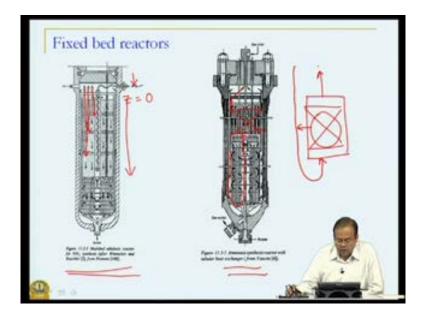
Chemical Reaction Engineering Prof. Jayant Modak Department of Chemical Engineering Indian Institute of Science, Bangalore

Lecture No. # 33 Autothermal reactors

Friends, in the last session, we looked at the design of reactor for reversible exothermic reaction; and towards the end, we said that there are different ways of operating us reactors for such reactions; and one of them is making use of the energy that is generated, because of the exothermic nature of the reaction to pre-heat the reactant. So, our idea was the following that we saw in the reactor, we need temperatures at a higher level at the beginning, and then progressively reduce the temperature towards the exit of the reactor.

So on one hand, we have requirement for pre-heating the reactor to a high temperature, but on the other hand as the reaction proceeds, there is lot of energy that is generated, because the reaction is progressing. So, we can then combine these two processes namely, in order to pre-heat the reactant, so that they enter the reactor at a high temperature; we can make use of the energy that is released during the reaction itself, instead of using an external source of energy. So, these kinds of reactors are referred to as autothermal reactors, and they lead to some special design features, which we will see in today's session. But before we do that, let us look at how they actually the reactor for this kind of reaction actually is operated?

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So, what you see here is two kinds of reactors this one, we discuss last time that is what is what is being done here is the reactants are entering at this point and they are passing through the catalyst bed in this particular direction, but instead of putting all the reactants at the inlet, what we conventionally understand as inlet let us say axial position z equal to 0, instead of doing that, you have several tubes in which cold reactants are added in the middle of the reactor. So, what happens is suppose we pass certain initial reactant over here the reaction takes place, there is no heat removals so temperature rises, so then you premix with a fresh feed, so that temperature goes down and then there by achieve the lowering of the temperature. Now, this second operation over here is the autothermal operation that we are going to look at in detail today.

So, what is being done in these reactor is that this is our catalyst bed, this is our catalystbed but it it is packed in the tubes and surrounding this tube is a shell, through which the reactant actually enters, it it goes down and then there is a heat exchanger and then goes through the through the catalyst bed or in other words what we are doing essentially is that, if this is my catalyst bed then before the reactants get into the reactor, I pass it through the shell and then pass the reactant so that the reaction takes place. So, what happens here in this portion in this portion the reaction takes place, energy is generated that is transferred to the reactant which is flowing in the shell. So, that the reactant gets pre-heated before it enters the enters the reactor. So, this is the operation which we are going to see in today's session.

So, let us try to look at, look at how these reactors behave and will make take help of simple mass and energy balances to understand how these how these reaction is taking place.

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C=C Reactor

So, to simplify the matter, let me just show one bed of catalyst, and surrounding shell in which my reactants are going to enter. So what I am going to do is I have my reactants at temperature T1 f and concentration C 1 f, which are going to flow through this empty shell, before it enters the reactor. So, let us say that keeping in mind that a reactor inlet we always put it at axial position 0, so let us put that as 0 and let us say my catalyst bed is of the length length L. So, now in the shell, let us say that my temperature is T 1 of z, because my temperature is is temperature is changing along with this axial position at the inlet it is T 1 f, but through the shell it is T 1 T 1 of z what happens to my concentration? I am not changing my changing my concentration so concentration so at this particular point, at this particular point, we have some temperature let us say T 1 0 and concentration C 1 f, which enters into my into my reactor.

Okay Now, this T10 and C1 f enters my enters my reactor and what happens here let us say that my concentration now will change. So, let say that concentration in the reactor is C1 and temperature is T2 both are functions of functions of z. So, my products will come out over here and let us say my temperature that comes out is T2 l and concentration is

some C1C1L. So, we have now actually coupled the heat transfer and reaction, so what is happening that energy that is generated will get transferred to the shell or the cold reactant, that is flowing through the through the shell.

