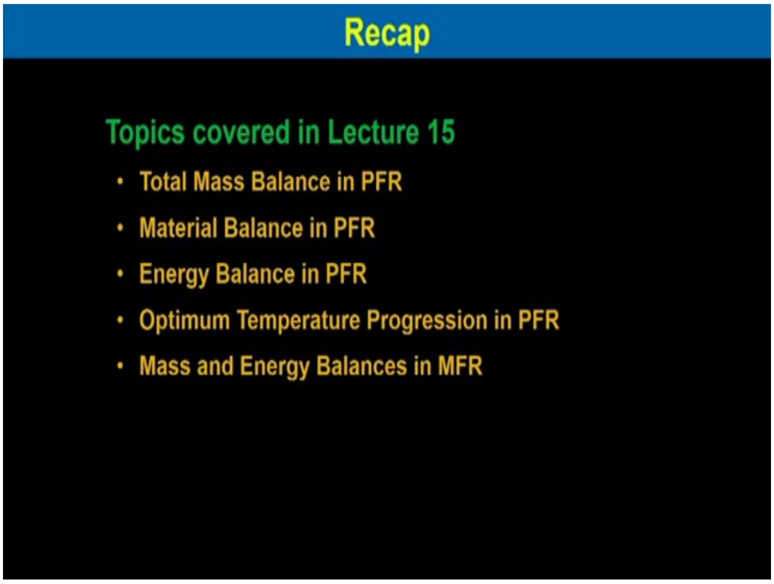
Chemical Reaction Engineering - I
Professor Bishnupada Mandal
Department of Chemical Engineering
Indian Institute of Technology Guwahati

Lecture 26 - Ideal and Non-Ideal Mixed Flow Design and Multiple Steady States

Welcome to the 16th lecture of module 4. In this module we are discussing reactor design. Before going to this lecture let us have brief recap on our previous lecture.

(Refer Slide Time: 00:58)



Recap

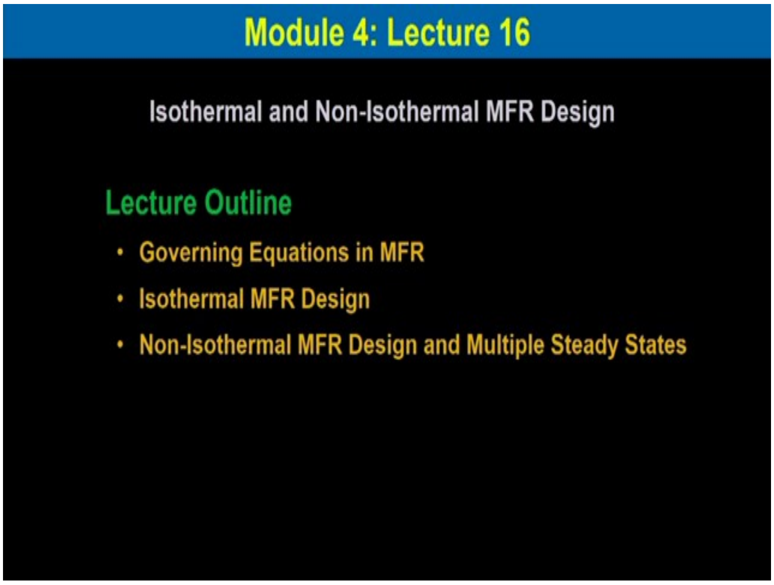
Topics covered in Lecture 15

- Total Mass Balance in PFR
- Material Balance in PFR
- Energy Balance in PFR
- Optimum Temperature Progression in PFR
- Mass and Energy Balances in MFR

In the last lecture we have mainly covered mass balance in plug flow reactor, material balance in plug flow reactor. Then energy balance in plug flow reactor then we have seen the optimum temperature progression in plug flow reactor. As we have discussed before, the performance equation or the species mole balance equation are similar to that of a batch reactor for a constant volume systems and for a single reaction the relations between the temperature and the concentration is similar to the batch reactor.

So we have seen how the temperature progression in case of the PFR changes for different reactions like endothermic, exothermic, irreversible and reversible reactions. We have discussed mass and energy balance in CSTR or mixed flow reactor MFR.

(Refer Slide Time: 02:15)



Module 4: Lecture 16

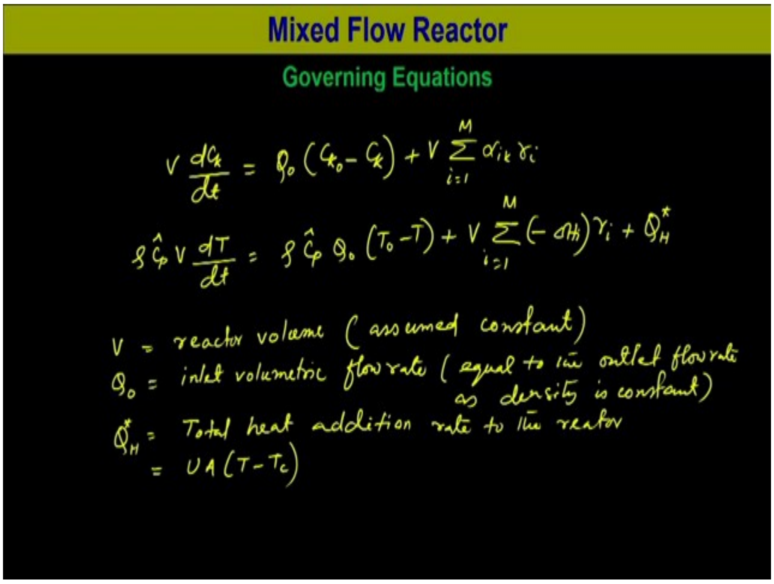
Isothermal and Non-Isothermal MFR Design

Lecture Outline

- Governing Equations in MFR
- Isothermal MFR Design
- Non-Isothermal MFR Design and Multiple Steady States

In this lecture we will consider isothermal and non-isothermal mixed flow reactor design that is CSTR design. So the brief lecture outline would be governing equations in mixed flow reactor, then we will consider design for isothermal mixed flow reactor and then finally we will consider non-isothermal mixed flow reactor and happenings of multiple steady states in a CSTR.

(Refer Slide Time: 02:54)



Mixed Flow Reactor

Governing Equations

$$V \frac{dC_k}{dt} = Q_0 (C_{k_0} - C_k) + V \sum_{i=1}^{M} \alpha_{ik} r_i$$

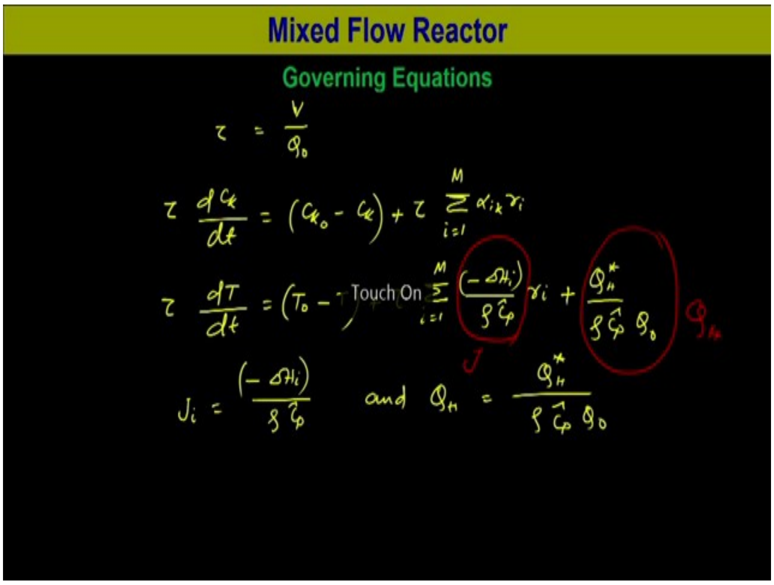
$$\rho \hat{C}_p V \frac{dT}{dt} = \rho \hat{C}_p Q_0 (T_0 - T) + V \sum_{i=1}^{M} (-\Delta H_i) r_i + Q_H^*$$

V = reactor volume (assumed constant)

Q_0 = inlet volumetric flow rate (equal to the outlet flow rate as density is constant)

