Module - 4
Lecture - 20
Concentration Profile

In the last lecture we non-dimensionalized the mass balance or the mole balance for the diffusion and simultaneous reaction happening inside the catalyst pellet. And we initiated the process of solving the model equation. And we defined the key parameter which characterises the diffusion and reaction process that is happening inside the catalysts, which is the thiele modulus; which captures the ratio of the surface reaction rate to the diffusion rate.

The value of thiele modulus signifies whether the internal diffusion is rate controlling or the surface reaction is rate controlling. We also observed that if thiele modulus is very large then it is the internal diffusion which is rate controlling and if the thiele modulus is small it is most likely the surface reaction which is actually rate controlling. So, let us move further and solve the model equation and then we look at how the concentration depends upon the position and what kind of insights we can obtain from them.

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So, the dimensionless model equation that captures the diffusion in the reaction process is d psi square by d lambda square, – + 2 by lambda into d psi by d lambda – phi 1 square psi = 0. And we introduce this dimensionless quantities. We introduce this, where the dimensionless quantities psi is essentially C A by C A S and lambda is r by capital R.

We then introduce the transformation y = psi times lambda, which essentially led to reduction of this model equation into d square y by d lambda square – phi 1 square y = 0. Now, what is the solution of this equation? It is a very simple 2 point boundary value problem. And so, the general solution of this equation is, y = A 1 cos hyperbolic phi 1 lambda + B 1 sin hyperbolic phi 1 lambda.

Because we know that y = psi times lambda, we can now find out that psi is = y by lambda, which is essentially A 1 by lambda cos hyperbolic phi 1 lambda + B 1 by lambda into sin hyperbolic phi 1 lambda. So, now we need to find these constants. We need to find these constants to get the final expression where we can now find out what is psi which is the ratio of the concentration, as a function or position, which is the essentially represented in this quantity lambda.

So, let us find out A 1 and B 1. How do we find A 1 and B1? For that we need to use the boundary conditions. Let us first look at the first boundary condition we want to look at, we want to use. So, the first boundary condition we want use is;

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The concentration C A is finite at r = 0, which means that the dimensionless quantity psi is finite at lambda = 0. So, if I look at the solution expression, the general solution expression, psi is = A 1 by lambda, cos hyperbolic, phi 1 lambda + B 1 by lambda, sin hyperbolic phi 1 lambda. So, at lambda = 0, what is the value of cos hyperbolic? So, cos hyperbolic phi 1

lambda; when we set lambda $= 0$, it means that, when we set this to be 0, so, it means that cos h hyperbolic 0, essentially is $= 1$.

And what about sin hyperbolic? So, sin hyperbolic phi 1 lambda; when we set this to 0, we essentially get sin hyperbolic of 0, is essentially $= 0$. What about 1 by lambda? 1 by lambda essentially tends to infinity. At lambda $= 0$, that is at the centre of the catalyst pellet, 1 by lambda essentially tends to infinity. So, what we have is that, in this boundary condition, at lambda $= 0$, that is at the centre of the pellet, this first term essentially tends to infinity.

The first term, because we have a 1 by lambda term here, this quantity essentially tends to infinity. And this quantity actually is bounded. So therefore, in order for the solution to be finite, because we specify that the psi has to be finite at lambda $= 0$. It cannot be an infinite value. So, the only way by which we can achieve finite value, if one of the terms is actually infinity is, if the coefficient corresponding to that particular term is actually $= 0$.

So therefore, setting A $= 0$. So, this psi is finite at lambda $= 0$, can be achieved by setting this constant, this integration constant A 1 $= 0$. So, once we substitute this, we will find that the, we will find that psi is;

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So, we set A 1 $= 0$. So, we find that psi is essentially B 1 divided by lambda, into sin hyperbolic of phi 1 lambda. So, how do we find B 1 now? How to find B 1? So, we can use the other boundary condition. There is another boundary condition which is available. What

is the other boundary condition? The other boundary condition is psi = C A by C A S. That is = 1 @ lambda = 1.

So, we can substitute that here. So, substituting that, you will get 1 is = B 1 divided by 1 into sin hyperbolic phi 1 into 1. So, which is essentially means that B 1 is = 1 by sin hyperbolic of phi 1. Okay. So, we have now found out both the constants. What are the constants? A 1 is 0 and B 1 is = 1 by sin hyperbolic of phi 1. So, we can now substitute this back into the solution. So, when we substitute this back into the solution, we will see that psi is essentially = A 1 is 0.