So, we would like to now, set up mass and energy balances for these for these reactors. So, this is my reactor R, so let us see, what happens for my reactor, what is happening in the reactor? The reaction is reactions is taking place and for sake of simplicity let us say that our reaction is A 1 going to A 2 exothermic reaction. So, if my velocity is let us say u over here in this of this fluid then I will consider a simple Plug Flow Reactor, no mass transfer resistances for for sake of this illustration. So, my concentration will change according to my rate of rate of reaction and what happens to the energy balance? My energy balance will take form of this is what we had we had seen earlier.

This is my energy content which is changing along the axial direction, this is my heat of heat of reaction and therefore, because of reaction there is some energy that is liberated and this is the energy, that is getting transferred from from the from the reactor to the gases that are flowing in the in thein the shell.

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Heat Exchanged (GP) $U \frac{dT_1}{dz} = -\frac{4U}{4z} (T_2 - T_2)$ Z = 0 $C_1 = C_{1f}$ $T_1(0) = T_2(0) = T_{10}$ Z = L $T_1(Z = L) = T_{1f}$

Now, let us let us write a similar balance for my Heat Exchanger, what is happening in my Heat Exchanger? There is no reaction, so concentration remain same as C 1 f only energy is getting transferred from the reactor side to the gasses, that are flowing into the into the shell side. Again the energy content minus we were assuming the velocity

remains the same, so the size of this tube and and let us say the shell is the diameter is same, so u remains the same and we have a energy transfer from the reactor to the to the shell side. Notice here, the negative sign has come, because if we take the velocity u in this direction as positive, the velocity has to be minus u in the in the reverse direction, because the flow direction itself is isis different. So now, let us let us try to write these are two energy balances and and the mass balance, so we need boundary condition boundary conditions for this. So what all what all do we know?

For example, we know that the concentration at the inlet of reactor is C 1 f that is my feed condition. So, I can safely write at my at my inlet of the reactor concentration is C 1 f. What about temperature T 1 0? I do not know what that temperature is, because all I know is what are my feed conditions so, I know what is a temperature at z equal to L or or at this location, but I do not know what would that temperature be at z equal to 0, but I do know that the temperature of the gaseous stream coming out at z equal to 0 here is the same as temperature of the gaseous stream that is entering the reactor over here. So, I can write a coupled equation namely, the temperature of the gaseous stream that is entering the reactor and which is some value T10, I do not know what that value is, but I do know that T1 at z equal to 0, must be T 2 at z equal to 0.

So, this is my boundary condition at at z equal to 0 and what is happening at the z equal to L? We need three boundary conditions: we have 1, 2 and we have another boundary condition namely the inlet temperature is known to me. So, my temperature of the gaseous stream in the shell side, at z equal to L is T 1 f that that much I know. So, now if we look at look at these three balances and corresponding corresponding boundary conditions, we see that we have a coupled boundary condition problem. Why coupled boundary condition? Because typically if we have a differential equation and if you know all the conditions that is all the boundary conditions at one point, then that is namely let say entry of the reactor which is what typically happens when you have a single pass reactor or normal tubular tubular reactor.

But in this particular case, we have a tubular reactor alright, but we need three boundary conditions, but we do not know them at any of the inlet or exit point. But we know them some at the inlet point and some at the exit point, that is this we know at the inlet point; this we know at the exit point and therefore, we call such problems as coupled or two

point boundary value problems. So, we have set of differential equations we want to solve them, but we do not know what this what this solution is, so how do we how do we solve such problems numerically?

Numerically, we can we can solve these problems in the following manner: and it has to be done in an iterative iterative manner that is one way of doing it, other is to solve a two point boundary value problem, but that is too mathematical. So, let us try to look at iteratively how we can we can solve this problem? If you if you look at look at what is happening over here? Let us say, that I assume some value of T 1 0, and that is my starting point.

