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Lecture - 22 Multiple Reactions System – I

So, let us talk about the multiple reaction system in this particular lecture under the head of polymer reaction engineering. So, before we start, let us have a look about that what we studied previously. We discussed about the various performance equation attributed to the recycle reactor.

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Then we studied about the concept of autocatalytic reactor and their performance equation and which is the best reactor scheme is suited for our optimised reaction system. Now, what we are going to study in this lecture that is attributed to the multiple reaction system having the parallel, series, complex, independent type of system and then we will have the discussion about the quantitative treatment of various product distribution.

Because this is again a very much important in case of a multiple product stream being generated in due course of time in a particular reactor system.

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Multiple reactions

❖ Multiple Reactions

- \checkmark In the single reaction system, the flow pattern within the vessel affect's the performance (size) of the reactor and there is needs of only one rate expression to describe its kinetic behavior.
- \checkmark In multiple reaction system more than one reaction occurs simultaneously.
- \checkmark Multiple reactions required more than one rate expressions to describes its kinetics behavior.
- \checkmark The reactor size and distribution of product are effected by the flow pattern in reactor.
- There are both desired and undesired reaction taking places simultaneously in multiple reaction systems.

So, let us have a discussion about the multiple reaction. Now, usually in a single reactor system or reaction system the flow pattern within the vessel sometimes it affects the performance or the size of the reactor. And there is a need of only one rate expression to describe its kinetic behaviour. That is quite obvious because there are certain mathematical tool which can accommodate only one rate expression.

You cannot afford to have multiple rate equation because of the complexity of the nature. Now, in multiple reaction system more than one reactions occur simultaneously. So, you need to take care of all those reaction system or reaction parallely. Now, multiple reactions sometimes require more than one rate expression to describe its kinetic behaviour, thus making the system more and more complicated in the nature.

So, the reactor size distribution of the product, they are sometimes affected by the flow pattern in the reactor. Because, see there are multiple variables in those reactor system and those multiple variable also affect the performance equation also affects the rate expression. So, they are both desired and undesired type of a reaction sometimes you may interested or some time you may not interested. And these reaction may take place during the course of the multiple reaction system simultaneously.

So, when we talk about this particular concept, there is a requirement of a minimization of undesired side product because it is quite obvious that if you are looking for the efficiency of the reactor system, if you are talking about the best conversion or a yield of a reaction system,

then you have to take care of this particular undesired side products and you have to curtail these things.

So, the size of reactors sometimes again play a very vital role. Now, to maximise the desired product, sometimes you need to optimise the size of a reactor. Concentration terms, sometimes they are more convenient to deal with multiple reaction rather than the conversion terms although you cannot verify the effect of conversion in the multiple reaction system. But this for the dealing aspect or for the development of any mathematical equation, these concentration terms are more convenient to handle.

Now, there are relative rates are involved in the analysis of reaction. Now, in this particular concept, we will study that termination of the reactor size, how we can deal with the product distribution concept. Now, these are things are quite essential because ultimately they affect the separation process. They affect the various other allied processes in C 2. Now, these type of multiple reactions sometimes can occur usually either by the by themselves or in PR or altogether.

So, there are various permutation combination or various classification or various types of multiple reactions like parallel reaction, series reaction, complex reactions and some time independent reaction. So, let us start with the parallel reactions. In this type of reaction, reactant is usually consumed by 2 different reaction pathway to form different type of products.

Now, these type of reactions are sometimes called as the competing reactions. Now, let us see about the chemical equations in which you can represent the parallel reaction system. **(Refer Slide Time: 04:50)**

Now, here, if we are having one reactant and this may participate in 2 aspect, this are that is the desired product. And sometimes, it may gives you the undesired one, side reaction based product etcetera, undesired product. Now, it can be represented sometimes if we wish to write in terms of reaction engineering concept, then it may be represented as like this. This one is a desired one and it is undesired one.

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If you see that sometimes, we need to write the corresponding rate equation for the formation of a desired product versus undesired product. So, now, we can write these equations like rR is equal to dC_R upon dt $k_R C_A^{al}$. Now, you see here, this is the rate equation for the desired one and this is a concentration, concentration approach. So, this may be termed as the equation number 1.

