Chemical Reaction Engineering - II
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Lecture – 37
Use of Experimental Data

Friends, let us look at how to obtain the limiting cases from the experimental data that is what whether the reaction is under diffusional limitations or under the surface reaction limiting conditions and how it depends upon various parameters of the system. So, first let us consider the external mass transport limited case.

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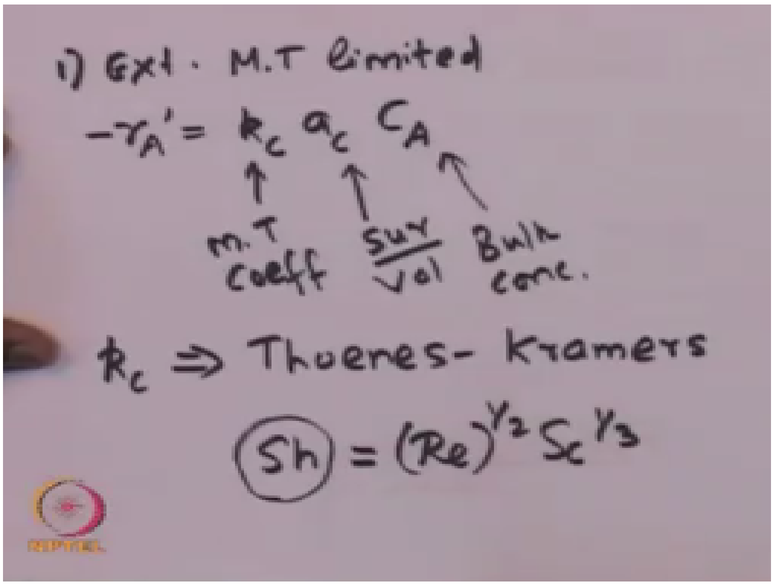

1) Ext. M.T limited

$$-r_A' = \underset{\substack{\uparrow \\ \text{m.T} \\ \text{coeff}}}{k_c}\ \underset{\substack{\uparrow \\ \text{sur} \\ \overline{\text{vol}}}}{a_c}\ \underset{\substack{\nwarrow \\ \text{Bulk} \\ \text{conc.}}}{C_A}$$

$k_c \Rightarrow$ Thoenes- Kramers

$$\boxed{Sh} = (Re)^{1/2} Sc^{1/3}$$

Now, here in the under the external mass transport limitations, the reaction rate is given by Kc ac * CA where Kc is the mass transport coefficient, ac is the surface to volume ratio and CA is the bulk concentration now, Kc can be estimated using appropriate correlations such as the Thoenes Kramers correlation; can be estimated using the Thoenes Kramers correlation now, the correlation is as follows.

It says that the Sherwood number should be = Reynolds number to the power of 1/2 multiplied by the Schmidt number to the power of 1/3 so, the mass transport coefficient is embedded in Sherwood number while other properties like velocity etc. they are all embedded in Reynolds number and the Schmidt number. So, now looking at the functional form of these 3 terms, we could be; we would be able to discern how the mass transport coefficient depends upon various parameters such as the diameter of the particle.

Or the temperature of the; temperature at which the reaction is being conducted etc. and then find out what is the relationship or functional dependence of the overall reaction rate on various systems parameters such as the diameter of the particle and velocity of the; velocity with which the fluid is flowing into the reactor.