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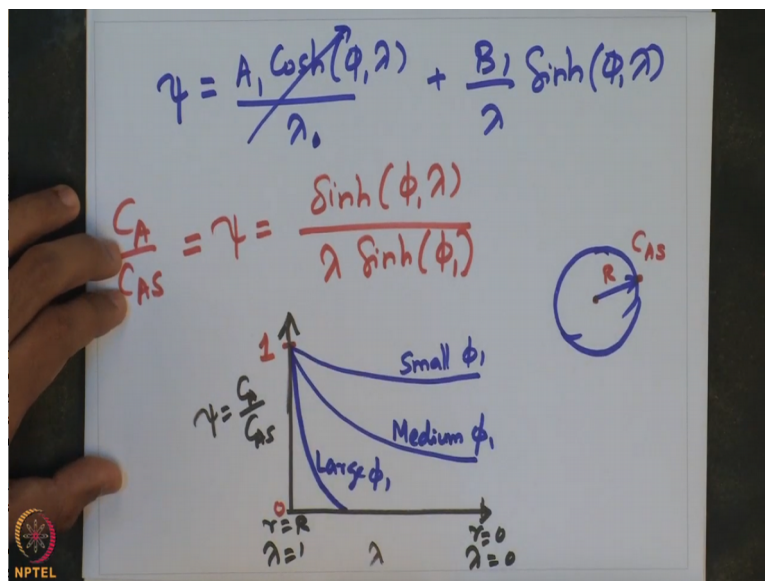
So, the first, the first term essentially goes away. So, A 1 cos hyperbolic phi 1 lambda by lambda. So, that essentially goes away. That goes away. + B 1 by lambda into sin hyperbolic of phi 1 lambda. So, we can now substitute B 1 here. So therefore, psi is essentially = sin hyperbolic phi 1 lambda divided by lambda into sin hyperbolic of phi 1. And this is nothing but C A by C A S.

So, this expression essentially captures the concentration as a function of the radial position inside the pellet. Now, let us try to sketch this profile here. So, how will this profile look like? So, let us say that we have radial position here. Let us say lambda is here. So, r = 0 or lambda = 0. And let us say that r = capital R or lambda = 1. So, recall that, I am plotting in, from r = capital R, which is the surface of the pellet, to the centre of the pellet.

So, let us sketch the pellet for the sake of convenience, to understand this. So, here is a pellet. And the radius of the pellet is R. So, I am now plotting the profile from the outer edge of the pellet, all the way to the centre of the pellet. So, the concentration of the pellet at the surface is C A S. So therefore, clearly this value should be = 1. So, this goes between 0 and 1. And if the concentration of this is essentially 1 here.

And so, the typical profile that one would get is, we will get a profile which looks like this. Now, suppose if I have to increase my thiele modulus. If I have a very large thiele modulus, then what will be the kind of profile that one can get? So, for large thiele modulus, which means that the diffusion is actually controlling the overall reaction rate, the typical profile that one will observe is actually this.

So, this is for large phi. And for a small phi, one actually would observe this kind of a profile. So, one can say that, this is for some medium value of phi 1. So, this picture, this sketch of the C A S, C A by C A S; so, this is essentially, this axis is psi = C A by C A S. So, this profile of concentration versus position actually gives tremendous insights into what is actually happening inside the catalyst pellet.

Suppose, if we look at this picture here, where the catalyst pellet is, the system is operating at large thiele modulus, then what one can observe is that the concentration drops to very close to 0 value at a very small region inside the exterior surface of the pellet. Which means that the reaction is essentially happening very close to the exterior periphery of the reactor. And so, if thiele modulus is very large, then the diffusion process is actually very very slow.

The diffusion rate is very slow. So therefore, the species which is diffusing, as soon as a small quantity of the species diffuses from the exterior surface, close to the exterior surface inside the catalyst pellet; And because the surface reaction is relatively rapid, the reaction would happen immediately and the concentration of the species will essentially drop down to 0, very close to the exterior surface.

And that aspect is quite nicely captured by the curve that we have seen here. On the other hand, what happens when the thiele modulus is small? When the thiele modulus is very small, then the diffusion rate is sufficiently higher compared to the surface reaction. So

therefore, sufficient quantity of the species would always be present everywhere inside the catalyst. It diffuses fast enough, so, before the reaction happens.