 = = 1…………..(1)

Now, sometimes we have been look into the disappearance of reactant A, because it is being consumed in due course of time during the reaction and usually it is the sum of the formation of the product r and S usually represented by the rate equation. So, sometimes we can write this rs is equal to dC_s upon dt ks C_A . Now, this is equation number 2. Now, if we talk about the disappearance rate, then the rest equation can be represented as $-r_A=r_R + rs$.

$$
r_S = \frac{dC_A}{dt} = C_A^{a2} k_S \dots \dots \dots (2)
$$

$$
-r_A = r_R + r_S
$$

$$
-r_A = C_A^{a1} k_R + C_A^{a2} k_S \dots \dots (3)
$$

If we take the help of equation 1 and equation 2, so, in that case we may write -rA is equal to $k_R C_A^{a1}$ + $k_S C_A^{a2}$, that is equation number 3. Now, here the C_A, C_R, C_S they are the concentrations of A, R and S, usually represented in moles per litre. Similarly, k R, k S the specific rate constants of desired product stream and undesired product stream. And small a 1 and small a 2 are the respective order for the formation of the reaction for desired one and undesired one.

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Now, let us talk about the series reactions. Now, when we go into the details of the series reaction, this type of reactions, the reactant is consumed to a product or produced an intermediate product sometimes, which can react to further to form another product. So, these reactions are also called the consecutive ones. Suppose, you are having any reactant and then you are forming another product this may be consumed over the period of time, these are may be termed as the intermediate products.

So, now here, how you can represent mathematically? So, if we try to write these series reaction, which can be represented as A that is converted into R and sometimes it may lead to form the undesired one, undesired product. So, this is k_R , this is obviously a desired one and then this is ks and this is the undesired product.

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Now, when we talk about the mathematical representation or when we talk about the rate equation for the decomposition of reactant A, then it can be represented as r_A is equal to $-dC_R$, minus sign is quite obvious because A is being consumed in due course of time. That is a dC^R upon dt $-k_R$ CA^{a_1} . That is the equation, my equation number 4. Now, the rate of formation of the intermediate R and the final maybe the undesired product but is can be represented as r_R is equal to dC_R upon dt.

That is k_R C_A^{a1} – k_sC_A^{a2}. Now this is my equation number 5 and rs dC_s upon dt C_A^{a2}, that is my equation number 6.

Rate equation for decomposition of reactant A

$$
r_A = -\frac{d c_R}{dt} = -C_A^{a1} k_R \dots \dots (4)
$$

Rate of formation of intermediate R and unwanted producto S

$$
r_R = \frac{dC_R}{dt} = C_A^{a1}k_R - C_A^{a2}k_S \dots \dots (5)
$$

$$
r_S = \frac{dC_S}{dt} = C_A^{a2}k_S \dots \dots (6)
$$

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Now, sometimes we may we may need to handle the complex reaction in which both the series and parallel reactions are involved. And sometimes, they are designed as a complex reaction to make them product distinct more and more perfect in nature. So, we can have this equation or the representation of the complex reaction system like $A + R$ that is the k_1 and then S may further react with the desired product one. So, it may gives you this one. So, this is one of the way through which you can represent the complex reaction system.

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Another one is attributed to the independent one. Now, these are the reactions that occurred at the same time, but neither the reactant nor product react with themselves or one another. So, both the streams are altogether different. Now, sometimes mathematically, you need to represent all those things further generation of rate expression and further the calculation of optimization of and the performance of those reactions.

In that case, you can represent like this that this A is dissociated to form $B + C$ under the rate constant of k_1 and then another thing that is the D, this may be get dissociated over the period of time to give you E and F. So, both the reaction streams if you see that both the reactants reaction streams are altogether different.

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Now, then we may have to look into the desired and undesired product obviously. Even as an engineer, one must have looked into the desired one and undesired must be minimised. But unless otherwise, we do not have any clue that what are the desired, undesired products are being found in due course of time then we will not be able to to get the optimization when and we may not be able to get the desired design of those reaction media.

So, therefore, their knowledge their mathematical representation should be taken into account. So, in the multiple reaction usually a reactant can be consumed to form a desired product which obviously, we want to produced and undesired product, obviously, we are not looking for unwanted. But because of the presence of some impurity, because of the presence of some side reaction, because of the some other reversibility, it may get involved, it may get formed during the course of reaction.

In that case, we have to write all those things. So, you see that here we are having one parallel reaction stream where A is get converted into the desired product R with the rate constant k_R and undesired product ks rate constant. Now, here you see that here we are having the desired one and undesired one. And unfortunately, this R is get dissociated over the period of time to get the to give you the undesired one.

So, in that case you are having your rate constant with you, so that you can optimise the things accordingly, so that we can improvise the reaction media.

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Now, let us have a look about this if there is a greater amount of undesired things and as product form, then the larger amount of economy is needed to spend to separate it from the desired product. So, your your reaction battery or reactor battery will not be economically feasible. So, there is a need to minimise the formation of undesired one and fix the reaction condition in such a way that the maximum desired product need to be formed.