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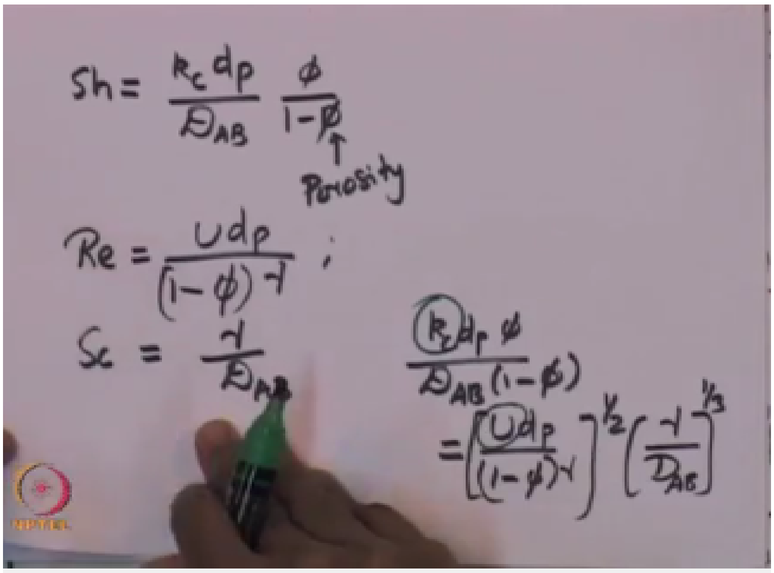

$$Sh = \frac{k_c d_p}{\mathcal{D}_{AB}} \frac{\phi}{1-\underset{\substack{\uparrow \\ \text{Porosity}}}{\phi}}$$

$$Re = \frac{u d_p}{(1-\phi)\nu} ;$$

$$Sc = \frac{\nu}{\mathcal{D}_{AB}}$$

$$\frac{\boxed{k_c} d_p \phi}{\mathcal{D}_{AB}(1-\phi)} = \left[\frac{\boxed{u} d_p}{(1-\phi)\nu}\right]^{1/2} \left(\frac{\nu}{\mathcal{D}_{AB}}\right)^{1/3}$$

So, now if I look at the expression for Sherwood number, you see that the Sherwood number is given by mass transport coefficient Kc multiplied by the diameter of the particle dp divided by the equimolar counter diffusivity with DAB multiplied by phi divided by 1 – phi, here phi is refers to porosity of the bed and it does not represent the Thiele modulus here, phi is the porosity of the bed.

And Reynolds number is given by u times dp, u is the superficial velocity, dp is the diameter of the particle, diameter of the catalyst pellet in which the catalytic reaction is being conducted divided by the 1 – phi, where phi is porosity; porosity * nu which is kinematic viscosity and similarly, Schmidt number is given by kinematic viscosity divided by the equimolar counter diffusivity of the species A that is of interest.

So from here, we can now write the all these plug in all this expression in the Thoenes Kramers correlation, we find that Kc dp * phi divided by DAB * 1 - phi that should be = u dp/ 1- phi * nu to the power of 1/2 multiplied by nu/ DAB to the power of 1/3rd so that is the dependence of the mass transport coefficient where here Kc refers to the mass transport coefficient and this is the functional dependence of mass transport coefficient on the terminal velocity u and dp and other parameters.

So, from here we can discern that the mass transport coefficient K is now a proportional to Kc is proportional to square root of u where u is a superficial velocity and also it is proportional to 1/ square root of dp, Kc is proportional to 1/ square root of dp. Now the; if I look at the reaction rate, reaction rate is Kc * surface area per unit volume multiplied by the corresponding concentration CA.

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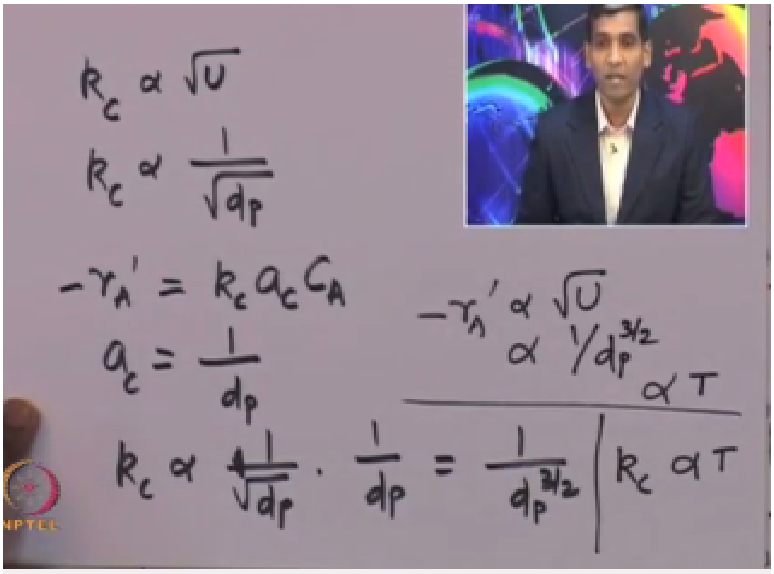