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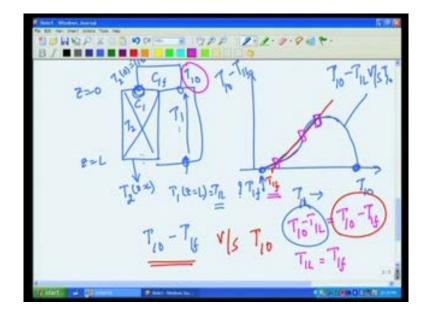
Z = 0 $C_1 = C_{1f}$ $T_1(0) = T_2(0) = T_{10}$ Z = L $T_1(z = L) = T_{1f}$ Assume Tro Int mass k energy from Z=0 to C, (Z=L), T, (Z=L), T_2(Z=L) T. (2=L)=711 (is two

So, I will say that first step is assume T 1 0, if I assume T 1 0 then I know everything that needs to be solved, because I know I know three conditions, this concentration is C 1 f, T 1 0 is T 1 0, because I have assumed some value and T 2 0 is T 2 0. So, I can integrate these equations in a single direction. So, that now this becomes an normal boundary condition problem, no 2 point boundary condition problem if I assume T 1 0. So, then I integrate mass and energy balance from z equal to 0 to z equal to L. So, I will then know C1 at z equal to L, T 1 at z equal to L and T2 at z equal to L, that is if I assume value of T10 over here then I can simply solve this three energy balance mass and energy balances in a forward direction from z equal to 0 to z equal to L and get these get these values.

Now, of these three conditions I know, what should my T 1 at z equal to L, because well let us call this as T 1 L and according to what I know that value should be T 1 f, right that is temperature temperature of this reacting stream at z 1 equal to L is fixed, that is my feed condition so T 1f.So, by integrating these these these equations if I know my T 1 0 it should match with T 1 f.

Now, how do I know that that it will definitely match that will depend upon how good is your guess of T 1 0 or in other words after integrating I will check this namely, I will say, this particular value is this equal to T 1 f if answer to this question is yes, I have solved my problem. But, if answer is no, answer is no that means my initial guess of T 1 0 was not correct. So, I will go back make another assumption on T 1 0 and go on repeating this process till I get T 1 at z equal to L,, T 1 at z equal to z equal to L matches with T 1 f and that is how I will numerically, numerically solve this problem.

Now, before we before we look at look at how we solve this problem numerically and look at the numerical solution let us let's try to try to look at look at how do we what kind of qualitative information can we can we get and to do that, what I am going to do is? And let us say whether this works? It did not work. So let me let me redraw all over again.



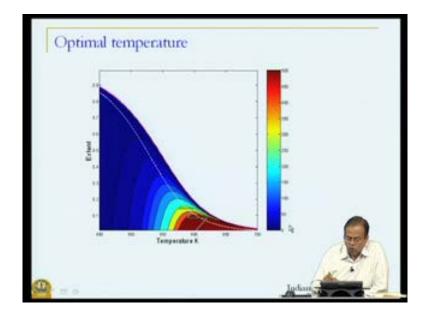
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So, what we said was this was my this was my reactor, this was my shell T 1 at z equal to L is T 1 f this is my z equal to L; this is my z equal to 0; this is my temperature T 1 here,

T 2 here and concentration C1 here. So this was flowing like this, so here the temperature is T10 and T2 at 0 is also T 1 0 by doing this I will get by my iterative iterative procedure Whatever I said will get T 2 at z equal to L, T 1 at z equal to L and let us call this as T1L, this is what we ultimately want.

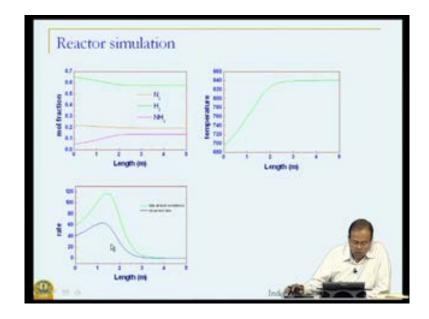
So, let us so this has to match with T1f is what we want to check by doing an iterative scheme in which we will assume T10 integrate these equations in a forward direction from z equal to 0; to z equal to L, get T1L and try to see whether that matches with matches with T10. So, now let us qualitative try to see, what behavior will I get, if I try to solve these equations? So, on x axis let us put T 1 0 and on y axis let us put T 1 0 minus T 1 L. T 10 minus minus T 1 L. And let us try to look at qualitatively what what these these solutions solutions will be like. Now, let us let us again this is all qualitative argument let us assume, that my T 1 0 is very low myT 1 0 is very low and we saw that if the temperatures are low, the reaction rates are also also very low right.

