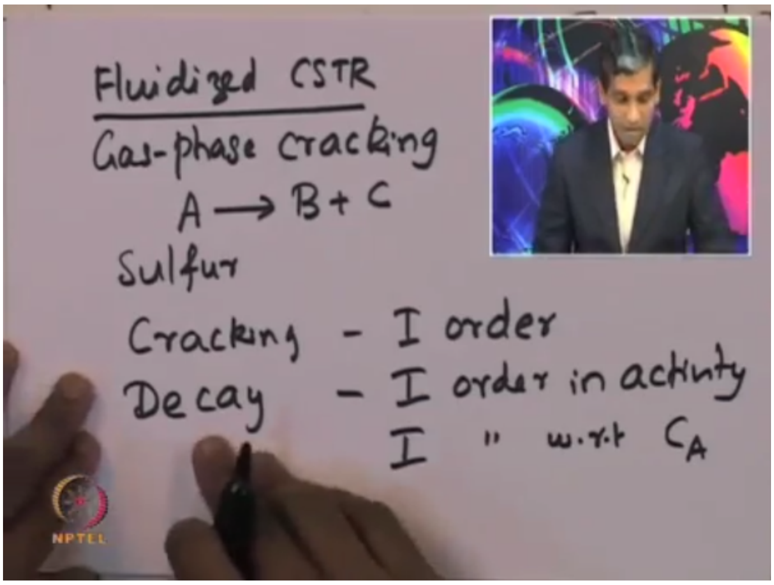
Chemical Reaction Engineering - II
Prof. Ganesh A Viswanathan
Department of Chemical Engineering
Indian Institute of Technology - Bombay

Module - 4
Lecture - 16
Catalyst Deactivation IV: Reactor Design

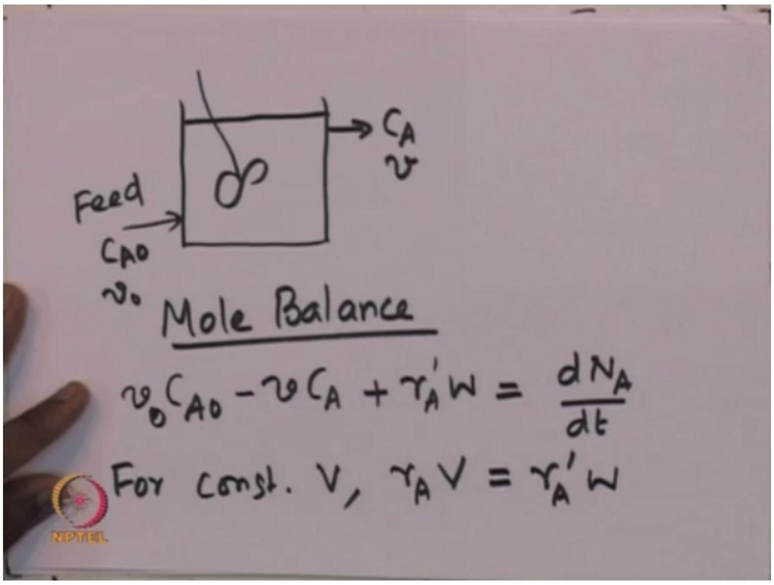
(Refer Slide Time: 00:34)



Fluidized CSTR
Gas-phase cracking
$A \longrightarrow B + C$
Sulfur
Cracking - I order
Decay - I order in activity
I " w.r.t C_A

So, let us consider a fluidized CSTR. And let us assume that a gas phase cracking reaction where A goes to B + C is occurring in this fluidized CSTR. And let us assume that the feed contains a sulphur which is, which acts as a poison for the catalyst. And also assume that the cracking is a first order process. And if we assume that the decay, catalytic deactivation or decay of the catalyst is first order with respect to first order in activity. And it is first order with respect to concentration of species A in the gas stream. So now, we can actually, so the schematic of fluidized CSTR, it looks like this.

(Refer Slide Time: 01:45)



Mole Balance

$$v_0 C_{A0} - v C_A + r_A' W = \frac{dN_A}{dt}$$

For const. V, $r_A V = r_A' W$

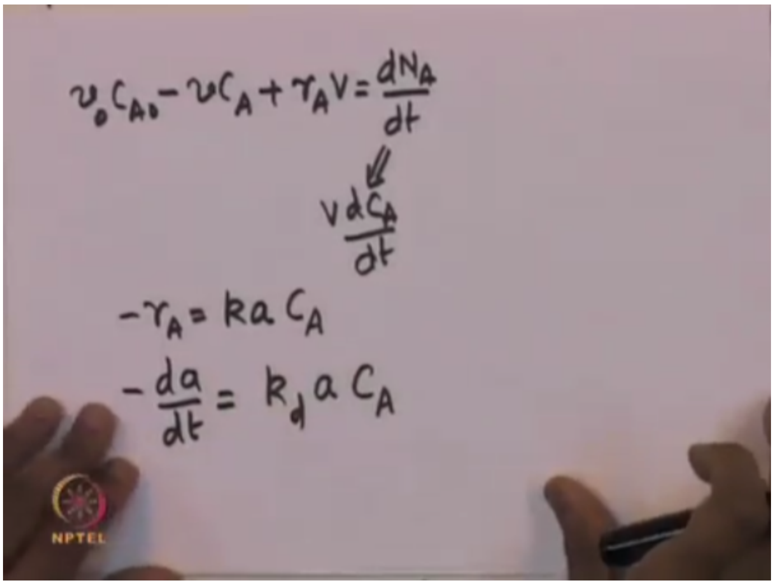
Where you have a fixed volume, fixed volume for the CSTR. It is well mixed. And you have a feed which goes in and let us assume that C A nought is the concentration of the feed at the inlet. And v nought is the flow rate, volumetric flow rate of the feed at the inlet. And C A is the concentration of the product stream or concentration of species A in the product stream. And v is the volumetric flow rate with which the fluid stream leaves the fluidized CSTR.

