Advanced Chemical Reaction Engineering

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Lecture - 11
Catalyst Deactivation – I

Welcome to this edition of chemical reaction engineering. In this edition will be looking at deactivating catalytic systems are of course, I mean deactivating catalytic systems are not new to us. I mean chemical process industry has may great straights in this areas of catalyze catalysis and, so on. But our concern here is how do we deal with designs for deactivating catalyze and then how do we manage systems in which there is catalyze deactivation and, so on. So, will try to go through this in a simple way, so that we get a grip on what happens in, so on.

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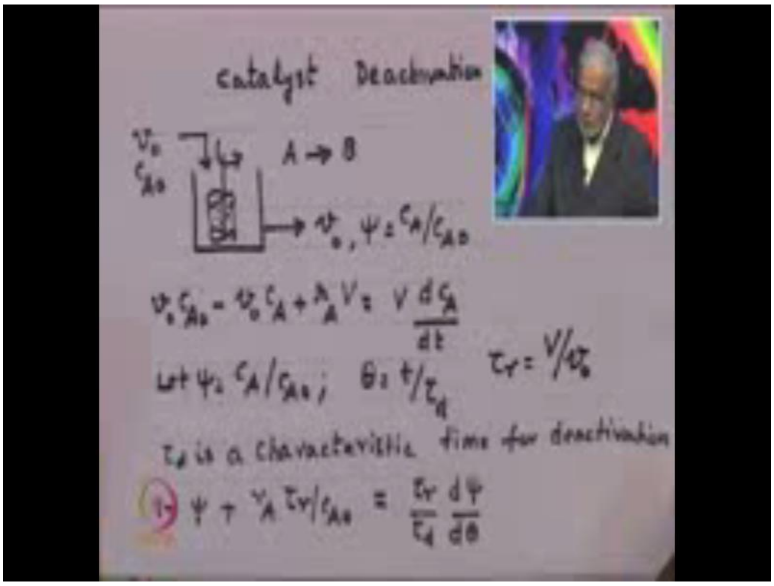

Catalyst Deactivation

v_0, C_{A0} ; $A \to B$; $\to v_0, \psi = C_A/C_{A0}$

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

Let $\psi = C_A/C_{A0}$; $\theta = t/\tau_d$ $\quad \tau_r = V/v_0$

τ_d is a characteristic time for deactivation

(1) $1 - \psi + r_A \tau_r / C_{A0} = \frac{\tau_r}{\tau_d} \frac{d\psi}{d\theta}$

So, we will begin at let us look at this problem of our interest is that we have a catalyst which deactivates. And we want to understand what is the kinetics of catalytic deactivation why this, required? It is required, because that data would be that model, the data whatever is useful for us to design systems in which catalyst undergoes deactivation. So, to be able to quantitate situation like this what we got here is a stirred tank there is a stirrer and the ban the stirrer has small basket which contains the catalyst. Now, this stirrer is spinning the idea of making expensive, so that the temperature and conversation inside the equipment remains reasonably the same everywhere. So, that our data can be meaningfully useful rather purposes we have feet coming in at a certain concentration and going out of certain concentration. And that is the reaction density taking place inside this equipment. And we want to quantitate the extent to which catalyst deactivates we want to make seeks measurement, so that we make use of it in other systems designs and, so on. So, we able to do this I have little down the material balance for material coming in input its output v naught c naught is the inputs.

So, many moles per time are going out and this is the rate at which chemical reaction is occurring where r A is a rate function v is the volume of the equipment. In this case this volume refers to volume of the catalyst. And this is the euquimulation term which is v term d by d t as c A of taking v outside the derivative, because v is constant without taking the outside. And I have written v naught same as the inlet in the outlet and the assumption that that is not much volume change because you looking at the reaction which is A to B. Now, we want sort of taking forward by way some simple manipulations. So, I set this psi is c A by c A 0 is not dimensional and I have define a what is called as characteristic time tau d is the characteristic time for deactivation what is mean by characteristic time? For example, in our commercial processes or catalyst perhaps loss per year sometimes 2 years why the reaction time? That means the time that these gases spread inside the equipment and the time these gases spreading inside the equipment it generally quite small.

But what is really great interest was is what is the time for which the catalyst would last. So, it next senses for us we able to look at what happens to this equation in the time scale of deactivation that time scale is taken as tau d what is tau d? Tau d is the characteristic time for deactivation for example, if the catalyst lost for 1 year our characteristic time is 1 year that is the meaning of tau d. So, what we have done here is that we have done non-dimensionalsation of urological time d with respect to the characteristics time for deactivation that is theta. So, what we have done? We defined a variable psi this c A by c A 0 we defined a variable theta which is t by tau d therefore, we can now, write this equation in form like this 1 minus psi r A tau r c A 0 tau r by tau d d psi by d theta what is tau r? Tau r is volume of by v 0. In this case this v refers to the volume of catalyst that we have put inside the equipment. Now, if you look at this equation here let me go to the next line, because that.

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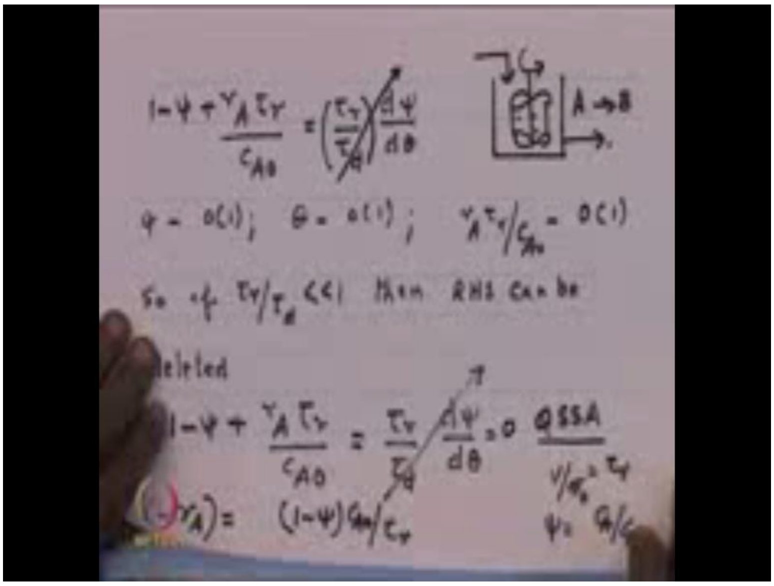

$1-\psi+\frac{r_A\tau_r}{c_{A0}}=\cancel{\left(\frac{\tau_r}{\tau_d}\right)}\frac{d\psi}{d\theta}$

$\psi = O(1)$; $\theta = O(1)$; $r_A\tau_r/c_{A0} = O(1)$

So if $\tau_r/\tau_d \ll 1$ then RHS can be deleted

$1-\psi+\frac{r_A\tau_r}{c_{A0}}=\cancel{\frac{\tau_r}{\tau_d}\frac{d\psi}{d\theta}}=0$ QSSA

$(-r_A) = (1-\psi)c_{A0}/\tau_r$

$V/q_0 = \tau_r$

$\psi = c_A/c$

So, we have the unsteady state representation of us state time we have a state time. Here that is not forget our system we have this state tank our catalyst are sitting here material is coming in material is going out it will do action A by to B. So, this represent 1 minuses psi r A tau c A by c A 0 equal to tau r by tau d d psi by d theta is this statement of the unsteady state material balance for the material happening inside this reaction equipment. Now, if you look carefully what will be find? We find that the order of magnitude of psi is the order of magnitude is 1 why it is 1? psi is c A by c A 0 at that psi can go to 1 I mean c A by c A 0 can be 1 therefore, values are roughly of the order of magnitude 1. If you look at theta this ratio at best can be 1, so the order of magnitude is 1. Once again we recognize this r A tau r by c A 0 what is tau r? Tau r some kind of a reaction time we can all say the inverse of the reaction time great constant therefore, what this whole thing refers to is that is some kind of a radio of reaction rate at divide by the maximum reaction rate that is the kind of meaning is gives also has an magnitude of 1.

So, what we saying is that in this unsteady state representation of the material balance for the third tank all the terms are first terms is magnitude 1 order of magnitude 1 order of magnitude 1 order of magnitude 1 order of magnitude 1 order of magnitude 1. Only thing that is not this tau r by tau d you see all terms being of the order of magnitude of 1. IF any of this terms at very small we can knock them out. For example, if we find this term tau r by tau d is very small. Then we can knock out this tau that is the point we trying to get a gross what we saying is that and the non dimensional representation we able to look at the values of the each term. And says the order of magnitude is it all made of 1 any term which is very small we can knock out and therefore we can understand what happening to this system and goes conditions and which this particular Assumption holds on. Other word in this particular case tau r by tau d less than 1 means that is this right hand side can be knocked out therefore, we can look at the material balance as equal to 1 minus of psi r A tau r by c A 0 equal to 0 equal to 0. Since the right hand is near very small we call it is equal to 0.

Then this equality becomes 0 we call this as the quality steady state approximation. On other words what we trying to say here is that and the condition the tau r by tau d is very small the accumulation inside the reaction equipment can be neglected. Therefore, we might be able to quite satisfactorily say that 1 minus of the psi plus r A times tau r by c A 0 equal to 0. On other words we can say r A equal to 1 minus of psi multiplied by c A 0 divided by tau r. So, what we trying to say here is the fouling. Now, here it is an instant of a reaction with under goes with a catalyst under goes the deactivation which means what? The reaction rates keep on changing, because the catalyst is losing it is activity. Now, our interest in this whole problem is we able to measure this catalyst deactivation and quantitate this through a model with this why we are doing all this experiment. So, what we are saying now, is that under conditions where tau r by tau d is very small tau r by tau d is very small. Accumulation of material inside the equipment is very small therefore, we can neglect it.

And therefore, reaction rate r A can be measure simply by measuring the right hand side. Do will know the right hand side the answer is we know c A 0 we know psi, because psi is c A by c A 0 c A is will be measure tau r what is tau r? tau r is simply v by v 0 we said all these v by v 0 is tau r. And then psi is c A by c A 0 and both these are measured quantities. And as a result we able to measure the reaction rate and at anytime therefore, use the catalyst deactivates which means the reaction rate gives changing with time. Now, we are able to measure what is the reaction rate ((Refer Time: 09:49)) of time, because all the points all the quantities in the right hand side is known to cut this long story short. What we are trying to say here is even for the case F a deactivating catalyst. Under Assumption of quality study state which means that the accumulation inside the equipment is small we can measure reaction rate simply by measuring psi which is c A c

A by 0 c A is measured c A 0 is measured tau r is measured. Therefore, all the quantities in this right hand side is known. And therefore, reaction rate is known therefore, we are able to quantitate reaction rate of the function of time this is what we are trying to say having said this. So, what we are saying now, we have a catalyst which is deactivating our interest is to measure how this deactivation is taking place? For doing that what are we doing? We are measuring reaction rate.