Q_H^* = Total heat addition rate to the reator

$= UA(T - T_c)$



Mixed Flow Reactor

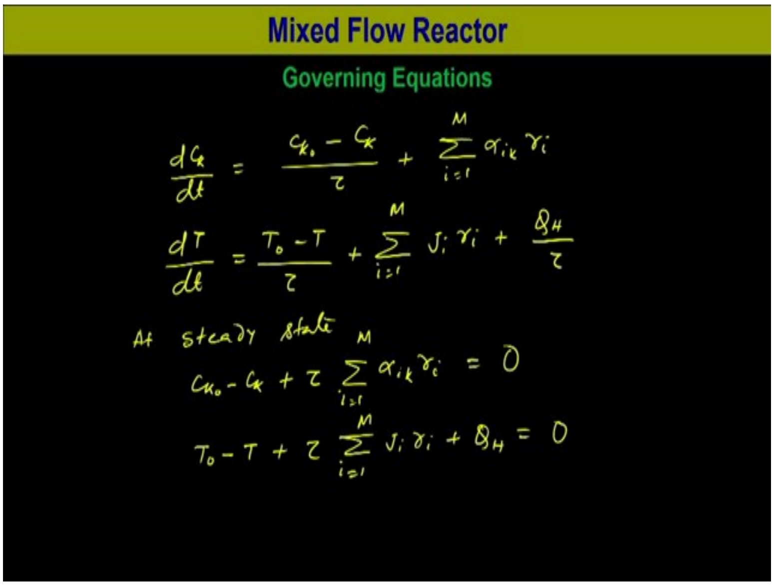
Governing Equations

$$\tau = \frac{V}{Q_0}$$

$$\tau \frac{dC_k}{dt} = (C_{k0} - C_k) + \tau \sum_{i=1}^{M} \alpha_{ik} r_i$$

$$\tau \frac{dT}{dt} = (T_0 - \text{Touch On} \sum_{i=1}^{M} \underset{J}{\boxed{\frac{(-\Delta H_i)}{\rho \hat{C}_p}}} r_i + \boxed{\frac{Q_H^*}{\rho \hat{C}_p Q_0}}\; Q_H$$

$$J_i = \frac{(-\Delta H_i)}{\rho \hat{C}_p} \quad \text{and} \quad Q_H = \frac{Q_H^*}{\rho \hat{C}_p Q_0}$$



Mixed Flow Reactor

Governing Equations

$$\frac{dC_k}{dt} = \frac{C_{k0} - C_k}{\tau} + \sum_{i=1}^{M} \alpha_{ik} r_i$$

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + \sum_{i=1}^{M} J_i r_i + \frac{Q_H}{\tau}$$

At steady state

$$C_{k0} - C_k + \tau \sum_{i=1}^{M} \alpha_{ik} r_i = 0$$

$$T_0 - T + \tau \sum_{i=1}^{M} J_i r_i + Q_H = 0$$

So let us consider mixed flow reactor governing equations. In the last lecture in mass and energy balance for CSTR we have derived the species mole balance equation and the energy balance equation. Now if the density of the inlet stream and the outlet streams are constant, in that case we can assume constant heat capacity and other physical properties.

Then we can write the equation as, for species mole balance it would be

$$V \frac{dC_k}{dt} = Q_0 \left(C_{k0} - C_k \right) + V \sum_{i=1}^{M} \alpha_{ik} r_i$$

So this is species mole balance equation. Now the energy balance equations would be

$$\rho \hat{C}_p V \frac{dT}{dt} = \rho \hat{C}_p Q_0 \left(T_0 - T \right) + V \sum_{i=1}^{M} \left(-\Delta H_i \right) r_i + Q_H^*$$

So here V is the reactor volume and it is assumed constant, and Q_0 which is given over here is basically the inlet volumetric flow rate. So Q_0 is the inlet volumetric flow rate and this is equal to the outlet flow rate because the density is constant. So this is equal to the outlet flow rate as density is constant. Q_H^* is basically the total heat addition rate to the reactor. So this would be positive for heating and negative for cooling.

The heat addition to the surface as we have done before that

$$Q_H^* = UA\left(T - T_c\right)$$

Now we can define the residence time as we have done for the plug flow reactor. So we can write the residence time τ which is equal to

$$\tau = \frac{V}{Q_0}$$

And then we can write the earlier equation, the species mole balance will be

$$\tau \frac{dC_k}{dt} = \left(C_{k0} - C_k\right) + \tau \sum_{i=1}^{M} \alpha_{ik} r_i$$

Similarly the energy balance equation can be written as

$$\tau \frac{dT}{dt} = \left(T_0 - T\right) + \tau \sum_{i=1}^{M} \frac{\left(-\Delta H_i\right)}{\rho C_p} r_i + \frac{Q_H^*}{\rho C_p}$$

Now if we want to simplify this relation we can define another term J which is, you can write

$$J_i = \frac{\left(-\Delta H_i\right)}{\rho C_p}$$

and Q_H we can write,.

$$Q_H = \frac{Q_H^*}{\rho C_p}$$

So this term is J and this term as Q_H. Now if we substitute these terms over here we can write

$$\frac{dC_k}{dt} = \frac{\left(C_{k0} - C_k\right)}{\tau} + \tau \sum_{i=1}^{M} \alpha_{ik} r_i$$

And this would be, energy balance equation would be

$$\frac{dT}{dt} = \left(\frac{T_0 - T}{\tau}\right) + \sum_{i=1}^{M} J_i r_i + \frac{Q_H}{\tau}$$

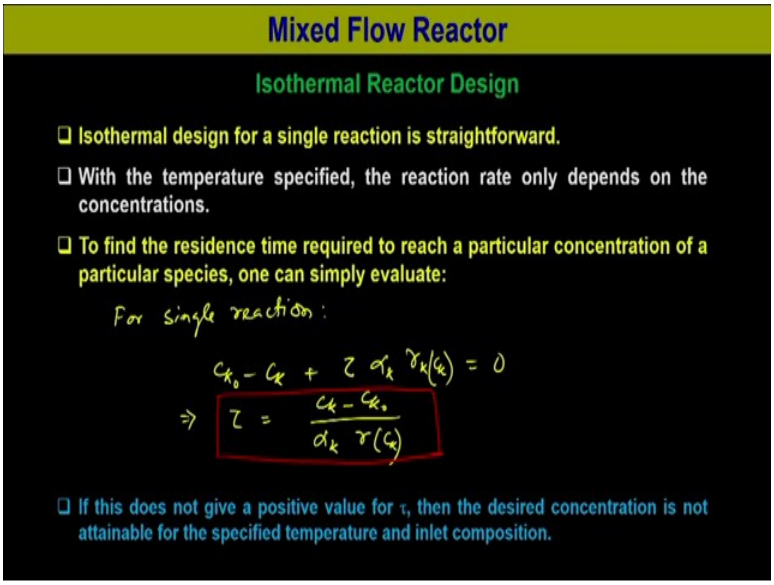
Now if we consider steady state, so at steady state

$$C_{k0} - C_k + \tau \sum_{i=1}^{M} \alpha_{ik} r_i = 0$$

Similarly the energy balance equation would be

$$T_0 - T + \tau \sum_{i=1}^{M} J_i r_i + Q_H = 0$$

(Refer Slide Time: 13:20)



Mixed Flow Reactor

Isothermal Reactor Design

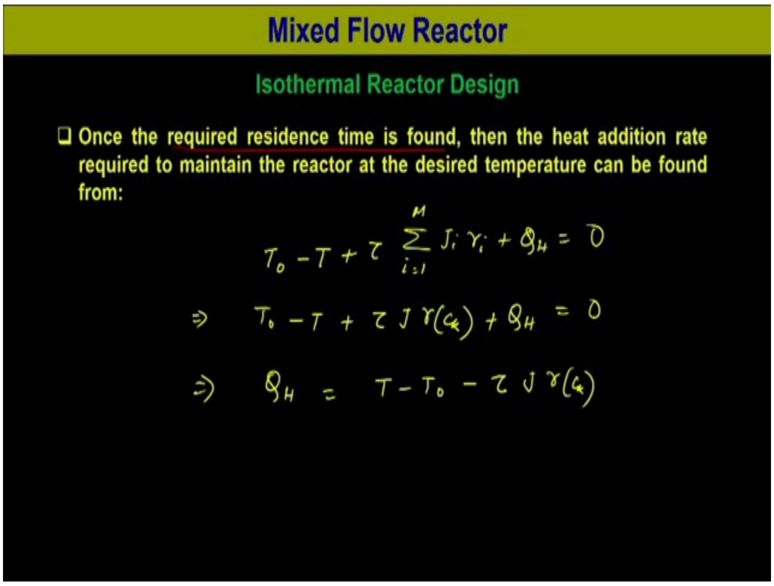
- Isothermal design for a single reaction is straightforward.
- With the temperature specified, the reaction rate only depends on the concentrations.
- To find the residence time required to reach a particular concentration of a particular species, one can simply evaluate:

For single reaction:

$$C_{k_0} - C_k + \tau \alpha_k r_k(C_k) = 0$$

$$\Rightarrow \boxed{\tau = \frac{C_k - C_{k_0}}{\alpha_k r(C_k)}}$$

- If this does not give a positive value for τ, then the desired concentration is not attainable for the specified temperature and inlet composition.