$$k_c \propto \sqrt{U}$$

$$k_c \propto \frac{1}{\sqrt{d_p}}$$

$$-r_A' = k_c a_c C_A$$

$$a_c = \frac{1}{d_p}$$

$$-r_A' \propto \sqrt{U}$$

$$\propto 1/d_p^{3/2}$$

$$\propto T$$

$$k_c \propto \frac{1}{\sqrt{d_p}} \cdot \frac{1}{d_p} = \frac{1}{d_p^{3/2}}$$

$$k_c \propto T$$

So, now the; from here we can see that the area per unit volume is given by 1/dp and therefore, the reaction rate therefore, the mass transport coefficient Kc is proportional to square one; 1/ square root of dp * 1/dp, so that will be given by 1/ dp to the power of 3/2, so that is the functional form of the mass transport coefficient on the diameter of the particle, so it is dp to the power of 3/2.

Now, similarly one can see that the mass transport coefficient is typically proportional to the temperature at which the reaction is being conducted so therefore, from here we can see that the reaction rate is proportional to square root of u which is the superficial velocity with which the fluid is flowing into the reactor and also it is proportional to 1/dp to the power of 3/2 and it is also proportional to the temperature at which the reactor is being operated.

So that provides the functional form of the reaction rate dependence of the reaction rate on various parameters of the system.

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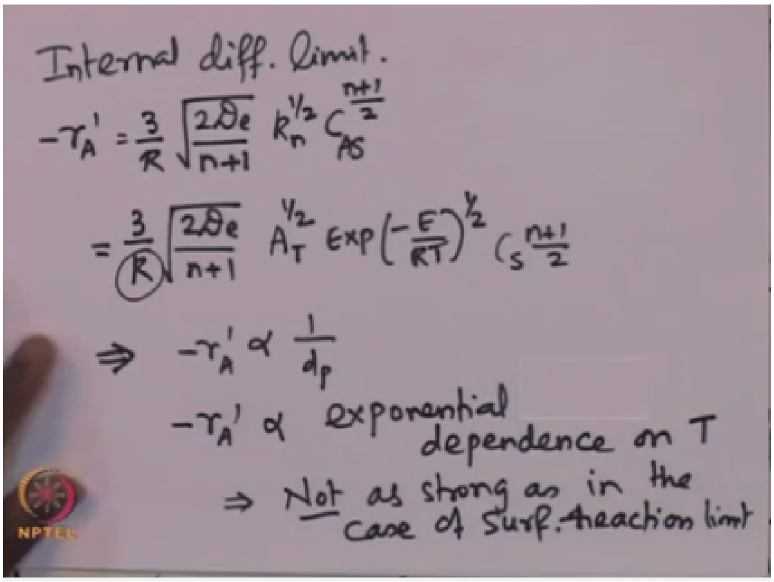

Internal diff. limit.

$$-r_A' = \frac{3}{R}\sqrt{\frac{2D_e}{n+1}}\, k_n^{1/2}\, C_{AS}^{\frac{n+1}{2}}$$

$$= \frac{3}{\textcircled{R}}\sqrt{\frac{2D_e}{n+1}}\, A_T^{1/2} \exp\left(-\frac{E}{RT}\right)^{1/2} C_S^{\frac{n+1}{2}}$$

$\Rightarrow -r_A' \propto \frac{1}{d_p}$

$-r_A' \propto$ exponential dependence on T

$\Rightarrow$ Not as strong as in the case of surf. reaction limit

So therefore, now next if we look at the internal diffusional limitations, then the reaction rate is for any nth order reaction is given by rA prime, it is = 3/R that is the radius of the pellet; catalyst pellet that is being used into square root of 2 times the diffusivity; effective diffusivity of the species divided by n + 1 multiplied by Kn to the power of 1/2 where K is the nth order reaction rate constant multiplied by the surface concentration CAS to the power of n + 1/ 2.