Now, a simple mole balance can be written for this system. So, the mole balance is the rate at which species enters the, molar rate at which the species enters the reactor which is v nought into C A nought. v nought has the units of volume per time. Let us say metre cube per time. And the C A nought which is the concentration is moles per unit volume. – whatever rate at which the, molar rate at which the stream leaves the reactor, which is v which is the volumetric flow rate with which the stream leaves the reactor.

And C A is the concentration with which, at which it leaves the reactor. + the rate of generation of the species A. That is = the rate of change of the number of moles of A with respect to time, which is the accumulation term. Now, for constant volume, which is true for a CSTR for constant volume, the rate multiplied by rate in terms of the volume, that is moles per unit volume per time, multiplied by the volume should be = the rate defined in terms of the catalyst weight.

That is the moles of a reactor per gram weight of the catalyst per unit time, multiplied by the weight of the catalyst. So, these 2 has to be equal. So, incorporating this equality into the mole balance, we can rewrite the mole balance as:

(Refer Slide Time: 03:56)



$$v_0 C_{A0} - v C_A + r_A V = \frac{dN_A}{dt}$$

$$\Downarrow$$

$$V\frac{dC_A}{dt}$$

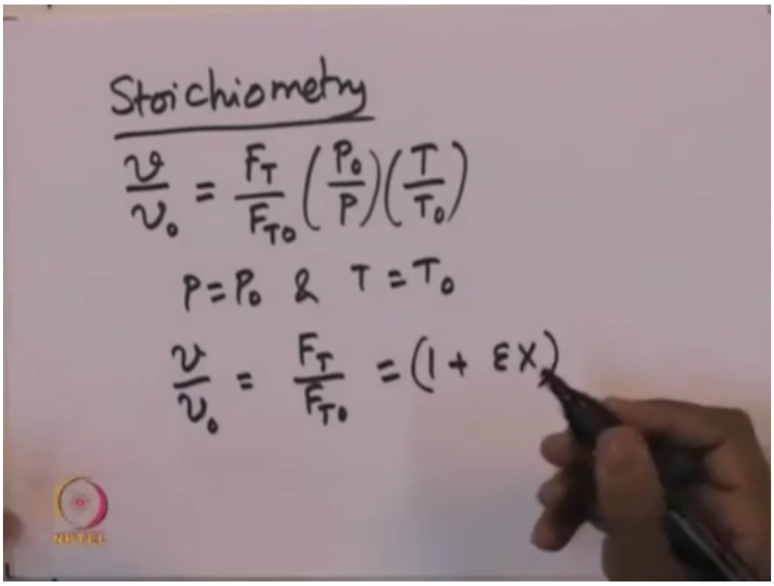
$$-r_A = k a C_A$$

$$-\frac{da}{dt} = k_d a C_A$$

v nought into C A nought – v into C A + r A into V. And that is = d N A by d t. Now d N A by d t can actually be written in terms of the concentration of the species. And so, that will be V into d C A by d t. So now, the rate at which the reaction occurs, that is the rate of consumption of species A is – r A = the corresponding specific reaction rate multiplied by the activity of the catalyst multiplied by the concentration of the species C A.

And the corresponding decay law is given by d a by d t. That is = the decay constant multiplied by the activity of the catalyst multiplied by the concentration of A in the gas phase. Now, if we know the rates of this reaction, that is the reaction rate, then next step we need to do in terms of designing the reactors, we need to use the stoichometry and related these terms here.

(Refer Slide Time: 05:06)



Stoichiometry

$$\frac{v}{v_0} = \frac{F_T}{F_{T0}}\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$$

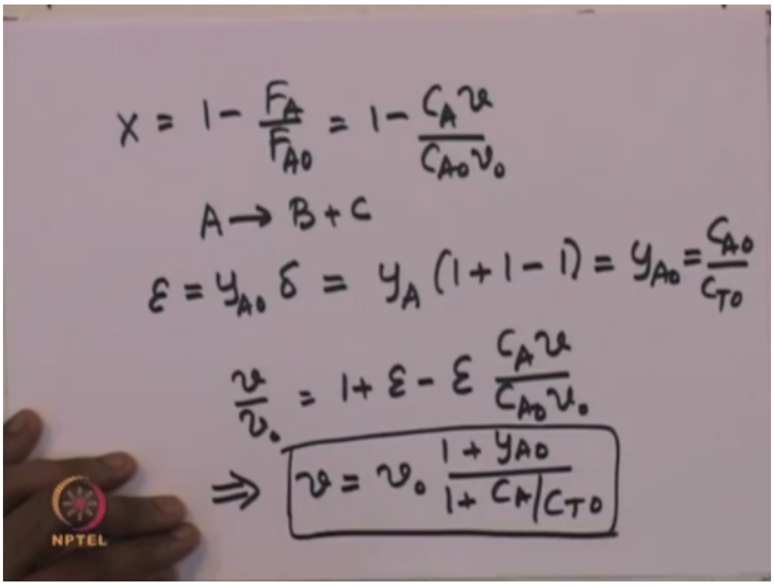
$P = P_0$ & $T = T_0$

$$\frac{v}{v_0} = \frac{F_T}{F_{T0}} = (1+\varepsilon X)$$

So, using stoichiometry we can find that the volumetric flow rate of the stream that leaves the reactor divided by the volumetric flow rate of the stream that enters the reactor should be = the molar flow rate F T with which these species leaves divided by the, it is the ratio of the total molar flow rate of the outlet stream divided by the total molar flow rate of the inlet stream multiplied by the P nought by P which is the total pressure at the inlet divided by the total pressure at the outlet multiplied by T by T nought.

So, at constant pressure if P = P nought and at isothermal conditions T = T nought. So, v by v nought simply reduces to F T by F nought F T nought which is nothing but 1 + the net fractional change in the number of moles because of the reaction multiplied by X.