Mixed Flow Reactor

Isothermal Reactor Design

- Once the required residence time is found, then the heat addition rate required to maintain the reactor at the desired temperature can be found from:

$$T_0 - T + \tau \sum_{i=1}^{M} J_i r_i + q_H = 0$$

$$\Rightarrow T_0 - T + \tau J r(C_k) + q_H = 0$$

$$\Rightarrow q_H = T - T_0 - \tau J r(C_k)$$

Now let us consider a single reaction for isothermal reactor design. So if we consider a single reaction then the solution or design of the isothermal reactor is very straightforward. So with the temperature specified the reaction rate only depend on the concentration. So the earlier species balance equation that is

$$C_{k0} - C_k + \tau\alpha_k r_k\left(C_k\right) = 0$$

So for single reaction we can write

$$C_{k0} - C_k + \tau\alpha_k r_k = 0$$

So when it is isothermal conditions then rate of reaction will only depend on the concentration. So this r_k is a function of concentration only. So if this is the relations for the single reaction, so if we rearrange for tau we can write, so we can write from here

So this is the relation.

$$\tau = \frac{C_{k0} - C_k}{\alpha_k r_k\left(C_k\right)}$$

So to find the residence time required to reach a particular concentration of a particular species one simply evaluate tau. Now if this tau does not give the positive value then the desired concentration is not attainable for the specified temperature and inlet composition. So this way we can design the isothermal reactor for a particular residence time to obtain the conversion, desired conversion.

But if we consider the energy balance equation, once we get the required residence time then the heat addition rate required to maintain the reactor at the desired temperature can be obtained from the energy balance equations. So we had energy balance equation,

$$T_0 - T + \tau \sum_{i=1}^{M} J_i r_i + Q_H = 0$$

Now since it is isothermal, so and single reaction we can write this relation as

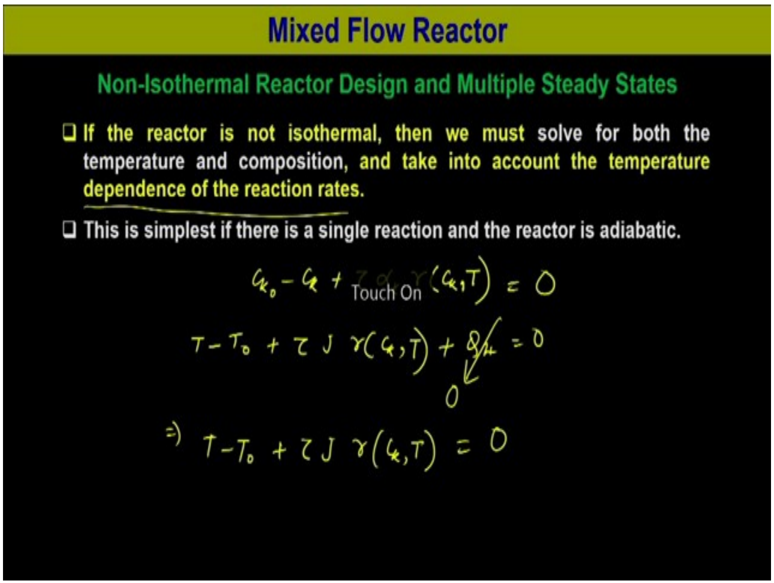
$$T_0 - T + \tau J r\left(C_k\right) + Q_H = 0$$

So from here we can get

$$Q_H = T - T_0 - \tau J r\left(C_k\right)$$

Q H is equal to T minus T naught minus tau J r is a function of concentration. So to obtain the required heat addition rate which is required to maintain the desired temperature we can calculate from the energy balance relation for a single reaction. So we can see that the isothermal reactor design is very straightforward. So now we will consider non-isothermal reactor design and multiple steady states.

(Refer Slide Time: 18:57)



Mixed Flow Reactor

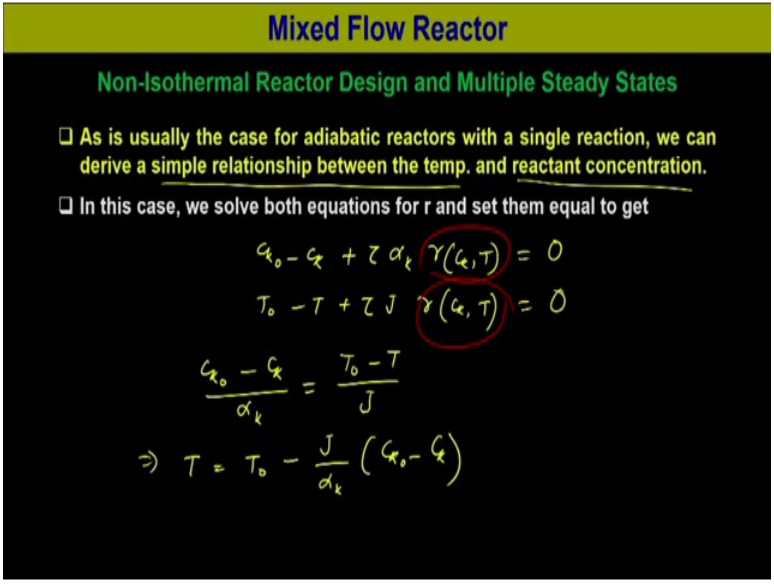
Non-Isothermal Reactor Design and Multiple Steady States

- ❑ If the reactor is not isothermal, then we must solve for both the temperature and composition, and take into account the temperature dependence of the reaction rates.
- ❑ This is simplest if there is a single reaction and the reactor is adiabatic.

$$C_{k0} - C_k + \tau \alpha_k r(C_k,T) = 0$$

$$T - T_0 + \tau J r(C_k,T) + \underset{0}{\cancel{Q_H}} = 0$$

$$\Rightarrow T - T_0 + \tau J r(C_k,T) = 0$$



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ❑ As is usually the case for adiabatic reactors with a single reaction, we can derive a simple relationship between the temp. and reactant concentration.
- ❑ In this case, we solve both equations for r and set them equal to get

$$C_{k0} - C_k + \tau \alpha_k \boxed{r(C_k,T)} = 0$$

$$T_0 - T + \tau J \boxed{r(C_k,T)} = 0$$

$$\frac{C_{k0} - C_k}{\alpha_k} = \frac{T_0 - T}{J}$$

$$\Rightarrow T = T_0 - \frac{J}{\alpha_k}(C_{k0} - C_k)$$

If we consider the reactor is not isothermal then we must solve for both the temperature and composition and take into account the temperature dependency of the reaction rates. So now the rate is not only depend on concentration it will also depend on the temperature. So this is simplest if there is a single reaction and the reactor is adiabatic in nature.