So that is the rate law now, the rate constant actually follows Arrhenius type dependence on the temperature so therefore, we can rewrite this expression as 3/R * square root of 2 times De divided by n + 1 multiplied by the frequency factor AT to the power of 1/2 * exponential of –E/ RT to the power of 1/2 * Cs to the power of n + 1/ 2, so that is the expression, so given that the where E is the activation energy and T is the temperature at which the reactor is being operated.

So, from here one can discern that the rate of reaction rA is proportional to 1/ diameter of the particle dp because of this functional dependence on because of this term 3/R and also the rate of reaction is; has an exponential dependence on the temperature at which the reactor is being operated, it is important to also note that diffusivity is also a function of temperature.

So, this suggests that the unlike in the case of external mass transport control situation in the internal diffusion control situation, the reaction rate does not depend upon the superficial velocity with which the fluid stream is being flown into the reactor. Now, it should be noted that here the exponential dependence is exponential to the power of 1/2, so therefore the exponential dependence on temperature is not as strong as in the case of surface reaction limited situations.

So, therefore we can see that the reaction rate in the case of internal diffusional limitations is 1/dp and it depends exponentially on the temperature at which the reactor is being operated.

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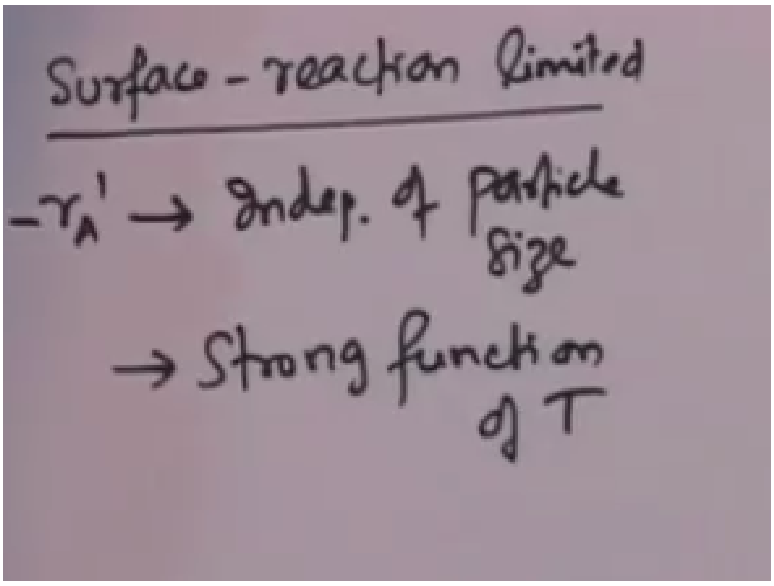

Surface - reaction limited

$-r_A' \rightarrow$ Indep. of particle size

$\rightarrow$ Strong function of T

So, next let us look at the surface reaction limited case so, in the surface reaction limited case, the reaction rate is now is independent of the size of the particle, it is independent of the particle size and it is a strong function of the temperature at which the reactor is being operated so now, if you put them all together, if you put all of these 3 dependencies of the reaction rate on various systems parameters for all these 3 cases together, we can now form a table which captures the dependence of the reaction rate on various parameters.