(Refer Slide Time: 06:15)



$$X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{C_A v}{C_{A0} v_0}$$

$A \to B + C$

$$\varepsilon = y_{A0}\delta = y_A(1+1-1) = y_{A0} = \frac{C_{A0}}{C_{T0}}$$

$$\frac{v}{v_0} = 1+\varepsilon - \varepsilon\frac{C_A v}{C_{A0} v_0}$$

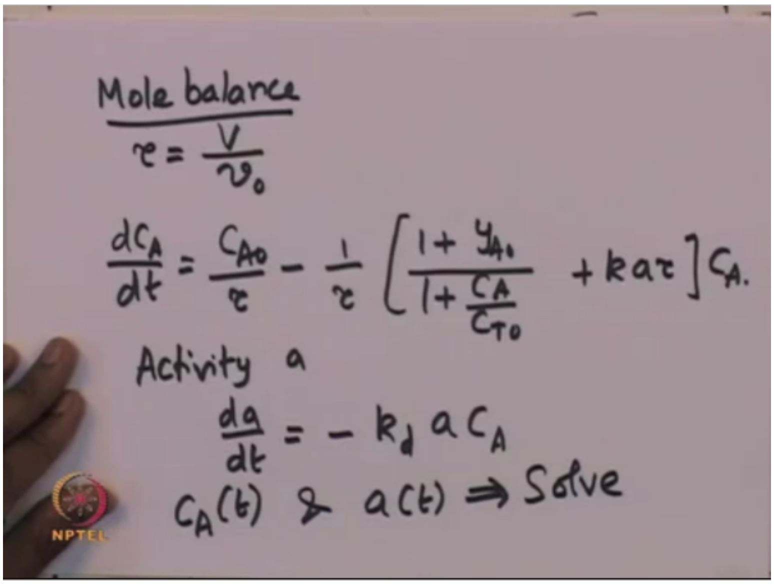
$$\Rightarrow \boxed{v = v_0 \frac{1+y_{A0}}{1+C_A/C_{T0}}}$$

So, now the conversion X is = 1 – F A by F A nought. So, that is the conversion. And that is = 1 – C A into v divided by C A nought into v nought. Now, remember that the reaction that we are looking at is A giving B + C. So, therefore the net fractional change in the number of moles is given by the overall mole fraction of A multiplied by these change in number of moles which is = y A into 1 + 1 – 1.

That is = y A nought which is given by C A nought by C T nought which is the, C A nought is the is the concentration of the species in the inlet stream and C T nought is the total concentration at the inlet stream. So, by using this expression we can rewrite v buy v nought as 1 + epsilon – epsilon into C A into v divided by C A nought into v nought. Which is; and from here, we can easily deduce that the volumetric flow rate of the stream that leaves the reactor should be = v nought into 1 + y A nought divided by 1 + C A by C T nought.

So now, so plugging in all these volumetric flow rate expressions in terms of concentrations etcetera into the mole balance.

(Refer Slide Time: 07:57)



Mole balance

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

$$\frac{dC_A}{dt} = \frac{C_{A0}}{\tau} - \frac{1}{\tau}\left[\frac{1+y_{A0}}{1+\frac{C_A}{C_{T0}}} + k a \tau\right] C_A.$$

Activity a

$$\frac{da}{dt} = -k_d\, a\, C_A$$

$C_A(t)$ & $a(t) \Rightarrow$ Solve

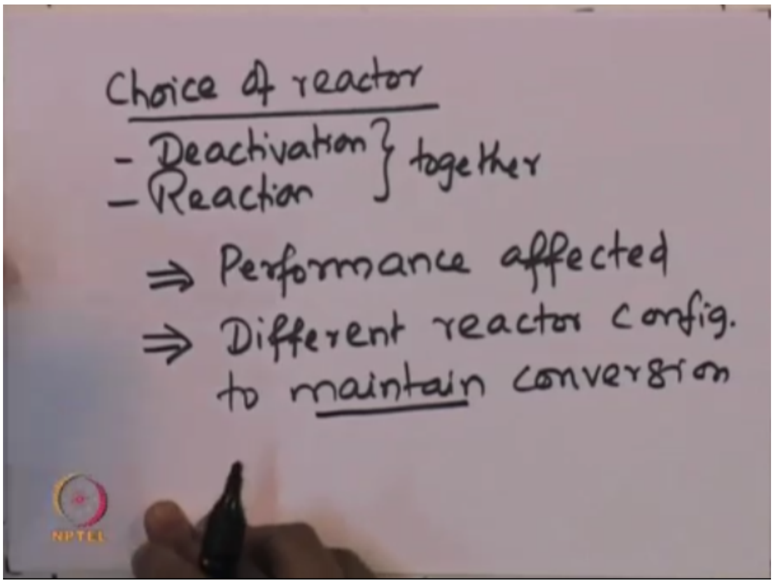
We can rewrite the mole balance as, we can rewrite the mole balance after defining a residence time tau which is the time that the fluid element bends inside the reactor. Which is given by volume of the reactor divided by the inlet volumetric flow rate. And so, the mole balance will be d C A by d t. That is = C A nought by tau – 1 by tau into 1 + y A nought divided by 1 + C A by C T nought + k into a into tau into C A.

And the activity is given by, activity a can be found from the decay rate expression for the catalyst. That is d a by d t = – k d into a into C A. So, these 2 equations essentially characterise the simultaneous deactivation and the catalytic reaction which is happening in the reactor. And so, if one needs to obtain the dependence of concentration on time and the activity on time, then one needs to solve these 2 equations, solve the equations simultaneously.

And one should be able to obtain the concentration profile as a function of time and the activity profile as a function of time. So now, we observed that the catalytic deactivation is a very serious problem, because it poses a strong major problem in terms of maintaining the conversion of the desired products. And as a result, it has a strong effect on the economic, economy of the company which is actually producing that particular product.

So, therefore it has a strong effect on the economics of that particular product. And as a result, choice of reactor is extremely important which will help in minimising or avoiding the deactivation process.

