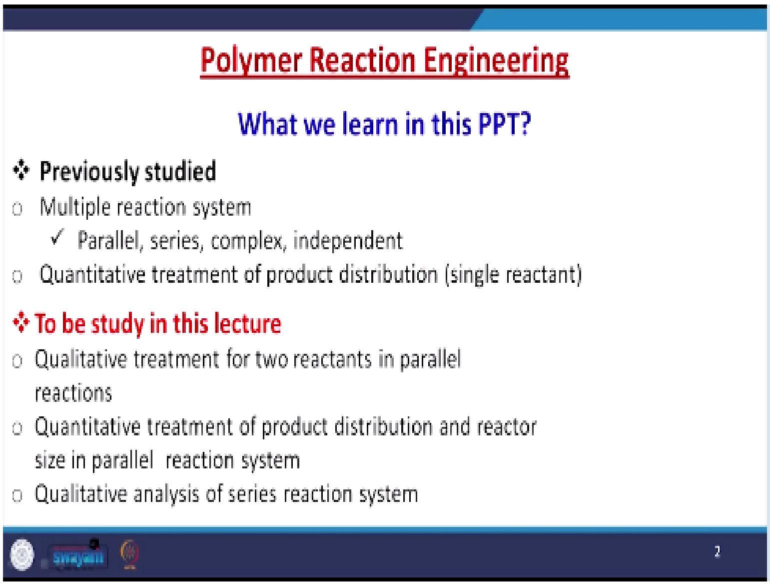
Polymer Reaction Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology Roorkee

Lecture – 23
Multiple Reactions System - II

Welcome to the second part of multiple reaction system under the head of polymer reaction engineering. Now, before we proceed further, let us look at what we studied previously. We had gone through the concept of multiple reaction system.

(Refer Slide Time: 00:40)



Polymer Reaction Engineering

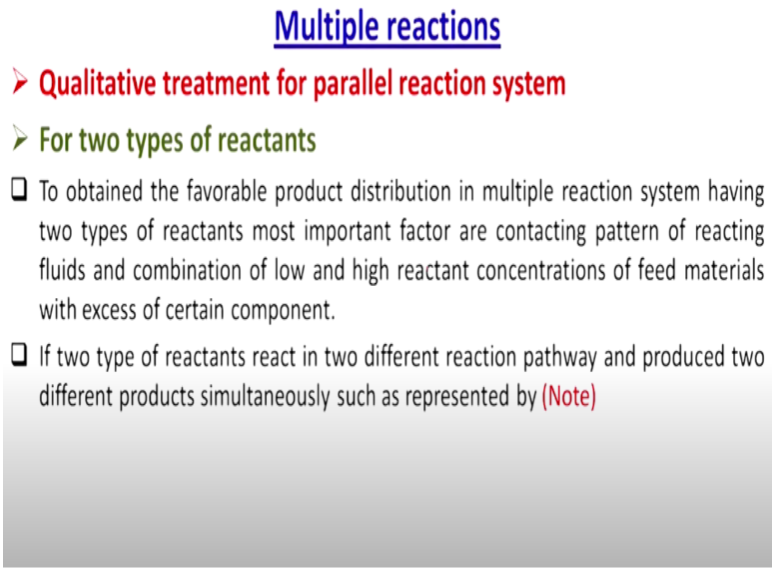
What we learn in this PPT?

- Previously studied
  - Multiple reaction system
    - ✓ Parallel, series, complex, independent
  - Quantitative treatment of product distribution (single reactant)
- To be study in this lecture
  - Qualitative treatment for two reactants in parallel reactions
  - Quantitative treatment of product distribution and reactor size in parallel reaction system
  - Qualitative analysis of series reaction system

Under this slide, we discussed about the parallel, series, complex, independent type of reaction system. Then we perform the quantitative treatment of product distribution under the head of single reactor and system. Now, in this particular lecture, we are going to discuss about the qualitative treatment for 2 reactants in parallel. Because this is one of the most common tool in all kinds of reaction engineering concept, especially polymer as well as in the chemical reaction engineering concept.

Then we will discuss about the quantitative treatment of product distribution and reactor size in parallel reaction system. We will discuss about the qualitative analysis of series reaction system. So, all these things, we will try to cover in this particular lecture.

(Refer Slide Time: 01:34)



Multiple reactions

- **Qualitative treatment for parallel reaction system**
- **For two types of reactants**

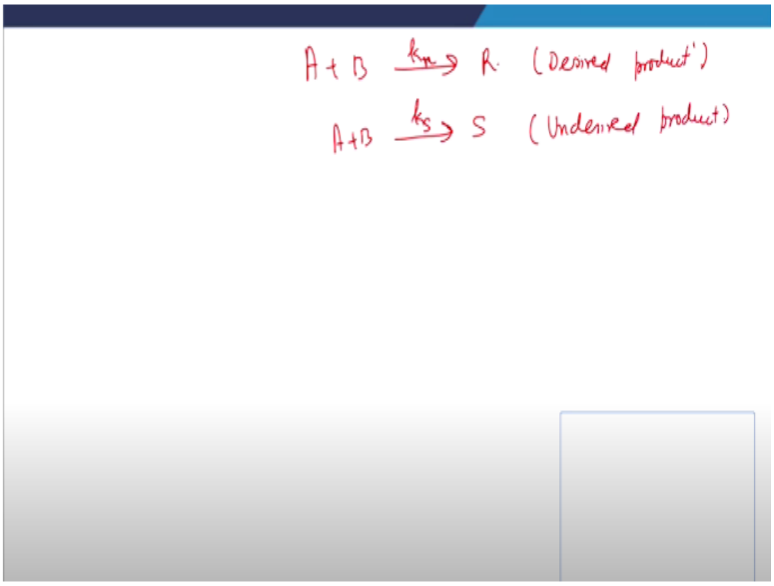
☐ To obtained the favorable product distribution in multiple reaction system having two types of reactants most important factor are contacting pattern of reacting fluids and combination of low and high reactant concentrations of feed materials with excess of certain component.

☐ If two type of reactants react in two different reaction pathway and produced two different products simultaneously such as represented by (Note)

Now, let us have a concept of a qualitative treatment of parallel reaction system. Now, there are 2 types of reactants, let us see. Now, to obtain the favourable product distribution in multiple reaction system, having 2 types of reactions. Most important factor, they are contacting pattern of reacting fluid and the combination of low and high reacting concentration of feed material with excess of certain components.

Now, see, one thing is that you are having 2 different reactants and you are looking for a favourable product distribution that is quite obvious for the economy of any kind of system. If 2 types of reactants, they react in 2 different reaction pathway and produce 2 different products simultaneously.

(Refer Slide Time: 02:30)

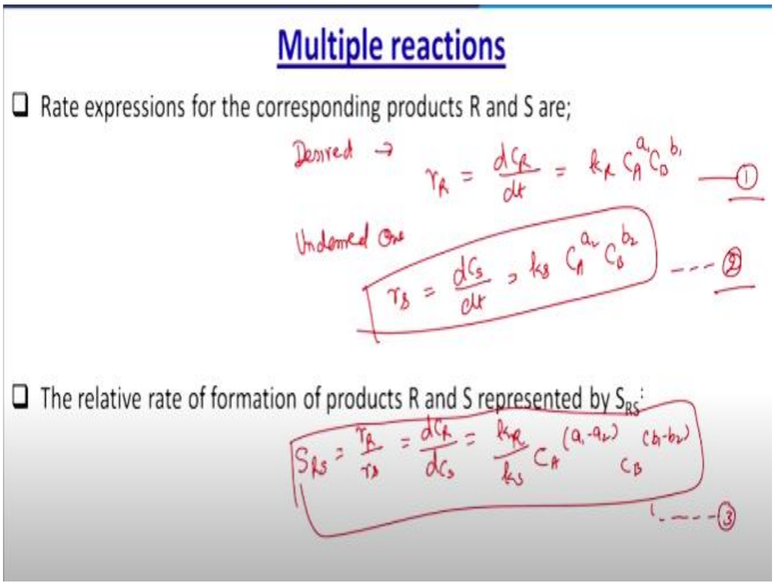


$A + B \xrightarrow{k_R} R$ (Desired product)

$A + B \xrightarrow{k_S} S$ (Undesired product)

These can be represented as A + B k_R, they are giving that is the desired product and A + B k_S, they are giving the undesired product.

(Refer Slide Time: 02:56)



Multiple reactions

❑ Rate expressions for the corresponding products R and S are;

Desired → $r_R = \frac{dC_R}{dt} = k_R C_A^{a_1} C_B^{b_1}$ —①

Undesired One $r_S = \frac{dC_S}{dt} = k_S C_A^{a_2} C_B^{b_2}$ ---②

❑ The relative rate of formation of products R and S represented by S_{RS}:

$S_{RS} = \frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_R}{k_S} C_A^{(a_1-a_2)} C_B^{(b_1-b_2)}$ ---③

Now, sometimes when we talk about these desired one and undesired one, people are always looking for the rate expression and when we try to write the rate expression for the corresponding product of R and S, remember R, we are representing as the desired one and S, we are representing as the undesired one. So, the rate equation for the desired one can be written as r_R = dC_R/dt k_R C_A^{a1} C_B^{b1} and sometimes you may write like equation number 1.