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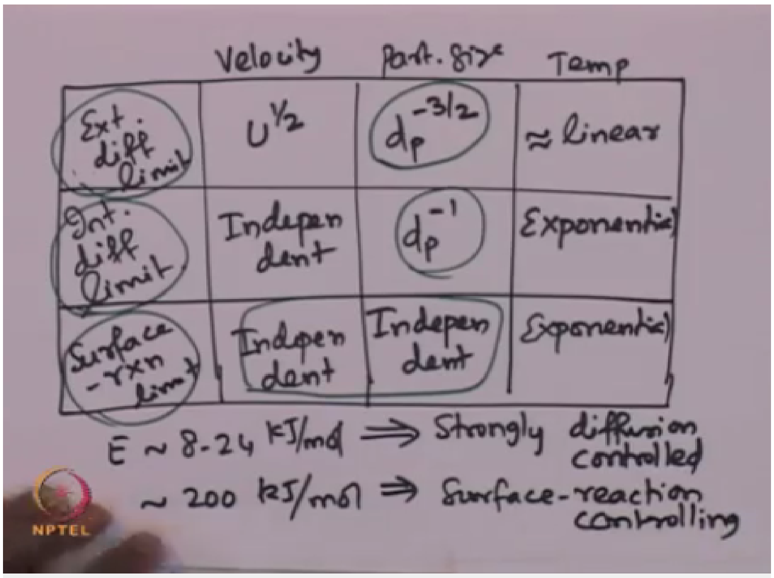

	Velocity	Part. size	Temp
Ext. diff limit	$U^{1/2}$	$d_p^{-3/2}$	≈ linear
Int. diff limit	Independent	d_p^{-1}	Exponential
Surface -rxn limit	Independent	Independent	Exponential

$E \sim 8\text{-}24$ kJ/mol ⇒ Strongly diffusion controlled

~ 200 kJ/mol ⇒ Surface-reaction controlling

So, now let us draw a table, so let us look at the external diffusion, the case of external diffusional limitations under the external diffusional limitations, what is its functional dependence on the velocity; its u to the power of 1/2 so that is the functional dependence on velocity and if I look at the particle size, it depends upon dp to the power of – 3/2 and then on temperature, it is approximately linear.

So, the reaction rate is approximately linear with respect to temperature in the external diffusional limitation case next, if we look at the internal diffusional case; diffusional limitations case, the reaction rate is now independent of velocity, it is independent of the velocity with which the fluid is being pumped into the reactor and it is a function of dp to the power of - 1 and it depends exponentially on the temperature, it is an exponential dependence on the temperature.

Now, if you look at the surface reaction case; surface reaction limited case, then it is independent of the velocity with which the fluid is being flown into the reactor, it is independent of that and it is also independent of the particle size and it has a strong exponential dependence on the temperature so therefore, if the reaction is being performed, the first step would be to perform the reaction at a certain velocity and different diameter of the particle.

Now, if you look at the different diameter of the particle, if the reaction rate by decreasing the particle size it correspondingly uses this expression of dependent, this shows this dependence of 1/dp then, it suggests that the particular reaction is under the internal diffusional limitations. Now, if it has a functional dependence of dp to the power of – 3/2 then, it suggests that it is an exponentially; external diffusion limited situation.

Now, if it is independent of the particle diameter, if is completely independent of the particle diameter then it; the current conditions suggest that the experimental conditions are essentially it is a; it is under the reaction; surface reaction limited situation. So, as a rule of thumb, if the activation energy is of the order of 8 to 24 kilo joules per mole, if that is the order of magnitude.

Then it means that the reaction is actually strongly under strongly diffusional limitations; strongly external diffusion control regime that is external mass transfer controlling, it is under strong diffusion control regime however, if it is about 200 kilo joules per mole then more often than likely it will be a surface it will be under surface reaction controlled regime, so the reaction will be surface reaction controlling.

So, this table summarizes the functional dependence of various parameters and how can an experiment be designed using these from these parameters in order to estimate whether the reaction is likely to be external diffusion limited or internal diffusion limited or the surface reaction limited.