(Refer Slide Time: 10:09)



Choice of reactor

- Deactivation } together
- Reaction

⇒ Performance affected

⇒ Different reactor config. to maintain conversion

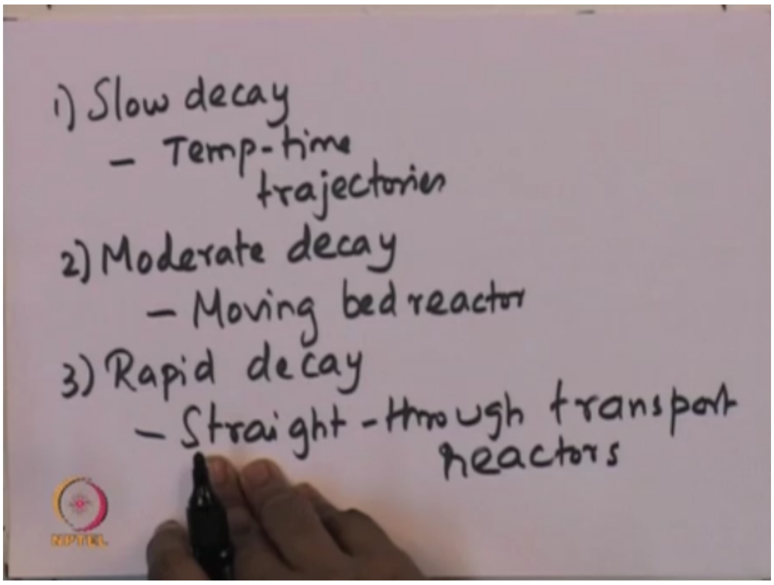
So, the choice of the reactor, so, what we going to discuss now is to look at, how can we use a particular choice of a, how can we decide what should be the choice of the reactor that will help in minimising the deactivation of the catalyst and with the objective of maintaining the conversion of the desired product. So, we know that deactivation and reaction, they occur together, they occur simultaneously.

So, therefore the performance is severely affected. And the, as an offset, one could actually use different reactor configuration to maintain the conversion. So, what we are going to discuss now is to look at what are the different types of configurations that one has to use in order to minimise the deactivation of the catalyst or rather in order to maintain the conversion, desired conversion.

So, suppose if the decay is very slow, so naturally the choice of the reactor and the necessary steps that one has to take depends upon the speed with which the catalyst gets deactivated. So, if the decay is very slow, then what really works is the, is basically the, using a temperature time trajectory where the feed stream is constantly preheated at and the temperature is increased slowly in order to minimise the deactivation and thereby maintain the conversion of the reaction which is happening inside the reactor.

Suppose if the decay is moderate, it is a moderate decay, then it is suggested to use a moving bed reactor. And we are going to look at the design of this. The moving bed reactor can be used in order to minimise the deactivation. And then, if it is a rapid decay of the catalyst, then one needs to use a straight through transport reactors. This classification is based on the deactivation time scales as dictated by the corresponding decay constant. So, let us look at the slow decay, first case of slow decay. Suppose if the catalyst is decaying very slowly.

(Refer Slide Time: 13:22)



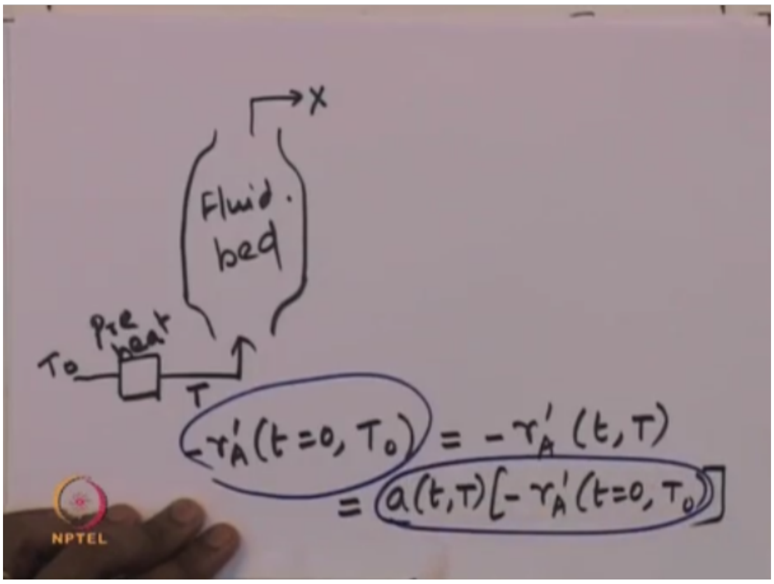
1) Slow decay
  - Temp-time trajectories

2) Moderate decay
  - Moving bed reactor

3) Rapid decay
  - Straight-through transport reactors

So, if it is a slow decay system, then the, in order to maintain a constant conversion the strategy is to increase the reaction rate by slowly increasing the temperature, slowly increasing the feed temperature. So, this, by slowly increasing the feed temperature, one could actually increase the reaction rate and thereby maintain the required conversion. And so, the classical setup which helps in such kind of a design is basically a fluidized bed. In fact, in many fixed bed reactors as well, such a strategy is employed.