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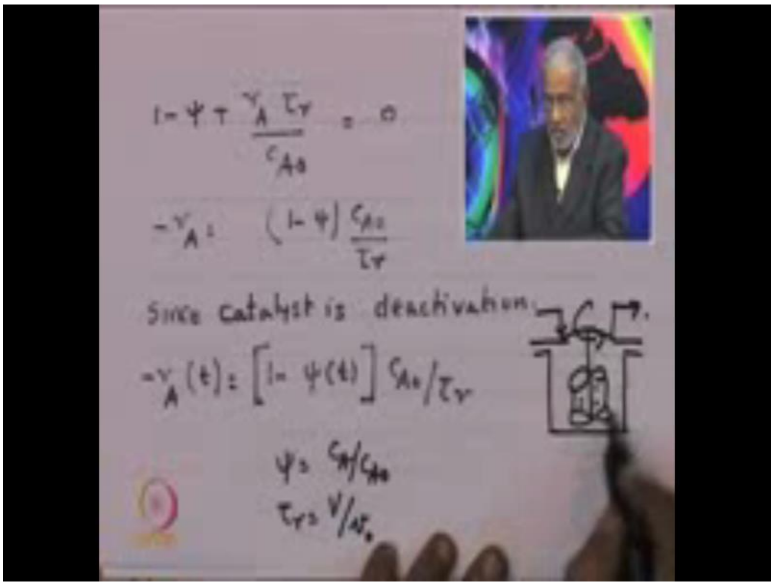

$$1 - \psi + \frac{r_A \tau_r}{c_{A0}} = 0$$

$$-r_A = (1 - \psi) \frac{c_{A0}}{\tau_r}$$

Since catalyst is deactivation

$$-r_A(t) = [1 - \psi(t)]\, c_{A0}/\tau_r$$

$$\psi = c_A/c_{A0}$$

$$\tau_r = V/v_0$$

How do we measure reaction rate? By measuring all the quantities on the right hand side what are the quantities on the right hand side psi which is c A by c A 0 which is c A by c A 0. And then tau r which is v by v 0 v is the volume of the catalyst v is the volumetric flow. Therefore by measuring on men the quantities in the right hand side we are able to measure reaction rate at the functional time. Therefore, the data that is required for us to quantitate catalyst deactivation is in front of us. That is the advantage of what will call as a state tank. State tank as you can see here this state tank, because we are able to put our catalyst inside this basket. We are able to split around we can put it in an equipment and put our material inside. And then take out of material and by appropriately changing this storage excreta we can measure reaction rates reaction rates, but different conditions of the system of our interest. Having said this let this look at some interesting features that might be a interest to us.

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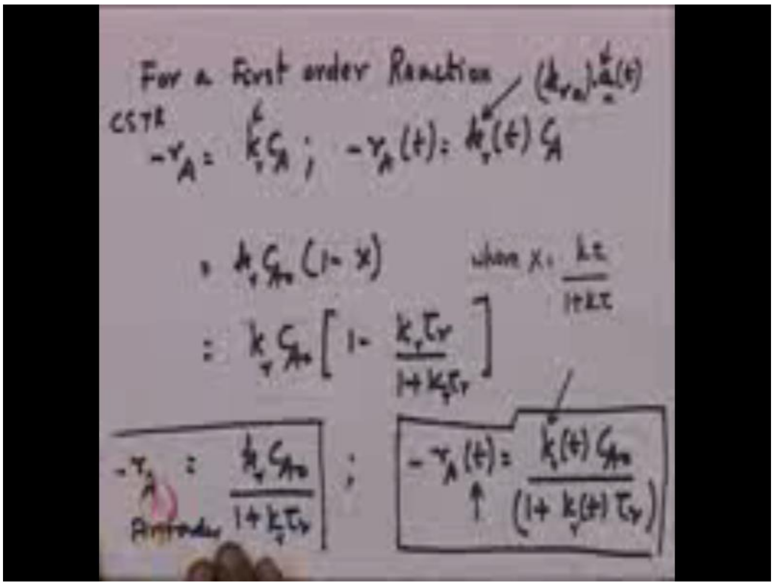

For a First order Reaction

CSTR

$-r_A = k_r C_A ; \quad -r_A(t) = k_r(t) C_A \quad (k_{r0}) \cdot a(t)$

$= k_r C_{A0} (1 - x) \quad$ when $x = \frac{k\tau}{1+k\tau}$

$= k_r C_{A0} \left[1 - \frac{k_r \tau_r}{1 + k_r \tau_r} \right]$

$\boxed{-r_A = \frac{k_r C_{A0}}{1 + k_r \tau_r}} \; ; \; \boxed{-r_A(t) = \frac{k_r(t) C_{A0}}{(1 + k_r(t) \tau_r)}}$

[illegible]

Let us say if this reaction of that we are studying A goes to B let us say this is the first order reaction. If this is the first order reaction we know from our basic understanding that the rate the x the conversion is given by k tau divided by 1 plus k tau. On other words if it is the first order reaction then our conversion does not depend upon concentration. It only depends upon what is call as the residence time and the reaction rate constant that is were as first order reaction. Suppose you have a second order reaction you notice for second order reaction we can do all these. The extent of reaction x depends upon what is the composition at the inlet? Depends upon the composition at the left for the PFR this for A PFR this is for a CSTR. This is our rating for a CSTR what I am trying to say here is we can devise experiments to understand what is the extent to which reactions occurring? We can measure those reactions depending upon the devise. If it is the CSTR we measure conversion like this if it is the PSR and the second order reaction we measure conversation like this.

So, depending upon the order of reaction the dependents of concentration with appears suitably in our expression for conversion, in our expression for a constant for the rate of reaction. For example, if we our PFR and if we our rate function is k c A squared as a return here then the rate function will contain the concentration term in the second part. So, these things you know the point of trying to draw this attention in this case is that if we have a first order reaction then there are certain benefits in terms of managing it. If it is second order there is little bit more complicated if you want to draw attention to those differences by quite in this out. Let us continue let us say we continue with our first order representation for the movement. So, we have a first order reaction in which the catalyst and goes the activation. Now, if you say that the rate of reaction r A is given by k r times a were k r is the rate constant then we know that, because of this of the deactivation this rated which comical reaction occurs changes.

It changes, because this rate constant to changing with time see that is why we are seeing the fact of the changes in the rate constant, because of that the reaction lost in changing. Now, I just put it is likely different form make it easiest to understand, so I would put it in this form r A which is rate of chemical reaction is k r times c A. And I have replace a in this form, because we know all these from our first order understanding. Therefore, the rated which chemical reaction occurs for a first order process is given by this. And then since the deactivation is occurring we can now, see that the reaction rate at anytime depends on the rate constant k r which is the function of time multiplied by c A 0 divided by k r is the function of time multiplied by the residence time. Now, sometimes it is difficult to understand this why is rated constant of function of time? The rate constant is function of time is, because our rate constant actually consist of a k r 0 multiplied by a term which is called activity. Because of the fact that this activity is the function of time this product is the function of time.

This is why we see, because this k r is the function of time, because k r is k r 0 is multiplied by this activity which is changing, because of the process we find that reaction k r is changing which time. Because a which changing it is time and therefore, reaction rate is changing which time. So, what is that we are saying now? But if we have a catalyst which is deactivating then reaction rate would changing time our interest in the whole exercise is that can we quantitate. And find a model which takes care of this deactivation phenomenon. If you can do that then the lot of thing that we do in reactive design operation evaluation and, so on which make the whole thing much easier. And that is the object of this particular module. So, call stating at once again we are used stating that reaction rate is k r c A 0 divided 1 plus k r tau for the first order reaction first order first order in a CSTR. All these are in a CSTR we are, so these all in a CSTR. Now, if this reaction is undergoing deactivation then we recognize that this is going to change with time, because k r is going changing with time. So that is only, so these 2 are representations in which in here we have recognize the deactivation occurring. Here we have recognize the deactivation is not occurring see we have 2 say statement of the same situation what we saying now what we saying now?

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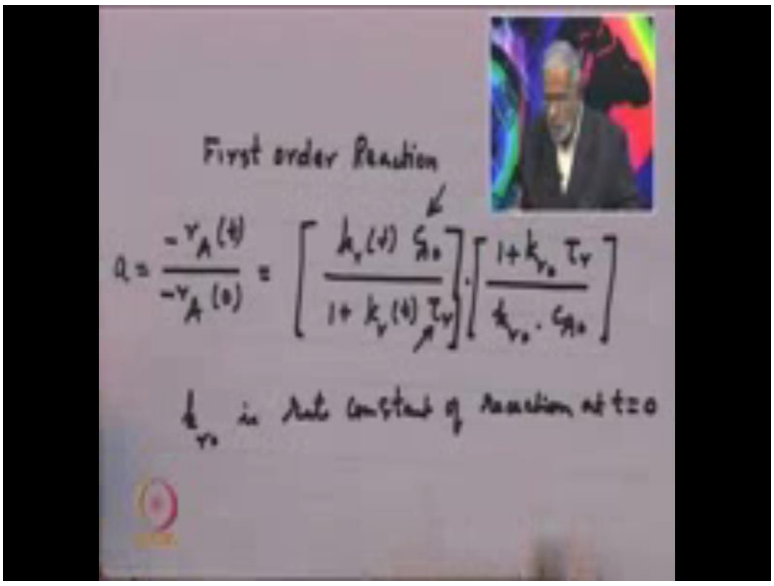

First order Reaction

$$a = \frac{-r_A(t)}{-r_A(0)} = \left[\frac{k_r(t)\, C_{A0}}{1 + k_r(t)\, \tau_r}\right] \cdot \left[\frac{1 + k_{r0}\, \tau_r}{k_{r0} \cdot C_{A0}}\right]$$

k_{r0} is rate constant of reaction at t=0

We have said just now that reaction rate is changing with time. So, we would like to know what is the reaction rate at any time divided by what is the reaction rate at the 0 time. So, what is the meaning what meaning can we attach to reaction rate at any time to reaction rate at 0 time? By definition it is activity of the catalyst, so we can say the this is the activity of the catalyst. The activity the catalyst is reaction rate at anytime divided by reaction rate at 0 time. Now, just now we derived what is reaction rate at anytime which is these function k r c A 0 divided by 1 plus k r tau and what is reaction rate at 0 time? It is 1 plus k r c A k r 0 which means that at 0 time we have taken this k r As k r As k r 0 and therefore, average little this form. So, if we ask you know this quantity r A what is the functionality on which this function this a depends? Now, we can tell by looking at the right hand side that the right hand side depends on number of factor very clearly depends upon temperature. Because k r is involved very clearly we can expect ((Refer Time: 18:36)) depends upon concentration, because c A 0 is involved. Now, we can say since tau r is involved.