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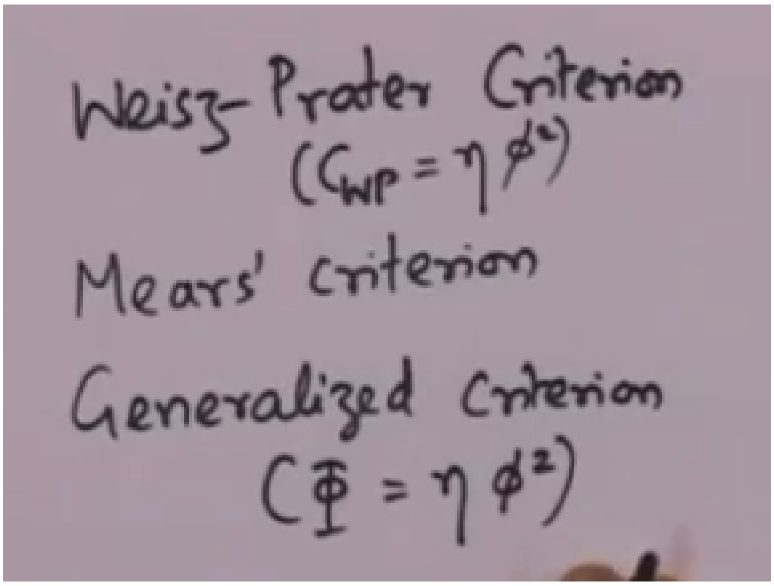

Weisz-Prater Criterion

($C_{WP} = \eta \phi^2$)

Mears' criterion

Generalized Criterion

($\Phi = \eta \phi^2$)

So, now summarizing what we have learnt about various criteria is; we have looked at the Weisz-Prater criterion, we looked at Weisz-Prater criterion, it essentially uses a parameter CWP which is equal to the effectiveness; internal effectiveness factor multiplied by the corresponding Thiele modulus and this does not work and for all types of rate loss, it works for certain type of rate loss where the effectiveness factor Thiele modulus behaviour is monotonic.

And then we looked at the Mears' criterion; Mears' criterion to discern from experimental data whether it is external diffusion controlled or not and then we looked at the generalized criterion where once again parameter capital phi which is equal to the overall effective; which is equal to the local effectiveness or internal effectiveness factor for any general reaction mechanism multiplied by the Thiele modulus of that particular general mechanism.

So that particular product gives you a factor called capital phi which is used in; which is used as a general criterion, so if phi is < 1, then it is considered that the diffusional limitations does not exist and if it is > 1 then, the diffusional limitations; strong diffusional limitations exist in the particular type of reaction. So, now once we know how to identify whether the reaction is under the diffusion or the internal limitation; internal diffusional limitation or external diffusional limitation or surface reaction limited conditions then one may use these kind of information such as the effectiveness factor into the reactor design.

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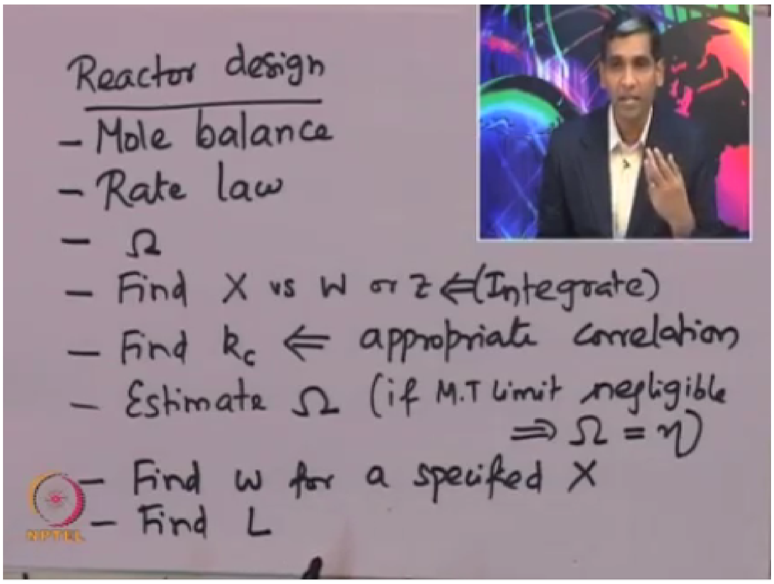

Reactor design

- Mole balance
- Rate law
- Ω
- Find X vs W or z ⇐ (Integrate)
- Find k_c ⇐ appropriate correlation
- Estimate Ω (if M.T limit negligible $\Rightarrow \Omega = \eta$)
- Find w for a specified X
- Find L

So, the general algorithm to perform a reactor design; general algorithm to perform a reactor design is first one; writes a mole balance; a mole balance is written and then the rate law is identified and then based on the rate depending upon the experimental data, one may be able to find out whether it is external diffusion controlled or internal diffusion controlled, so based on that we can find out what is the expression for the overall effectiveness factor which incorporates all types of limitations.