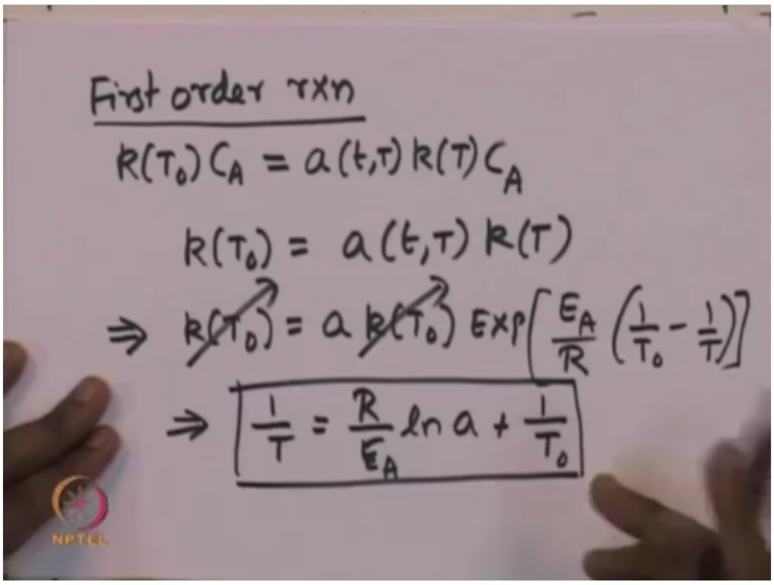
(Refer Slide Time: 14:14)



Suppose, if this is a fluidized bed, it is a fluidized bed reactor, and then a preheater is added to the inlet stream. So, suppose the inlet stream is entering the preheater at certain initial temperature T nought, then, as the reaction proceeds the preheater constantly increases the temperature of the inlet stream so as to maintain a certain fixed conversion X. So, which means that the reaction rate at t = 0, that is at the start of the reactor, at the temperature T nought should be = the reaction rate at certain other time and certain other temperature T.

And in terms of using the rate law that we have derived for catalyst deactivation, the rate law for the reaction when the catalyst deactivation is simultaneously occurring. So, that will be a into t , T. So, now the activity is a function of both time and temperature. And so, – r A into t = 0 , T nought. So, these 2 quantities has to be equal in order to obtain the desired conversion. This quantity must be = this quantity in order to obtain the desired conversion, in order to maintain the desired conversion.

(Refer Slide Time: 15:54)



First order rxn

$$k(T_0)C_A = a(t,T)\,k(T)\,C_A$$

$$k(T_0) = a(t,T)\,k(T)$$

$$\Rightarrow \cancel{k(T_0)} = a\,\cancel{k(T_0)}\,\exp\left[\frac{E_A}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]$$

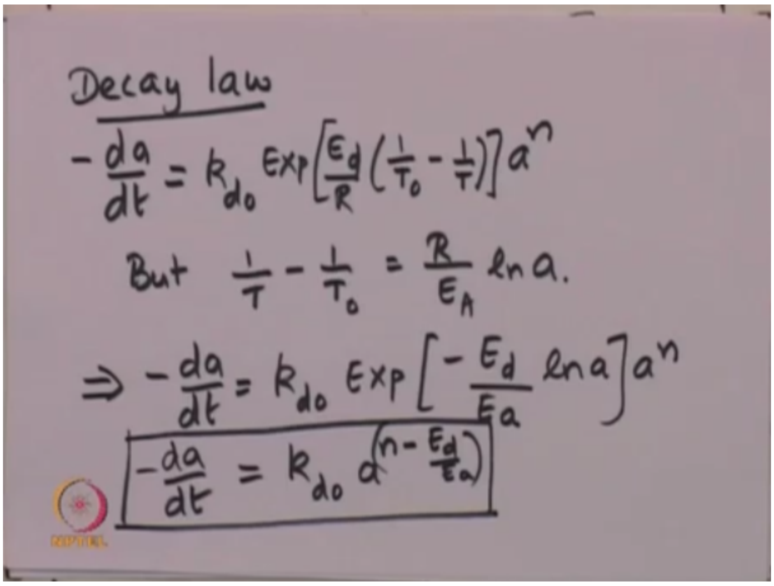
$$\Rightarrow \boxed{\frac{1}{T} = \frac{R}{E_A}\ln a + \frac{1}{T_0}}$$

So now, if you assume that it is a first order reaction; and also, if we neglect the concentration variations, then we can write k of T nought into C A should be = the activity of the catalyst multiplied by the k that is the specific reaction rate at a particular temperature multiplied by the corresponding concentration C A. So, if we neglect the variations in the concentrations, then we can write that K T nought should be = a into k of T.

But we know from the Arrhenius dependence of the specific reaction rate that we can rewrite this expression as k into T nought. That is = a into k T nought, multiplied by exponential of E A which is the activation energy for that reaction divided by R into 1 by T nought – 1 by T. So, cancelling these 2 we can write, we can now find an expression that relates the local temperature that is the temperature at which the reactor is being operated with the activity and the temperature when the reaction was started.

So, 1 by T should be = R by E A which is the activation energy of that particular reaction into lon a – + 1 by T nought. So, this is the relationship between the temperature at which the reactor has to be operated and the activity as a function of activity and the initial temperature T nought. So now, if we look at the decay law which basically characterises the deactivation of the catalyst.

(Refer Slide Time: 17:45)



Decay law

$$-\frac{da}{dt} = k_{d_0} \exp\left[\frac{E_d}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]a^n$$

But $\frac{1}{T}-\frac{1}{T_0} = \frac{R}{E_A}\ln a.$

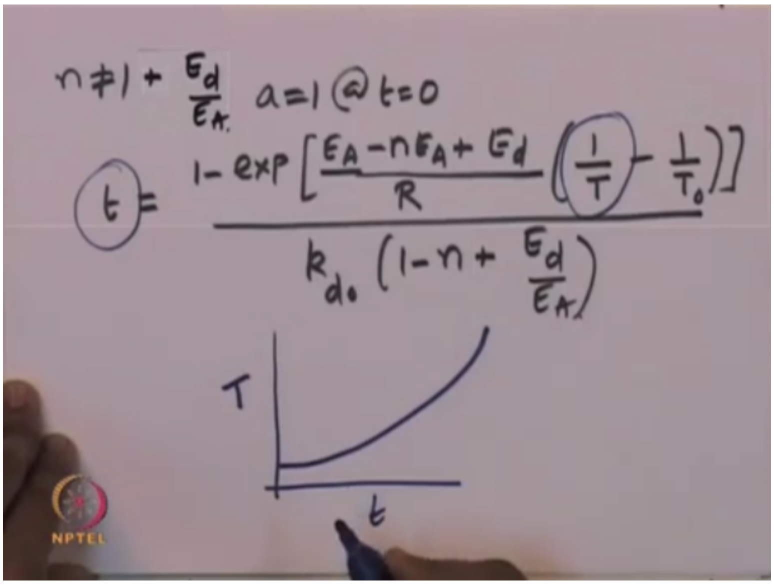
$$\Rightarrow -\frac{da}{dt} = k_{d_0} \exp\left[-\frac{E_d}{E_a}\ln a\right]a^n$$