So, we can in general say that this function this quantity A depends upon the composition of the system in which the reaction is taken place which is temperature and composition. Now, that composition is determine by residence time therefore it as the indirect depend upon dependence on the residence time. So, what we are trying to say here is that we want to quantitate how activity of the catalyst changes and what is that function which determines the determines this deactivation rate phenomena? So, if you look at the right hand side the right hand side if you can measure and quantitate then will able to get A as a function of time in data for which we can model. So, this is what you want to do in this let us go further and see what we can do with it. So, let us just look at what is the phenomena we are trying to understand?

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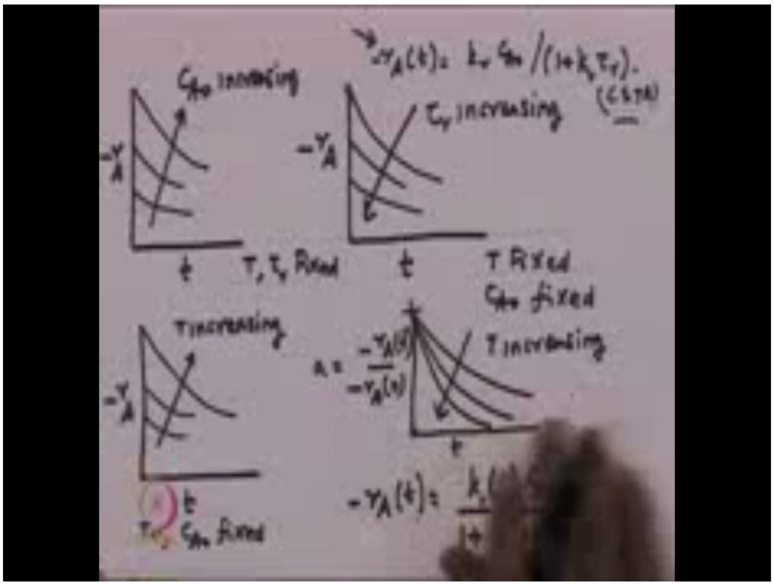

The phenomena we trying to understand is what happens to r A as a function of time as a increases? We know that just looking at i just write this function once again here, so that we can remember this we write it here r A as a function of time is for A first order K r c A 0 divided by 1 plus k r tau r this is in a CSTR all this in a CSTR. So, if you look at this function in say what happens to r A as a function of time as c A increases? We can see very clearly that the reaction rate will be increase, therefore we will get curves like this. Now, suppose we keep temperature constant c A c A 0 as constant and change or increase the residence time then we will get curves like this.

On other words for A given the 1 residence time it will be this for the higher residence time it will be this another residence time it will be this. Because the simply by looking at this expression we can tell what is the direction in which the rate function will move? Similarly when time temperature is increased will see behavior like this that at high temperature it will be like this or low temperature it will be like this. So, what we trying to say now is that? If we have a first order reaction we can measure r A is a function of time and then we can plot these to understand how the reaction rate is changing with time?

And once we do that then we can measure what is called as activity what is activity? It is reaction rate at any time divided by reaction rate at 0 time. Now, moment if do it in this form you will find that at 0 time all th the activity at 0 time should be should be 1. So, we can actually normalize we point to that we can normalize the activity as 1, so that we can plot the all the data in 1 curve. So, that is the advantage of this normalization, so what we are try to do is that we are try to conduct an experiment.

In this experiment we have done in a CSTR what is the advantage of doing this in a CSTR? We are able to take maintain temperature to that level that we want and then we are able to change the flow rates or residence time. And therefore, we can measure reaction rate under different conditions. Now, when we do reaction rate at different conditions we said that we can normalize that reaction rate at 0 time and we make plots like this. What we are saying here is that if we normalize at 0 time we can say that the activity at 0 time is 1 it is a normal cloture the activity 0 time is 1. In that case we can plot all of them using the same plot or we can plot differently, but choice is ours. So, what we tying to say is that we can plot activity as a function of time of our different conditions. Now, having done this we have activity as a function of time.

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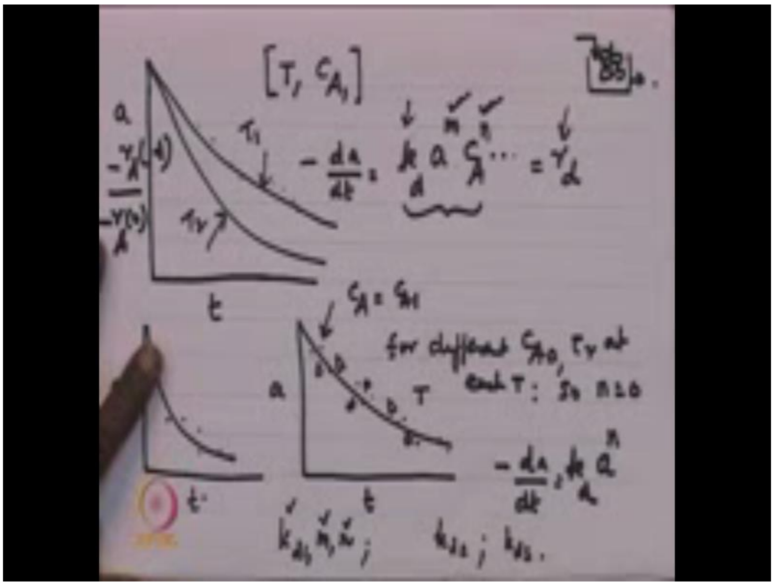

For different conditions what are the conditions under which we have done the experiments? We have done the experiments for different times, we have done the conditions for different compositions, we have done the experiments for let us say for these 2 for the moment. And maybe it is activity as, so or model we need a model let us say that model is this. The rate at which the activity changes minus of d by d t of d a by d t is this r d and r d is given by this function k d time k to the power of m c A to the power of n we do not know that function. So, we want to find out what is m, what is n, what is k d, that is our object of doing this whole experiment. Suppose we find then will you make A plot of a verses time we get a curve like this that the points like this we get a curve. Let us say this corresponds to an experiments correspondent to c A some c A 1. Now, we repeat this for Another set of experiments in which we put c A equal to some c A 2 then we get let us says all these triangles.

Let us say c A equal to c A 3 we get let us say all these star. Now, when we do a experiments and different conditions let us say this is for 1 temperature then we can do for another temperature we can do for another temperature let us say it is very sharp. A verses t some data like this, so what are essence we are able to do this experiments is that we are able to get a verses t. And, because of this experimental data we are able to determine what is the value of m, what is the value of n, what is the value of k d at different temperatures? So, what we are got some our experiments we find k d m n this, so our deactivation experiments. Essentially what is the experiment we have done r A time t divide by r A time 0 and made a plot of a verses time. And we got data at 1 temperature may be this may be temperature t 1 and this may be temperature t 2. So, from the data of a verses t be fitted the curve fitted this curve to this to this model and found out k d m and n and then k d values at 1 temperature that is a k d 1. Similarly another temperature we got k d 2 and that temperature k d 3 and, so on.

So, on other words we had value of k d at different temperatures and m and n. So, the whole object of doing this CSTR kind of experiments is that CSTR allows us to operated constant temperature comfortably. And therefore, we are able to make composition measurements comfortably we are able to make changes in the external environment comfortably. Therefore, we are able to get lot of data which panes a great variety of compositions and temperatures. So, that we can fit to this model and find out k d at different temperatures find out m and n and we think I mean most of the data is suggest that m and n values is to be main reasonably consistent across all the conditions. Therefore, we have a value of m a value of n and value of k d for different temperatures. Now, what we normally do is that we look for a dependents of temperature on and dependents of k d on temperature.

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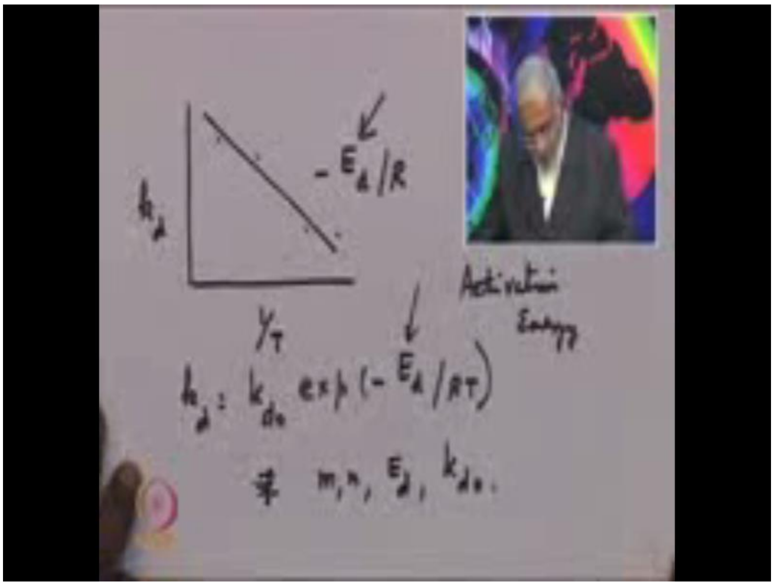

And this is something that we have learned from our early chemical kinetics that rate constants were against temperatures typically have an armies kind of dependents. And it is it is not a usual to find this kind of dependence and then we in fitted to the model like this we find what is called as the activation energy for deactivation? So, what we get from this experiments we are able to find out, because we know the value of k d at different temperatures, because they this measurements have been done different temperatures. And we found out the k d from our fitting we have plotted k d verses 1 by t and we find this kind of linearity and then from the linearity slope we find out what is e d at the activation energy for deactivation. So, to cut this long story short what we have done is the following what we have done is we have done an experiments in a CSTR. We have done measurements at different compositions in different temperatures. From that reaction rates at different temperature different conditions we have found out normalize that reaction rate with respect to 0 time reaction rate in found out activity as a functional time.

