

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

Lecture No. # 09
Complex Reactions - Introduction

Friends, let us continue our discussion on reaction engineering and today we will start looking at complex reactions. So, what we have looked at so far was basic review of material that you would have learnt in your first undergraduate reaction engineering course.

In which we saw how we represent a reaction, how we monitor the progress of the reaction, how thermodynamics plays an important role in determining what conversions we will get and then thereby determining what operating conditions we should use for our reactions. We also saw different kinds of kinetics and then finally, how we use this information to design the reactors, we focused or rather we limited our attention to ideal reactors namely, stir tank reactor and a plug flow reactor.

We also saw how kinetics determines which of these two reactors is better, as for as obtaining higher conversions or lower residence times are required. But as I had mentioned in my first class, that we hardly ever encounter a single reaction that will be carried out in isolation of any other reactions, when it comes to chemical reacting engineering practice.

Or in other words, we have lot of complex reactions and thereby kinetics, which is not a straight forward or as simple as for example, for an elementary reactions, where molecularity and order is same. So, what we will do in next couple of lectures is to look at some of the ideas that are used, when one encounters complex reactions. How do we simplify the analysis of such complex reactions and we look at few typical examples, which will illustrate these ideas more clearly.

So, we will begin our discussion by looking at few examples of complex reactions or what are the situations under which we encounter these reactions.

(Refer Slide Time: 02:47)

Complex systems - Examples

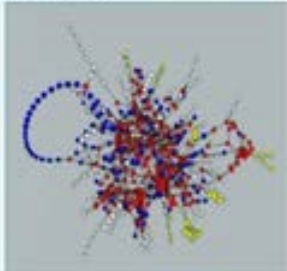
➤ Large number of reactions and reactants

Thermal cracking of alkanes

$$C_3H_8 \rightarrow C_3H_6 + H_2$$
$$C_3H_8 \rightarrow C_2H_4 + CH_4$$
$$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$$

Cracking of crude to petrol

Metabolic network inside cell



Let us start our discussion by we will first look at the examples then look at the analysis of some simple complex systems. That is complex systems, but very simple representation or as simple system as possible. Then we look at the kinetics by way of examples of chain reactions, catalysis, polymerization and we will also discuss about lumping analysis. When it when we encounter lot of complex reactions.

So, let us start with an example of complex systems. And the first set of example that I have put up over here, is an example where we have large number of reactions and reactants products and so on. So, typical example would be thermal cracking of alkenes. So let us say, we start with butane or propane, what gives rise to propylene then propane can also gives rise to ethylene plus methane, then propylene plus ethylene can react to give ethane plus propylene and so on.

What is conveyed in this example is that there are large number of reactants, large number of products and large number of reactions, occurring all occurring simultaneously. So, that is one example of what is meant by complex reactions. The second example, I would like to focus is cracking of crude oil to petrol. Now, this example is quite unique, in the sense that when we talk about crude oil to petrol. We really do not know the chemical formula for crude oil or for petrol.

Rather there is no single quantity or single chemical species which we say is a crude oil and which we can say is petrol. But rather what we have is mixture of different chemical species, which together constitute what we call as a crude oil or petrol and so on. For example, one way of putting all these species together is by number of carbon atoms that they have. So for example, we can say that lubricating oils for example, are all C 20 to C 70 compounds or gas oil or petrol is gasoline is a C 4 to C 12. Then we have light gases and liquids which is C 1 to C 4, kerosene for example, C nine to C 14 and so on and so forth. So, there are numerous chemical species, which are grouped together and we call them as gas oil, gasoline, liquefied gas or kerosene and so on.

So now a problem arises, while defining the kinetics of such processes, that we do not have well defined chemical species. And naturally chemical well defined chemical products. And therefore, there are no well defined reactions, but still we have to design a cracker or reactor for converting crude oil to petrol, otherwise, how would you drive from your home to your work place.