And then find the; by solving the mole balance you can use this overall effectiveness factor and you can find out what is the rate law based on the observable quantities such as the bulk concentration and then we can find what is the relationship between the conversion X by taking stoichiometry into account versus the weight of the catalyst which may be used for conducting the reaction to attain a certain conversion.

Or the position inside the reactor then, following which the; which can be obtained by integration of the mole balance, so integrate the mole balance and one can get the relationship between X and the weight of the catalyst or the position inside the catalyst. Now, the position at which the desired exit conversion can be achieved is; what is the length of the reactor that needs to be designed or that is the required length of the reactor for attaining a certain conversion.

Then, the next step is to find the mass transport coefficient Kc, this can be obtained using various correlations one may use the appropriate correlations now, if it is not external mass transport control, then the mass transport coefficient really does not play much role here, so in that case this step can be ignored and the effectiveness factor will simply be equal to the internal effectiveness factor.

And so, the overall effectiveness factor will simply be equal to the internal effectiveness factor, so then the next step is to estimate based on the various properties and the parameters and next step is to estimate the overall effectiveness factor, if mass transport limitations are negligible, then an overall effectiveness factor is approximately equal to the internal effectiveness factor and then next step is to find the weight of the catalyst for a specified conversion and then find the length of the reactor.

So, this is the general recipe for performing a reactor design in order to obtain the design parameters such as how much weight of catalyst is required to obtain a certain conversion, what should be the length of the reactor to obtain the desired conversion. So, now let us look at a little bit more details of packed-bed reactor and the design of packed bed reactors.

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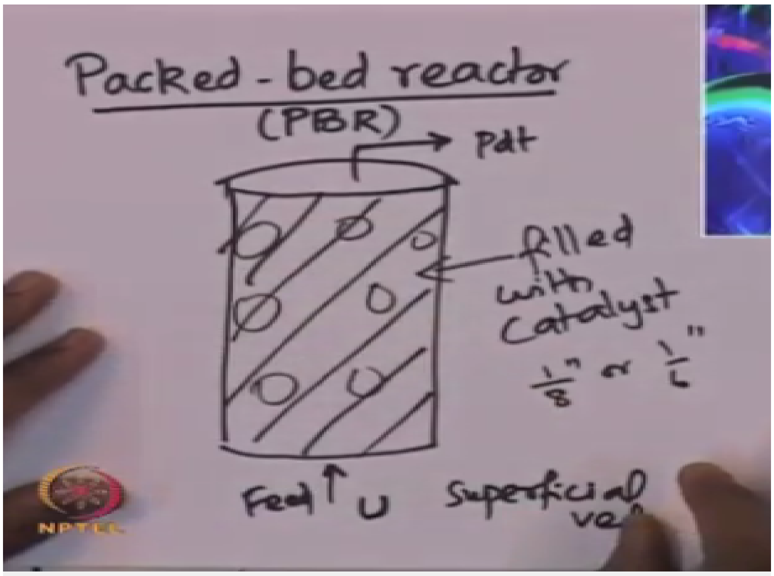

The packed bed reactor hereafter will simply be referred to as PBR which stands for packed bed reactor, so packed bed reactor is essentially a tube which is filled with catalyst inside and the reactants are flown from one end and the gas stream the reactant species present in the gas stream they go into the catalyst and then get adsorbed on to the site of the catalyst and the reaction occurs and soon after the reaction occurs the product leaves the catalyst.

And then moves into the gas stream and the product leaves the reactor, so it is essentially a tube, it is a tube which is filled with catalyst pellet, so these are catalyst pellets, so the catalyst pellets may be spherical, it may be small cylindrical, there are various types of shapes that may be used depending upon the nature of the reaction that is being conducted and the typical size of the catalyst if it is a spherical particle or the approximate hydraulic radius would be about 1/8th inch or 1/6th inch that is the typical size of the catalyst that is actually being used inside a commercial packed-bed reactor.