Desired product

$$r_R = \frac{dC_R}{dt} = k_R C_A^{a1} C_B^{b1} \text{.............}(1)$$

Undesired product

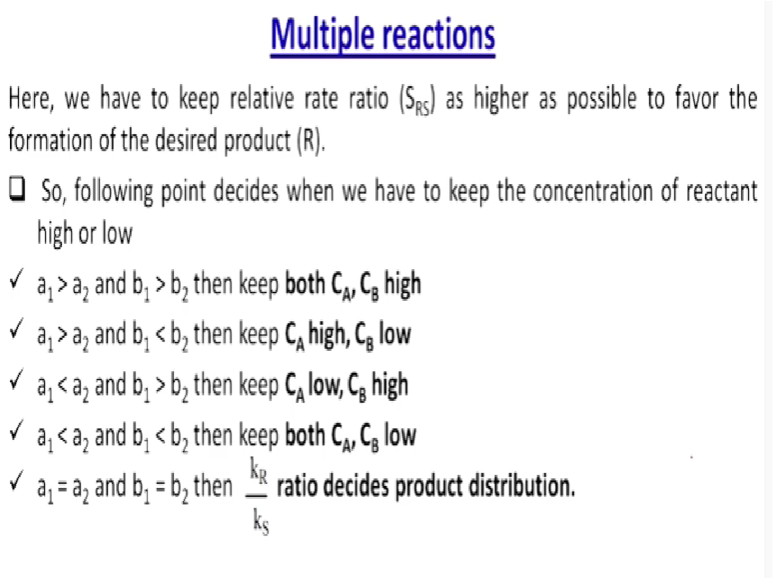
$$r_S = \frac{dC_S}{dt} = k_S C_A^{a2} C_B^{b2} \text{.............}(2)$$

And if you try to write for the undesired one, then we can write r_S is equal to dC_S upon dt k_S C_A^{a2} C_B^{b2}. This you can represent like a equation number 2. Now, sometimes we may have to look into the relative rate of formation of product R and S usually represented by S_{RS}. So, this relative rate of formation of product R and S, now, if we divide this equation 1 with equation 2, we may have this S_{RS} is equal to r_R upon r_S is equal to dC_R upon dC_S is equal to k_R upon k_S C_A^{a1} minus a_2 and C_B b_1 minus b_2.

Now, this is my desired equation for the S RS and let us represent this equation as equation number 3.

$$S_{RS} = \frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_R}{k_S} C_A^{(a1-a2)} C_A^{(b1-b2)} \text{………}(7)$$

(Refer Slide Time: 05:03)



Multiple reactions

Here, we have to keep relative rate ratio (S_{RS}) as higher as possible to favor the formation of the desired product (R).

☐ So, following point decides when we have to keep the concentration of reactant high or low

✓ $a_1 > a_2$ and $b_1 > b_2$ then keep **both C_A, C_B high**

✓ $a_1 > a_2$ and $b_1 < b_2$ then keep **C_A high, C_B low**

✓ $a_1 < a_2$ and $b_1 > b_2$ then keep **C_A low, C_B high**

✓ $a_1 < a_2$ and $b_1 < b_2$ then keep **both C_A, C_B low**

✓ $a_1 = a_2$ and $b_1 = b_2$ then $\frac{k_R}{k_S}$ **ratio decides product distribution.**

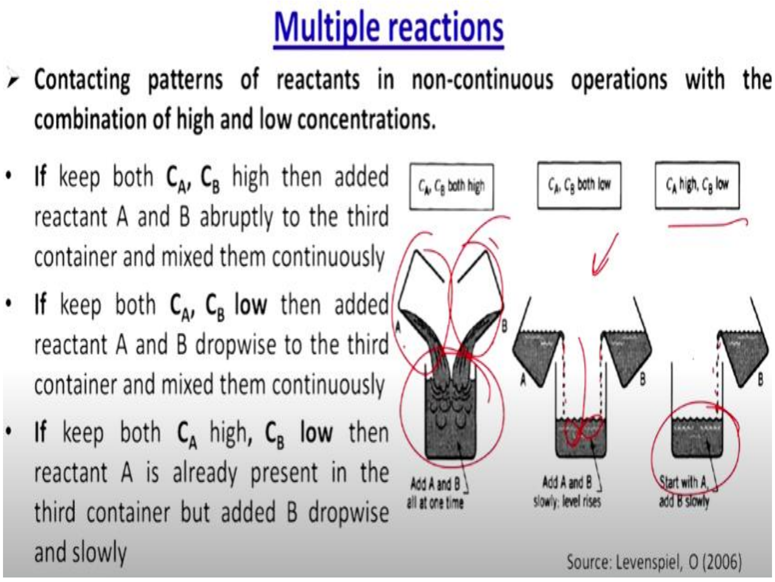
Now, here, we have to keep the relative rate ratio S_{RS} as high as possible to favour the formation of the desired product. Because, see in the numerator we are having r_R. So, therefore, we must maintain this ratio on the higher side. Therefore, the following points usually decide when we have to keep the concentration of reactant high or low. Now, if a_1 is greater than a_2 and b_1 is greater than b_2, then keep both the concentration C_A and C_B high.

Now, if there is another possibility that a 1, may have greater even, is greater than a 2 then and b_1 is less than b_2, then you may need to keep the C_A high and C_B low. Now, if a_1 is less than a_2 and b_1 is greater than b_2, then you need to keep C_A low and C_B high. Similarly, if a_1 is less than a_2 and b_1 is less than b_2, then keep both C_A and C_B as low as possible.

And sometimes one last option is there. When a_1 is equal to a_2 and b_1 is equal to b_2, then k_R upon k_S ratio decides the product distribution. So, these 6 or 5 or 6 parameters and approaches, they decide about the favourable product distribution condition. Now, sometimes during the multiple reactions, you need to look into the cantatrice pattern of reactants in non-continuous operation with the combination of high and low concentration.

Now, you need to go for various permutation and combination. You may have to keep your C_A and C_B high. You may need to keep C_A and C_B both low and you may need to keep the C_A high and C_B low. Now, if you keep both C_A and C_B high, then added reactants A and B abruptly to the third container and mix them continuously. So, this is a usual protocol.

(Refer Slide Time 7:24)



Multiple reactions

- Contacting patterns of reactants in non-continuous operations with the combination of high and low concentrations.

- If keep both C_A, C_B high then added reactant A and B abruptly to the third container and mixed them continuously
- If keep both C_A, C_B low then added reactant A and B dropwise to the third container and mixed them continuously
- If keep both C_A high, C_B low then reactant A is already present in the third container but added B dropwise and slowly

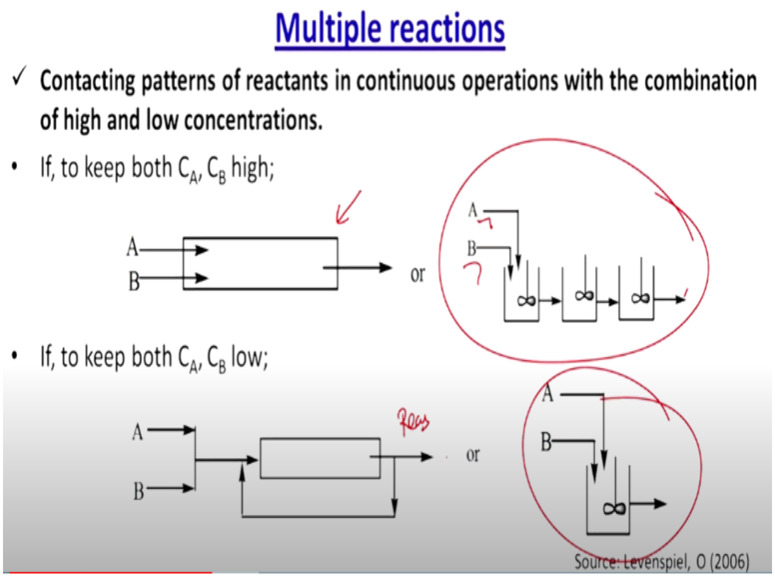
Source: Levenspiel, O (2006)

Now, here you see that instantaneously, you need to pour all these contents of A and B into another container or additional container. Now, if both C_A and C_B low that is in this condition, then added reactants A and B drop-wise, you can add these all these things in A drop-wise manner to the third container and mix them continuously. Now, if you decide to keep both C_A high and C_B low that is in the third container, then you need to start with A and you need to add B very slowly, so, all in a drop-wise.

Now, this is usually this protocol decides about your product favourable conditions. So, sometimes, you have to be a bit choosy about these kinds of protocols and adoption of these protocol is extremely important for the product, final product outcome or a final product distribution. Now, when we are talking about the contacting pattern and sometimes, we need to deal with the continuous operation with the combination of high and low concentration.

Now in that case, sometimes you need to design your own reactor battery. Now, there are again various combinations or various permutations are available for these kinds of approaches.