So in absence of precise information about chemical species, how does one design reactor? How does one determine the kinetics? And this is where lumping that I was referring to comes into picture. More close, example, is the metabolic network inside the living cell. And the cartoon that you see over here is actually a map of all reactions that take place inside the cell. In fact, it may not be even all reactions, but whatever we know for example, in an equalize cell. So, the circles that you see are the species, different colored circles denoting different kinds of species proteins, polysaccharides, and fat fats and so on. And the lines which connect these circles represent actually the reactions.

So, there is a huge or large number of reactions, thousands. We have to analyze these reactions; we have to design systems which make use of these living cells. So, how does one determine the kinetics of such processes? That is a challenge, but fortunately our training in reaction engineering gives us a lead to how we can handle such complex situations. So, this is one class of one example, where you have large number of reactions and reactants, examples where reactants and reactant are well defined such as thermal cracking of alkane. An example where they are poorly defined such as crude oil to petrol and so is the case of metabolic network inside the cell.

(Refer Slide Time: 08:23)

Complex systems - Examples

► Chain reactions

Thermal decomposition
 $CH_3CHO \rightarrow CH_4 + CO$

Auto-oxidation
 $R-H + O_2 \rightarrow ROOH$

Polymerization
 $styrene \rightarrow poly(styrene)$

$\gamma = K (CH_3CHO)^{3/2}$

Another class of reactions that are often encountered or what we call chain reactions, and there are few examples, which illustrate or which are based on chain reaction mechanisms. For example thermal decompositions, acetaldehyde giving rise to methane and carbon monoxide. Auto oxidation process that is a hydrocarbon or H incorporates oxygen within itself and gives rise to a chemical called, oxidized chemical called R O O H. And this compound is so called, the reaction is so called auto oxidation, because this particular compound contains both the fuel, that is the hydrocarbon R H and the oxidant namely the oxygen. So, you have in one place oxygen and the fuel. And I leave it to your imagine to figure out what may happen.

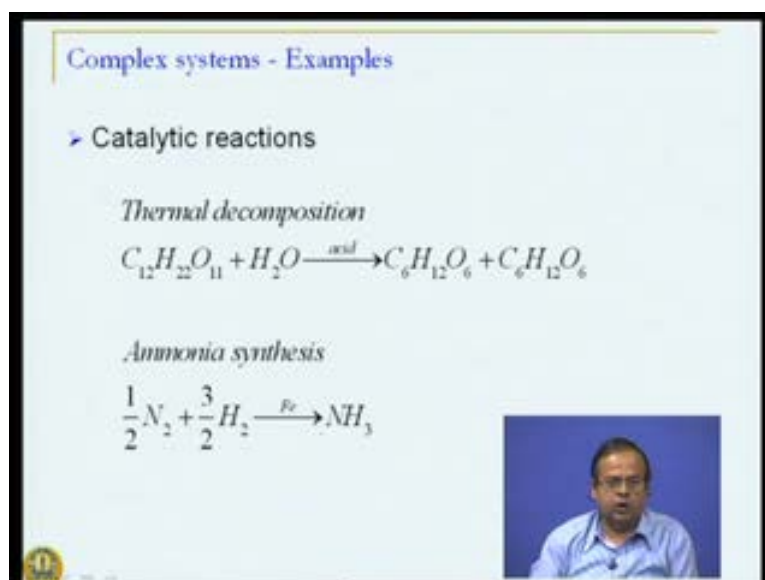
Incidentally these oxidation reactions are important for our well being as well. You might have seen advertisement saying take antioxidants or some vegetables such as spinach or carrot have good are good antioxidants. Reason for that, we will come to with the example is that we want to prevent such auto oxidation of organics in our body. Because that leads to deterioration of various organic molecules and we want to avoid that. But third reaction is of course, polymerization reactions styrene going to polystyrene and there are several other reactions.

Now on face of fate these reactions may appear simple. Take an example of acetaldehyde decomposition. One could argue that this is a fairly simple example, where you have one molecule of acetaldehyde giving rise to one molecule of methane and one

molecule of carbon monoxide. So, I can expect for example, my reaction rate to be simply R equal to K into concentration of acetaldehyde. Indeed, this would have been the case, if the reaction was an elementary reaction.