$$\boxed{-\frac{da}{dt} = k_{d_0}\, a^{\left(n-\frac{E_d}{E_a}\right)}}$$

So, if we look at the decay law; so, – d a by d t is given by k d nought multiplied by exponential of E d by R which is again the specific decay constant is also depends on temperature using the Arrhenius type expression into 1 by T nought – 1 by T multiplied by a to the power of n. But, we know using the rate law we can relate the temperatures using the expression 1 by T – 1 by T nought. That is = R by E A into lon a.

So, by substituting this expression, we find that – d a by d t, that is = the specific deactivation constant multiplied by exponential of – E d which is the activation energy for the deactivation of the catalyst multiplied divided by E a into lon a into a to the power of n. So, this is = k d 0 into a raised to the power of n – E d by E a. So, this expression provides a way to find out what is the dynamics of the activity as a function of time. Now, if n is not = 1, that is the order of the decay or deactivation as a function of the activity is not = 1.

(Refer Slide Time: 19:41)



$n \neq 1 + \frac{E_d}{E_A}$ $a = 1$ @ $t = 0$

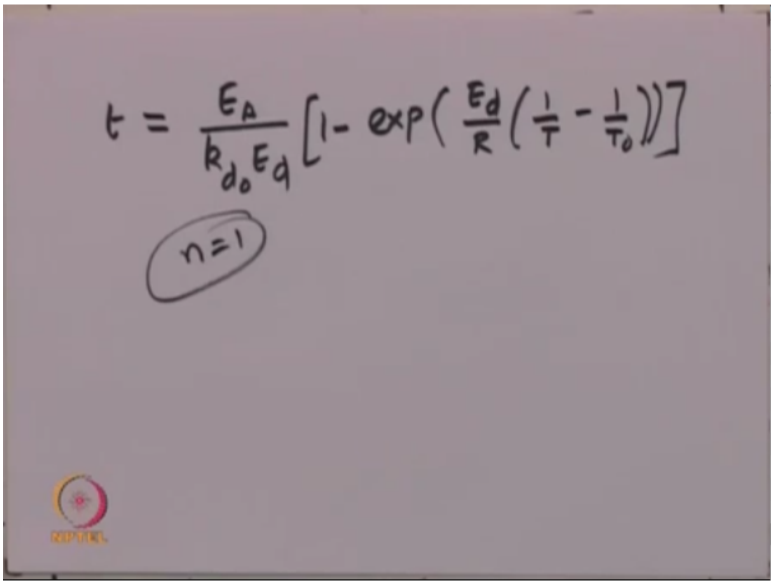
$$t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}\left(1 - n + \frac{E_d}{E_A}\right)}$$

Then, with assuming that the activity is 1 at time t is = 0, the expression can be integrated and found that t = 1 – exponential of E A divided by E A – n into E A + E d. That is the activation energy for the decay divided by R, into 1 by T – 1 by T nought, the whole divided by k d 0 into 1 – n + E d by E A. So, this provides, this expression provides a relationship as to how the temperature has to be changed as a function of time.

So, this provides a relationship of how the temperature has to be increased in order to maintain a certain fixed conversion or desired conversion. Note that this relationship is valid only for independent deactivation. So, this kind of an expression provides an industry operating person as to how much the temperature has to be increased or how much preheating has to be done in order to maintain the conversion of the desired products.

So now, if I look at the if I plot this as a function of time and temperature; so, this is the kind of profile that you will, that I will get. So, if the catalyst deactivation is very slow, then I can maintain the conversion by actually increasing the temperature of the gas that comes into the reactor and the kind of profile and the kind of temperature in raise as a function of time is captured in this graph here. So, suppose if it is a first order decay process, if the deactivation kinetics is directly proportional to the catalytic activity and if the exponent is 1.

(Refer Slide Time: 21:39)

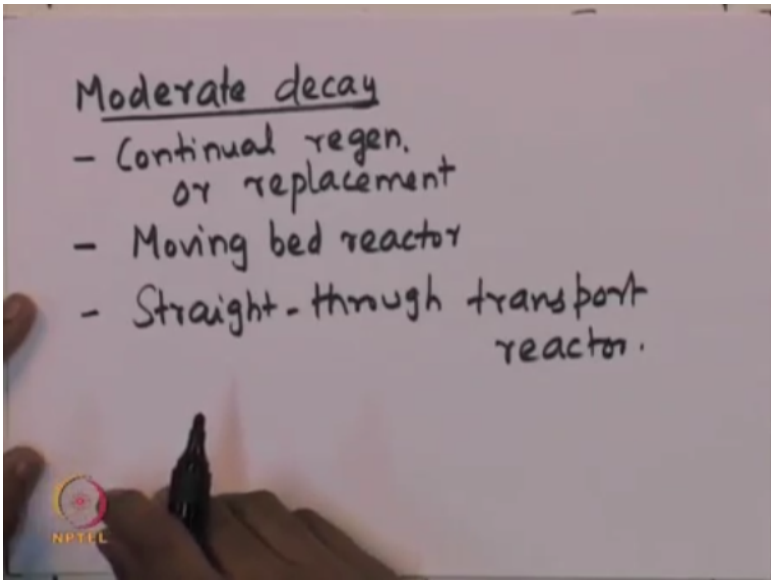


$$t = \frac{E_A}{k_{d_0} E_d}\left[1 - \exp\left(\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)\right]$$

$$\boxed{n=1}$$

Then the relationship between the temperature and the time at which the temperature has to be changed is given by E A divided by k d nought into E d multiplied by 1 – exponential of E d by R into 1 by T – 1 by T nought. So, that is the expression one would get and that sort of tells you what is the how the temperature has to be increased as a function of time when n = 1. That is the, that is basically the first order dependence on the, of the deactivation kinetics on the activity of the catalyst. Now, as a next step we look at what is the, what kind of configuration that one has to use if the decay is moderate or a rapid deactivation of the catalyst.