Now, these reaction conditions we can discuss in the later on because it involves mathematically rigorous mathematical approach. Now, before we go into the these mathematical approach, let us have a look about the qualitative analysis of the product distribution.

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Now, see this qualitative analysis is again very important of the product distribution because suppose, you are having one product, one reactant which is get dissociated over the period of time one is the desired product stream and other one is the undesired product stream. Under this head, you need to have a product distribution profile because this is giving you R and S, both are coming under the head of the product stream.

So, you must have a proper product distribution profiling or you have the product profiling system with you. So that you can have a knowledge that how much quantity of the desired product being produced and how much is the undesired one. So, this gives you the series and a parallel concept gives you about this particular concept and in this particular approach when you try to develop the mathematical equation.

In that case, you must have a knowledge about all the rate constants being involved whether it is a desired one or the undesired one.

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Now, let us consider into the mathematical approach like considering the decomposition of a reactant A into the path and we are having the desired and undesired one. Now, the rate of disappearance of A is the sum of the rate of formation of desired one and undesired one. So, in that case $-$ r_A, minus sign is put forward just A is being disappeared over the period of time during the reaction time.

$$
-r_A = r_R + r_S
$$

$$
-r_A = k_R C_A^{a1} + k_S C_A^{a2}
$$

Rate equations for formation of the desired prodcut 'R' can be written as;

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

Then this is the r_R that is the rate of desired one and this one is the rate of undesired one. Now, if we introduce the rate constant, then the equation my equation will become like this. Now, the rate equation for the formation of the desired product R, this can be written as like this. **(Refer Slide Time: 15:41)**

Now, if we try to write the rate equation for the undesired product, we can represent this equation by rs is equal to dCs upon dt is equal to ks CA^{a2} . And also if we divide the rate equation for the desired product with the undesired one, then we may get the relative rate of formation of desired to undesired product that is sometimes referred to as SRS. And this can be represented like this particular equation.

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

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Now, S_{RS} is equal to r_R upon r_S dC_R upon dC_S. This is the undesired one and this is equal to k_R upon ks that is the rate constant CA^{a1-a2} . Now, this is the equation number 7.

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

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Multiple reactions

 \checkmark To maximize the desired product 'R' the rate selectivity parameter S_{RS} should be as larger as possible and we have to maintain this ratio always greater than one to obtained the desired product.

Where,

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- k_{R} , k_{s} , are the reaction rate constant for desired (R) and undesired products (S)
- \bullet a₁ and a₂ are the respective order for desired reaction and undesired reaction
- C_{α} , C_R, C_S, are concentrations for reactant A, desired product R and unwanted product S respectively
- \checkmark In the above equation for selectivity parameter (S_{RS}), C_A, is only the factor which can be adjust and controlled as at a given temperature whereas, K_{R} , K_{S} , a_1 , a_2 all are constant for a specific system.

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Sometimes, because there is an engineering perspective, we need to maximise the desired product. So, therefore, the selectivity parameters, they also play a very vital role and this SRS should be as large as compared to other one. And my focus should be like that it should be as large as possible. So, we have to maintain these this ratio always greater than one to obtain the desired one.

Now, if you look into this particular equation, then we find that there are several terms which we need to address like k_R , k_S . They are the reaction rate constant for the desired react product and undesired product; a₁ and a₂, they are the respective orders of the desired reaction and undesired reaction. Now, remember when we talk about the multiple reaction, we need to take care of all these respective orders whether some one reaction may have the order of 1 and another one may have the order of 2.

Then C_A, C_R and C_S are the concentration of the reactant A, desired product R and undesired product S. So, therefore, in this equation, we may have to look into the selectivity panel parameters. Now, C^A is only factor which can be adjusted and controlled as at a given temperature when k_R , k_S , a_1 , a_2 all are constant for a specific system. Therefore, when we look into the desired product, it can be obtained by the controlling the concentration of reactant A. **(Refer Slide Time: 18:13)**

That means when we talk about this controlling the concentration of reactant A, that means we are zero down that things. If you see that the mathematical equation, it consists of a lot of parameters. But, and all those parameters, if we consider all those parameters at a time, then it definitely my mathematical equation will become so complex in nature then sometimes the solution will not be easy.

So, therefore, we narrowed down the things and now that things are that we are concentrating towards the reactant A concentration. Now, sometimes you need to keep the concentration of a load, so, you can use the mixed flow reactor. You can maintain the high conversion. There may be a chance that you may increase the inert in the feed, or decrease the pressure in the gas phase system if you are handling that gas system in this one.