But it turns out that the kinetics is actually raise to 3 by 2. Now, where did this 3 by 2 come about, from where did it arise? So, what happens in this auto catalytic reactions or catalytic or rather chain reactions is that, these reactions actually take place through a series of many reactions, which involve formation of a free radical. Then that free radical somehow interacts with your reactant gives rise to more free radicals and products. And this cycle may continue for a long time or forever, if it does not come to an end. We will see the example of this little later on, but these all leads to complex kinetics.

(Refer Slide Time: 11:50)



Complex systems - Examples

> Catalytic reactions

Thermal decomposition

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{acid}} C_6H_{12}O_6 + C_6H_{12}O_6$$

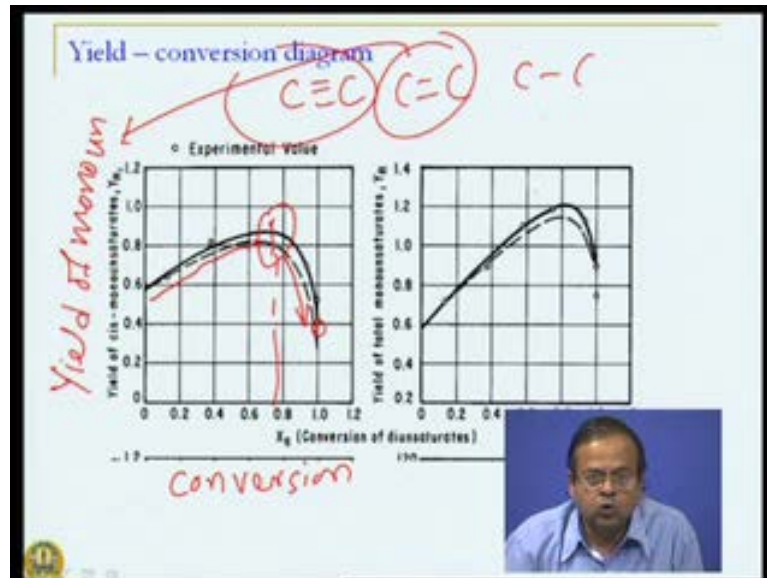
Ammonia synthesis

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \xrightarrow{Fe} NH_3$$

Then of course, we have catalytic reactions catalyst as you know is a compound, which does not influence the equilibrium of the reaction. That it does not change the equilibrium conversion, but it reduces the activation energy and brings about the reactions at reasonably faster rate, compare to what would have happened, if the catalyst was not present. And there are several examples, for first example is hydrolysis of sucrose giving rise to 2 C 6 compounds. Ammonia synthesis, where nitrogen and hydrogen combine to give ammonia, in presence of iron catalyst. The first example is presence of acid catalyst. So, they are two examples, one homogeneous catalysis that is

this sucrose hydrolysis and the other one heterogeneous catalysis gas solid, because catalyst is a solid. And these gives rise to various complex kinetics.

(Refer Slide Time: 13:03)



