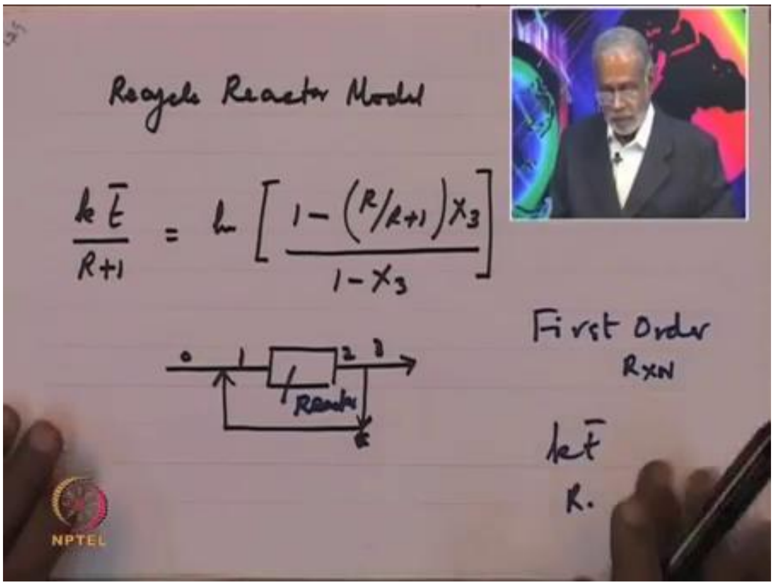
So, we have the completely segregating model, base come interlay from the R T D data there is no other modeling parameters. Then we have the tanks in series model which involves a number of tanks as a modeling parameter. Or you have the action dispersion model, where the dispersion coefficient of Peclet number, which is the inverse of dispersion coefficient. And it is used as a modeling parameters. The three ways of understanding what is called as the real reactors.

Please recall, what we have been saying so far. That if you have a dispersion model, then this psi C A at L divided by C A 0 you already derived this, which is equal to 4 times q exponential P e by 2, divided by 1 plus q whole squared exponential P e q by 2 minus 1 minus q whole squared exponential minus of P e q by 2. You have derived this, where q squared is given by 1 plus 4 k tau bar divided by P e, where this is residence time. We have said all these is not new to us, where P e is the Peclet number.

So, in other words, what we saying is that, for a dispersion model be the performance of the equipment psi, which is C A L by C A 0 is given by the right hand side, where our parameters are q and P e. Both q and P e are numbers that we know about our reactor. That means, if you have an equipment, whose P e and q are known then the dispersion model will be able to tell us, how this system will perform.

So, this is one way of understanding that movement of q and P e are known, we know how to characterize our system. Now, instate of dispersion model, suppose we look at a recycle reactor model. What it been trying to say here is that we can look at a real equipment in various ways. Dispersion model is one way of looking at it. Of which way, we have already said what that model all about.

(Refer Slide Time: 43:57)



Recycle Reactor Model

$$\frac{k\bar{t}}{R+1} = \ln\left[\frac{1-\left(R/R+1\right)X_3}{1-X_3}\right]$$

First Order Rxn

$k\bar{t}$

R.

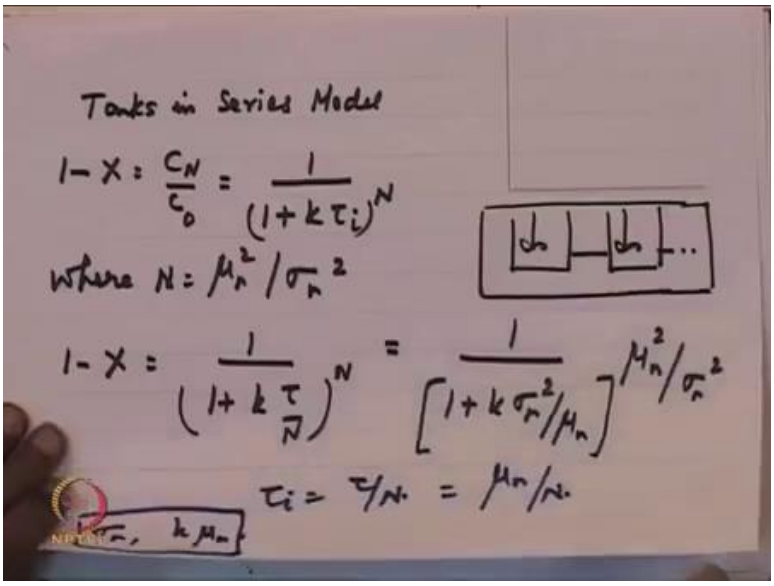
Now, similarly we can look at the same equipment as a recycle reactor model, where this is the recycle reactor, this is the reactor, this is our reactor. We can look at these reactor as a recycle reactor, where r is a recycle ratio and the performance that means, what is the conversion that you will get at the exit x 3 can be given by this equation, for a first order reaction. This for a first order reaction, all these we are doing it for a first order reaction.