So if you consider the earlier species mole balance equation for a single reaction which we have derived that is

$$C_{k0} - C_k + \tau \alpha_k r(C_k, T) = 0$$

But energy balance equation that is

$$T_0 - T + \tau J r(C_k, T) + Q_H = 0$$

Since the reactor is adiabatic so this $Q_H = 0$ and we can write

$$T_0 - T + \tau J r\left(C_k, T\right) = 0$$

So this is our species mole balance equation and this is energy balance equation for a single reaction adiabatic, so non-isothermal systems. Now as we have considered before for the usual case of the single adiabatic reactions we can derive a simple relationship between the temperature and reactant concentration. So here we solve both equation for r and then set equal to get the desired relations. So our relation is

$$C_{k0} - C_k + \tau \alpha_k r\left(C_k, T\right) = 0$$

And another relation we have,

$$T_0 - T + \tau J r\left(C_k, T\right) = 0$$

Now from these two if we equate this rate then we can obtain the relation between this is

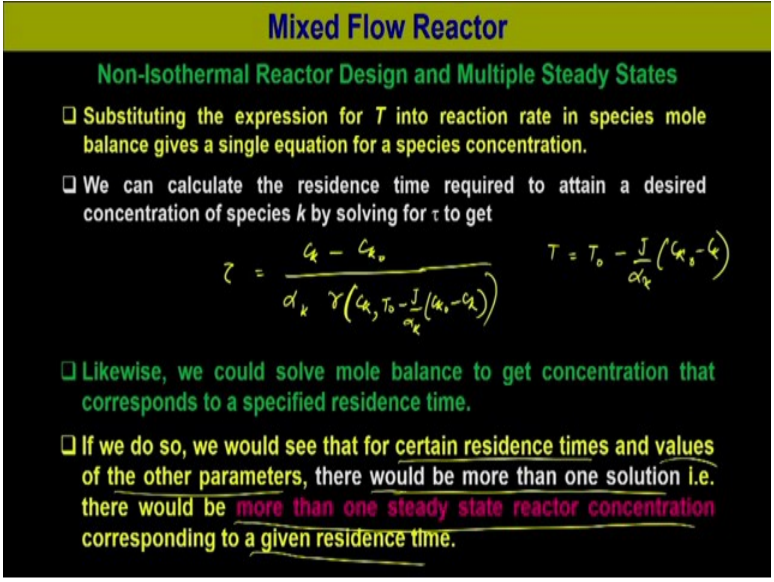
$$\frac{C_{k0} - C_k}{\alpha_k} = \frac{T_0 - T}{J}$$

Or from here we can write

$$T = T_0 - \frac{J}{\alpha_k}\left(C_{k0} - C_k\right)$$

So we have a relations between concentration and temperature. Now if we substitute this T in the reactor species mole balance equation then the equations will be only dependent on concentration.

(Refer Slide Time: 23:47)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ☐ Substituting the expression for *T* into reaction rate in species mole balance gives a single equation for a species concentration.
- ☐ We can calculate the residence time required to attain a desired concentration of species *k* by solving for τ to get

$$\tau = \frac{C_k - C_{k_0}}{\alpha_k \, r\left(C_k, T_0 - \frac{J}{\alpha_k}\left(C_{k_0} - C_k\right)\right)} \qquad T = T_0 - \frac{J}{\alpha_k}\left(C_{k_0} - C_k\right)$$

- ☐ Likewise, we could solve mole balance to get concentration that corresponds to a specified residence time.
- ☐ If we do so, we would see that for certain residence times and values of the other parameters, there would be more than one solution i.e. there would be more than one steady state reactor concentration corresponding to a given residence time.

So we can reduce from the two variable rate equation rates to single variable. So substituting the expression for T into rate into species mole balance gives a single equation for a species concentration. We can then evaluate the residence time required to attain a desired concentration of species k by solving for τ . So we will get

$$\tau = \frac{C_{k0} - C_k}{\alpha_k r_k \left(C_k \right)}$$

Then rate of reactions which is a function of concentration and temperature, the temperature relations we have obtained

$$T = T_0 - \frac{J}{\alpha_k} \left(C_{k0} - C_k \right)$$

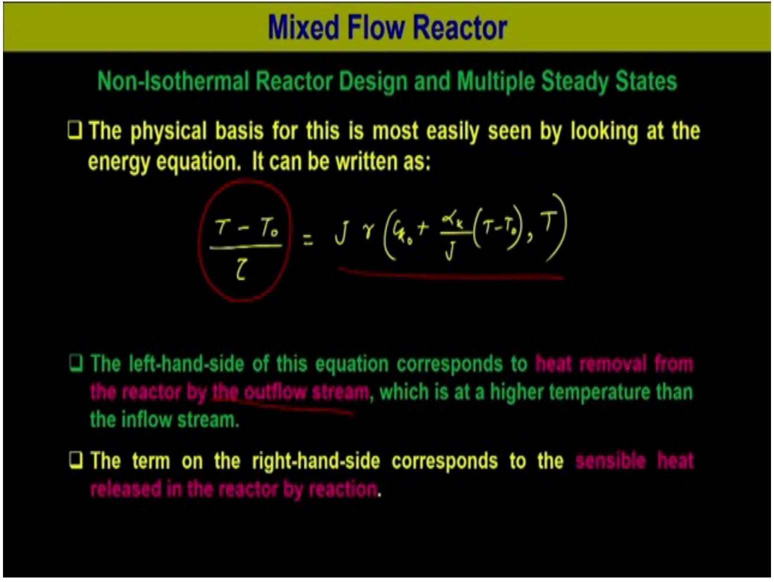
So this r, if we substitute this temperature here so this r will be only function of concentration. So we can write

$$T = T_0 - \frac{J}{\alpha_k} \left(C_{k0} - C_k \right)$$

So this is the equation of tau. So like this we could also solve the mole balance to get the concentration that correspond to a specified residence time. If we do so, what we will observe for a certain residence time and values of the other parameters there would be more than one solution. That is there would be more than one steady state reactor concentration corresponding to a given residence time.

So at a given residence time we would obtain multiple steady states if we solve the equation. We will see more detail in our couple of slides.

(Refer Slide Time: 26:15)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ❑ The physical basis for this is most easily seen by looking at the energy equation. It can be written as:

$$\frac{T - T_0}{\tau} = J\, r\left(C_{k0} + \frac{\alpha_k}{J}(T - T_0), T\right)$$

- ❑ The left-hand-side of this equation corresponds to heat removal from the reactor by the outflow stream, which is at a higher temperature than the inflow stream.
- ❑ The term on the right-hand-side corresponds to the sensible heat released in the reactor by reaction.

Let us see the physical basis of it which can be mostly seen from the energy balance equation. So the energy balance equation we can write

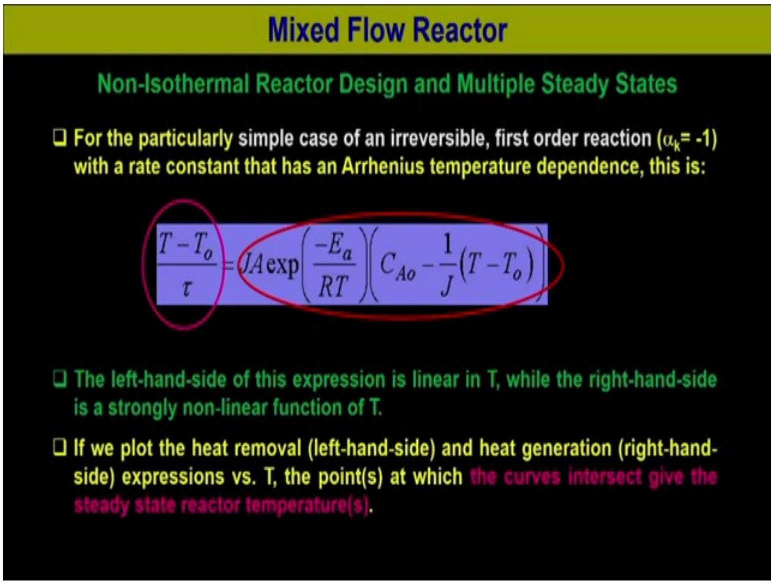
$$\frac{T_0 - T}{\tau} = Jr\left(C_{K0} + \frac{\alpha_k}{J}\left(T - T_0 \right), T \right)$$

So here the r is made only the temperature dependency, single variable, so the relations between temperature and concentration is substituted over here.

So r is function of temperature only. So this is from the energy balance equation. The left hand side of this equation corresponds to this part, is corresponds to the heat removal from the reactor by the outflow streams. We have a temperature which is coming at the inlet is T_0 and the T is the temperature of the reactor. It is same as the outflow and tau is the residence time. So the left hand side basically represents the heat removal by the reactor, heat removal from the reactor by the outflow streams which is at higher temperature than the inflow streams.