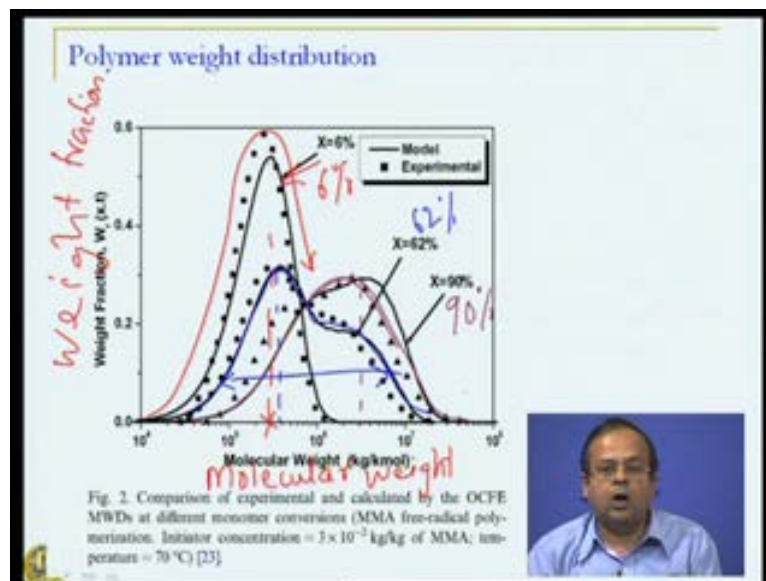
Now, one may ask question. So, what if the reaction is complex? I mentioned few examples; I will now mention the consequences of complexity of the reaction. Now, here are few examples which tell us what happens, if there are complex reactions which are encountered. And the first example that you see over here is an example of hydrogenation of oils or unsaturated fatty acids or oils to saturated fatty acids. And what you see on the X axis is the conversion and what you see on the y axis is the yield of mono unsaturated.

What our oils or a naturally occurring fatty acids what they have, is they could have up to 2 or 3 double bond bonded carbon species. So, this is die-unsaturated, this is mono unsaturated and of course, if it is double bond or triple bond, it is a saturated fatty acid. What we see on the on the y axis is the yield of mono unsaturated and for health reasons and otherwise, it is desirable to have higher mono unsaturated in our oils and fats. Now, if we start with unsaturated fatty acids, something like this and convert it by way of hydrogenation. So, you go from mono to, I mean d I to mono to saturates by adding hydrogen. If you go on adding hydrogen and go on converting this unsaturated, so that is what is the conversion on the X axis, what is the yield of mono unsaturated that we get. That is C double bond, C kind of compounds. and what we see here is that, as we

increase the conversion **as we increase the conversion** the yield of mono saturates increase, but that is true only for conversions up to 70-80 percent. Any conversion of unsaturated beyond this 78-80 percent actually reduces the yield of unsaturated, mono unsaturated.

In other words, if we want high levels of mono unsaturated chemicals or mono (()) fatty acids, then we do not want 100 percent conversion of unsaturated. Because 100 percent conversion of unsaturated, actually gives you less mono unsaturated compared to 80 percent conversion. So, there is an optimal conversion which is to be decided upon. This is a result of several reactions taking place and competing mechanism. So, this is one consequence or in other words, design of reactant now is no longer focused on converting di-unsaturated to 100 percent, because that would give us less yields.

(Refer Slide Time: 16:42)



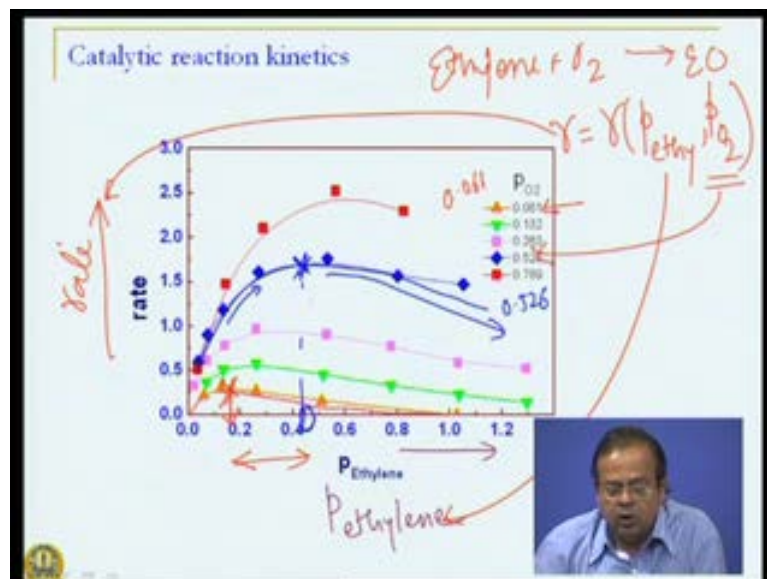
The second example is a polymerization example. And this is a figure in which see when you typically carry out polymerization reaction, you do not get a single product. You get a distribution that is polymer segments with differing number of monomers. And therefore, molecular weight of those segments is also different and their fractions actually change. So, what we are seeing here is for example, on the X axis is the molecular weight of the polymer fragment. And what you are seeing on the y axis is the weight fraction.