From the activity as a functional time data we have fitted to a model like this and found out the value of m n and k d this k d is the different temperatures. And then we have plotted this k d verses 1 by t and found out the activation energy for deactivation. So, that our deactivation experiments gives us what is called as m n and E d and K d 0, so these 4 parameters come from our deactivation experiments. Now, the question I mean the reason why we have done all these things is to be able to understand how deactivating catalytic reaction systems perform number 1.

Number two more importantly can we ensure that in spite of deactivation our process runs as per design. Because after All we have designed it for, so many dons per day. And if we does not give as that that many dons per day clearly in our economics stone work out for us. And our process equipments that we have put in place or not performing to the optimality that we have design for. Therefore, our prime interest in looking at catalyst deactivation is to be able to understand them number one. Of course, number two to able to make good use of that information, so that our designs or as for our requirements, now we want to address that question by just looking back at what we have done.

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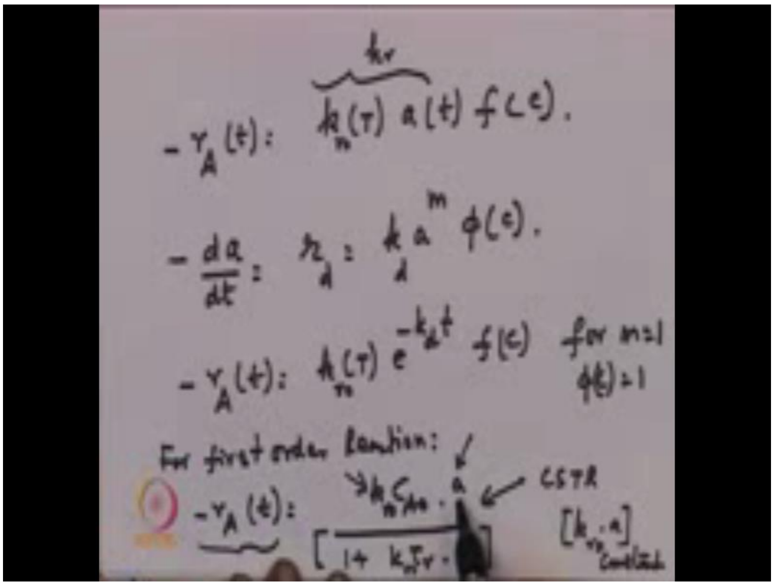

What we have done? If we recall a little earlier we said our reaction rate in we did this for the case of CSTR and just see we wrote this for the case of CSTR. We said our reaction rates can be described by k r c A 0 divide by 1 plus k r T r, so I put k r 0 here multiplied by a. So, notice here the k r 0 k r 0 times a is our k r on other words this is our k r that we have been taking about. Now, what we are trying to say here is that if I ask you I want to keep the left hand side constant irrespective of what happens to the catalyst? So, what is the kind of answer that we can think of? If r A has to remain constant which means what then only our designs will give us the production that we have design for, so left hand side must stay constant which means what?

On the right hand side the term k r 0 times a should not change, so we should have k r 0 times a should be constant. Only then the reaction rate as a function of time will not change. Only then our equipments will deliver productivity that we have design for. On the words what we trying to say here is that in the case of deactivating catalytic systems we recognize that the catalyst deactivate therefore, activity will change. But is it something we can do to ensure that k r 0 times a does not change. On other words can we see what we can do to this product k r 0 times a. So that k r 0 times a does not change a might decrease, but which means what we trying to say here is that can we increase k r 0, so that it is able to compensate for the loss of activity. This is the point that you like to investigate understand and see how best we can integrates these ideas into a design. Let us go forward what are we saying now?

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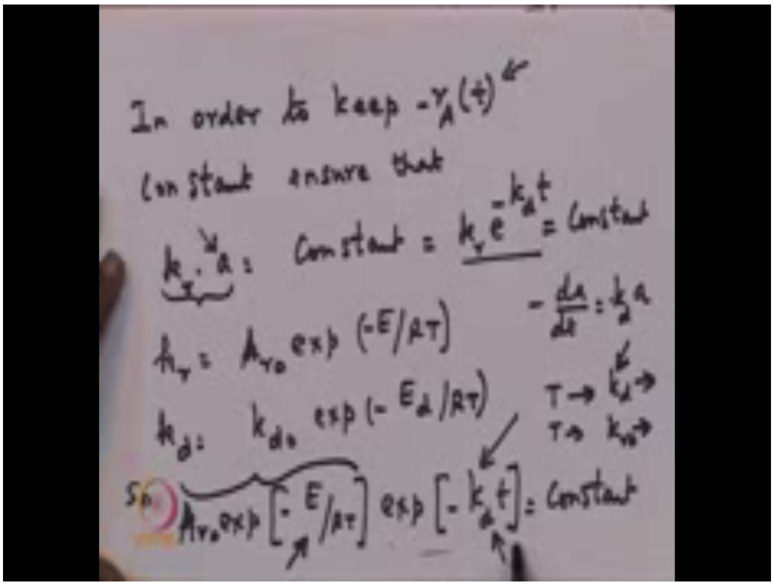

In order to keep $-r_A(t)$ constant ensure that

$k_r \cdot a =$ Constant $= \underline{k_r e^{-k_d t}} =$ Constant

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

$k_r = A_{r0} \exp(-E/RT)$

$k_d = k_{d0} \exp(-E_d/RT)$

$T \to k_d \to$

$T \to k_{r0} \to$

So $A_{r0} \exp[-E/RT] \exp[-k_d t] =$ Constant

What are we saying now is that our reaction rate r A it is changing with time and this something that we have to accept. Because as the process is running due to variety of factors on the catalyst sintering may be may be co deposition may be may be poising we do not know where it could be different situations the activity is on the way down. So, in order to be able to a null infect of decrease in activity what is being suggested is that if you can keep this k r times a constant. On other words if this product is kept constant then very clearly as you can see here when you can keep this k r 0 times k constant or we can keep k r A constant then clearly the right hand side does not change. And therefore, left hand side does not change therefore; our production will be as per design. On other words what we are trying to stay here is that the strategy for managing deactivation should be the keeping this k r times a constant. Moment we do that we have a way of managing deactivation.

Now, how do we do this? What is being is jested is if we assume that this a is decay exponentially which means what we are saying that d a by d t d a by d t equal to k d times a therefore, a is decay exponentially. If a decay exponentially then we can write k r times a equal to k r time e d t therefore, this must be held constant how do we heat keep it constant?? We keep it constant the recognizing that k r which is rate constant which is in armies k a r 0 time exponentially e by r t and k d is given by this expression. Therefore k r times a can be written as the what are written here k r 0 exponentially by r t and exponentially k d t where this k d as an armies dependents as mention here. So, if we look at the last line here what we are saying here is that while this term decreases with time to will, because of k d. This term increases the temperature, because it is very strong functional temperature. If this product as to stay constant it only means that the effect of temperature on increasing this quantity more than makes up for the effect of decrease in this term.

Because of effect of temperature let we state this once again. We know that as temperature rises as T raises k d increases and also as T raises k r also increases. But what is to been happen in real life is that increasing k r increasing k r 0s of k r 0. Because of temperature is generally much larger than the effect of k d increase in the activity of the catalyst. On other words what we saying is that when we rise take temperature from x 1 to x 2 the increasing the first term. You see this first term increases second time also may decreases you know because of raising temperature. But the increase in the first term compensates for the decrease in the second term, so that the product is kept constant. On other words what we are trying to say here is that deactivation data that we gather from our experiments gives us deactivation parameters. Similarly, reaction rate data the absence of catalytic deactivation gives you reaction rate parameters.

So, we have reaction rate parameters we have deactivation parameters what is being said is that when increase temperature, the rate constant in the reaction rate sys increases. Similarly, when you increase temperature the rate constant in deactivation also increases, but what is important to recognize is that the effect of increase in the rate constant. Because of increasing the temperature compensates for the decrease in the activity, because of increasing deactivation rate constant. So that the product can be help constant, so that our designs ensures the reaction rate does not change with time. Moment reaction rates do not change which time then our designs gives us productions that we have design for. And therefore, our economics and our optimality the excreta that we have taken to account none of them affected. We take an example to illustrate how this is actually achieved and some of the issues that arise from some of it are features. So, let me illustrate this through an example.

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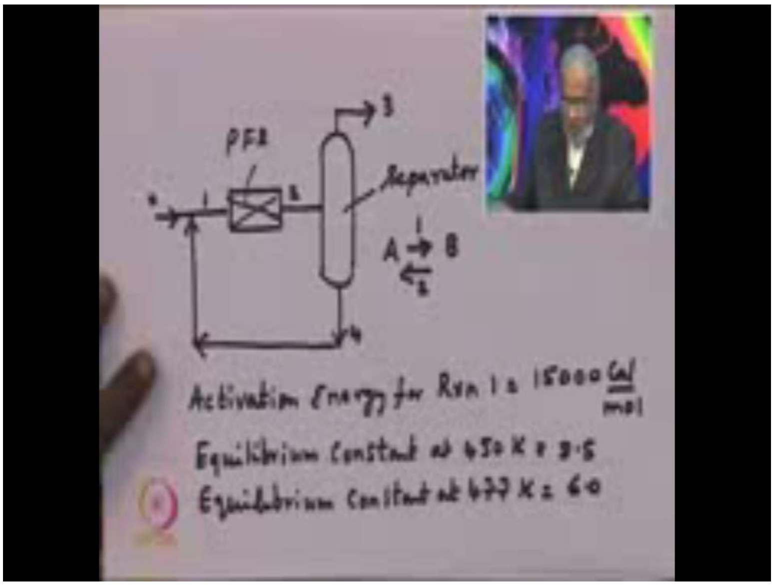

Activation Energy for Rxn 1 = 15000 $\frac{cal}{mol}$

Equilibrium Constant at 650 K = 3.5

Equilibrium Constant at 677 K = 6.0

What I want to do now, is to illustrate interesting example of catalyst deactivation that we might have to encounter in process design, process evaluation, and process optimization and, so on. So, here is an instants of a of a illustration were you have PFR is a plot floor reactor calling PFR. It has a catalyst which deactivates. Now, here is a separated what you have? We have a plot floor reactor and a separator. Now, we have this reaction A going to B, so there are A going to B in it is a reversible reaction there. For every reaction this is reaction 1 and reaction 2 and the data basic data is given activation energy for reaction 1 is given equilibrium constants are given at 2 temperatures and, so on. Now, the situation of our interest is the falling. Catalyst deactivates, so in a process in catalyst is deactivating that after sometime the activity of the catalyst is quite and not satisfactory to be able to make curve good use of the transmit equipment.