We can do for others, but is what is important this to understand the fundamental. Therefore, we have done for a first order reaction. It says k t bar by R plus 1 is given by the right hand side, where x 3 is the conversion at position 3. On other words, what we are saying is that, if we know the rate constant k t, k t bar which is the rate constant multiplied by residence time. And r is a recycle ratio, there are two parameters. What are that two parameters, k times t bar and then R.

If we know k t bar at R and then we can say, how the reactor will perform. That means, we can find out what is the extent to, which the reaction takes place moment k t bar and R determined through an appropriate experiment. This is another way of understanding a real vessel. On other words, point we are trying to put across is that. Suppose, we have a real equipment, which is giving you a conversional of x 3, for which you know what is k t bar from our experiment.

Then we can tell, what is the recycle ratio there is the appropriate to this process, that is the another way of understanding the real equipment. They another way understanding the real equipment is the following.

(Refer Slide Time: 45:36)



Tanks in Series Model

$$1 - X = \frac{C_N}{C_0} = \frac{1}{(1 + k\tau_i)^N}$$

where $N = \mu_n^2 / \sigma_n^2$

$$1 - X = \frac{1}{\left(1 + k\frac{\tau}{N}\right)^N} = \frac{1}{\left[1 + k\sigma_n^2/\mu_n\right]^{\mu_n^2/\sigma_n^2}}$$

$$\tau_i = \tau/N = \mu_n/N$$

$\boxed{\sigma_n,\ k\mu_n}$

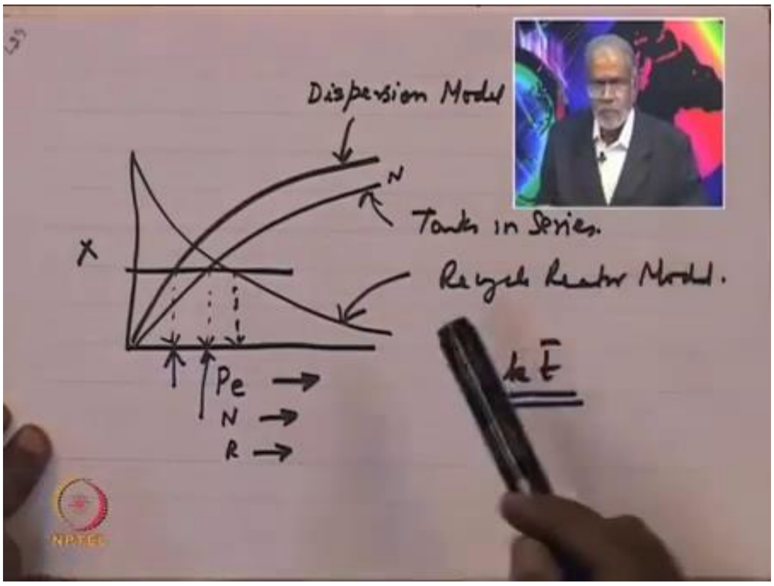
In tanks in series model, what we do is that. We have a real equipment, which we think can be model as is a stirred tank, which means we have done experiments on the real equipment. And we find, the conversion is x. And as per this tanks in series model, which we have already derived 1 minus of x is given by 1 plus k tau i to power of N, where N can the given by this equation ((Refer Time: 46:05)) derived N is equal mu n squared by sigma n squared.

And tau i equal to and we also know that tau i equal tau by N. And what is tau, tau is equal to mu n by N, where mu is the first movement of the tracer responds. On other words, what we are trying to say here is that. If you have a real vessel and you want to model this as a tanks in series model. So, if you understand from your experiment what is the extent of reaction you observed, the using that data, you will be able to tell how many tanks are required to model this equipment.

So, if you look at the final expression 1 minus of x equal to this. If you look at this, if 1 minus of x equal to 1 by all these parameters k sigma n and mu n. So, how many parameters are involved here. Some the number of parameters involved here is sigma n k mu n are the two parameters. So, if you know, these two then we can tell, how this tanks in series model would perform. So, we talked about three models, now dispersion model they recycle reactor model, tanks in series model.

On other words, if have a real equipment you can use any of these models to understand how real equipment it is performing. And that is the idea of trying to develop models to describe real equipments.