(Refer Slide Time 9:01)



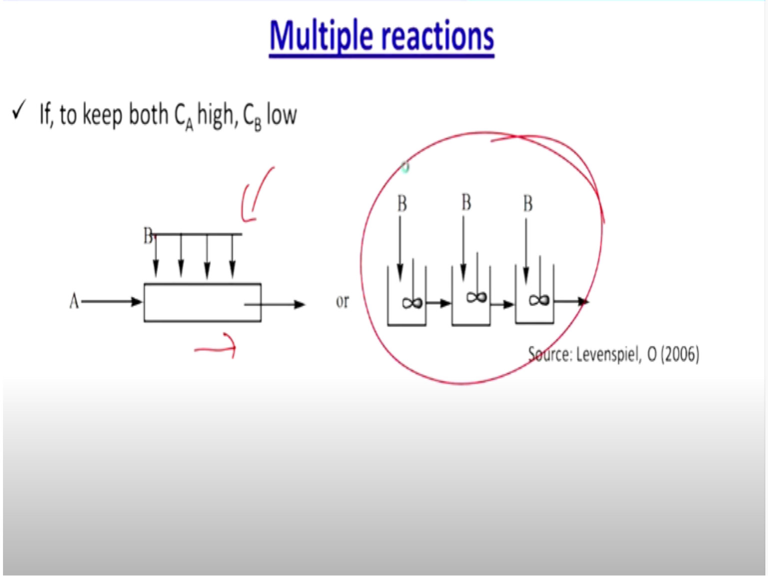
Multiple reactions

- ✓ Contacting patterns of reactants in continuous operations with the combination of high and low concentrations.
- If, to keep both C_A, C_B high;
- If, to keep both C_A, C_B low;

Source: Levenspiel, O (2006)

Now, if to keep both C_A and C_B high, then you may have either this type of a tubular reactor or you may have this reactor battery where you are putting both A and B the reactor and then you can treat all around. Now, if to keep both C_A and C_B low, then you may need to have this type of recycle approach or you may have this particular type of approach which we discussed in previous slide.

(Refer Slide Time: 09:26)



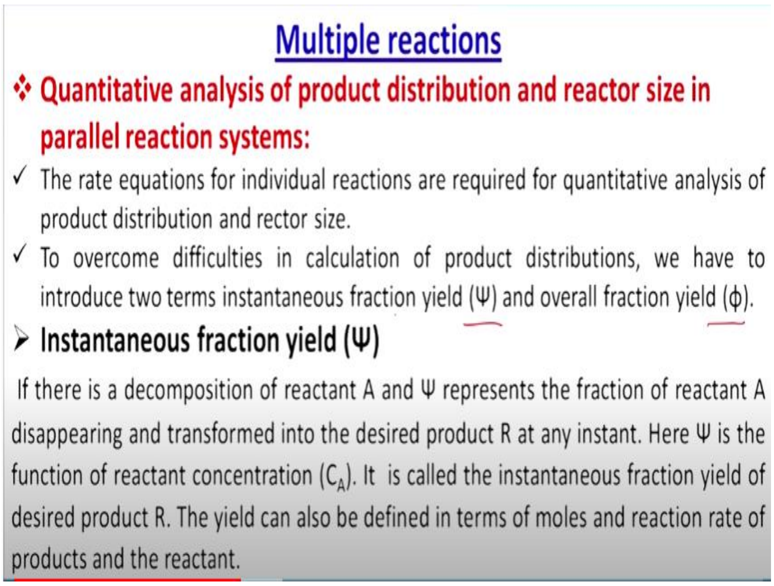
Multiple reactions

- ✓ If, to keep both C_A high, C_B low

Source: Levenspiel, O (2006)

Now, if you are intended to keep both C_A high and C_B low, then in that case, you may have this option that you can drop or you can put or you can pour this B into this continuous fashion and you may have multiple opening through which you can distribute the B all around this reactor or you may have this type of reactor battery for making the product condition favourable.

(Refer Slide Time: 09:52)



Multiple reactions

❖ **Quantitative analysis of product distribution and reactor size in parallel reaction systems:**

✓ The rate equations for individual reactions are required for quantitative analysis of product distribution and rector size.

✓ To overcome difficulties in calculation of product distributions, we have to introduce two terms instantaneous fraction yield (Ψ) and overall fraction yield (ϕ).

➢ **Instantaneous fraction yield (Ψ)**

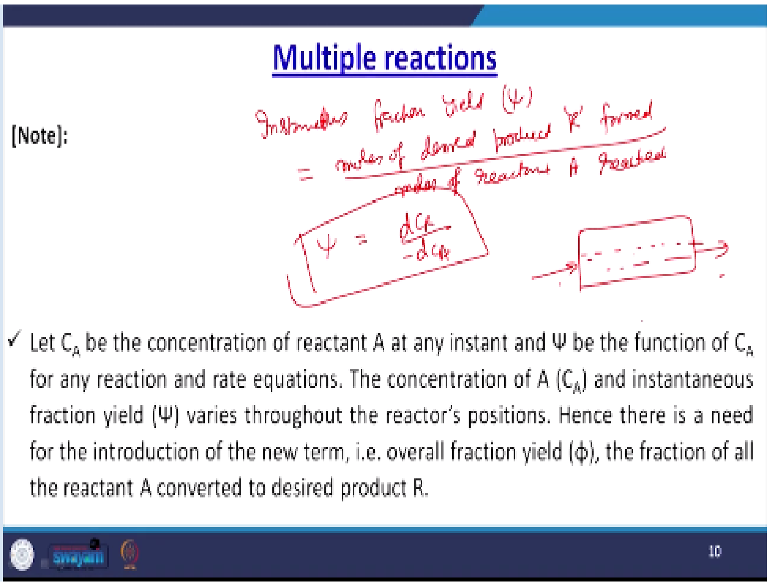
If there is a decomposition of reactant A and Ψ represents the fraction of reactant A disappearing and transformed into the desired product R at any instant. Here Ψ is the function of reactant concentration (C_A). It is called the instantaneous fraction yield of desired product R. The yield can also be defined in terms of moles and reaction rate of products and the reactant.

Now, let us have a look about the quantitative analysis of product distribution and reactor size in parallel reaction system. Now, the rate equations for individual reactions, they are required for the quantitative analysis of product distribution in a reactor size. Now, sometimes these poses various issues in the reactor geometry. Now, to overcome the difficulties in calculation of product distribution, we have to introduce 2 terms instantaneous fraction yield that is chi and Overall fraction yield that is phi.

So, you need to put these things into mind. Now, let us have a look about the instantaneous fraction yield that is represented by this chi. Now, if there is the decomposition of a reactant, A and chi represents the fraction of reactant A disappearing and transformed into the desired product r at any instant. So, when we talk about the chi, the here, chi is the function of reactant concentration that is usually referred as C_A. It is called the instantaneous fraction yield of desired product r.

So, if you recall that we are terming that A + B, they are converting into R and S where R is the desired product and S is the undesired product. So, this chi deals that how much fraction of desired product being achieved in the due course of reaction. Now, this yield can also be defined in terms of moles and a reaction rate of product and the reactant.

(Refer Slide Time: 11:42)



Multiple reactions

[Note]:

Instantaneous fraction yield (Ψ)

$= \frac{\text{moles of desired product 'R' formed}}{\text{moles of reactant A reacted}}$

$\boxed{\Psi = \frac{dC_R}{-dC_A}}$

✓ Let C_A be the concentration of reactant A at any instant and Ψ be the function of C_A for any reaction and rate equations. The concentration of A (C_A) and instantaneous fraction yield (Ψ) varies throughout the reactor's positions. Hence there is a need for the introduction of the new term, i.e. overall fraction yield (ϕ), the fraction of all the reactant A converted to desired product R.

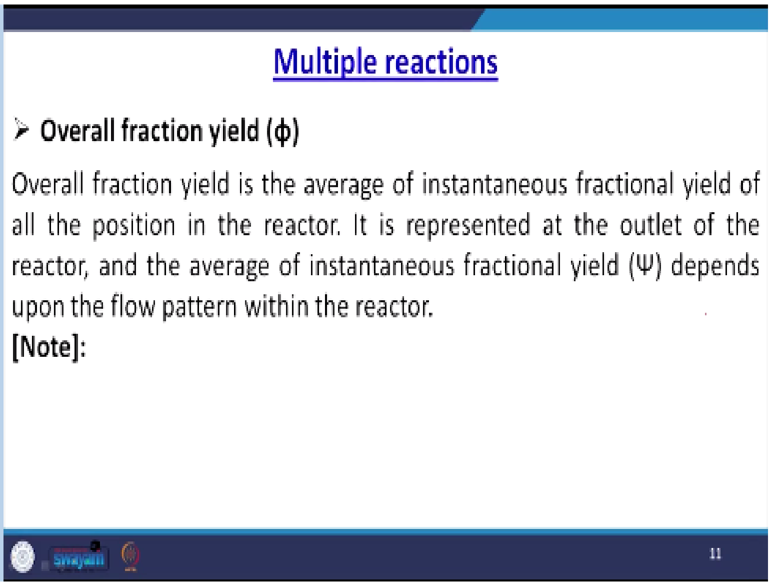
Now, sometimes, if we try to put this thing in a mathematical approach, then instantaneous fraction yield chi may be given as moles of desired product R formed during the course of reaction divided by moles of reactant A whatever reacted and this represented as chi is equal to DC$_R$ upon minus dC$_A$. Now, if C$_A$ be the concentration of reactant A at any instant and the chi is the function of C$_A$ that we have already shown in this equation.

$$Instantaneous\ fraction\ yield\ (\Psi) = \frac{moles\ of\ \ desired\ R\ formed}{moles\ of\ A\ reacted} = \frac{\mathrm{dC_R}}{-\,\mathrm{dC_A}}$$

The concentration of A that is C$_A$ and instantaneous reaction yield varies throughout the reactors position. Therefore, there is a need for the introduction of a new term that is overall fraction yield is always evident and this represented by phi, this is the fraction of all the reactant A converted to the desired product. Now, this sometimes people may ask that why there is a need of this additional thing?