Therefore, you might want to think about disposing it and buying a fresh package of catalysts. Catalyst being expensive there are processes available in which catalyst can be regenerated. And you might want to see whether a regeneration process can be thought of, so that you can regeneration use of catalyst. Here is an instants of a problem in which problem statements says that this catalyst deactivates and then this the data and fresh catalyst is spend catalyst is available. And when you regenerated spend catalyst it has n types of activity what is important for us. In this particular problem is to find out whether the regeneration process that we have put in place is satisfactory for our economic for satisfactory for which some data is given what is the data given? The data says the following.

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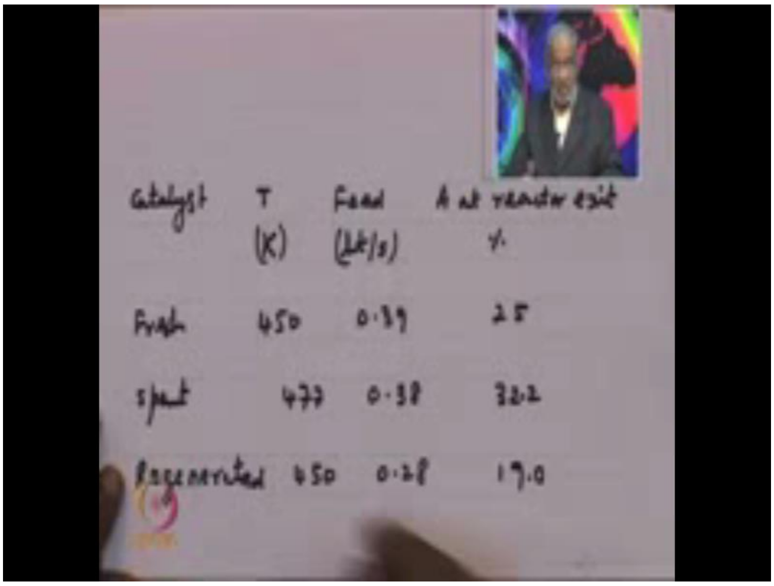

Catalyst	T (K)	Feed (Lit/s)	A at reactor exit %
Fresh	450	0.39	25
Spent	477	0.38	32.2
Regenerated	450	0.28	19.0

It’s says the following. It that here is the catalyst fresh catalyst spent catalyst regenerated catalyst the performances given. Now, we are asking to judge whether the regeneration process that we have adopted is good enough to be purchased. Now, whenever you want to evaluate we must say what is the criteria on which you will judge the regeneration process. The kind of criteria that is jested in this particular exercise is the following it is says the following.

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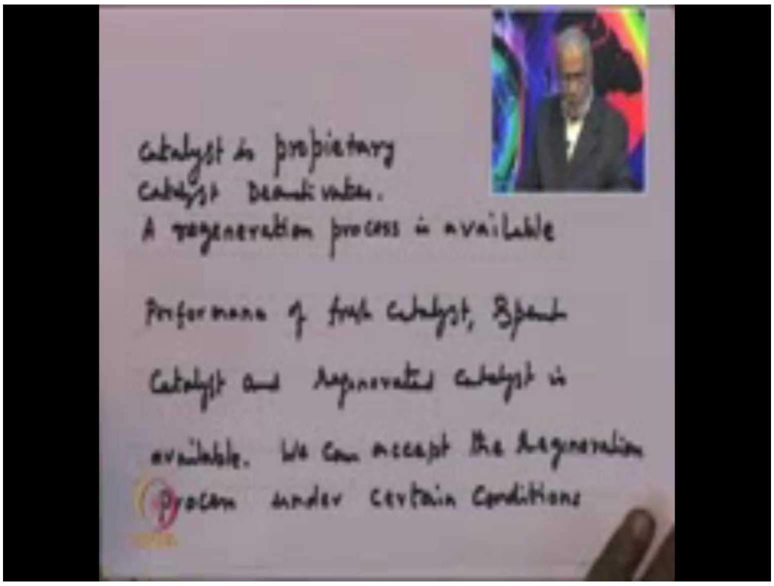

Catalyst is propietary
Catalyst Deactivates.
A regeneration process is available

Performance of fresh catalyst, Spent
Catalyst and Regenerated catalyst is
available. We can accept the Regeneration
Process under certain Conditions

It’s says the catalyst that we are using in this reactors preparatory the catalyst under goes the deactivation. And the regeneration process is available and it is says that we can accept the regeneration process.

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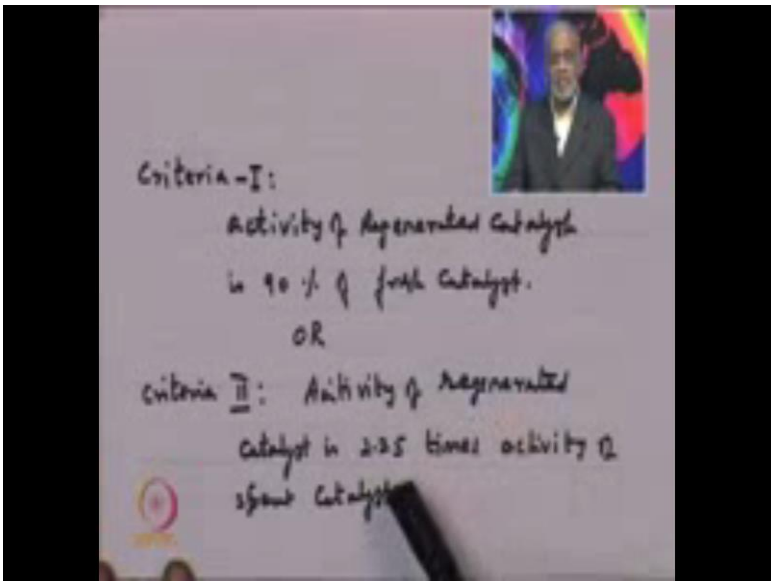

Criteria-I:
Activity of Regenerated Catalyst
is 90 % of fresh Catalyst.
OR
Criteria II: Activity of Regenerated
catalyst is 2.25 times activity of
spent Catalyst

If the regenerated catalyst has 90 percent activity of fresh catalyst what are we saying? What we saying is that we will accept the regeneration process if the activity of the regenerated catalyst is 90 percent of fresh catalyst. Alternatively if the activity of the regenerated catalyst is 2.2 5 times the activity of fresh of the spent catalyst also we will accept the process. So, what is being said is the data that is in front of us we have to evaluate the data on fresh catalyst, spent catalyst and regenerated catalyst with respect to the 2 criteria mention here which means what? We must judge the activity of regenerated catalyst estimate the activity based on the data given and see whether it is 90 present of the fresh catalyst. Or you can check the activity of regenerated catalyst and see whether it is 2.2 5 times or more then the activity of spend catalyst. If either of these 2 criteria's are meat we are willing to accept the regeneration process.

On other words what we are trying to say here is that we have to deal with deactivating catalyst in our industry. So, we need a systematic procedure to evaluate process data. Now, here is an instant of process data in front of us all the data is given to us. Now, we have to setup the design equations to see how shall we evaluate the performance of the catalyst and different conditions that is given in front of us. So, this is what we want to do now that means the following. That we have a catalyst which is fresh performs like this we have a catalyst which is spent performs like this.

We have a regenerated catalyst which is performs like this we have to see the 3 data and advise weather we should by the regeneration process if, so why if not why not? This is the kind of the questions that we want to answer. Let us get a head with this problem how do we solve this problem? Now, to be able to solve a problem in reacted design react optimization react evaluation and, so on we have to develop equations that will describe performance of this equipment. This is all once we have the equations that describe the performance then we can answer various kinds of questions. So, we will go through the algebra as it is required to set off the design equation for understanding the performance of this equipment which is a PFR containing a deactivation catalyst. Let us see how we can do this.

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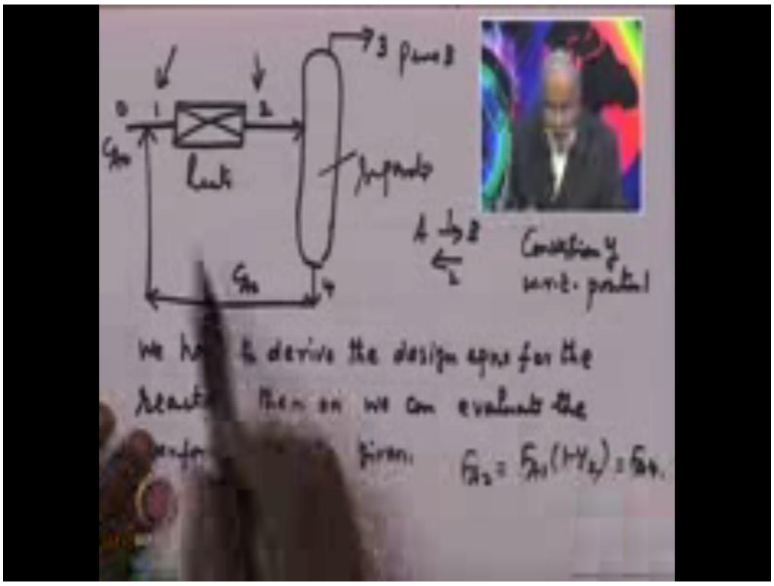

we ha[illegible] to derive the design eqns for the reacto[illegible] then on we can evaluate the perfor[illegible] given. $F_{A2} = F_{A1}(1-Y_2) = F_{A4}$.

So, to do this, so what I have done is of course, I have done this drawn this same figure once again may be a meaning. So, we have this catalyst have denoted this is 0 1 2 3 4. Now, there few things that we can recognize very quickly without losing too much time and this is the separator this a reactor. Now, this is pure B now since this is pure and this is c A 0 is coming in. So, we can say that is since B is fully recovered this stream it is only c A 0 this common sense. Because c it is B is fully recovered our reaction is a going to B and B going to A therefore, this is c A 0 it is something very elementary nothing very complicated. Now, we can write material balances at various points.