(Refer Slide Time: 47:46)

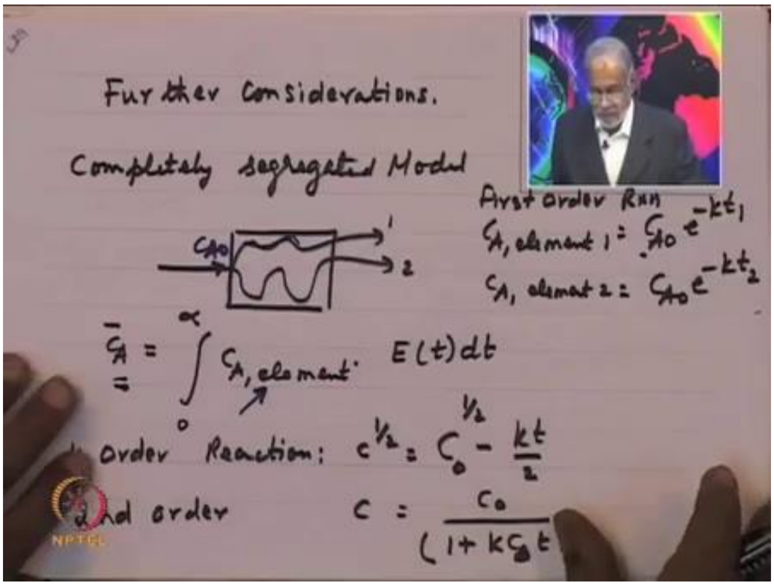


So, just to summarize what we are saying is, would be saying is that. Suppose, we have a real equipment giving conversion of x. And corresponding in different Peclet number, corresponding to different tanks in series number of tanks are corresponding to different recycle ratio. For example, suppose let us say our conversion that is excepted that is been observed from experiment is x this is the conversion.

And you can notice here, if it is a desperation model, it will give us a Peclet number corresponding to this, which means this particular Peclet number would be able to describe that equipment. Or if it is a tanks in series model, this particular number of tanks will be able to describe the equipment. Or if it is a recycle reactor model this recycle ratio will be able to the describe that particular equipment. Given that what is the value of the k t bar, which is the residence time multiplied by the rate constants.

In other words, if you know the residence time multiplied by the rate constant. If this number is given, then you can tell what will be the conversion or you will be able to tell what is the Peclet number corresponding to a given extent of reaction. Or what is the number of tanks required to describe this under the tank in series model. Or the recycle ratio there is a required to describe it, under the recycle a reactor model. In other words, what is important to recognized here in that. A real equipment can be describe many models. And then, we can choose model that we thing is most appropriate for a description. And three models have been described here. Dispersion model, tanks in series model and recycle reactor model.

(Refer Slide Time: 49:29)



Further considerations.

Completely segregated Model

First order Rxn

$C_{A,\text{element }1} = C_{A0} e^{-kt_1}$

$C_{A,\text{element }2} = C_{A0} e^{-kt_2}$

$$\bar{\bar{C_A}} = \int_0^\infty C_{A,\text{element}} \cdot E(t)\,dt$$

order Reaction: $c^{1/2} = C_0^{1/2} - \frac{kt}{2}$

2nd order $c = \frac{c_0}{(1 + kC_0 t}$

Having said this, there are few points that we want to take it a forward a little. Let us say, we have an equipment and which we want to describe by what is called the completely segregated model. What is the complicatedly segregated model, the completely segregated model tells us, that the fluid elements, that is entering the reaction equipment they go through the equipment and a merge. Another fluid element goes through the equipment and a merges.

And these fluid elements as per this model, it is assumed that they do not recognize the existence, which other as it goes through the equipment at is that completely segregated as the move through the equipment. And the mix only at the exit this is the model. What happens, this is how we are visualizing what happens in the equipment. Therefore, if as per the assumption this fluid element goes through the equipment and emerges without recognize the existence of the other element.