The reason is that, when you are moving from this station to this station, then the concentration of A may vary all around this reactant and therefore, when we talk about because it represents the instantaneous things, so, when obviously, for the designing pattern, we always look for the overall fraction yield. In that case, you need to have another function that is called the phi.

(Refer Slide Time: 13:39)



Multiple reactions

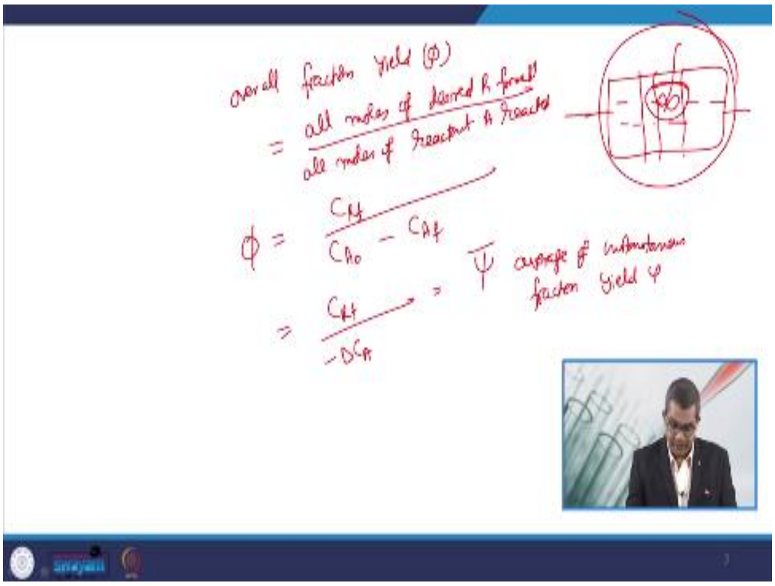
- **Overall fraction yield (ϕ)**

Overall fraction yield is the average of instantaneous fractional yield of all the position in the reactor. It is represented at the outlet of the reactor, and the average of instantaneous fractional yield (Ψ) depends upon the flow pattern within the reactor.

[Note]:

So, this phi is the overall fraction yield. Now, this overall fraction yield is the average of instantaneous fractional yield of all the portion in the reactor. So, whatever portion you have discussed, it carries out all the information of the entire reactor system. Now, it is represented as at the outlet of the reactor and average of instantaneous fractional yield chi depends upon the flow pattern within the reactor.

(Refer Slide Time: 14:17)



overall fraction yield (ϕ)

$$= \frac{\text{all moles of desired R formed}}{\text{all moles of reactant A reacted}}$$

$$\phi = \frac{C_{Rf}}{C_{A0} - C_{Af}}$$

$$= \frac{C_{Rf}}{-\Delta C_A} = \bar{\Psi}$$

average of instantaneous fraction yield φ

So, let us think in this direction that like this is your reactor and as I told you that instantaneous the chi represents the instantaneous 1 and sometimes, it depends on the flow behaviour or the flow pattern within the reactor. Now, if you are having any kind of say, mixing protocol over here, then the chi may be, may have more or a lower value. It may not be having the constant value throughout the reactor.

And phi represents the entire segmentation. Now, mathematically, we can write the chi as overall fraction yield phi that is equal to all moles of desired R formed divided by all moles of reactant A reactor. Now, this may be represented as C_{Rf} that is the the R represent that desired component that is formed and f represents the formation. C_{A0} that is the initial concentration of A and this is the final concentration of A.

So, that is the phi or this is C_{Rf} upon minus delta C_A and sometimes, it may represent the average of instantaneous fractional yield chi.

$$overall\ fraction\ yield\ (\phi) = \frac{all\ moles\ of\ \ desired\ R\ formed}{all\ moles\ of\ A\ reacted}$$

$$= \frac{C_{R_f}}{C_{A_0} - C_{A_f}} = \frac{C_{R_f}}{-\Delta C_A} = \overline{\Psi} \qquad (1)$$

Where,

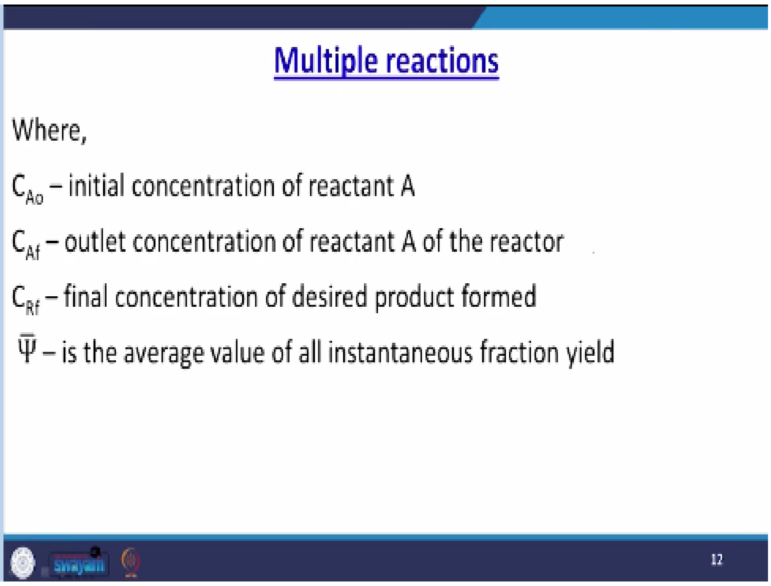
C_{Ao} – initial concentration of reactant A

C_{Af} – outlet concentration of reactant A of the reactor

C_{Rf} – final concentration of desired product formed

$\overline{\Psi}$ – is the average value of all instantaneous fraction yield

(Refer Slide Time: 16:03)



Multiple reactions

Where,

C_{Ao} – initial concentration of reactant A

C_{Af} – outlet concentration of reactant A of the reactor

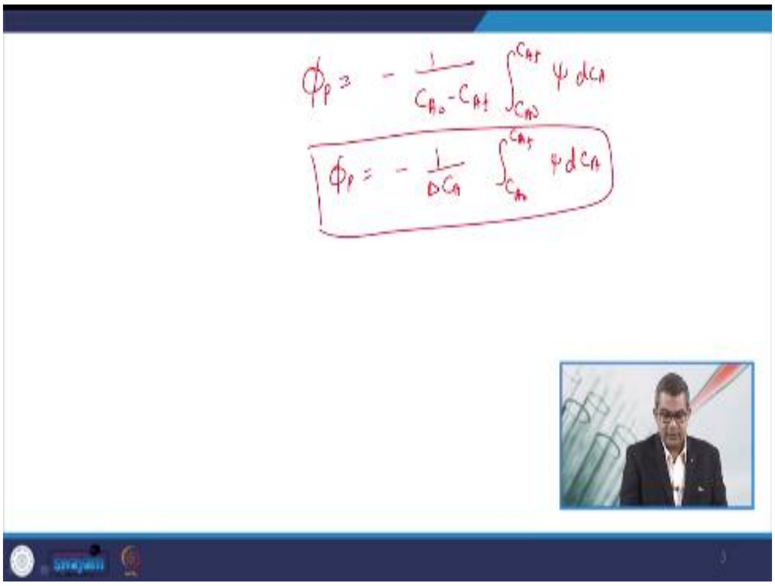
C_{Rf} – final concentration of desired product formed

$\bar{\Psi}$ – is the average value of all instantaneous fraction yield

Now, here these things C_{A0} that is the initial concentration of reactant A. C_A f that is the outlet concentration of reactant A of the reactor. C_{Rf} that is the final concentration of desired product form and bar chi is the average value of all instantaneous reaction yield. Now, let us have a look about the product distribution profile. The product distribution profile and product distribution and reactor size for plug flow and or batch reactor, they can find out with the help of overall fractional yield.

So, that is why the overall fractional yield is quite important in all kinds of reactor pattern. Now, let us have a look about this plug flow reactor first. So, for plug flow reactor the concentration of a reactant A changes progressively as it passes through the reactor length, which we have already discussed the quantitative relationship of PFR, you can write like this.

(Refer Slide Time: 17:06)



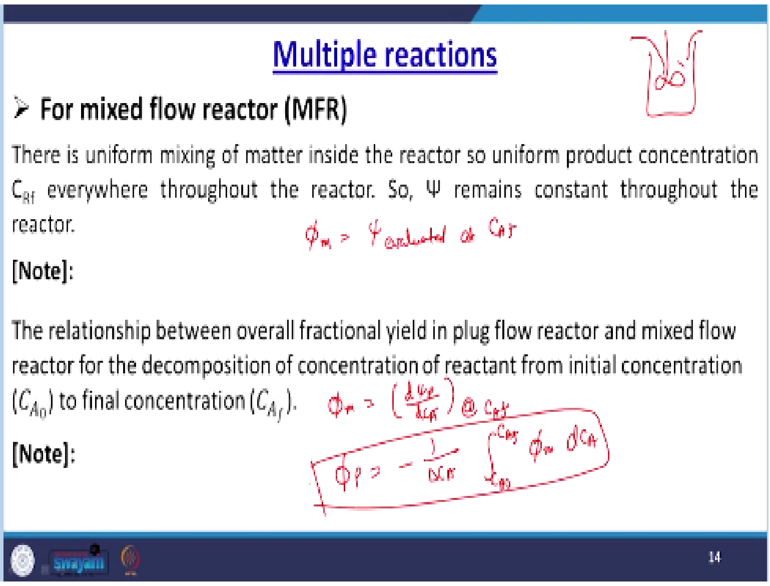
$$\phi_p = -\frac{1}{C_{A0}-C_{Af}}\int_{C_{A0}}^{C_{Af}} \psi \, dC_A$$

$$\boxed{\phi_p = -\frac{1}{\Delta C_A}\int_{C_A}^{C_{Af}} \psi \, dC_A}$$

Phi p is equal to minus 1 upon C_{A0} minus C_{Af} integration of C_{A0} to C_{Af} chi dC_A. Now, this phi p is equal to 1 upon delta C_A, C_{A0}, C_{Af} chi dC_A. So, this is the relationship the plug flow reactor.

$$\phi_P = \frac{-1}{C_{A_0} - C_{A_f}} \int_{C_{A_0}}^{C_{A_f}} \Psi \, dC_A = \frac{-1}{\Delta C_A} \int_{C_{A_0}}^{C_{A_f}} \Psi \, dC_A$$

(Refer Slide Time: 17:38)



Multiple reactions

- For mixed flow reactor (MFR)

There is uniform mixing of matter inside the reactor so uniform product concentration C_{Rf} everywhere throughout the reactor. So, Ψ remains constant throughout the reactor.