And therefore, it is the reaction which is actually controlling the overall reaction rate. And that is nicely captured by this picture here. And note that there is another useful insight that one can actually derive from this graph. If thiele modulus is very small, then the reaction is essentially happening everywhere inside the catalysts pellet, which means that all surface which is available for the reaction, inside the catalyst pellet, is available and is being used for the reaction to be conducted.

On the other hand, if the thiele modulus is very large, as you can see from this curve here, only a small fraction of the overall catalysts which is available for reaction is actually being utilised. The reaction is essentially completing very close to the exterior surface of the catalyst pellet. And this actually offers very useful insight in terms of the way the catalyst can be designed.

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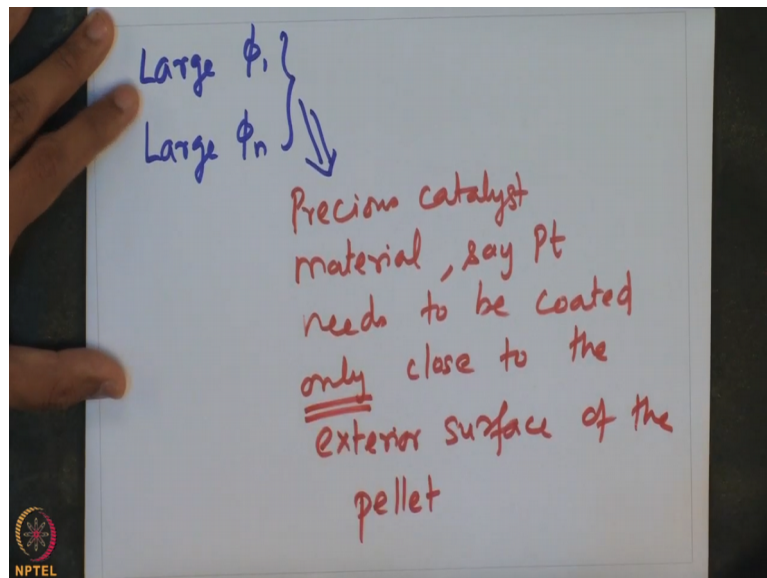
For instance, if the thiele modulus is very large, for large thiele modulus, if for some reason the system is actually operating under large thiele modulus or in general for an nth order reaction; Let us say the thiele modulus is very large, in for an nth order reaction, then if one desires to actually coat the precious catalyst material on the support, let us say alumina or some other support, then if the thiele modulus is very large, then it makes sense to just coat the precious metal only close to the exterior surface of the catalyst pellet.

And there is no need to impregnate the precious metals, which is very expensive, in the way interior of the catalyst pellet, when thiele modulus is very large. And this is because the catalyst pellet is not completely utilised when the thiele modulus is very large. It is only those regions which is close to the exterior surface is being utilised to its maximum extent.

So, when thiele modulus is very large, then it provides a useful suggestion that the precious metal catalyst, precious catalyst material, say platinum needs to be coated only close to the exterior surface of the pellet. It is not required to actually coat or impregnate the catalyst pellet everywhere inside the catalyst pellet. On the other hand, if the, let us say the thiele modulus is very small;

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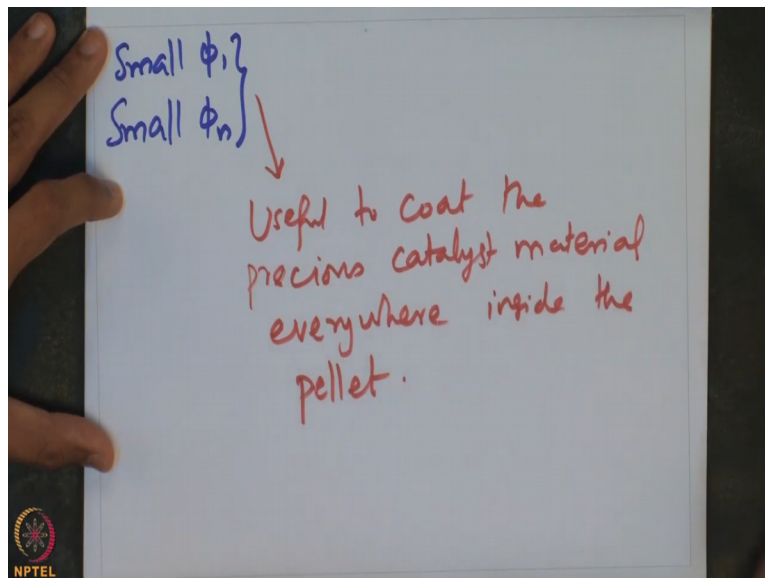
Say it is small phi 1 for a first order or in general, small phi n for any nth order reaction. Then in this case, it is actually necessary to coat the catalyst particle, precious catalyst metal, everywhere inside the catalyst. And this is because for small thiele modulus the reaction is happening everywhere inside the catalyst pellet. And so, if the coating of the precious metal catalyst is not done at every location inside the catalyst pellet, then the reaction is not happening.