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I mean if you do not recall, we will go back to go back to temperature versus rate and these are my rate contours, colors, low rate to very high rate, so if my temperatures are low, let us say let us say something like this then I see my reaction rate is also also very low.

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So, I would then expect that my reaction will be very slow in the reactor my reactionwill be very slow in the reactor and therefore, at low values of low values of T 1 0 very little reaction reaction in the in the reactor. So, my T1L very little reaction means what, very little heat generation, so very little heat transferred to the shell, so my T 1 at this point will be pretty much close to T 1 at z equal to L, because there is very little reaction; there is no heat generation. So, no heat exchange or heat transfer which will pre-heat the reactant. So at a low value of low value of T10, my T 1L will be pretty much close to T10, because very little reaction so no change in temperatures across this entire length.

So, that is that is one limit, let us look at the other possible limit and if we say, if my temperature is is very high, so high that for the given composition of the feed that temperature happens to be my equilibrium corresponding point on these violet curve. So, let us say that given this given this composition of the inlet composition of the inlet my temperature is this particular value, this value over here T 1 0.

So, what will happen if my entry temperature conditions are such that the reaction is at equilibrium, because I am putting this point on contour of rate equal to 0. So, if at the entry point I have already achieved my equilibrium, then what will happen in my reactor? In my reactor no reaction can take place because, if the conditions here are such that at the entry points are such that we are at equilibrium then reaction cannot even start. So, there again would not be any reaction through the entire reactor, so again no heat

transfer to the shell side, again the inlet temperature T 1 0 here will be pretty much close to T 1 L, that is we will have some point like this, at very high T 1 0, let me let me repeat this repeat this argument argument once again, we are saying that we are assuming some value of T 1 0, integrating these equations and getting the value of T1 at z equal to L, that is T 1 L and plotting T 1 0 against T 1 0 minus T 1 T 1 L.

Now, what kind of solutions can we expect you will have to actually numerically integrated, but some qualitative field we can get by considering the extreme cases namely, if temperature T 1 0 is low then the extent of reaction will be very low, because rate constant are low. Hence, there would not be hardly any difference in condition from the z equal to 0, z equal to L or in other words hardly any reaction in the reactor therefore, hardly energy energy transfer from the reactor to the reactant and therefore, hardly any increase in temperature from T1L to T 1 0. So, we will have a point somewhere like this, where T10 is pretty much close to T 1 L.

Let us consider other extreme where T 1 0 value is so high and is of a specific value such that, this T 1 0 corresponds to the temperature which is at which equilibrium is achieved visa vice the inlet composition. So, corresponding to C 1 f, if T 1 0 value is such that the equilibrium is already achieved at the inlet point. So if equilibrium is already achieved at the inlet point. So if equilibrium is already achieved at the inlet point. So no heat transfer, so once again T 1 0 will be same as T 1 L and so as we change my T 1 0 now, the solution it turns out looks something like this. So, both had low and high assumed value of T 1 0, the excess T 1 0 is same as T 1 L and then it goes through a through a maximum.

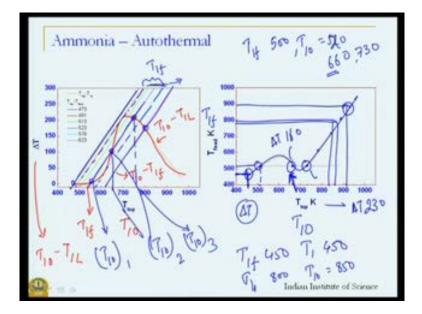
Now, on the same plot, let we plot T 1 0 minus T1f and let me use different color to do that. So, now I am trying look at I have already plotted for example, over here this particular plot is T 1 0 minus T 1 L versus T 10. I am now going to plot T 1 0 minus T 1 f versus T 1 0. Now, what will be the value of this function? This function will have value 0, when T10 is equal to T 1 f. So, let say that this is that point T 1 f that is my feed condition and what is this line? This is just a straight line starting with T 1 f. I am going to cheat little bit to just just to make a point. So, blue line is my T 1 0 minus T 1 L, my red line is Ismy is my straight line T 1 0 minus T1f versus T 1 0 and what does these intersection points indicate?