The term on the right hand side, this part corresponds to the sensible heat released in the reaction, in the reactor by the reaction. So the right hand side which represents the sensible heat released during the chemical reactions in the reactor.

(Refer Slide Time: 28:53)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- For the particularly simple case of an irreversible, first order reaction (α_k= -1) with a rate constant that has an Arrhenius temperature dependence, this is:

$$\frac{T-T_o}{\tau} = JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{Ao}-\frac{1}{J}(T-T_o)\right)$$

- The left-hand-side of this expression is linear in T, while the right-hand-side is a strongly non-linear function of T.
- If we plot the heat removal (left-hand-side) and heat generation (right-hand-side) expressions vs. T, the point(s) at which the curves intersect give the steady state reactor temperature(s).

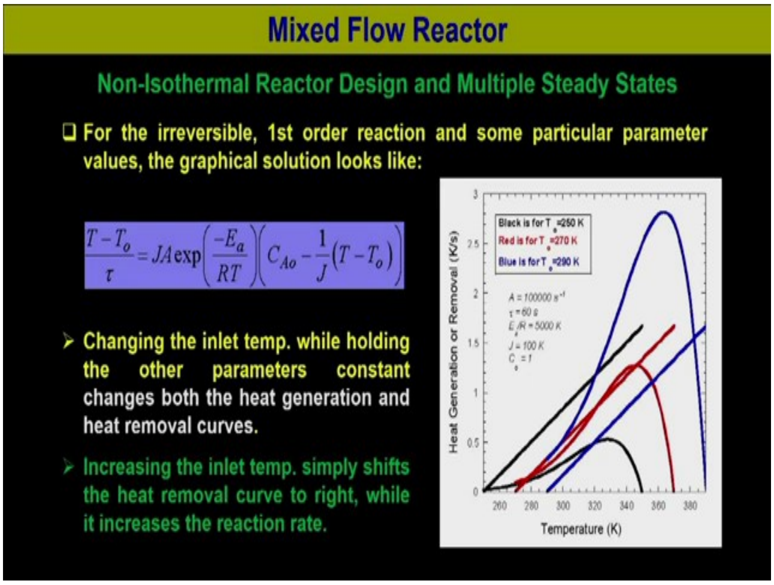
For a particularly simple case if we consider an irreversible first order reaction where $\alpha_k = -1$ with a rate constant that has an Arrhenius temperature dependency if we write, then the relations between temperature and rate of reaction would be like this, or the energy balance equations would be like this.

$$\frac{T_0 - T}{\tau} = JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{A0} - \frac{1}{J}\left(T - T_0\right)\right)$$

So this is the energy balance equation for an irreversible first order reactions with a stoichiometric coefficient is -1. The left hand side of this expression, this is $\frac{T_0 - T}{\tau}$ is linear in T while the right hand side, here, this is a strongly non-linear function of T because of the Arrhenius relations. So this is strongly non-linear in nature.

The right hand side, that is $\exp\left(\frac{-E_a}{RT}\right)$. So now if we plot the heat removal, that is the left hand side and the heat generation that is on the right hand side of this equation with respect to temperature the points at which the curves intersect, both the heat removal and the heat generation curve, the left hand side curve if we plot with respect to temperature and the right hand side with respect to temperature, the points they intersects is the steady state conditions or the steady state temperature of the reactor.

(Refer Slide Time: 31:11)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- For the irreversible, 1st order reaction and some particular parameter values, the graphical solution looks like:

$$\frac{T-T_o}{\tau} = JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{Ao} - \frac{1}{J}(T-T_o)\right)$$

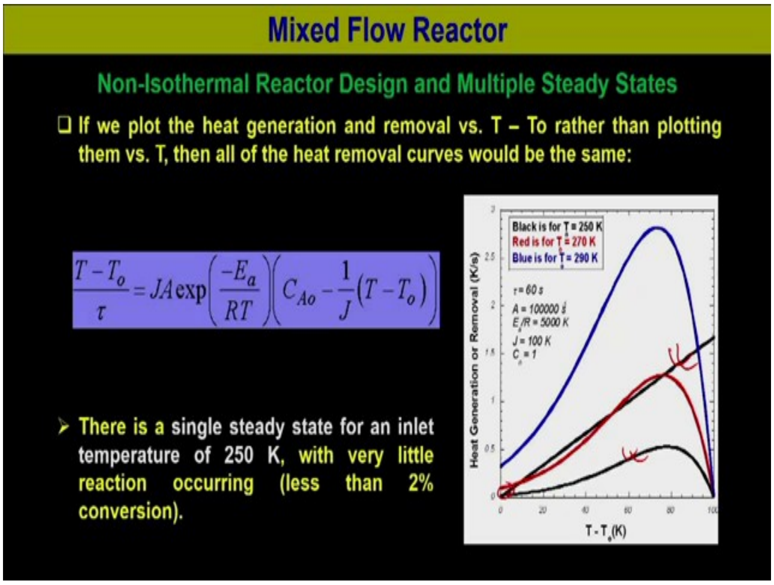
- Changing the inlet temp. while holding the other parameters constant changes both the heat generation and heat removal curves.
- Increasing the inlet temp. simply shifts the heat removal curve to right, while it increases the reaction rate.

Now for the irreversible first order reaction some particular parameter values, the graphical solution should be look like this. So here this is our energy balance equation and this is the, y axis over here is heat generation or removal in terms of Kelvin per second and on the x axis the temperature is plotted. So with respect to temperature heat generation or heat removal is plotted over here with a particular values of Arrhenius constant, exponential factor A and E_a activation energy, by RT so that is given over here and tau is the residence time, J which we have defined earlier that values is also given.

Initial concentration is taken as 1. So with these values if we change the initial or inlet temperature to the reactor what will happen? So changing the inlet temperature while holding the other parameter constant changes both the heat generation and the heat removal curve. We can see, so this black curve represents the left hand side that is the heat removal with respect to temperature at 250 degree Kelvin. Then the red straight line, because that is the linear with respect to temperature, left hand side curve. At 270 it is the red one, and at 290 it is the blue one, the straight line.

So both are, as we change the inlet temperature holding all other parameters constant, both the curve, the right hand side curve and the left hand side curve are shifting towards the right. Now increasing the inlet temperature as we have said, it simply shifts the heat removal curve to right while it increases the reaction rate.

(Refer Slide Time: 33:34)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ☐ If we plot the heat generation and removal vs. T – To rather than plotting them vs. T, then all of the heat removal curves would be the same:

$$\frac{T-T_o}{\tau} = JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{Ao}-\frac{1}{J}(T-T_o)\right)$$

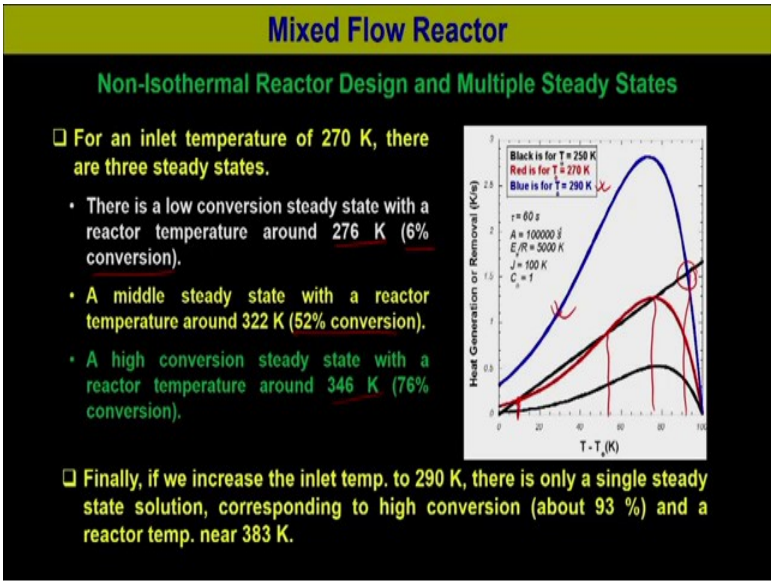
- ➢ There is a single steady state for an inlet temperature of 250 K, with very little reaction occurring (less than 2% conversion).