Whereas the system is actually facilitating the situation where the reaction can happen everywhere. And so, it is necessary to use, to coat the catalyst material at every location inside the catalyst. Otherwise the productivity is actually severely sacrificed. So, in the case of small phi n, it is useful to coat the precious catalyst material everywhere inside the pellet. So, such kind of insights actually is very useful in designing the way in which the catalyst can

be used and in fact it is helpful in deciding what is the nature of the coating of the catalyst that needs to be performed, in order to take care of the conditions in which the reaction is actually happening. So, what we are going to see next is an important concept called the effectiveness factor.

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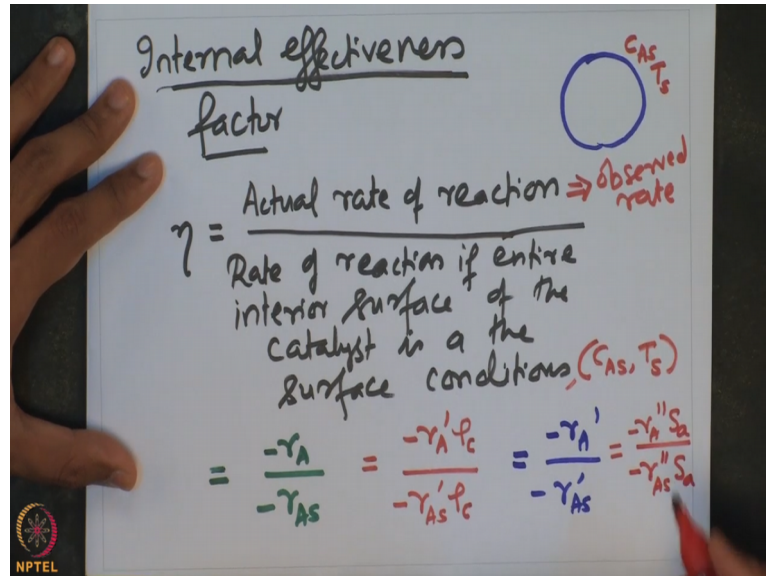
So, the internal effectiveness factor is essentially defined as the, the overall rate. So, typically the symbol that is used is eta. And this is defined as the ratio of actual rate of reaction, divided by the rate of reaction if the entire interior surface of the catalyst is at the surface conditions. Let us try to understand this definition. So, suppose we have a catalyst pellet here and there is reaction that is happening inside.

And the concentration of the species at the surface is C A S. Let us say that the temperature of the fluid at the exterior surface is T S or temperature of the exterior surface of the catalyst is T S. Now, the overall reaction or the actual rate at which the reaction happens could be controlled by diffusion; it could be controlled by surface reaction; we do not know. Depends upon the conditions in which the system is actually operated and depends upon the system that is being considered.

On the other hand, suppose let us say, we create a situation where the entire catalyst is actually maintained at the concentration of the species at the surface and the temperature of every location of the catalyst, is the temperature of the catalyst surface. Now in fact, is it possible to achieve in practice? Yes, it is. If suppose let us say, I conduct the reaction at a very high temperature, then the diffusion rate of the species is going to be much higher.

And in that situation the diffusion rate may be much faster compared to the surface reaction rate. And so, before the reaction happens, the species is actually available at every location inside the catalyst, at the same concentration as that of the surface concentration. So therefore, when we say that the rate of reaction if entire interior surface of the catalyst is at surface condition, what we really mean is that the species is actually at concentration C_S everywhere and the temperature everywhere is actually T_S.