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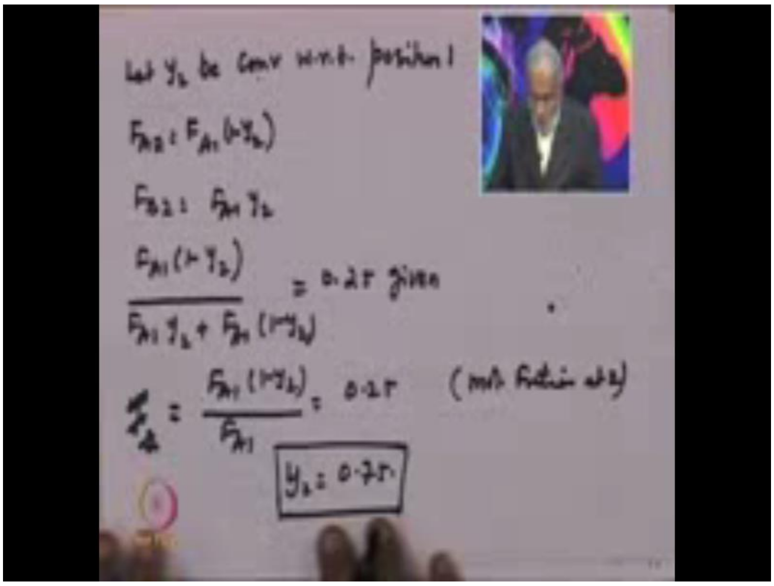

Let Y_2 be conv w.r.t. position 1

$F_{A2} = F_{A1}(1-Y_2)$

$F_{B2} = F_{A1}Y_2$

$$\frac{F_{A1}(1-Y_2)}{F_{A1}Y_2 + F_{A1}(1-Y_2)} = 0.25 \text{ given}$$

$$x_A = \frac{F_{A1}(1-Y_2)}{F_{A1}} = 0.25 \quad \text{(mole fraction at 2)}$$

$$\boxed{Y_2 = 0.75}$$

So, I have done just fairly elementary, so this is not difficult to do. So, please notice here this is 0 this is position 1 position 2. Now, we have defining conversion conversions at defining with respect to conversion y defined with respect to position 1 what do we mean/? What we mean is that if I want conversion at position 2 and our references as position 1 then I say F a 2 equal to F 4 F a 1 multiplied by 1 minus of y 2. That is what I am saying that is what I have written F a 2 is F a 1 is multiplied by 1 minus of y 2 y is dives that that is how we are defining conversion here. Similarly, if I ask you what is F b 2? Let this what is the amount of B at position 2 we say that f b 2 is F a 1 times y 2, because whatever A is disappearing it becomes b. So, it is, so F a 1 and F a 2 and f b 2 or F a 1 1 minus of y 2 and F a 1 1 minus of y 2.

If I ask you please look at this data it says composition at reactor exit is 25 percent, so if composition is 25 percent means what? This is the gas is reaction therefore, if I find mole fraction this is the number of moles they exit. So, if this is this is mole fraction y 2, so what is this equal to this is not y 2. This ratio is equal to this 1 minus F a 1 1 minus y 2 dived by F a 1, because these 2 F a 1, so this is mole fraction. So, mole fraction at 2, so mole fraction at 2 is 0.25 that is the data given please this data is given this given here. Therefore, you can find out from this that y 2 value at react to the exit is 0.75 what are we saying what we saying is that if I give you mole fraction at position 2 I can calculate conversion simply from the relationships.

Therefore, if I say mole fraction is 0.25 then conversion is 0.75. On other words what we are saying is that in this x data mole fraction at reactor exit is if 75 percent means our conversion is having 25 here. It is 32.2 mean conversion is 67.8 in this is 19 percent means our conversion is 81 percent. So, this is the kind of the data that is given that is what we are saying. So, what we are tried to say is we found a value of y 2, because that is given 2 us in the form. The data we have converted the data into value of y 2, so that we can go-ahead and doing the evaluation. Now, let us go forward what we us now, saying is what we us now, saying is all right. Now, we know how to make good use of the data only we have to write various simple expressions for various flows. So, that we can understand what is going on in the equipment? So, please once again look out our look out our figures.

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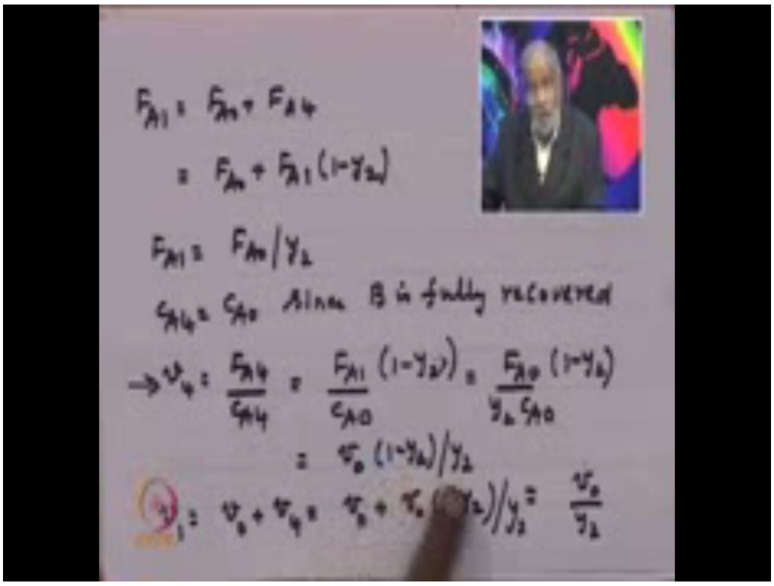

$$F_{A1} = F_{A0} + F_{A4}$$
$$= F_{A0} + F_{A1}(1-y_2)$$
$$F_{A1} = F_{A0}/y_2$$
$C_{A4} = C_{A0}$ since B is fully recovered
$$\rightarrow v_4 = \frac{F_{A4}}{C_{A4}} = \frac{F_{A1}}{C_{A0}}(1-y_2) = \frac{F_{A0}}{y_2 C_{A0}}(1-y_2)$$
$$= v_0(1-y_2)/y_2$$
$$v_1 = v_0 + v_4 = v_0 + v_0(1-y_2)/y_2 = \frac{v_0}{y_2}$$

So, that we can understand what we are saying here is that F a 1 is F a 0 plus F a 4 please see here F a 1 this is F a 1 F a 1 is equal to what is coming at 0 and what is coming at 4? So, F a 1 is F a 0 plus F a 4 and what is the F a 4? We know that F a 4 is only F a 2, because all the 2 here will come to 4 what is F a 2? We just now said F a 2 equal to we say equal to F a 1 times 1 minus of y 2 we said that just therefore, and similarly, what is coming here all the 2 that is coming here is also going to coming here. Therefore, F a F a 2 is also equal to F a 4 is also equal to F a 4 therefore, what is coming at position 1 is F a 4 which is F a 1 time 1 minus of y 2 plus F a 0. Therefore, simplifying you find F a 1 that means molar flow at position 1 is simply F a 0 is divided by y 2 what we are saying is that from elementary material balance we find out what is coming at position 1? Now, what is the concentration of A at position 4? We said all the B is fully recovered and therefore, the concentration at 4 is same as c A 0.

So, what we are saying now, is that c A 0 is c A c A 4 is c A 0 and therefore, we can calculate now, what is the flow at the position 4? By definition is F a 4 divided by c A 4 cur molar flow divided by concentration c A 4 is c A 0. Therefore, it is F a 4 means F a 1 times 1 minus of y 2 we are just now said that c A 4 is c A 0. Therefore, we find the molar flow at position 4 is v 0 times 1 minus of y 2 divided by y 2. So, what we are saying is that molar flow at position 4 we have found out as v 0 times 1 minus of y 2 divided by y 2 that is v a 4, so what is the molar flow at position 1? v 0 plus v 4 that is what we have done v 1 equal to v 0 plus v 4 when you do that we say it is equal to v 0 of y 2. In essence what we have done is that we have try to put all the term that are required for us in terms of quantities that we know from our experiments y 2 is known from our experiments, v 0 is known from our experiment. From our data v 0 is given y 2 is given therefore, we should express all numbers in terms of what we know that is what we are trying to do in this algebra. Having done that let us let us go forward what we saying now? What we saying now is that we from our material balance that concentration is 1 it is simply c A, 0 because this also c A 0.

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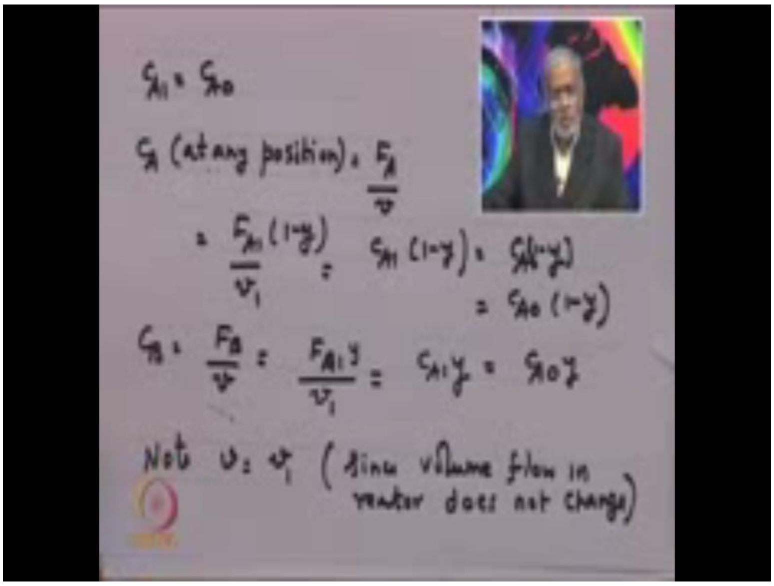

$c_{A1} = c_{A0}$

c_A (at any position) $= \frac{F_A}{v}$

$= \frac{F_{A1}(1-y)}{v_1} = c_{A1}(1-y) = c_{A1}(1-y)$

$= c_{A0}(1-y)$

$c_B = \frac{F_B}{v} = \frac{F_{A1}y}{v_1} = c_{A1}y = c_{A0}y$

Note $v = v_1$ (since volume flow in reactor does not change)

We know that c A 1 is c A 0 we know and what is the concentrated at any position? See after all if you want to write the design equation for s for a equipment we should know concentration at any position therefore, we have written what is c A? By definition is F a by v what is F a? F a 1 times 1 minus of y at any position what is v? Since there is no change in volumetric flow v at any position is v 1 which is coming in. On other words what we are saying is that in this PFR the flow at any position is same as v 1, because there is no volume change in the reaction. And what is the concentration at any position F a divided by v that is what I have written here. Therefore, concentration is F a by v which is c A 0 times 1 minus of y for component A and for b it is c A 0 times of y. Therefore, what we are tried to do is that we are now, able to express concentrations in terms of y. Now, we have expressed all the other flows in terms of con known quantities there 4 we are now in a position to be able to write the reactor design equation that is required to understand what is going on. So, this is what I have written here.