Now if we plot the heat generation and removal versus $T - T_0$ rather than plotting them versus T, then all the heat removal curves would be same because if we look into this equation, if we plot the left hand side with respect to $T - T_0$, even if we change the inlet temperature the left hand side will lie on the same line, that is on the black line shown over here.

So we could see there is a single steady state for inlet temperature of 250 at a very low conversion over here. That is the black curve at 250 and those, the right hand side curve which is the black one over here and this curve, the linear curve, left hand side curve they intersect at a point over here which is about 2 percent conversion. So there is a single steady state and low conversion steady state at a lower temperature.

So as you get over here, $T - T_0$ which is equivalent to, you can consider the conversion as well because the temperature difference and the concentration difference, they have a relationship we have derived for a single relation.

(Refer Slide Time: 35:12)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

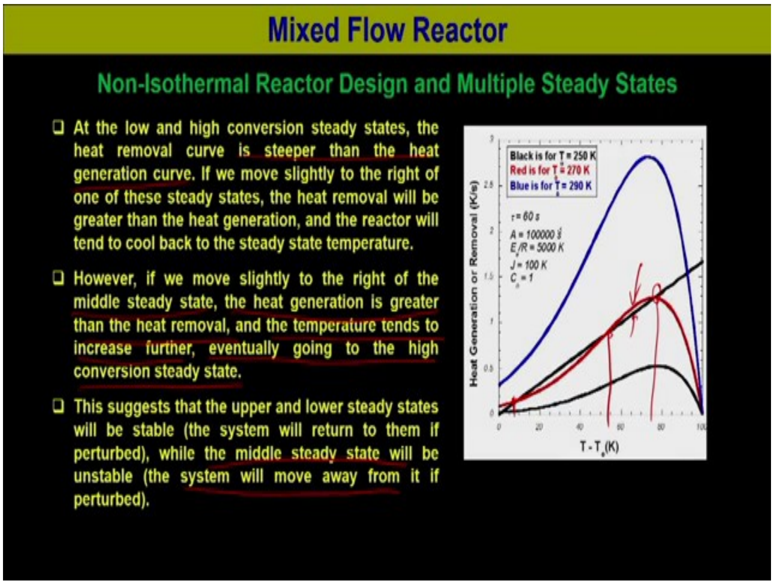
- ☐ For an inlet temperature of 270 K, there are three steady states.
  - There is a low conversion steady state with a reactor temperature around 276 K (6% conversion).
  - A middle steady state with a reactor temperature around 322 K (52% conversion).
  - A high conversion steady state with a reactor temperature around 346 K (76% conversion).
- ☐ Finally, if we increase the inlet temp. to 290 K, there is only a single steady state solution, corresponding to high conversion (about 93 %) and a reactor temp. near 383 K.

Now for inlet temperature say about 270 Kelvin there are 3 steady states. We can see over here. There is a low conversion steady state with a reactor temperature around 276 Kelvin so which is over here.

So this black curve that is also the red curve is merged on the left hand side curve which is merged with the same black line, and this is, this red curve is basically at T naught is equal to 270. So both the curves intersects at this point which is about, temperature would be around 276 Kelvin, so and the conversion is about 6 percent. Now at middle steady state with a reactor temperature around 322 Kelvin that is 52 percent conversion which is over here which is the temperature is around 322 Kelvin and the conversion is about 52 percent. Then we can see there is another intersection between these 2 curves.

A high conversion steady state with a reactor temperature around 346 Kelvin that is about 76 percent conversion. Now, finally if we increase the inlet temperature to 290 that is 290, the left hand side curve will superimpose on the black line, straight line and this blue line is basically at 290 on the right hand side curve, that is the heat generation curve and so heat generation curve intersects at this point. So that is corresponding to the high conversion steady state, only the single point which is about 93 percent and the temperature is near about 383 Kelvin.

(Refer Slide Time: 37:30)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- At the low and high conversion steady states, the heat removal curve is steeper than the heat generation curve. If we move slightly to the right of one of these steady states, the heat removal will be greater than the heat generation, and the reactor will tend to cool back to the steady state temperature.
- However, if we move slightly to the right of the middle steady state, the heat generation is greater than the heat removal, and the temperature tends to increase further, eventually going to the high conversion steady state.
- This suggests that the upper and lower steady states will be stable (the system will return to them if perturbed), while the middle steady state will be unstable (the system will move away from it if perturbed).

Now if we look into the details on it, the middle part that T naught is equal to 270 Kelvin for all the other parameter constant, we can see as we have said there are 3 intersections, so 3 steady states. So we have low and high conversion steady state, low and high conversion then this at low and high conversion steady state the heat removal curve is steeper than the heat generation curve.

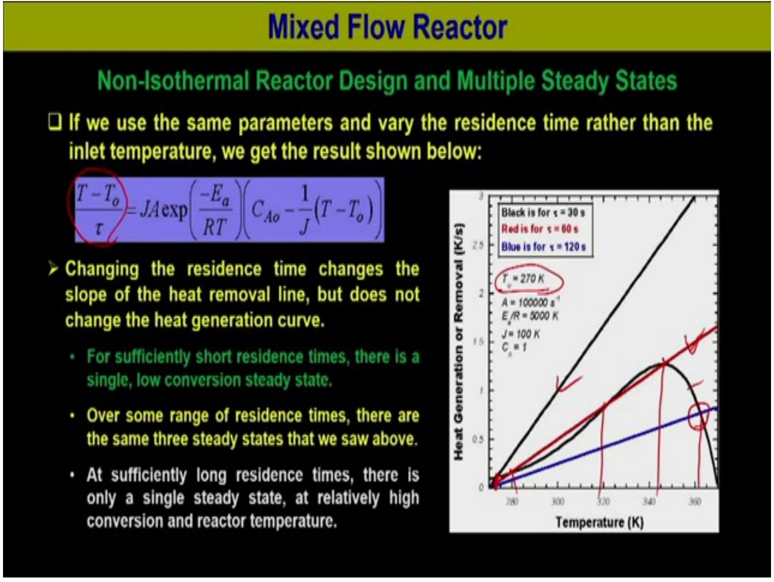
We can see the heat generation curve is the curve line over here, red line and heat removal curve is the black line shown over here. So from the point, low conversion point if we look, go forward towards right, we could see the black line is more steeper compared to the slope of the red line here. Similarly if we move towards the right from point, the high conversion point, the heat removal curve that is the black one is much steeper compared to the red one.

So that means the heat removal will be greater than the heat generation for these two points. So if the reactor is perturbed from these two points towards the right, the reactor, the heat removal will be higher so that the reactor will cool down to the steady states. So if we move slightly to right of the middle steady state the heat generation we can see over here. At this point the slope of the red curve that is the heat generation curve is higher than the black one; that is the heat removal.

So if heat generation is more then it will not come back. If we go right little bit, move forward towards right, it will heat up because the heat generation is more and it will reach to the higher steady state conditions. So if we move slightly to the right of the middle steady state the heat generation is greater than the heat removal. And the temperature tends to increase further, so eventually going to the high conversion steady state.

So from this observation this suggests that the upper and lower steady state will be the stable steady states. The system will return to them if it is perturbed. While the middle steady state will be unstable the system will move away from it if perturbed. So either it will go to the high conversion steady states or it will move towards the low conversion steady states.

(Refer Slide Time: 41:09)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ❑ If we use the same parameters and vary the residence time rather than the inlet temperature, we get the result shown below:

$$\frac{T-T_o}{\tau} = JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{Ao}-\frac{1}{J}(T-T_o)\right)$$

- ➢ Changing the residence time changes the slope of the heat removal line, but does not change the heat generation curve.
  - For sufficiently short residence times, there is a single, low conversion steady state.
  - Over some range of residence times, there are the same three steady states that we saw above.
  - At sufficiently long residence times, there is only a single steady state, at relatively high conversion and reactor temperature.