$\phi_m = \Psi_{\text{evaluated at } C_{Af}}$

[Note]:

The relationship between overall fractional yield in plug flow reactor and mixed flow reactor for the decomposition of concentration of reactant from initial concentration (C_{A_0}) to final concentration (C_{A_f}).

$\phi_m = \left(\frac{d\psi_p}{dC_A}\right) @ C_{Af}$

$$\boxed{\phi_P = -\frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \phi_m \, dC_A}$$

[Note]:

Now, let us have a look about for the mixed flow reactor. Now, there is a uniform mixing of the matter inside the reactor. Now, if you see, the mixed flow reactor, now here, this is the uniform mixing. So, you may experience the uniform product concentration C_{Rf} everywhere throughout the reactor. Therefore, chi remain constant throughout the reactor. So, if we try to write the equation, then we can say, like phi m for the m represents the mixed flow reactor, this is equal to chi evaluated at C_{Af}.

$$\phi_m = \Psi_{evaluated\ at\ C_{A_f}}$$

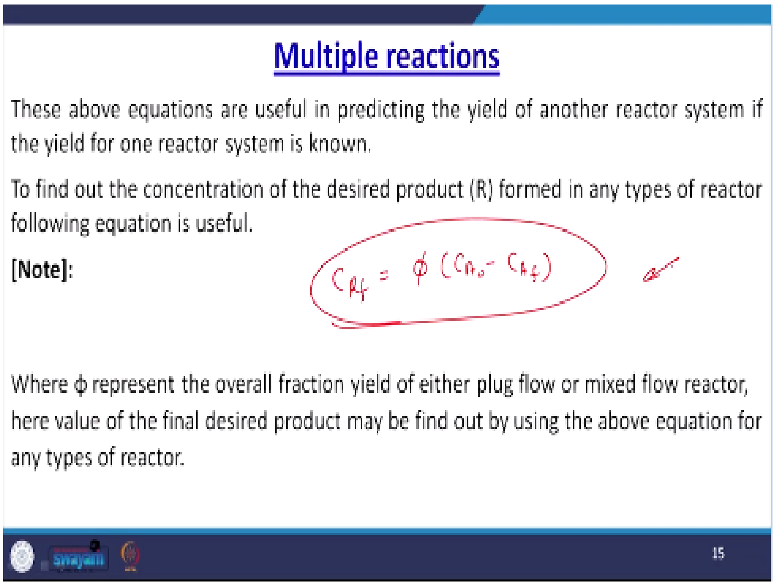
Now, sometimes, you may be interested to find out the relationship between the overall fractional yield in plug flow reactor and mixed flow reactor because the combination of these type of reaction is again more common and you may be interested to look mathematical approach of this type of combination or the reactor battery. So, for the decomposition of the concentration of reactant from initial concentration which is represented as C_{A0} to the final concentration C_{Af}.

And sometimes, it may be represented as phi m is equal to d chi p dC_A at C_{Af} and phi p is equal to minus 1 upon delta C_A, C_{A0} to C_{Af} phi m dC_A. So, this is the equation which is which categorically reflect this particular relationship.

$$\phi_m = \left(\frac{d\phi_P}{dC_A}\right) \text{at } C_{A_f}$$

$$\phi_P = \frac{-1}{\Delta C_A}\int_{C_{A_0}}^{C_{A_f}} \phi_m \, dC_A$$

(Refer Slide Time: 19:44)



Multiple reactions

These above equations are useful in predicting the yield of another reactor system if the yield for one reactor system is known.

To find out the concentration of the desired product (R) formed in any types of reactor following equation is useful.

[Note]:

$$\boxed{C_{Rf} = \phi(C_{A_0} - C_{Af})}$$

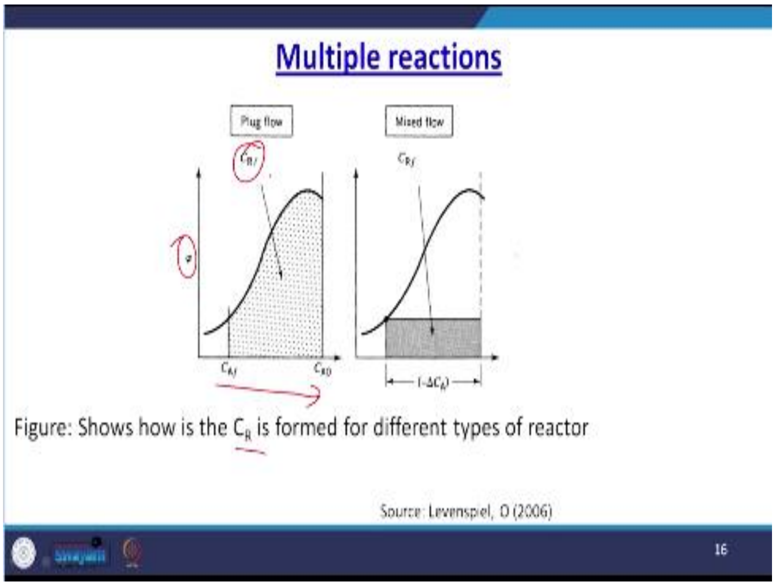
Where ϕ represent the overall fraction yield of either plug flow or mixed flow reactor, here value of the final desired product may be find out by using the above equation for any types of reactor.

Now, this equation is again useful in predicting the yield of another reactor system. Now, if the yield for 1 reactor system is known to you, then you can predict the another reactor system. Now, this is that is why these equations are quite useful. Now, sometimes you may be interested to find out the concentration of the desired product R formed in any type of reactor. Then you may require another set of equation that is represented as C_{Rf} is equal to phi C_{A0} minus C_{Af}.

$$C_{R_f} = \phi(C_{A_0} - C_{A_f})$$

So, this equation tells you that the reactor is your any kind of a reactor. Now, here the phi represents the overall fraction yield of either plug flow or mixed flow reactor. The value of the desired product may be find out by using this particular equation for any type of reactor.

(Refer Slide Time: 20:48)



Multiple reactions

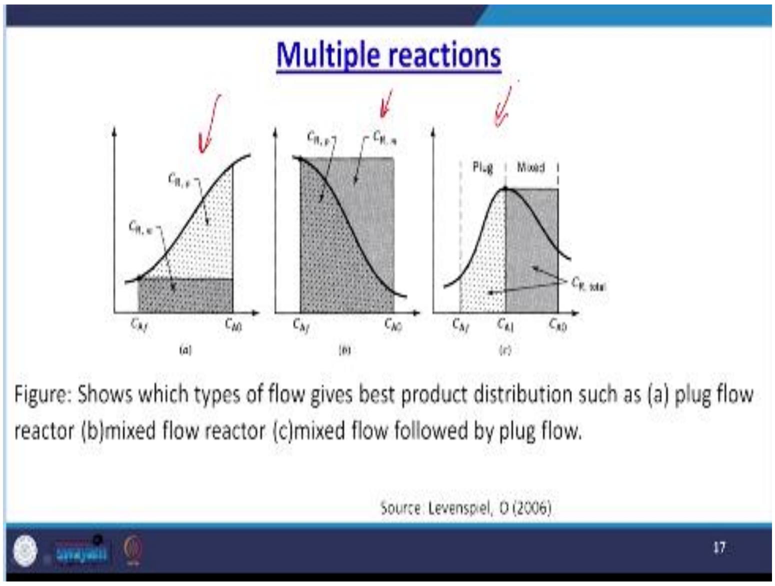
Figure: Shows how is the C_R is formed for different types of reactor

Source: Levenspiel, O (2006)

Now, you can see here, we have represented 2 figures, courtesy from Levenspiel. This shows that the C_{Rf} is formed for the different type of reactor. Now, here you see that the x axis represents the C_A and this is the chi. Now, you can see that in plug flow, you may have, you may experience this type of thing mixed flow, you may have this type of thing.

So, when we talk about the overall performance or overall things of any type of reactor in that case, the plot of this concentration of a reactant versus chi is always useful to give the proper reactor configuration or proper reactor battery designing.

(Refer Slide Time: 21:37)



Multiple reactions

Figure: Shows which types of flow gives best product distribution such as (a) plug flow reactor (b)mixed flow reactor (c)mixed flow followed by plug flow.

Source: Levenspiel, O (2006)

Sometimes, this approach gives you again an idea that what is the best product distribution profile. Sometimes the plug flow reactor, you may have over here, then you may have a mixed flow reactor, you may have over here and then followed by the mixed flow reactor followed by the plug flow reactor. So, sometimes you need to carry out such type of evaluation, such type of a calculation to assess that which kind of reactor configuration is useful for your desired product distribution.