Now, if you wish to keep the concentration of A on the higher side, then you may use the batch or a plug flow reactor. We have discussed the protocol of all these 3 reactors in the previous lecture, batch reactor, plug flow reactor, mixed flow reactor, etcetera. You may maintain the low concentration, you may remove the inert from the feed or you can stop the insertion of all inert to the feed, you may increase the pressure in the gas phase system.

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Now, there are various cases by which we can control the the formation of a desired and undesired product. One approach is that you can write this mathematical equation or we are having this mathematical equation with us that is S_{RS} is equal to rg upon rs and dC_R upon dC_S or go to $k_R/k_S C_A^{(a1 - a2)}$. Now, if we consider the first case, when we may have a 1 is greater than a 2. That is the desired reaction order is the higher than the undesired one that is obviously as an engineering perspective, it is more favourable condition.

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

So, in that case keep the concentration of reactant as high as posible. Now, it keeps the ratio high, this ratio on the higher side and favoured the desired product formation. Now, sometimes the use of batch or a plug flow reactor is always preferred to have in the minimum size because the concentration of the reactant sometimes drop progressively during the course of a reaction in the reactor mass. So, but sometimes you may not use the mixed flow reactor as the concentration of reactant is always at its lowest value that of the outlet concentration.

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Now, in other case when the a_1 is less than a_2 that means the desired reaction order is of lower order compared to the undesired one. Now, here, we need to keep the low concentration to favour the formation of a desired product. Now, you need to keep the selectivity parameter ratio as high as posible and you may require the larger mix flow rate and you may require the dilution in the feed stream.

Now, the last case is that in which we can have this a₁ is equal to a₂. That is the desired reaction order is of the same order as the undesired one. Now, here the product distribution is usually fixed by k_R upon k_S ratio and unaffected by the type of reactor being used. So, let us have a brief look about this the mathematical approach.

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Now, the desired rate for the case 3. Now, here r_R upon r_S that is equal to dC_R upon dC_S that is equal to k_R upon k_S that should be constant.

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Now, we may control the product distribution to by varying the ratio of a specific rate constant for desired and unwanted reaction and sometimes referred as k_R , k_S ratio. Now, there are a couple of cases through which we can address this particular issue by changing the temperature level of the system. Sometimes the activation energy, it play a very vital role. So, activation energy of 2 reactions, they are different and unknown the ratio that is the k_R upon k_S .

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So, in that case, we can write the things like controlling the product parameters like we can write k_R upon ks. That is k_{RO} e to the power – E upon RT, that is E_R, small r divided by k_{S0} e

to the power – Es upon RT. Similarly, k_R upon k_S is equal to k_{R0}/k_{S0} e to the power – (E_R – E_S) upon RT. So, this is my desired equation.

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Now, this ratio k_R upon k_S changes with the temperature and usually depends on whether the activation energy is greater or smaller than ES. So, if the activation of activation energy of the desired product is greater or smaller than the activation energy of undesired product. Now, when temperature rises in that case, the kR over ks ratio increases and in that case, the activation energy of the desired one is will be greater than activation energy of undesired one.

Now, if that case, the k_R upon ks ratio decreases, in that case, the activation energy of the desired product will be less than the undesired one. So, a higher temperature usually favours the reaction of higher activation energy and lower temperature usually favour the reaction of lower activation energy. Now, sometimes we may use the case 2 by using the catalyst although it is a very common phenomena in the industrial approaches.

Now, one of the most important feature of catalysts that is the selectivity in the pressing or deaccelerating the specific reaction. Sometimes, this may be much more effective way of controlling the product distribution than any of the method which we discussed. So, for parallel reaction system, the reactant concentration is usually the key to control the product distribution.

And a high concentration of reactant usually favours the reaction of higher order and a low concentration favours the reaction of a lower order. So, while concentration label has no effect on the product distribution, if reactions are of the same order.

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Multiple reactions

- \checkmark Case 2: by using the catalyst
- One of the most important features of a catalyst is its selectivity in depressing or deaccelerating specific reaction.
- . This may be a much more effective way of controlling product distribution than any of the method discussed.

[NOTE: For parallel reaction system, the reactant concentration is the key to control of product distribution. A high reactant concentration favor the reaction of higher order and a low concentration favor the reaction of lower order. While the concentration level has no effect on the product distribution if reactions are of same order.]

Now, in this particular segment, we discussed the other the various concepts attributed to the product distribution, the concepts attributed to the selectivity concept related to the various permutation and combination of a different type of reaction mechanism maybe with and we discussed all these things under the head of various cases.

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So, in case if you wish to have further study, we have enlisted couple of references for convenience. Thank you very much.