(Refer Slide Time: 22:32)

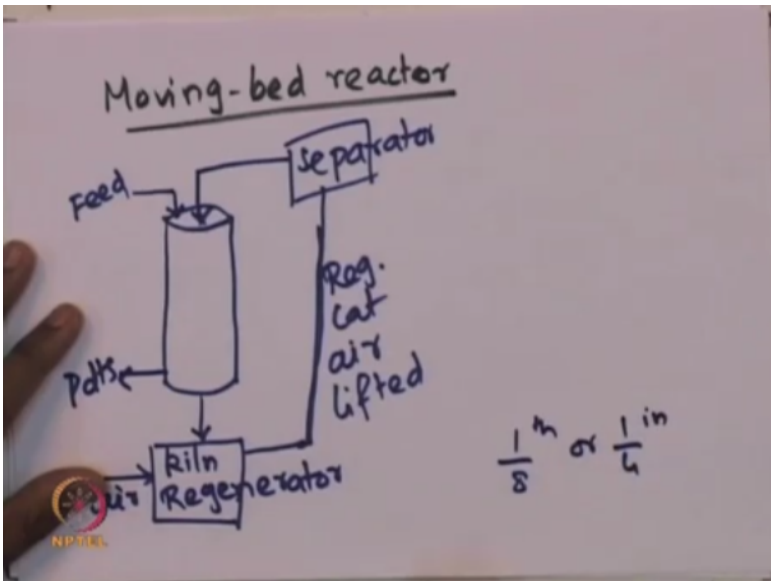


Moderate decay
- Continual regen. or replacement
- Moving bed reactor
- Straight-through transport reactor.

So, if you look at the moderate decay case, what is required here is because the deactivation is fairly quick, fairly rapid, then there has to be a continuous regeneration or replacement of the catalyst inside the reactor in order to maintain a certain conversion, certain desired conversion of the products, a certain desired conversion. And therefore the, it is require, it is important to have a continual regeneration or replacement of the catalyst.

And there are 2 types of configuration, 2 reactor configurations have been used. So, one is the moving bed reactor. And the second one is the straight through transport reactor. Straight, these are the 2 types of reactors which is useful when there is a moderate or rapid decay of the catalyst which is used in the catalytic reaction. So, the moving bed reactor in the way they could;

(Refer Slide Time: 24:03)

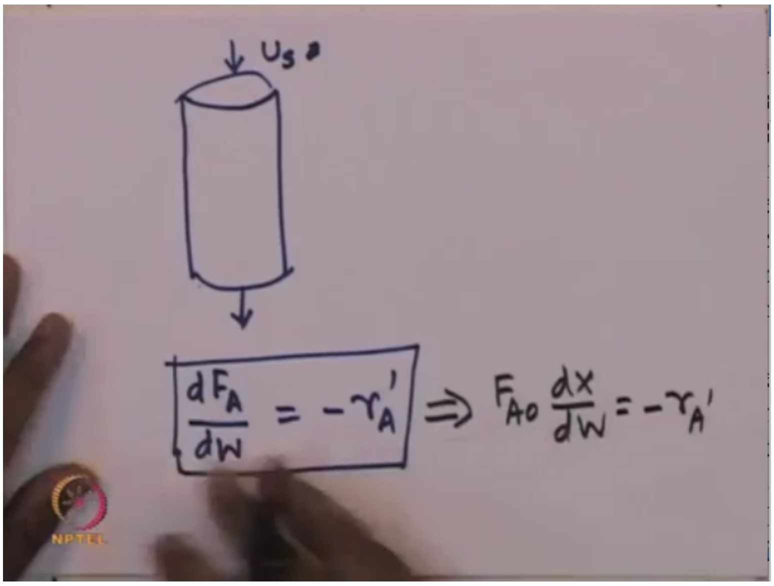


This is the moving bed reactor is basically a reactor where the catalyst is constantly replenished. And the way the catalyst is replenished is: Suppose, if this is the reactor, it is a cylindrical tube reactor. Suppose this is the reactor and the feed to the reactor is provided from the top. And the catalyst leaves the reactor and enters another chamber which is called a kiln. And this is used as a regenerator which regenerates the spent catalyst which is deactivated.

And air is passed through this regenerator. And once the catalyst is regenerated, the regenerated catalyst is circulated back. The regenerated catalyst is airlifted into another chamber which is called the separator chamber; so, it is a separator; into the separator chamber. And once the catalyst goes into the separator chamber, it pumps the catalyst back into the reactor. So, this is how the replenishment, constant replenishment of the catalyst occurs in a moving bed reactor.

And this helps in maintaining the conversion and the products are removed from the bottom of the reactor. So, the pellets, the catalyst pellets that are typically used is about 1 eighth inch or a 1 fourth inch. That is the tire typical size of the catalyst pellets that is used in these kinds of reactors. So now, let us try to write model equations in order to characterise the moving bed reactor and thereby maintain the conversion of the reactants into products.