Let us indicate them by different color what does this intersection point indicate? What

must be happening at these intersection points? At these intersection point, value of both the functions is identical. So, what does it mean? It means the intersection point T 1 0 minus T 1 L is equal to T 1 0 minus T 1 f, because this is my red line, this is my red curve, this is my blue curve and intersection points denote T 10 minus T 1 L is T 1 0 minus T 1 f or in other words these three intersection points denote T 1 L equal to T 1 f which is what the solution that we have been looking for.

Now, what what happened what happened is that, what this is saying is that for a given value of T1L, I actually have three different values of the temperature at the top T 1 0 corresponding to which reactions will will take place or in other words we will have once again multiplicity of steady state multiplicity of of uh steady state. Again a behavior which is similar to what we have seen earlier. let us Let us, look at the actual plots for ammonia synthesis and then things will become clear.

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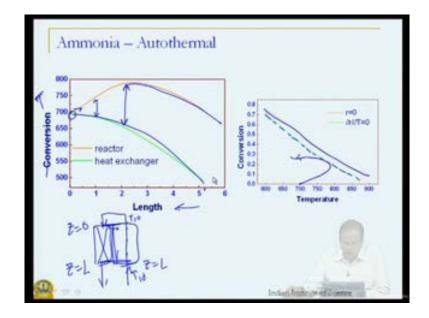
So, what we are what we are what we areuh seeing is, on the x axis is this the same thing actually, it is the value of T 1 0 that we have assumed and on the y axis on the yaxis that is over here we have T 1 0 minus T 1 L and this particular line over here is is representing T 1 0 minus T 1 L whereas, the straight lines of differing color are my T 1 0 minus T1 feed with different x intercept and the intersection point, I will just show typical ones, these are the three possible values of the of the top temperatures that we can we can have for this particular value of T 1 f. For example, if I choose this particular

value which is shown with a blue line blue line. So, I see that this intersects at three different locations and corresponding to this T 1 f. I have this T 1 0 1, another T 1 0 2 this particular temperature right and third possible temperature this particular value T 1 0 3.

Okay Now, what happens if I if I have my inlet temperature or oror the feed temperature as shown by this particular line, then I see the intersect only at one point even at this particular particularparticular point. Then these two cause, intersect only at one particular point whereas, for all the values of T 1 f between these two limits and what is this line? I have drawn this line is tangent to this curve at upper point and at lower points. So all the T1f values between this range we have possibility of three steady states and this is what is shown here. On the second figure, that is what we are seeing here is T1 feed versus top temperature T10. So, for a low value of low value of T 1 0 T 1 f, for a low value of T 1 f we have this value of T 1 f, for any T 1 f in this particular range in this particular range. We have three steady states we have 3 steady states that is three different possibilities of top temperature and for any any T 1 f greater than this value, that is on this side we are once again have single single temperature. So if you if you join all this, you will get a plot which looks something like this.

So, once again illustrating the fact that for low value of feed temperature, the top temperature will also be low right very little reaction. What is to be noted here is that is why, these delta T was delta T was shown over there. Here the delta T is very low right, but here also if you look at for example, if you look at the feed temperature of 500, I am just taking approximate, so feed temperature of 500. I can have three temperatures, top temperatures something close to let us say 520, this point something close to 520, then 660 let us say something close to that and something of a higher value let us say 730.

Ok If T 1 f is somewhere like 450, my top temperature is also 450 this particular point. But what about this point if T 1 f is let us say 800, this is not a very exact straight line. So, let us say if T 1 f is 800 my T 1 0 is something like 850 let us say, so what has happened delta T is small here and in fact if you if you go even further 900, the difference is almost vanishing. So, 900 T 1 f, T 1 0 is also 900, so very little reaction on both these sides or even here. But lot of reaction at this two particular points, how do I know there is lot of reaction you look at delta T. For example, delta T here the temperature difference between the inlet and exit is almost 160 degrees, with this this point this point delta T is even higher almost 230 degrees which is a indication that lot of reaction has has taken place. So, it turns out that from operating point of view, this is normally considered as an optimal optimal point, but whatever it is the point is,, we get three different possibilities and so we would have multiple steady states.