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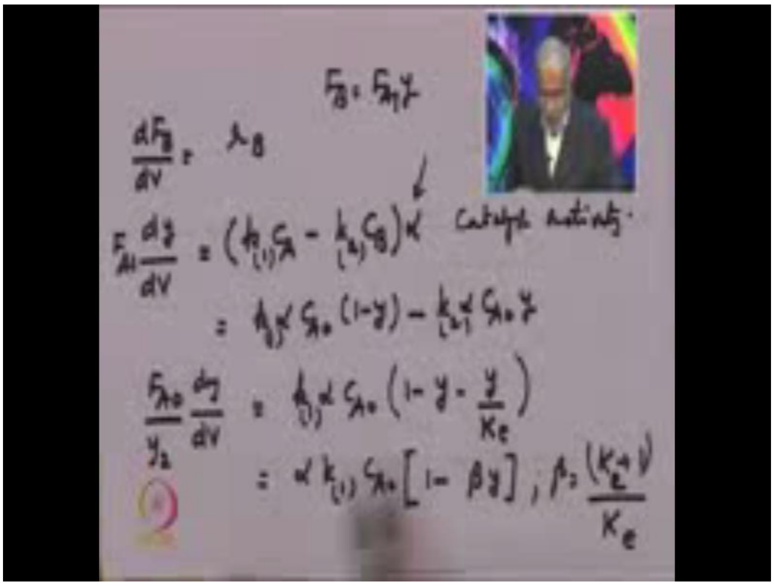

$$F_B = F_{A1} y$$

$$\frac{dF_B}{dV} = r_B$$

$$F_{A1}\frac{dy}{dV} = (k_{(1)}C_A - k_{(2)}C_B)\alpha$$

Catalyst activity

$$= k_{(1)}\alpha C_{A0}(1-y) - k_{(2)}\alpha C_{A0}\,y$$

$$\frac{F_{A0}}{y_2}\frac{dy}{dV} = k_{(1)}\alpha C_{A0}\left(1 - y - \frac{y}{K_e}\right)$$

$$= \alpha k_{(1)} C_{A0}[1 - \beta y], \quad \beta = \frac{(K_e+1)}{K_e}$$

So, our reactor design equation that d by d v of b is r b therefore, I have written f b we know that what is f b? By definition is F a 1 times y I have written that here, so F a 1, so time d by d v, so I have out all the terms and notice here that I have put 1 inside brackets to indicate that this refers to reaction and not position. So, this is reaction 1 this is reaction 2 and this term is a catalyst activity this is catalyst activity what we are saying here is that the reaction rate function r B depends on k 1 alpha times c A minus k 2 alpha times c B notice that the catalyst accelerates both the forward reaction and the reverse reaction.

See therefore, we find F a 1 d by d v is given by this expression. So, what we are now, we able to do is that we are able to write the design equations for the reactor in terms of y see d dived d v in terms of y. And all other terms excepting y are known that is the interesting point. That means we are able to write the design equation in terms of quantities that we know and the quantities we would able to measure in our experiment. So, this differential equation in this form we can see here F a 0 by y 2 divide d v equal to the right hand side. Now, we are able to integrate and then get the results in this form in which we required.

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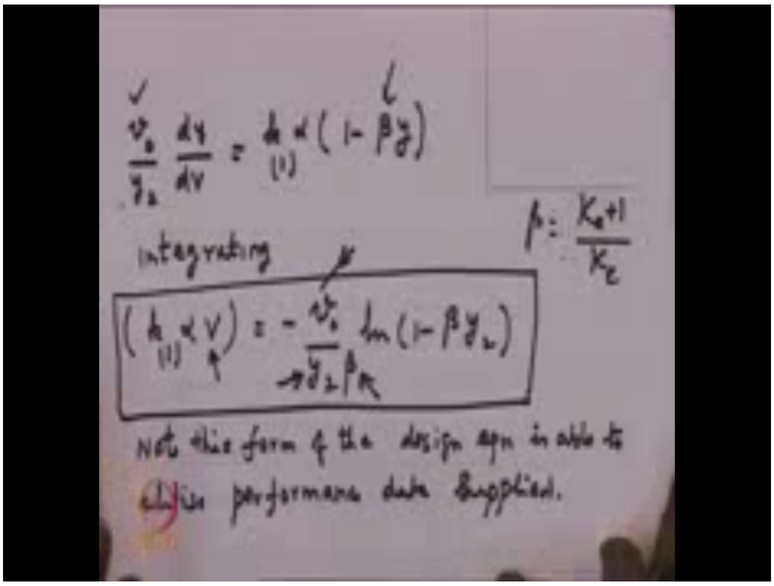

$$\frac{v_0}{y_2} \frac{dy}{dV} = k_{(1)} \alpha (1 - \beta y)$$

$$\beta = \frac{K_e + 1}{K_e}$$

integrating

$$\boxed{(k_{(1)} \alpha V) = - \frac{v_0}{y_2 \beta} \ln(1 - \beta y_2)}$$

Note this form of the design eqn is able to utilise performance data supplied.

When we go further we recognize that we are able to simplify the equations in terms of number that we know v 0 we know y 2 we know. Now, divide d v we can put in terms of beta is simply beta is simply k e plus 1 by k while k is equilibrium constant. Therefore the integrated form the integrated form of the equation which describes the performance of our equipment is given by this. Now, so what we have done? What we have done is that based on your understanding of reactions engineering we are able to write a design equation which is able to is describe our equipment. Notice here that k 1 is rate constants for forward reaction, alpha is activity the catalyst, v is the volume of the catalyst that we used our experiment, v naught is the volumetric flow at the inlet, y 2 is the extend of reaction at the reactor exit. Beta is simply k e by k plus, so all the terms we know see all these are given to us in the experimental data. The experimental data you can see here very clearly all this is given to us. Temperature is given, v naught is given this is v naught and what is this? This is actually this is a 1 minus of y 2 multiplied by 100.

So, everything is given understand, so 1 minus of y 2, so we will not write it like this. This that means if it is 25 percent is 0.25 1 minus of 0.25 is y 2 I mean all that, so what I trying to stay here is that the data that is given can be now, utilize to understand how this system is performing? To understand what is the activity of the catalyst, because our question is we have supposed to check the activity of the catalyst and compare with the criteria that are given to us. So, this equation x helps us to find out the activity of the catalyst, because all the rest of the quantities are known. And that is the important point of being able to formulate your mathematics, so that you are able to represent that physical system that is in front of you. Now, that we know all this we are now, in a position to make an evaluation of the data that is given to us.

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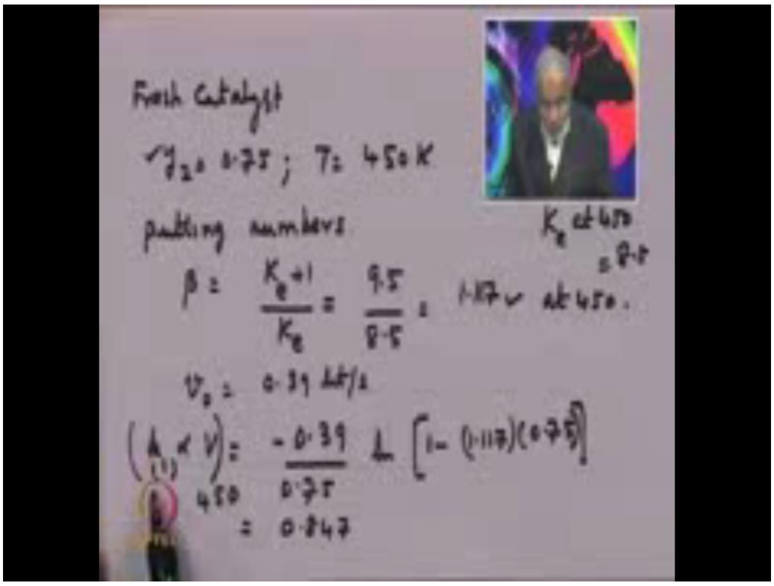

Fresh Catalyst

✓ $y_2 = 0.75$; $T = 450\,K$

putting numbers

K_e at 450 $= 8.5$

$$\beta = \frac{K_e+1}{K_e} = \frac{9.5}{8.5} = 1.117 \checkmark \text{ at } 450.$$

$v_0 = 0.39$ lit/s

$$(k_1 \alpha V)_{450} = \frac{-0.39}{0.75} \ln\left[1-(1.117)(0.75)\right]$$

$$= 0.847$$

So, let us evaluate the fresh catalyst. Fresh catalyst y 2 is given us 0.75, y 2 is given us 0.75 it is given us 25 percent therefore, 0.25 1 minus 0.25 is 0.75. Now, beta is k e plus 1 by k e beta values is given. You can see here our equilibrium constant k e at 450 is given us 8.5 therefore, 8.5 plus 1 is 9.5 therefore, beta is 1.17 at 450. So, we are able to calculate the value of k 1 alpha v at 450, because all the terms on the right hand side is given v naught is given y 2 is given beta is given everything is given on the right hand side. We can substitute and calculate the value of the right hand side which is comes out the 0.847. So, fresh catalyst k 1 alpha v given us we have found out as 0.847.