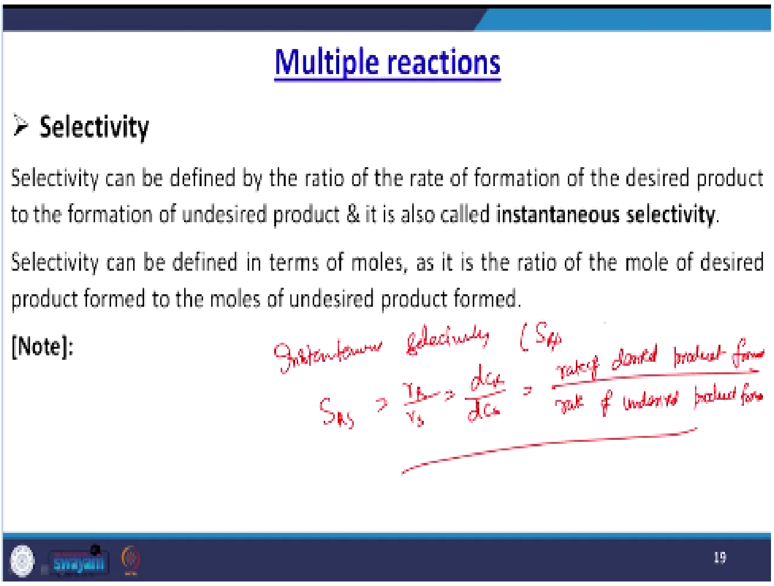
Now, these expressions whatever we discussed, they give us an idea for best selection of contracting scheme and allow us to relate the product to distribution from different type of reactors. Now, there is one condition that should be satisfied before say, we use these reactors or these relationships under the safe condition. One is, maybe like in the parallel reaction, no product should have effect on the rate to change the product distribution.

Now, to test this the product is stream added to the feed and verify that product distribution does not change. So, you need to look into this particular approach while assessing this particular approach. Now, so, whenever we talk about the fractional yield, the fractional yield of desired product R, this should be taken as a function of the reactant concentration A alone.

For more than 2 reactants, the fractional yield may be the function of one of the reactants consumed or all of the reactants. Now, when we talk about the reactor configuration and especially when we talk about the instantaneous phi or chi aspect, then selectivity is also very vital. Now, this can be defined as the ratio of the rate of formation of the desired product to the formation of undesired product and that is why it is sometimes, it is called the instantaneous selectivity.

Now, this selectivity can be defined in terms of moles as it is the ratio of the moles of desired product form to the moles of undesired product form.

(Refer Slide Time: 24:11)



Multiple reactions

- **Selectivity**

Selectivity can be defined by the ratio of the rate of formation of the desired product to the formation of undesired product & it is also called **instantaneous selectivity**.

Selectivity can be defined in terms of moles, as it is the ratio of the mole of desired product formed to the moles of undesired product formed.

[Note]:

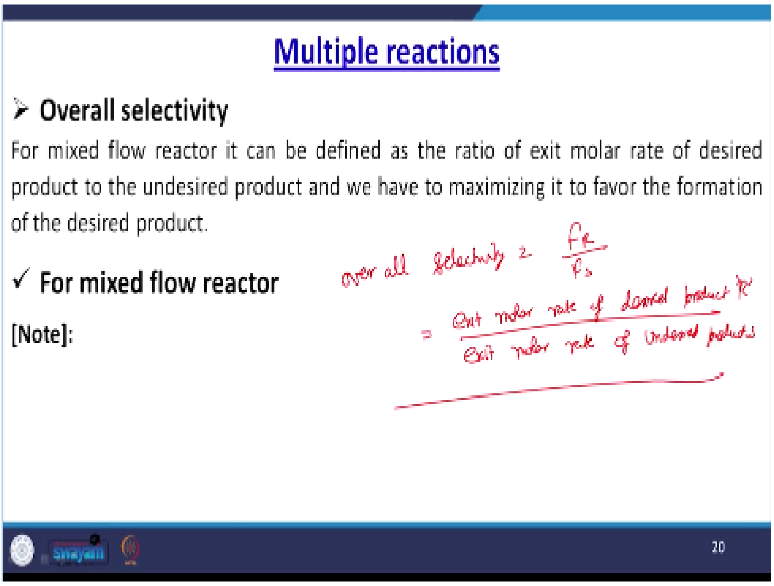
Instantaneous selectivity (S_{RS}

$S_{RS} = \frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{\text{rate of desired product form}}{\text{rate of undesired product form}}$

Now, let us give you a mathematical representation or a mathematical relationship of instantaneous selectivity. Now, this S_{RS} is represented as that is the rate of desired product found divided by the rate of undesired product found.

$$\text{Instantaneous selectivity } (S_{R/S}) = \frac{r_R}{r_S} = \frac{\text{rate of desired product formed}}{\text{rate of undesired product formed}}$$

(Refer Slide Time: 24:58)



Multiple reactions

- **Overall selectivity**

For mixed flow reactor it can be defined as the ratio of exit molar rate of desired product to the undesired product and we have to maximizing it to favor the formation of the desired product.

✓ **For mixed flow reactor**

[Note]:

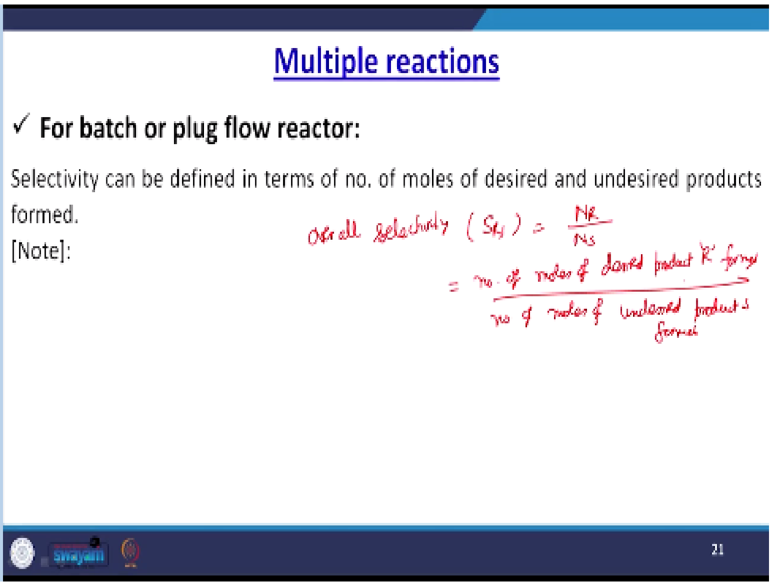
over all selectivity = $\frac{F_R}{F_S}$

$= \frac{\text{Exit molar rate of desired product 'R'}}{\text{Exit molar rate of undesired products}}$

Now, sometimes people may look into the overall selectivity. Now, overall selectivity is more common in the mixed flow reactor. So far, mixed flow reactor, it can be defined as the ratio of exit molar rate of desired product to the undesired product and we have to maximise it to favour the formation of the desired product. So, if we try to write the overall selectivity for mixed flow reactor, the overall selectivity F_R upon F_S that is equal to exit molar rate of desired product R divided by exit molar rate of undesired product S.

$$Overall\ selectivity\ (S_{R/S}) = \frac{F_R}{F_S} = \frac{exit\ molar\ rate\ of\ desired\ product\ R}{exit\ molar\ rate\ of\ undesired\ product\ S}$$

(Refer Slide Time: 26:03)



Multiple reactions

✓ **For batch or plug flow reactor:**

Selectivity can be defined in terms of no. of moles of desired and undesired products formed.

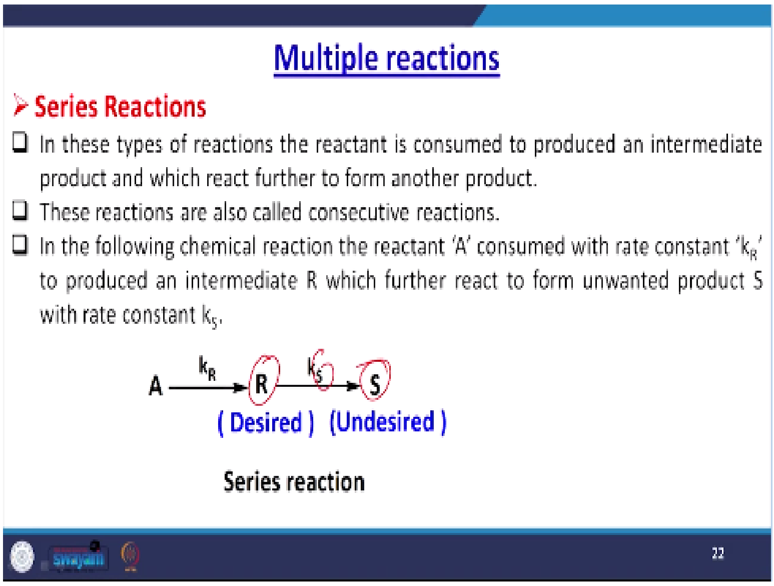
[Note]:

$$\text{Overall selectivity } (S_{R/S}) = \frac{N_R}{N_S} = \frac{\text{no. of moles of desired product 'R' formed}}{\text{no of moles of undesired products formed}}$$