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Let us wrap up this discussion by by looking at looking at how this temperature profiles profiles change? So what we are seeing here is conversion or rather this should be temperature temperature versus length of the reactor. So, once again this is my reactor right, this is my reactor this is my heat exchanger, so my reactants are going like this and coming out like this. So, this my z equal to 0, this is my z equal to z equal to L.

So, what we what we see is that, at the top z equal to 0? What we are seeing green is the temperature of the fluid in the heat exchanger and red is the temperature of the fluid in the reactor. So, what is happening to the temperature of the fluid? At the start or at the top both are both are both are same, but what is happening to the temperature in the shell? For example, in the shell there is no reaction, so there is continuous continuous exchange of feed. Now, let us let us just qualitative look at what is happening in the reactor, then we will go to the exchanger.

Now, at the reactor at this point at the inlet both this temperatures are same, the heat exchanger side and a reactor side, that means as little further down in the reaction. The thethe heat exchange rate at the inlet is 0, because there is no driving force, but there is

reaction there and reaction is generating energy. So, initially the rate of heat generation will exceed the rate of heat transfer and temperature will slightly slightly increase in the in the in the reactor.

Now, what is happening in the heat exchanger? The heat exchanger temperature here is the maximum, so there is there is a heat transfer so this is a lower temperature lower temperature and this is my feed. So, in the heat exchanger the temperature is continuously continuously decreasing, that is in this particular upward direction from z equal to L that is the exit to the to the entry to the reactor, temperature will continuously increase or from the entry of the reactor to the exit of the reactor, temperature will be continuously decreasing in the heat exchanger.

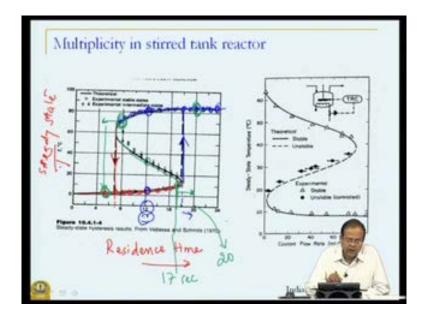
So, what is happening in the in the in the reactor? In the reactor, as I said initially temperature will increase, now it comes little further down. You see that the driving force, that is the temperature difference between the reactor temperature and the shell side temperature is now increasing and reaction rates is gradually decreasing. So, what will happen there will be a point where the driving force for heat transfer just matches with the generation, heat generation rate and beyond this point, because driving force is continuously increasing, the generation is continuously decreasing, the temperature in the reactor starts starts decreasing. Now, this is what we wanted for our reversible exothermic reaction anyway that is high temperature in the beginning and progressively progressively decrease in temperature.

So, this is how it is achieved by a single operation in which you pre-heat your reactant using the energy that is generated in the in the in the reaction. If you recall our discussion on extent of reaction and temperature, this is how things work here. This is my equilibrium line r equal to 0, this is the line when this is the line for which delta r delta T is equal to 0 and autothermal operation it actually if you if you if you if you plot conversion versus temperature, it it actually follows this particular trajectory, which is what we wanted by using adiabatic reactors or by by various different ways and this is now very conveniently obtained in an autothermal reactor reactor itself.

But autothermal reactors also leads to leads to the operation in which we have possibility of multiple steady states, where at two different that is starting for from same field temperature, we may actually have different different inlet and outlet, different outlet temperature and this is a fact that, we have to keep in mind while designing the autothermal autothermal reactors. So with this, we will conclude our discussion on autothermal reactors and we will go on looking at a different aspect of reactor reactor design namely, the safety considerations and reactor reactor design. So, we will start looking at that subsequently in in the existing, design consideration and and the safety.

Now, the idea idea in discussing this this particular topic is is very, very important, but very straight forward as well. Now, what we saw so far is how different kinds of reactor designs are carried out? We saw few case studies, we looked at the kinetics, we looked at reactor design mass balances and so on. Now, even though we try to design our reactors in as safe manner as possible there are always difficulties associated in controlling some of the reactions, which in a extreme case of complete control failure leads to tragic accidents such as Bhopal gas tragedy.