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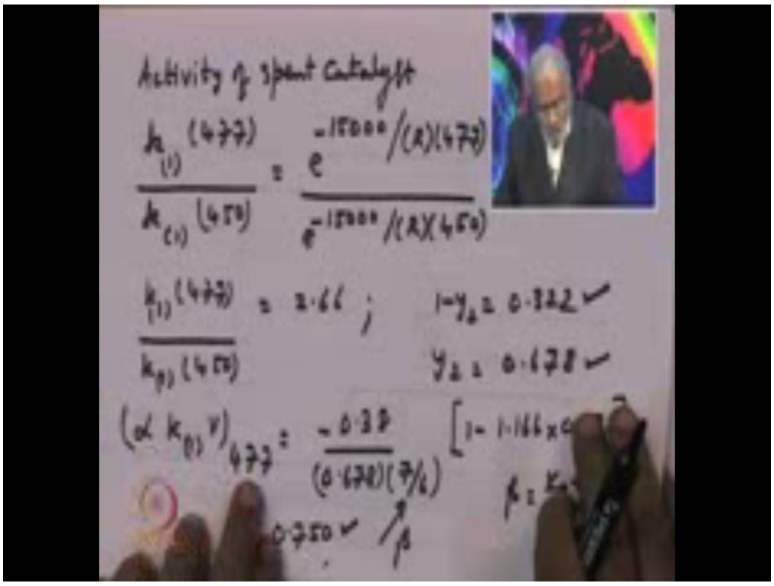

Activity of spent Catalyst

$$\frac{k_{(1)}(477)}{k_{(1)}(450)} = \frac{e^{-15000/(R)(477)}}{e^{-15000/(R)(450)}}$$

$$\frac{k_{(1)}(477)}{k_{(1)}(450)} = 2.66 \;; \qquad 1-y_2 = 0.322 ✓$$

$$y_2 = 0.678 ✓$$

$$(\alpha k_{(1)} v)_{477} = \frac{-0.33}{(0.678)(7/6)}\left[1 - 1.166 \times 0\right.$$

$$\beta = K$$

$$0.750 ✓ \quad \nearrow \beta$$

Similarly we can do for a spend catalyst. Spend catalyst data is also given when I do when we do the same thing. For spend catalyst we find the value for alpha k 1 v at 4 77 that terms go to be 0.750. Because y 2 is 0.322 is given and then be a this value of beta what is beta values? Beta value of calculated, because of the define the data given, so accordingly we find that the values are 0.678. I have not given the detail here 0.678 is y 2 and beta is the k e by k e plus 1 k e 1 plus k e which is beta at 477 it turns out to be 7 by 6. I have done this calculation the details are not given here you can check it for yourself, so what is an essence? It means is that at 477 spend catalyst our values of alpha k 1 v turns out to be 0.75. For spend catalyst it is sorry for spend catalyst 0.475 and for fresh catalyst we just now, said it is 0.847 we said that just now. Just now we said that fresh catalyst is 0847. Now, we have to do this same thing for the regenerated catalyst. Now, before we doing that let us just go forward a little and find out what is the activity of spend catalyst. Because this notice here that this at this alpha is that 477, so we always like to express in terms of fresh catalyst. So, we want to find out the value of alpha at 477, but we want to see what is alpha value with respect to our fresh catalyst?

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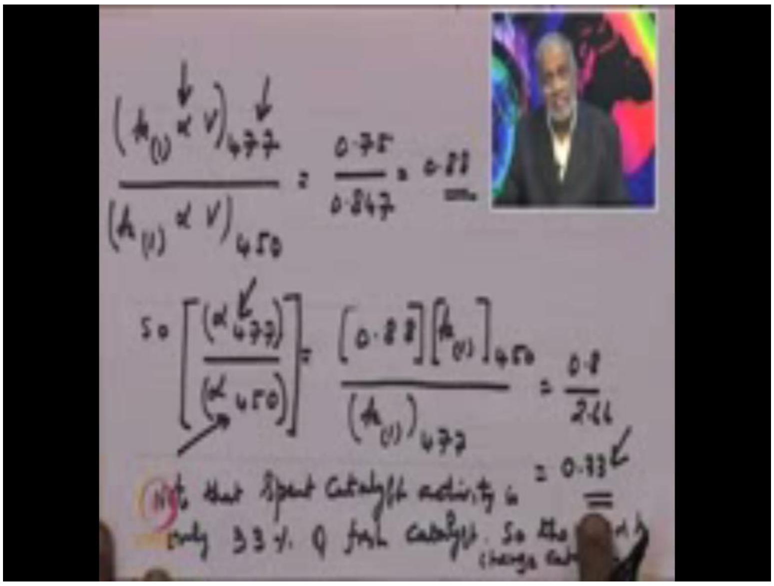

$$\frac{(k_{(1)}\alpha V)_{477}}{(k_{(1)}\alpha V)_{450}} = \frac{0.75}{0.847} = 0.88$$

$$\text{So}\left[\frac{(\alpha_{477})}{(\alpha_{450})}\right] = \frac{[0.88][k_{(1)}]_{450}}{(k_{(1)})_{477}} = \frac{0.8}{2.66} = 0.33$$

Note that Spent Catalyst activity is only 33 % of fresh catalyst. So the change

To do that I have just found out is k 1 alpha v divided by k 1 alpha v 450 this ratio is 0.75 a point is terms out be 0.88. So, what we are saying is that the value, so alpha at 477 divided by value alpha at 450 is actually what? k 1 k 1 at 450 I just multiplied by k 1 at 450 divided by k 1 at 477, so that I am able to find out what is the activity of catalyst at 477 in relation to activity at 450? And that terms out to be 0.33 what we are trying to say here is the following what we are trying to say here is that in this experiments in this catalyst evaluation we are given as spend catalyst we want to find out what is the activity of spend catalyst?

Now, we find that the spend catalyst is working at the 477 therefore, we want to check the activity of spend catalyst at 477 and you want to compare this activity of the catalyst at 450. And to do that is when we have done this through this manipulation. We have been able to find out what is the activity of spend catalyst at 477 in relation to the activity of the catalyst at 450 by multiplying by the appropriate reaction rates at the 2 temperatures that is what I have done. So, what we find? We find is that the activity of spend catalyst terms out to be 0.33. So, what we are saying here is that spend catalyst with respect to front catalyst is quite inactive and the reason why we are looking at the way of regenerating the catalyst. Let us go forward and look at the activity of regenerated catalyst.

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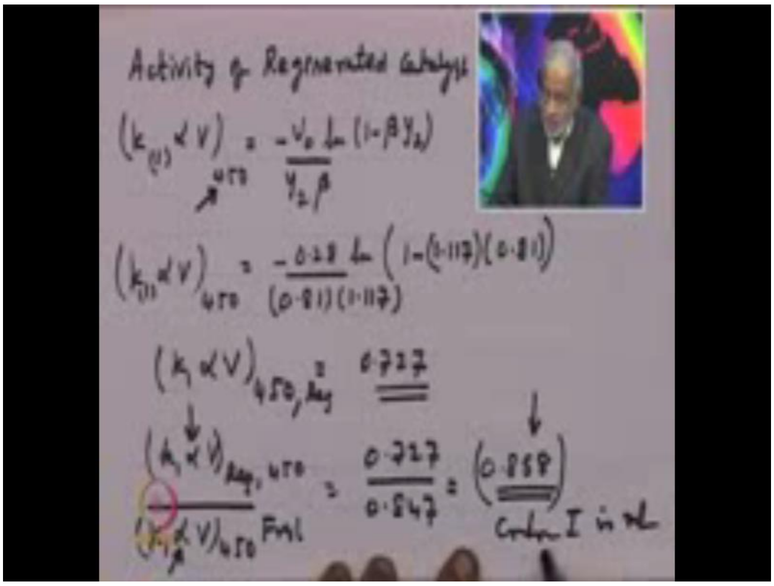

Activity of Regenerated Catalyst

$$(k_{(1)}\alpha V)_{450} = \frac{-V_0}{Y_2\beta}\ln(1-\beta Y_2)$$

$$(k_{(1)}\alpha V)_{450} = \frac{-0.28}{(0.81)(1.117)}\ln\left(1-(1.117)(0.81)\right)$$

$$(k_1\alpha V)_{450,Reg} = \underline{\underline{0.727}}$$

$$\frac{(k_1\alpha V)_{Reg,450}}{(k_1\alpha V)_{450}\ \text{Fresh}} = \frac{0.727}{0.847} = \left(\underline{\underline{0.858}}\right)$$

Criterion I is not

Now, the regenerated catalyst data is given at 450 the that in the right hand side all the data is given when you calculate we find that k 1 alpha v at 450 terms out to be 0727. Therefore, we can compare the k 1 alpha at 450 with fresh catalyst that terms out to be 0.858. On other words what we are saying now, is that the activity of is regenerated catalyst in relation to activity of fresh catalyst both are it is same temperature. It is not 0.9 we said we can accept the regeneration process if the activity is in 0.9 or higher. Now, it is only 0.858 and therefore, criteria 1 is not satisfied. So, criteria 1 is not satisfied, so that is the first point that we recognize now let us see about criteria 2 what is criteria 2.

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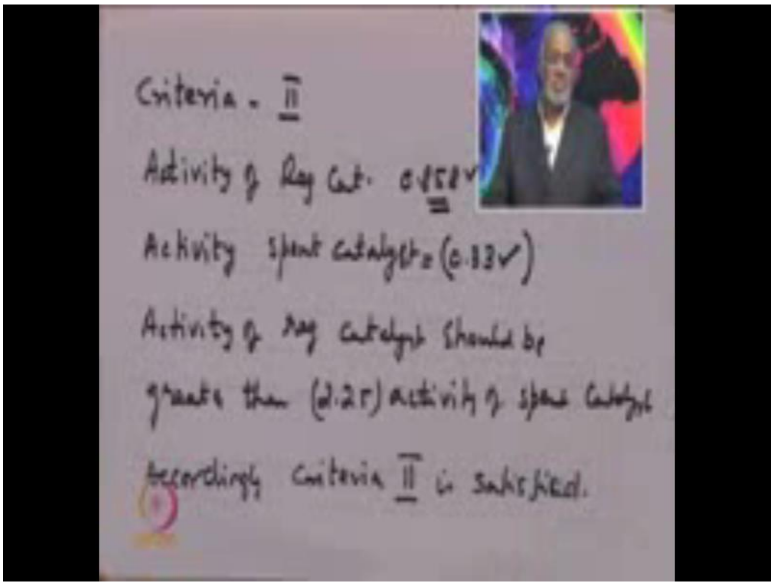

Criteria - II

Activity of Reg Cat. 0.858 ✓

Activity spent catalyst = (0.33 ✓)

Activity of Reg catalyst should be

greater than (2.25) activity of spent catalyst

Accordingly criteria II is satisfied.

So, criteria 2 says the activity of regenerated catalyst is 0.858 and activity of spend catalyst is 0.33. And criteria 2 say, if it is 2.25 times the activity of spend catalyst it is if you multiply 0.33 by 2.25 you find that is less than 0.858 therefore, at criteria 2 is satisfied. On other words what we are trying to say here is that how do the 2 criteria 2 is satisfied therefore, we can accept the regeneration process. So, by going through this whole exercise what we are try to bring out your attention is that in a deactivating catalyst; catalyst will deactivate. Therefore, you have increasing the temperature of operation of the catalyst and therefore, the spend catalyst when we are discarding it the temperature is 477 what is 450 initially? We have to rise it up to 477 to be able to take care of deactivation. On other words what we are trying to put a cross you here is that in deactivating catalytic systems increasing the temperature of operation, so as to a null the effect of catalyst deactivation is this strategy generally employed. But this strategy may not be successful for the entire duration of operation you may have to stop it. After sometime when the activity as spend of the catalyst is unsatisfactory you have to take it out and discard it or replace it by an appropriate regeneration process.

Thank you.