Now, sometimes you may look into the batch or a plug flow reactor selectivity, this can be defined in terms of number of moles of desired and undesired product form. So, let us look for this one for batch or a plug flow reactor. The overall selectivity that is equal to N_R upon N_S and this is number of moles of desired product R formed divided by number of moles of undesired product S formed.

$$\text{overall selectivity } (S_{R/S}) = \frac{N_R}{N_S} = \frac{\text{No of moles of desired product R formed}}{\text{No of moles of undesired product S formed}}$$

(Refer Slide Time: 26:57)



Multiple reactions

➢ **Series Reactions**

- ☐ In these types of reactions the reactant is consumed to produced an intermediate product and which react further to form another product.
- ☐ These reactions are also called consecutive reactions.
- ☐ In the following chemical reaction the reactant 'A' consumed with rate constant 'k_R' to produced an intermediate R which further react to form unwanted product S with rate constant k_S.

$$A \xrightarrow{k_R} R \xrightarrow{k_S} S$$

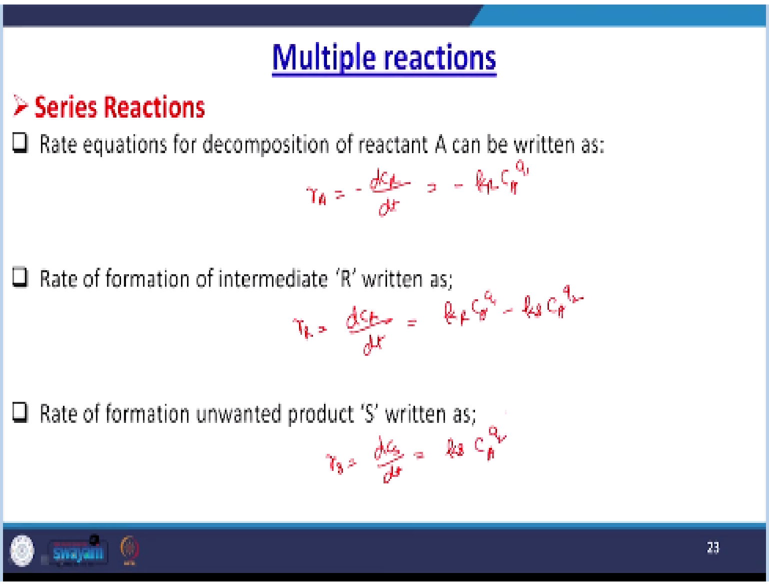
(Desired) (Undesired)

Series reaction

Now, sometimes we may need to look into the series reactions. Now, see, this type of a reaction, the reactant is consumed to produce an intermediate product which then further reacts with the under the given condition to form another product. So, in a layman's language, you may say that you are forming 2 products and one product is in due course of time disappears to form the final product. So, these reactions are sometimes called the consecutive reactions.

Now, if you see that this reaction, the chemical reaction, the reactant A is consumed with rate constant k_R to produce an intermediate R which is further disappears or further react to form unwanted product or sometimes represented as S with A rate constant k_S. So, this is termed as the series reaction.

(Refer Slide Time: 28:06)



Multiple reactions

➢ Series Reactions

❑ Rate equations for decomposition of reactant A can be written as:

$$r_A = -\frac{dC_A}{dt} = -k_R C_A^{a_1}$$

❑ Rate of formation of intermediate 'R' written as;

$$r_R = \frac{dC_R}{dt} = k_R C_A^{a_1} - k_S C_A^{a_2}$$

❑ Rate of formation unwanted product 'S' written as;

$$r_S = \frac{dC_S}{dt} = k_S C_A^{a_2}$$

When we talk about the mathematical representation of these series of reactions, so, the series reaction for the various component like decomposition of reactant A then the rate of formation of intermediate R or then rate of formation of unwanted product S, sometimes maybe written as like if you write to the rate equation for the decomposition of reactant A, then it can be represented as r_A is equal to minus dC_R upon dt that is minus k_R into C_A^{a1}.

Now, if we write the rate of formation of intermediate R, then it can be represented as r_R is equal to dC_R upon dt k_R C_A^{a1} k_S C_A^{a2}. Now, if we write the rate of formation of unwanted product S, it is not necessary that entire R may get consumed into in due course of time, then for unwanted S, we can write r_S is equal to dC_S over dt k_S C_A^{a2}. So, this is the mathematical representation of these series reaction.

Rate equation for decomposition of reactant A

$$r_A = -\frac{dC_R}{dt} = -C_A^{a1}k_R$$

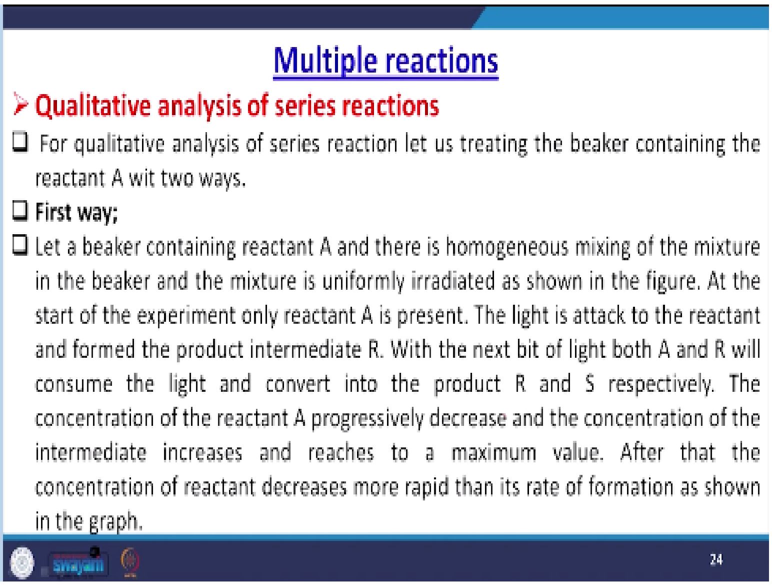
Rate of formation of desired product ‘R’

$$r_R = \frac{dC_R}{dt} = C_A^{a1}k_R - C_A^{a2}k_S$$

Rate of formation of undesired product ‘S’

$$r_S = \frac{dC_S}{dt} = C_A^{a2}k_S$$

(Refer Slide Time: 29:28)



Multiple reactions

➢ Qualitative analysis of series reactions

❑ For qualitative analysis of series reaction let us treating the beaker containing the reactant A wit two ways.

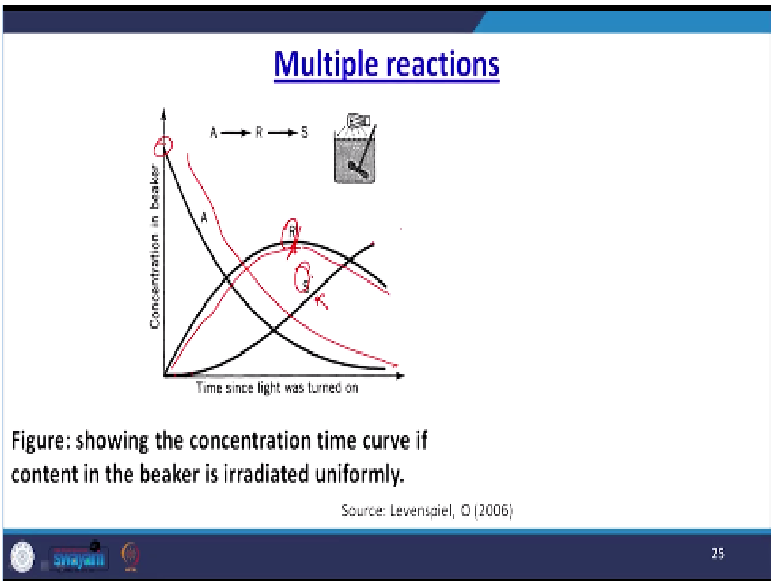
❑ First way;

❑ Let a beaker containing reactant A and there is homogeneous mixing of the mixture in the beaker and the mixture is uniformly irradiated as shown in the figure. At the start of the experiment only reactant A is present. The light is attack to the reactant and formed the product intermediate R. With the next bit of light both A and R will consume the light and convert into the product R and S respectively. The concentration of the reactant A progressively decrease and the concentration of the intermediate increases and reaches to a maximum value. After that the concentration of reactant decreases more rapid than its rate of formation as shown in the graph.

Now, let us have an analysis of qualitative approach of these reactions. So, for qualitative analysis of series reaction, we may treat the things in a beaker containing the reactant A with the 2 ways. One first way is that a beaker containing reactant A and there is a homogeneous mixing of mixture in beaker and the mixture is uniformly irradiated sometimes. Now, at the start of the experiment, the only rated A was present.

Now, when the light is attached to the reactant and formed the product intermediate R with the next bit of light both A and R will consume the light and convert into the product R and S respectively, so, partially the R and significantly S. Now, the concentration of the reactant A progressively decreases and the concentration of intermediate increases and reaches to a maximum value. After that the concentration of reactant decreases, more rapid then its rate of formation usually goes on increasing.