So, while designing the reactors we obviously do not design for such extreme cases, but one must be aware of the conditions under which we could have disaster on hand and this is what we are going to look at by with the help of few examples and why reactors behave in certain manner, which make it appear as if there is no control over the over the process.

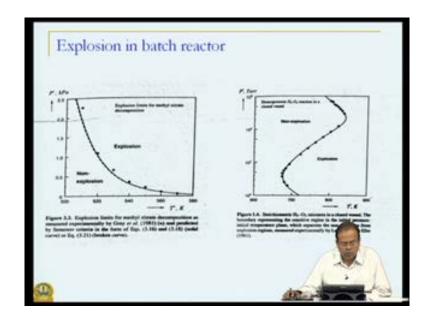


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So let us let us look at look at few examples, and this is this is an example, which we will we will first look at the actual example, and then try to understand, what is the reason

behind behind such behaviors.

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Now, first example is multiplicity of steady states in a stirred tank operation. Now, on face of it nothing can be simpler or at least it appears that operating a stirred tank reactor at a steady state is probably a very, very safe way of way of doing things. But that that is not necessarily always the case, so what we are what we are looking at is an example of sodium thiosulphate oxidation, the reaction is is not of that so important, but the phenomena, because this phenomena is observed for variety of different variety of different reactors and the first example what we are seeing is the operation of an adiabatic C S T R and what we see on the x axis, is the residence time and what we see on the on theor the y axis, is the steady steady state temperature. The steady state temperature on the y axis, and residence time on the on the x axis and these dots are are the this exothermic reversible reaction are the experimental points.

So, what we see is that, if we start increasing the residence time let us say residence time is very short, residence time is veryvery short then you expect very little reaction. So temperature in the reactor is also very very low and it remains low, if you keep increasing the residence time of course, temperatures are slightly slightly increasing, but they still on a on a lower side. But what we see is that, if we if we increase the residence time beyond these, let us say what looks like 18 18 minutes, the temperature suddenly goes to a very high value. So, there is a there is a sudden increase in temperature.

Let us repeat this process, but now in a reverse direction that is we have longer residence time, we have lot of reaction taking place. So, temperatures are fairly high and we now go on reducing the reducing the residence time and temperatures progressively progressively decrease, but once again there comes a point where if we reduce our residence time, below this particular value then temperatures suddenly go down and in fact, if you if you first of all so what do we see here we see a hysteresis, that increasing the temperature, increasing the residence time, first gives us gives us this particular branch of solutions and then suddenly the temperatures go to a very high high value, decreasing the residence time gives us high temperatures. But then suddenly temperatures go go down.

So what we do what we do see here for example, for a residence time of 12 seconds we see that there is a possibility of two different values of temperature in the reactor, one which is a very low value and one which is a which is a very high value. In fact it turns out that, if we use proper controllers we have a possibility of even a third value and there is another branch, which is which is in the in the in the middle or in other words, three different values of values of steady states.

Now, why is this? How is this connected to the design and safety, I talked about let us say that you had designed your reactor reactor to operate at this condition using this particular particular residence time. Now, what is residence time? Residence time is nothing but the volume divided by the volumetric flow rate. So, in the process, let us say that something happens; some fault develops into your pump, so your flow rate instead of what was desired is actually decreases, so what would it mean? It would mean that your residence time would increase, if the flow rate decreases, residence time increases and if residence time increase, is in brings it to this particular.

So let us say that you had design your process for 17 seconds residence time, but suddenly the residence time becomes 20 seconds, what you will have in your reactor is suddenly shoot up, because at this particular residence time the only steady state possible is this particular value. So what you had considered as a safe operation with temperatures hovering around at 10 degrees very low temperatures. Suddenly, you will find a small increase in in in in temperature; you will find that you have reached a very high value of temperature not a desirable situation. The same thing can be said over here if you are operating at this point and residence time suddenly comes down, you will have

completely shut off your your reaction.

Now, both turning on the reaction or shutting off could have implications in the entire process and therefore, one has to be clear as to what is causing this this multiplicity and what are the regimes? We will stop here for this session, but look at few examples, more examples before we start analyzing this reactor behavior. Thank you.