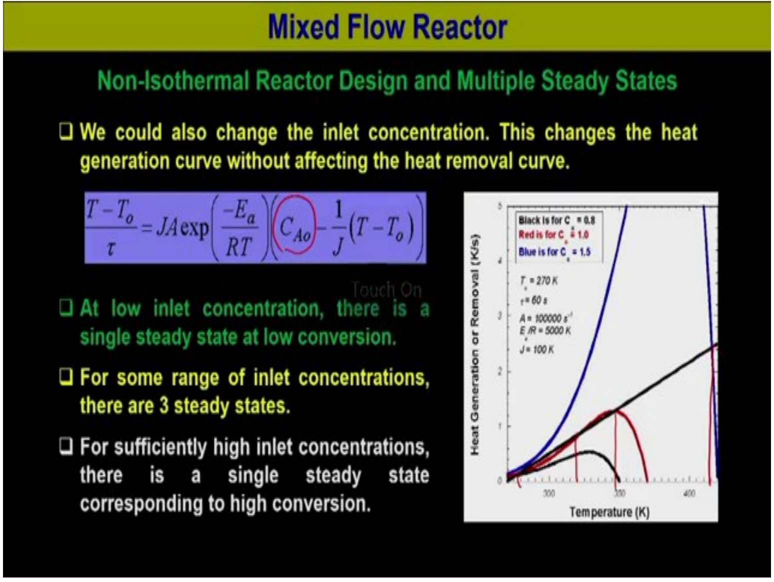
Now if we use the same parameter and vary the residence time rather than the inlet temperature, we can also see similar plot. So our equation is this, the energy balance equation and for a particular temperature that is inlet temperature is 270 Kelvin. Keeping all other parameters same, so we have considered inlet temperature keeping all other parameter constant where we observe the multiple steady states.

So we kept that inlet temperature constant at 270 Kelvin and all other parameters constant except the residence time. So we varied the residence time from 30 to 120 seconds. So changing the residence times the slope of the heat removal curve that is the left hand side over here, so changing the residence time the slope of the heat removal line will change but it does not change the heat generation curve.

So all the heat generation curve will be, will lie on the same line, only the left hand side with respect to temperature if we vary the residence time then the slope of the line, heat removal line will change. So we could see that for sufficiently short residence time, very small residence time when tau is equal to 30, so this is the line for the heat removal and the heat generation curve is this one, the black one. So this intercepts at this point. So we could see the low conversion steady states.

For some range of residence time there are same are 3 steady states that we saw earlier. So at tau is equal to 60 seconds the, this is the heat removal curve and the black one is the heat generation curve. So it intersects at three different points, so which is similar to the earlier. At sufficiently long residence time there is another intersection which is at the high conversion over here.

(Refer Slide Time: 43:57)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ☐ We could also change the inlet concentration. This changes the heat generation curve without affecting the heat removal curve.

$$\frac{T-T_o}{\tau}=JA\exp\left(\frac{-E_a}{RT}\right)\left(C_{Ao}-\frac{1}{J}(T-T_o)\right)$$

- ☐ At low inlet concentration, there is a single steady state at low conversion.
- ☐ For some range of inlet concentrations, there are 3 steady states.
- ☐ For sufficiently high inlet concentrations, there is a single steady state corresponding to high conversion.

Similarly as we have changed the temperature, inlet temperature then we have seen the inlet, the residence time and we can also change the inlet concentration. This changes also the heat generation curve without affecting the heat removal curve. So this is our energy balance equation. So we change the inlet concentration C_{A0} which is represented over here as C_0. So if we change keeping all other parameters constant where T naught is 270 Kelvin and tau is equal to 60 second, this two kept same as earlier where we observed the multiple steady states.

Now the inlet concentration can be varied from 1, 0.8 and 1.5. So if we do so, at low inlet concentration there is a single steady state at low conversion. So in this case if we change only the concentration we could only, the heat generation curve will change. But it will not change the heat removal curve because it is the, left hand side is not function of the concentration. So we could see that at, for some range of inlet concentration, that is at C_0 is equal to 1 there will be 3 steady states or 3 intersection between the heat generation and heat removal curve. For sufficiently high inlet concentration there is a single conversion over here, that is at high conversion.

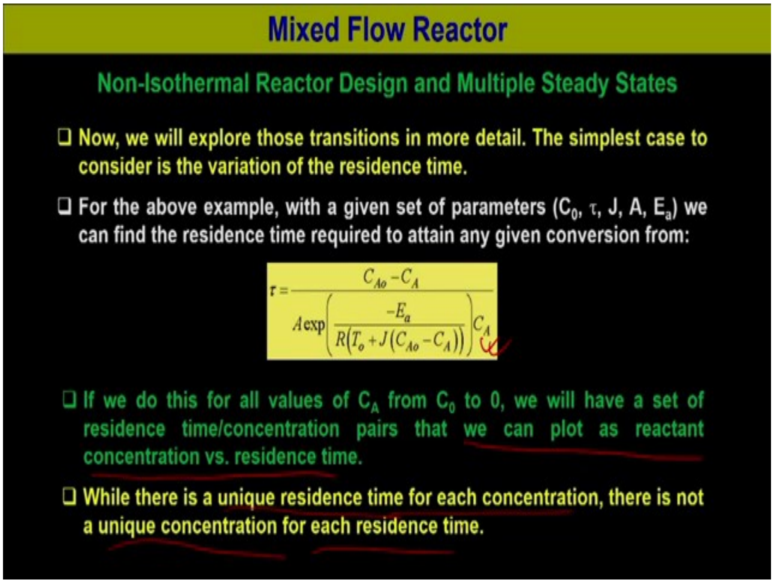
So far we have seen that for a particular condition or conditions in case of CSTR or the mixed flow reactor there are 3 different steady states and out of them two of their steady states are stable steady states and one steady state is unstable steady states which is generally not observed during the reaction and we have seen these effects, only the parameters we can vary. That is we varied the inlet concentration, inlet temperature and the residence time so, which we can control.

But the other parameters might change during this process that is the, say in case pre-exponential factor a, this may also change, decrease with time if we change the residence time, this may decrease with time because this may happen in case of the catalytic reactions where there is a catalyst deactivation. So in that case this may change. So those are the exceptions. So at this point we should remember that the case we discussed only for a single irreversible reactions.

If there is multiple reaction qualitatively might be similar observation might be, or would be seen but more complex behavior might be possible as well. Another thing is that if the reaction is not adiabatic, if it is not adiabatic then explicit heating or cooling term should be added in the heat removal expression. So if we add that, it will just and if that is constant, heat removal or heat for non-adiabatic system, if that part is constant it will just shift the heat removal curve and only it will change the slope of the curve.

Now these cases which we have considered is basically for the exothermic reaction where there is a heat generation. Now if the reaction is endothermic in nature rather than exothermic, in that case the heat generation curve would be negative. So only, we would, it is possible to get the single steady state with the reactor temperature lower than the inlet temperature because since the, it is the reaction is endothermic in nature, once the reaction will happen the temperature will come down from the inlet temperature. So we would obtain only the single steady states.

(Refer Slide Time: 49:57)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ❑ Now, we will explore those transitions in more detail. The simplest case to consider is the variation of the residence time.
- ❑ For the above example, with a given set of parameters (C_0, τ, J, A, E_a) we can find the residence time required to attain any given conversion from:

$$\tau = \frac{C_{Ao} - C_A}{A\exp\left(\frac{-E_a}{R\left(T_o + J\left(C_{Ao} - C_A\right)\right)}\right)C_A}$$

- ❑ If we do this for all values of C_A from C_0 to 0, we will have a set of residence time/concentration pairs that we can plot as reactant concentration vs. residence time.
- ❑ While there is a unique residence time for each concentration, there is not a unique concentration for each residence time.