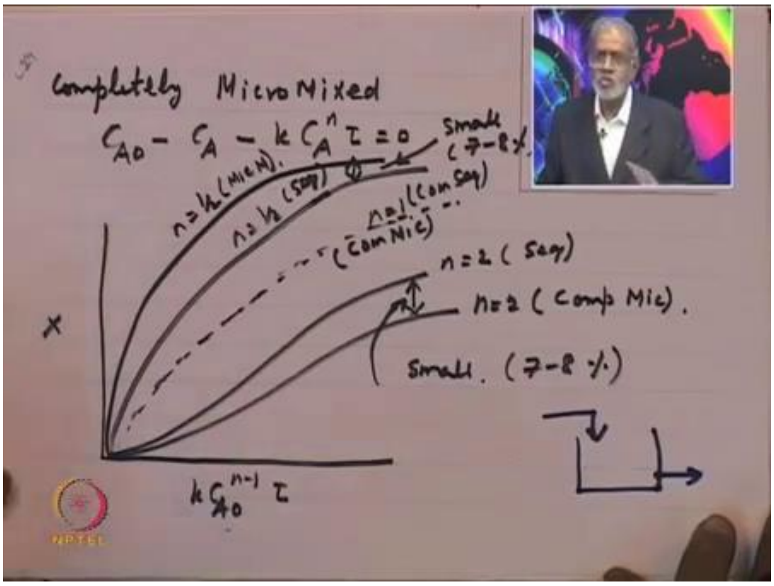
Then we can tell, that if it enters at C A 0 it would undergo chemical reaction, depending upon the time that is has spend it in the equipment. So, what is completely segregating model tells us is that, if you have a fluid element 1. Then it goes through the equipments start at C A 0 and reacts as per this first order model, if is the first order reaction and emergence like this. Another fluid element enters at C A 0, but spends time t 2 therefore, emergence with this kind of concentration.

Therefore, the mean that we see at the equipment will be what happens to each element multiplied by the time of residence of each element inside equipment. So, this is this is way we understand what is the called to completely segregated model. That the each element goes through and emerges without recognized existence the other therefore, what emergence at the exits is the value of each element multiplied by the timer of residence of the element.

This is if it is a first order reaction, then this C A element is given by the first order law. If it is half order reaction this C A element given by the half order law. If it is the second order reaction it is given by the second order law. So, what is what we are trying to say here is that? It is a completely segregated model is the description that we have chosen to understand the equipment.

Then the average that you would see at the exit, if C A element as described by whether it is a first order reaction, second order reaction or half order what our reaction in the case will be multiplied by the residence time distribution, fraction that spends fraction that stay the time assumed. That is the that is how we understand the completely segregated model. Now, we can also look at the same phenomena through what is called as the completely micro mixed model.

(Refer Slide Time: 52:28)



Completely Micro Mixed

$$C_{A0} - C_A - k C_A^n \tau = 0$$

So, the completely micro mixed what we do. We have material entering, material leaving and material reacting equal to 0 this is the completely micro mixed model. Once again, we can solve this and find out what is the x versus the reaction parameter. So, what we are saying is that. Whether, it is completely segregated model or completely micro mixed model in both cases, we can describe the reaction equipment in terms of conversion versus the reaction parameter.

Now, when we do this for the completely segregated model, we find that both are the completely segregated the model and completely micro mix model. For first order reaction ((Refer Time: 53:17)). On other words, whether we use completely segregated model or completely micro mix model. We have the same result first order process. Now, if it is second order process, we find that if it is completely segregated and completely micro mix there is difference about to 7 to 8 percent.

And if it is order of reaction less than 1, we also find the difference. Once again, we shown the deference 7 to 8 percent. On other words, what is being said of that when we try to describe the real equipment, by completely segregated model. Or describe the real equipment by completely micro mix model. The results are the not the same in the order of the reaction difference from 1. In the results are like the differences. But, that difference is both 7 to 8 percent.

We typically, the kind of variation that we ((Refer Time: 54:16)) except to the experiment. On other words, what we are trying to say of that you can used completely segregated model or the micro max model to describe the equipment. You will get answers, which are satisfactory, because fact that difference between the two models or generally, between the 7 to 8 percent, which might be will be accept to the range are the experimental error will be observe.

Then consist to not long story this short story what was the saying is we completely segregated model ((Refer Time: 54:49)) assumes that the fluid element mix only at the exits. And therefore, the average at the exit is what happens to reach element as per the order of reaction multiplied by the residence time distribution that gives us the averages. if it is the completely micro mix model, the assumption is that as soon as the completely assumption as soon entire mix, which called ((Refer Time: 55:17)) mixing.

In completely segregate, which called ((Refer Time: 55:19)) mixing. Is the ((Refer Time: 55:22)) mixing model completely micro mix model. What we find that be extension reaction again reaction parameter. When plotted we find the results are not the same.

There is a slide difference if order of the reaction difference model. In both cases, order of the reaction less than 1, the order of the reaction greater than 1 that the difference between the two models 7 to 8 percent. And therefore, in the range of experiment error that the participant. Therefore, for describing the real equipment we must like to used either completely segregated model are complete the micro mixed model.