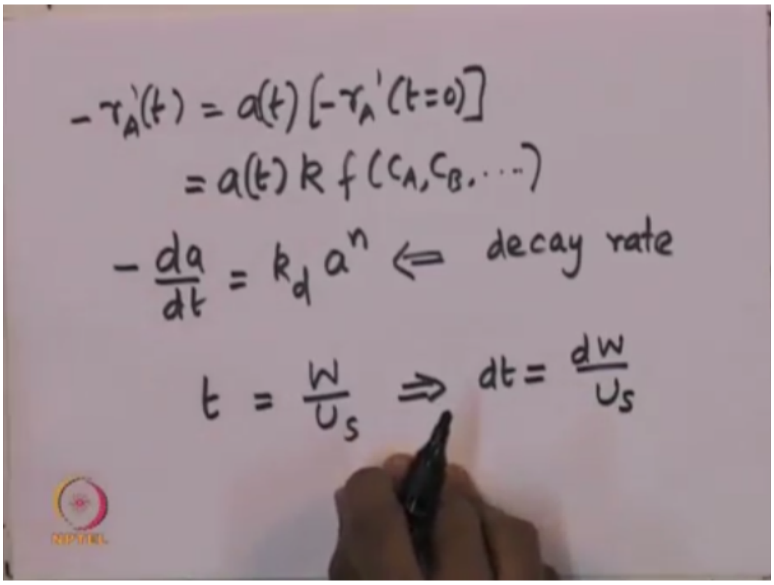
(Refer Slide Time: 26:08)



$$\boxed{\frac{dF_A}{dW} = -r_A'} \Rightarrow F_{A0}\frac{dx}{dW} = -r_A'$$

So, suppose if this is my reactor, and if the catalyst enters the reactor at a rate of U S. That is the mass of catalyst per unit time. And if it leaves at the same rate, then one can write a molar balance and obtain a an equation for the molar flow rate of the catalyst, molar flow rate of the species as a function of weight of the catalyst. So, this equation molar balance actually captures the dependence of the molar flow rate on the weight of the catalyst. And so, this can be rewritten as F A nought into d X by d W = – r A prime.

(Refer Slide Time: 27:10)



$$-r_A'(t) = a(t)\left[-r_A'(t=0)\right]$$

$$= a(t)\, k\, f(C_A, C_B, \cdots)$$

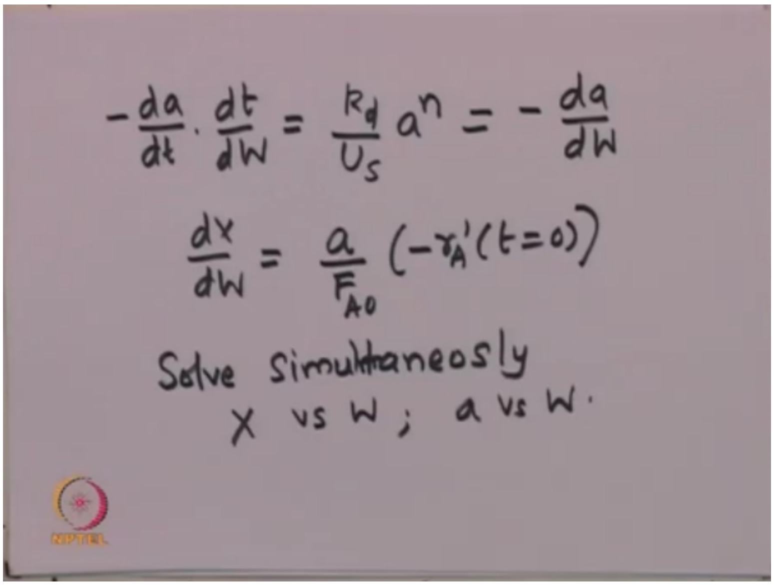
$$-\frac{da}{dt} = k_d\, a^n \Leftarrow \text{decay rate}$$

$$t = \frac{W}{U_s} \Rightarrow dt = \frac{dW}{U_s}$$

Now the rate of the reaction is now, can be written as – r A prime is = some activity of the catalyst a multiplied by the rate of the reaction at time t = 0. So, therefore it can be written as a of t into the rate constant k multiplied by some function of the concentration C A, C B etcetera. And the deactivation kinetics is given by d a by d t is = the deactivation rate, rate constant multiplied by a to the power of n. So, let us assume that this is the decay model. This is the decay rate.

This decay rate law is a simplified form and in general the decay rate can depend on reaction / product concentration. And so, the contact time needs to be related with the weight of the catalyst in order to characterise this particular reactor. So, the contact time of the reactor, contact time of the catalyst t is given by W by U S. And from here we can estimate that the, at a differential time the amount of catalyst that enters the reactor is given by d W by U S. So, from here, we can now rewrite the mole balance in terms of the catalyst which enters the reactor and also the decay rate law accordingly.

(Refer Slide Time: 28:44)



$$-\frac{da}{dt}\cdot\frac{dt}{dW} = \frac{k_d}{U_s}a^n = -\frac{da}{dW}$$

$$\frac{dX}{dW} = \frac{a}{F_{A0}}\left(-r_A'(t=0)\right)$$

Solve Simultaneosly

X vs W ; a vs W.

And the decay rate law is now given by d a by d t into d t by d W = k d divided by U S into a to the power of n. And that is nothing but d a by d W. So, that relates the, at decay of the catalyst as a function of the catalyst that is entering the reactor. And d X by d W is given by a by F A nought into – r A prime at t = 0. So, one has to solve these 2 equations simultaneously, these 2 equations need to be solved simultaneously to obtain X versus the weight of the catalyst and a versus the weight of the catalyst.

So, that characterises the moving bed reactor. So, once we know this, we can use this in design parameters in order to appropriately design the catalyst. So, what we have seen in today's lecturer is we have summarised the different types of deactivation of the catalyst. That is sintering ageing, fouling or coking process and poisoning of the catalyst. And we looked into the details of the mechanism of 2 types of poisoning.

One is poisoning if the poison is present in the feed or if the reactant or the product itself acts as a poison. And then we looked at a fluidized CSTR to incorporate the decay law which is based on the poisoning of the reactor and then poisoning of the catalyst. And then we proceeded to look at what are the different reactor configurations have to be used depending upon, because it depends upon the nature of the deactivation.

If the deactivation is slow then one can use the temperature time trajectory reaction system. Or if it is moderate or a fast reactor, one has to fast decay, then one has to use a moving bed reactor or straight through transport reactor. Thank you.