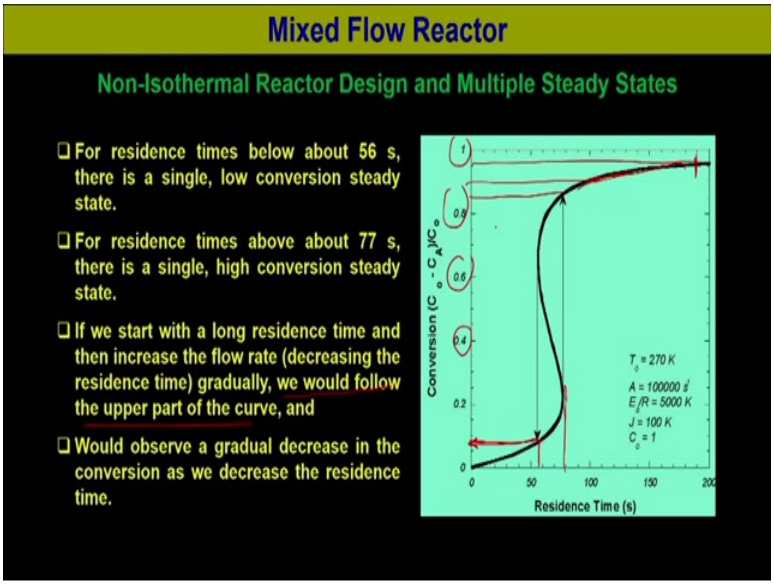
Now we will explore the transition in more detail. The simplest case to consider is the variation of the residence time. For the example, we have considered with a set of parameters that is C_0, τ, J, A and E_a, we can find the residence time required to attain any given conversion from this relation.

$$\tau = \frac{\left(C_{A0} - C_A\right)}{A\exp\left(\frac{-E_a}{R\left(T_0 + J\left(C_{A0} - C_A\right)\right)}\right)C_A}$$

So from this equation we can calculate the residence time with the particular parameters we have considered. If we do so for all values of C_A from C_0 to 0, we will have a set of residence time concentration pair. That we can plot as reactant concentration versus residence time. While there is a unique residence time for each concentration there is a unique concentration, there is not a unique concentration for each residence time.

So from this relation we can vary the concentration from C_0 to 0. So if we do so, from this expression we can calculate tau at different concentration. So we would have concentration and residence time pair and if we plot them we can see from there, for a unique residence time for each concentration we would obtain. But we may not get the unique concentration for each residence time.

(Refer Slide Time: 52:09)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

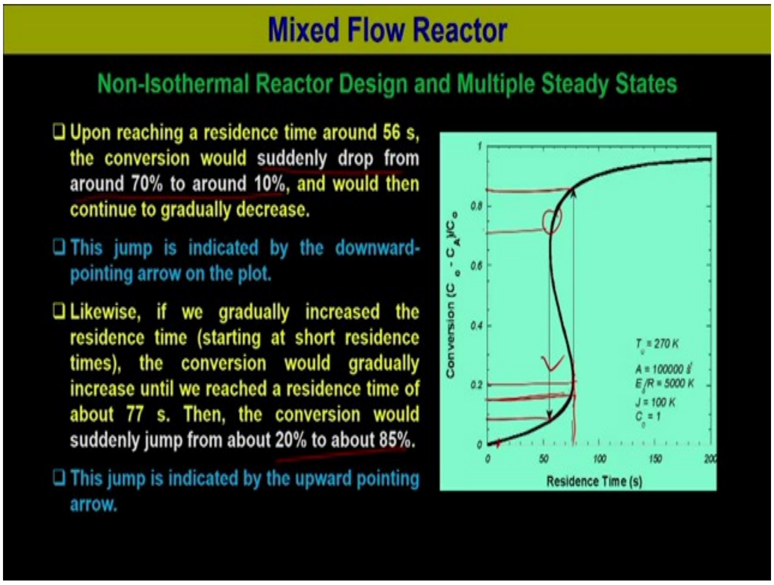
- ❑ For residence times below about 56 s, there is a single, low conversion steady state.
- ❑ For residence times above about 77 s, there is a single, high conversion steady state.
- ❑ If we start with a long residence time and then increase the flow rate (decreasing the residence time) gradually, we would follow the upper part of the curve, and
- ❑ Would observe a gradual decrease in the conversion as we decrease the residence time.

Let us see it. So this is the conversion, $\frac{C_0 - C_A}{C_0}$ versus residence time which was plotted. We could see from here, for a residence time below 56 seconds so over here there is a single low conversion steady state. So you could obtain the conversion from here. So this is 0, 20 percent conversion, 40 percent conversion, then 60, 80 and 100 percent conversion. So below the residence time 56 second we can obtain low conversion that is about 10 percent or so, 9 to 10 percent.

For residence time above 77 second that is over here, so you would obtain the high conversion steady states. If we start with a long residence time and then increase the flow rate, so initially we start with a very high residence time say here, so our flow rate is low. Now we increase the flow rate so our residence time of the reactant insider the reactor will decrease gradually, so we would follow the upper part of the curve. That means we would follow this curve.

And we would observe that a gradual decrease in the conversion. So we can see that, from here you have a conversion close to 90 percent and then it is decreased as you decrease the residence time. So conversion will gradually decrease.

(Refer Slide Time: 54:21)



Mixed Flow Reactor

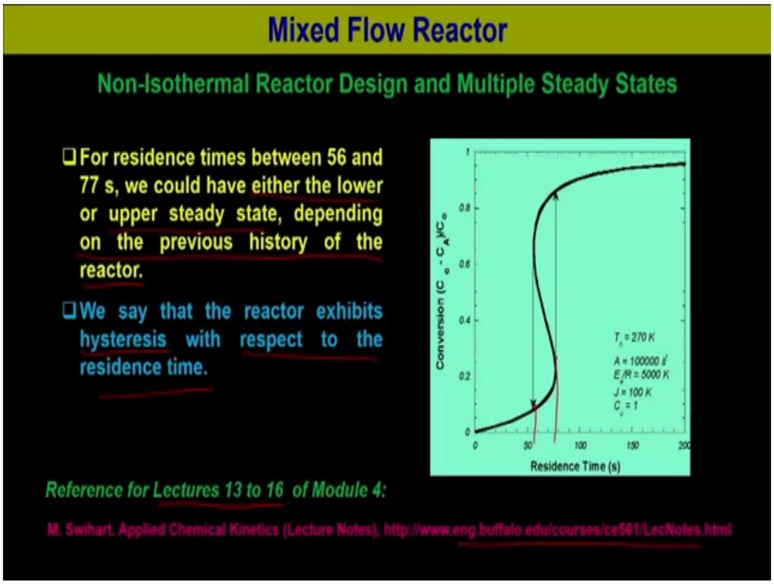
Non-Isothermal Reactor Design and Multiple Steady States

- ❑ Upon reaching a residence time around 56 s, the conversion would suddenly drop from around 70% to around 10%, and would then continue to gradually decrease.
- ❑ This jump is indicated by the downward-pointing arrow on the plot.
- ❑ Likewise, if we gradually increased the residence time (starting at short residence times), the conversion would gradually increase until we reached a residence time of about 77 s. Then, the conversion would suddenly jump from about 20% to about 85%.
- ❑ This jump is indicated by the upward pointing arrow.

Now if, upon reaching the residence time around 56 seconds over here the conversion would suddenly drop from around 70 percent to 10 percent, so which is over here. So conversion would suddenly drop from 70 percent to, so upon reaching the residence time around 56 seconds so which is over here and which is shown over here is black arrow, the conversion from 70 percent it is decreased to around 10 percent. And then it would continue gradually to decrease. This jump is indicated by the downward pointing arrow on the plot, so you could see over here.

Likewise if we gradually increase the residual time, that means we start at a very high flow rate so residence time is very low, so over here and then gradually increase until we reach a residence time of say, around 77 second, here then the conversion would suddenly jump from 20 percent to 80 percent, 85 percent. So from here it will jump to about 85 percent. So this jump is indicated by the upward pointing arrow, here.

(Refer Slide Time: 55:59)



Mixed Flow Reactor

Non-Isothermal Reactor Design and Multiple Steady States

- ☐ For residence times between 56 and 77 s, we could have either the lower or upper steady state, depending on the previous history of the reactor.
- ☐ We say that the reactor exhibits hysteresis with respect to the residence time.

Reference for Lectures 13 to 16 of Module 4:

M. Swihart. Applied Chemical Kinetics (Lecture Notes), http://www.eng.buffalo.edu/courses/ce561/LecNotes.html

For residence time between 56 second and 77 second, in between these two we could have either the lower conversion or upper steady states, upper conversion steady state depending on the previous history of the reactor.

So in this case we say that the reactor exhibit the hysteresis with respect to the residence time. So this is how we can observe in case of a CSTR, non-isothermal CSTR or mixed flow reactor the multiple steady state or multiplicity of a CSTR we could observe. The lectures which we have covered between 13 to 16 in this module is reference which is followed is the M. Swihart, Applied Chemical Kinetics, lecture notes which is from the University of Buffalo, lecture notes and the other part in this module we mostly considered on the Octave Levenspiel.

So this is end of the reactor design lectures. So thank you very much for attending this lecture and next module we will start with the non-ideal reactor design that is residence time distribution.