(Refer Slide Time: 31:02)



Multiple reactions

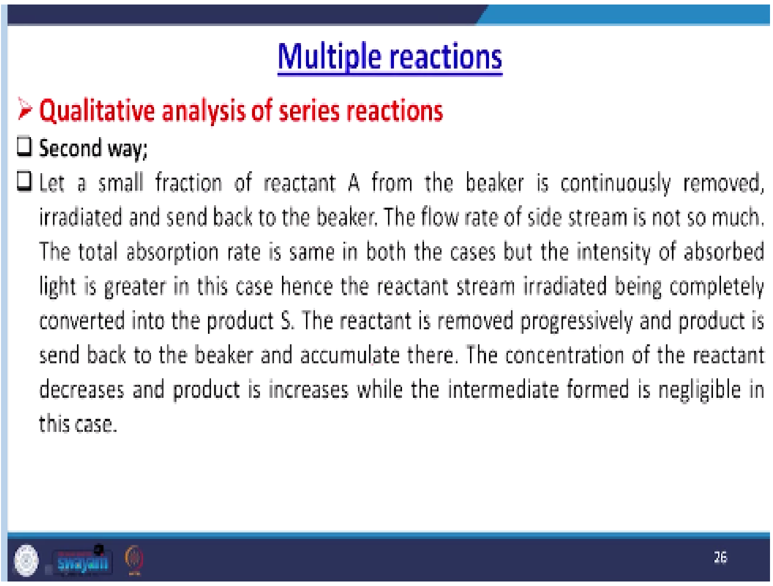
Figure: showing the concentration time curve if content in the beaker is irradiated uniformly.

Source: Levenspiel, O (2006)

Now, here this is the graphical representation what we have discussed that initially, you may have the concentration of A on the higher side and there was no R and S and progressively, it goes on decreasing and sometimes you may have a very low value and this intermediate goes on increasing and it reaches this maximum value and thereafter, it is having that tends to decrease.

Now, here, this S that is the unwanted product initially, it was having the 0% and then over the period of time, it gradually increases and it is having that that tendency towards increase as long as the sufficient quantity of R and sufficient quantity of A is available in the reaction mass.

(Refer Slide Time: 31:44)



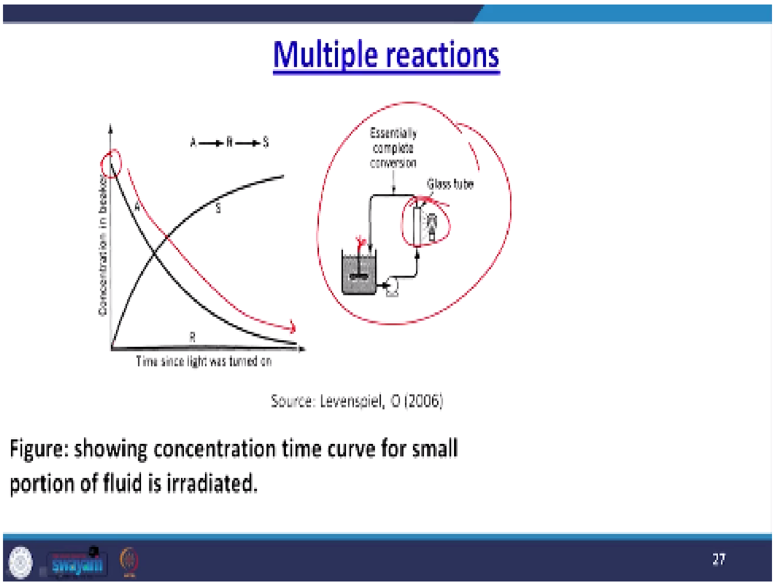
Multiple reactions

- Qualitative analysis of series reactions
- ☐ Second way;
- ☐ Let a small fraction of reactant A from the beaker is continuously removed, irradiated and send back to the beaker. The flow rate of side stream is not so much. The total absorption rate is same in both the cases but the intensity of absorbed light is greater in this case hence the reactant stream irradiated being completely converted into the product S. The reactant is removed progressively and product is send back to the beaker and accumulate there. The concentration of the reactant decreases and product is increases while the intermediate formed is negligible in this case.

Now, let us talk about the second way. Now, in the second way, let us take the small fraction of reactant A in a beaker and which is continuously removed and irradiated and sent back to the beaker. The flow rate of the side stream is not so much. So, the total absorption rate is usually seen in both the cases, but the intensity of absorbed light is usually greater in that case, therefore, the reactant is stream irradiated being completely converted into the product as.

So, the reactant is removed progressively and the product is sent back to the beaker, accumulate there. So, the concentration of the reactant decreases and product is increased while the intermediate form is negligible in that particular case. Now, let us have a look about this nothing.

(Refer Slide Time: 32:39)



Multiple reactions

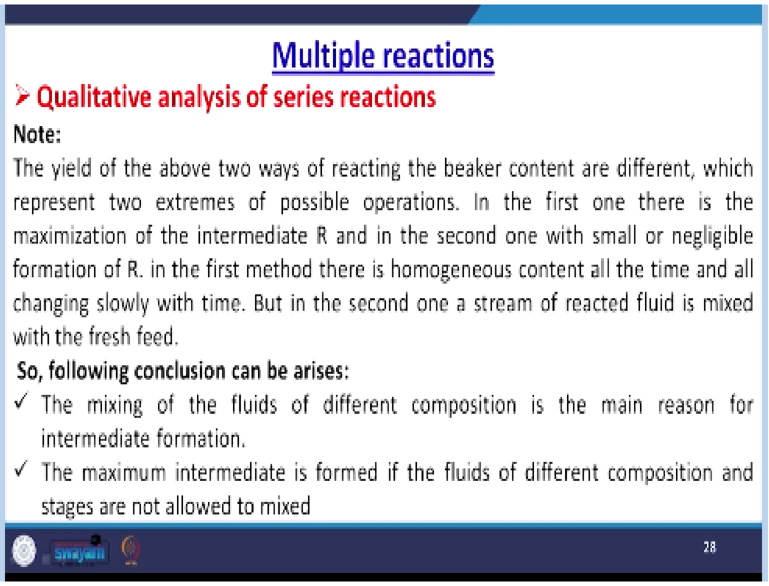
Source: Levenspiel, O (2006)

Figure: showing concentration time curve for small portion of fluid is irradiated.

Now, here, you are having the things inserted to this reactor, then they are sent back and here, you are irradiating the things and then you are making this particular cycle. Now here, you see that initially, you are having the reactant A right on the top at time zero. There was no conversion and then gradually tends to decrease and whatever R being formed, due to this cyclic approach, it reduces over the period of time.

Therefore, it is not having much concentration in the reactor mass and the product S is continuously being increased in due course of time.

(Refer Slide Time: 33:21)



Multiple reactions

➢ Qualitative analysis of series reactions

Note:

The yield of the above two ways of reacting the beaker content are different, which represent two extremes of possible operations. In the first one there is the maximization of the intermediate R and in the second one with small or negligible formation of R. in the first method there is homogeneous content all the time and all changing slowly with time. But in the second one a stream of reacted fluid is mixed with the fresh feed.

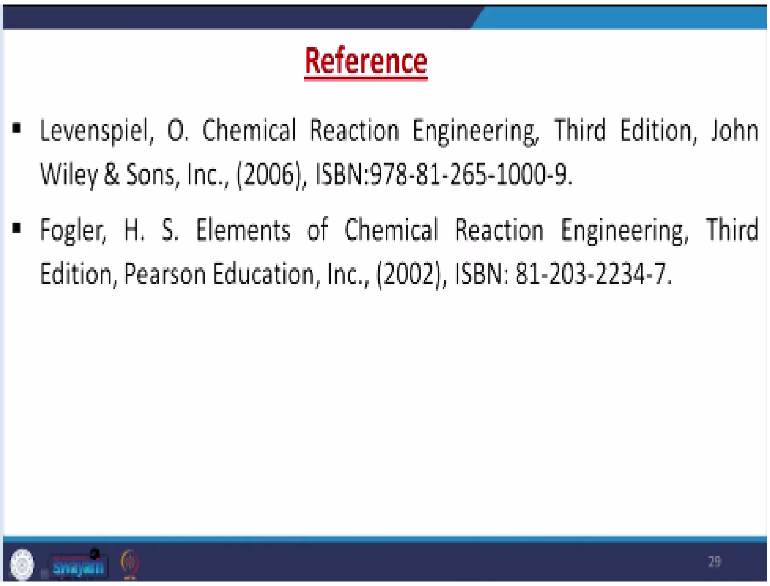
So, following conclusion can be arises:

- ✓ The mixing of the fluids of different composition is the main reason for intermediate formation.
- ✓ The maximum intermediate is formed if the fluids of different composition and stages are not allowed to mixed

Not last, we take the things in a different way that the yield of these about 2 way of reacting the beaker content they are different, which will present the 2 extremes of possible operation. In the first one, there is a maximisation of the intermediate R and then in the second one, with this small r negligible formation of R. In the first method, there is a homogeneous content all the time and all changing slowly with the time. But in the second one, the stream of reacted fluid is usually mixed with the fresh fluid, fresh, fresh fluid.

Now, therefore, we can conclude that the mixing of the fluid of a different composition is the main reason for the intermediate formation. Second is that the maximum intermediate is formed in the fluid of a different composition and stages are not allowed to mix.

(Refer Slide Time: 34:26)



Reference

- Levenspiel, O. Chemical Reaction Engineering, Third Edition, John Wiley & Sons, Inc., (2006), ISBN:978-81-265-1000-9.
- Fogler, H. S. Elements of Chemical Reaction Engineering, Third Edition, Pearson Education, Inc., (2002), ISBN: 81-203-2234-7.

Now, at last, if you wish to have further studies of this particular concept, especially series and parallel and what kind of configuration is useful, you may have look of these references which we listed in this particular slide. Thank you very much.