Now, the fluid stream may be flowing from the bottom of the reactor with let us say with the velocity; superficial velocity of u, so that is the superficial velocity and the product comes out from the top, so this is where the product comes out, the feed goes here, the feed stream goes in from here and then the product comes out from the top, so it may be that there may be different kinds of reactions that can be conducted inside such a packed bed reactor.

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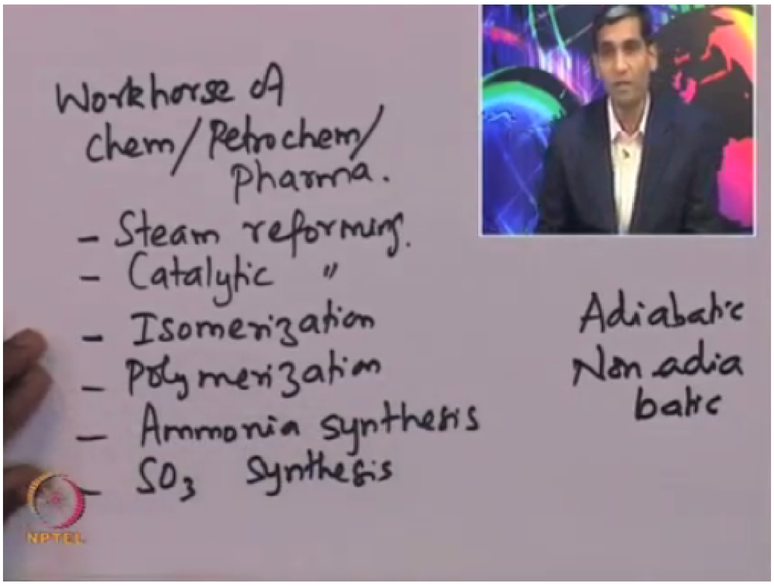

Workhorse of
Chem/Petrochem/
Pharma.

- Steam reforming.
- Catalytic "
- Isomerization
- Polymerization
- Ammonia synthesis
- SO_3 Synthesis

Adiabatic
Non adia
batic

So a packed bed reactor is actually the workhorse of chemical, petrochemical and pharmaceutical industries, so it is the workhorse of chemical, petrochemical and pharmaceutical industries / Pharma industries, it is used in many different processes, conversion of many different chemicals and a good example of that will be steam reforming, it is one of very good examples of situation where packed-bed reactor is used.

Then it is used for catalytic reforming; catalytic reforming process, it is used in isomerization process, it is used in polymerization process and it is used in ammonia synthesis, these are some of the examples where packed-bed reactor is routinely being used in industrial conditions; industrial settings, ammonia synthesis, it is also used in SO3 synthesis, so these are some of the examples of situations where packed-bed reactor is being used in reality.

And the packed-bed reactor can in principle be operated in a 2 modes; one can be operated in adiabatic mode or a non-adiabatic mode, so adiabatic mode is a situation where no heat that is actually lost from the reactor to the external surroundings, so that is called an adiabatic situation and another configuration is a non-adiabatic situation, where the reactor may not be conducted at an adiabatic conditions, the reactor maybe it is an exothermic reaction where there is a cooling fluid which is flowing in the jacket.

And it might be removing the heat that is being generated because of the exothermicity of the reaction now, this is required, this may be required under many situations because if there is an exothermic reaction, then the local temperature inside the reactor can actually increase and that may lead to if it crosses the melting point of the catalyst, then it may lead to melting of the catalyst or if it is present close to the walls and if it is an undesirable temperature, then it poses a very serious safety concern.

So, therefore it is very important to manage the heat inside the reactor and so a fluid is being circulated around and constantly the heat is being removed, if it is an exothermic reaction which generates heat due to the reaction so, there are generally 2 modes of operating; one is the adiabatic where there is no heat is removed from the reactor where the exterior of the tubular reactor is insulated and then, another situation where it is a non-adiabatic situation where the heat may be removed from the exterior walls of the tubular reactor.