And this actual reaction rate is essentially nothing but what is called as a observed reaction rate. What is the observed rate? So, we can now write this in terms of the quantities that we know. So, that should clearly be $= -r_A$ divided by $-r_{AS}$. So, this is the observed rate and this is the rate at which the reaction would happen if entire catalyst is actually at the surface conditions.

And this clearly should be also $= -r_A'$ into ρ_c, where the, now the r_A' is basically the rate at which the reaction happens, defined based on the mass of the catalyst. And so, I can now cancel this off, cancel the densities. And so, this is essentially $= -r_A'$ by $-r_{AS}'$. And that also is $= -r_A''$ into S_a divided by $-r_{AS}''$ into S_a.

Where S_a is the surface area of the catalyst and $-r_A''$ is essentially the rate at which the reaction happens, defined based on the per unit surface area of the catalyst. So, if that reaction rate is present, I can multiply that by surface area, to find out what is the rate at which the reaction is happening based on the weight of the catalyst.

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So, from here, one can clearly see that the effectiveness factor eta, is $= -rA$ divided by $-rAS$, which is the rate based on the surface conditions. And that should be $= rA$ prime by $-rAS$ prime. And that should clearly be $= -rA$ double prime divided by $-rAS$ double prime. So, this relationship or effectiveness factor which is conserved across the way the reaction rates are defined, can be used to find out what is the effectiveness factor; what is the internal effectiveness factor.

Now, it is often useful rather than looking at the actual rate, one can actually rewrite this as $-rA$ into the volume of the catalyst, divided by $-rAS$, into volume of the catalyst. Now, what is the reaction rate into volume of the catalyst? So, $-rA$ into volume of the catalyst is essentially tells me what is the moles of species reacted per unit time. So, if I call this as, let us say M A, which is the moles of the species that is undergoing reaction per unit time.

And similarly, I can now write $-rAS$, I can write $-rAS$, which is basically the rate at which the species is reacting if the entire surface is at the surface concentration. I can now write that as the moles of species reacted if surface conditions, divided by time. So if, let us say that I define this as M A S, I can now rewrite the effectiveness factor definition in terms of the actual moles that is undergoing the reaction.

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$$\eta = \frac{M_A}{M_{AS}}$$

$$M_{AS} = \text{moles of reacted if entire pellet is at the surface conc./time}$$

$$= k_1 C_{AS} \cdot V_G$$

$$= k_1 C_{AS} \cdot \frac{4}{3} \pi R^3$$

$$M_A$$

So, eta is essentially = M A divided by M A S. So, how do we find these 2 quantities? How do we find the moles of the species that is actually reacting? And how do we find the moles of the species that is reacting if the entire catalyst is actually at the surface concentration and surface temperature. So, let us start with M A S. M A S is essentially, is the moles reacted if entire surface is at the surface, entire pellet is at the surface concentration, per unit time.

So, if entire pellet is actually at the surface concentration, then it means that the reaction that is happening at every location inside the catalyst pellet, will be happening at the intrinsic rate. Therefore the reaction rate everywhere is essentially given by K into C A S. If I assume that it is a first order reaction, it will be k 1 into C A S. That will be the rate at which the reaction is happening at every location inside the catalyst pellet.

And that multiplied by volume of the catalyst will tell me what is the moles that is actually reacted, if the entire pellet surface is actually at the surface concentration and surface temperature. So, that should be = k 1 C A S into 4 by 3, pi R cube. So, next is to find out what is this M A, which is basically the moles of species that is actually undergoing reaction per unit time. So, it is a good time to summarise.

So. what we have seen in this lecture is, we have solved the model equation which captures the diffusion and the simultaneous surface reaction that is happening in the catalyst pellet. And we looked at the concentration profile and obtained insights on what should be the nature of the concentration profile if the thiele modulus is large versus thiele modulus is small. And we also understood what is the, what is its implication on the actual design.

That is, in terms of, what should be the nature of the impregnation or coating of the precious catalyst metal on the pellet support. And next we looked at what is the effectiveness factor. We defined effectiveness factor. And we looked at what is the, how to find out the moles of species that is actually undergoing reaction, if the entire surface is maintained at the, entire catalyst reacting surface is actually maintained at the surface concentration and surface temperature.

In the next lecture, we will actually find out what is the actual moles that is undergoing reaction. And we will define, we will actually find out the expression for the effectiveness factor. And will look at what is the importance of the effectiveness factor. Thank you.