This is an example of batch polymerization. And what we see here is data for example, when you run the reactor for a short time. So, your conversions are limited. So in this particular case, conversion is only about 6 percent. At that point of time, your molecular weight distribution is of this type. So, the mean or the maximum segments are of this molecular weight, whatever that value is between 10^5 to 10^6 .

But look at what happens as you run these reactors for a longer time. This distribution does not remain the same, when the conversion changes from 6 percent to 62 percent. For example, at 62 percent conversion **62 percent conversion** where distribution is now a completely different set of distribution. what we notice here is that still maximum is in the same range, maximum number of segments having molecular weight of somewhere in between 10^5 and 10^6 , but the spread has now increased compared to the previous 6 percent conversion. Things change even more, when if you wait for 100 percent conversion or 90 percent conversion of your monomer. Look at the distribution.

Now, distribution is quite broad, but also the segment with the maximum number of maximum weight fraction is now of the molecular weight between 10^6 , 10^7 , this particular one. So in other words, as the time progresses there is a distribution, but that distribution keeps changing. One would like to know how do we determine, how these distribution changes? And it of course, depends on the kinetics of the process.

(Refer Slide Time: 19:56)

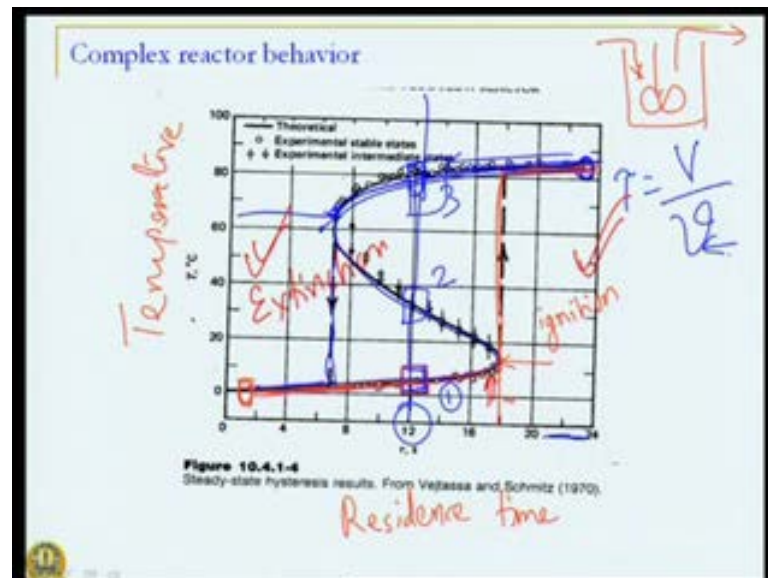


Let us take another example of oxidation of ethylene. What we are seeing here is an experimental data for partial pressure of ethylene **partial pressure of ethylene** in X axis. So, that is a representation of concentration and on the y axis, what we are seeing is the rate of reaction.

Our reaction is ethylene plus oxygen giving rise to ethylene oxide. The rate here depends on concentrations of both ethylene as well as concentration of oxygen. So, what is plotted here is the rate as a function of ethylene concentration at different values of oxygen concentration. So, these different colored symbols denote different values of oxygen concentration and what we see here is that when oxygen concentration is low, that is it is fixed at the low value, so this particular one the value is 0.061, partial pressure, then the rate follows this particular trend. As we increase the partial pressures of oxygen, there is a different value of dependency. For example, when partial pressure is 0.006, this is my rate of oxidation of ethylene as a function of ethylene concentration.

So now, we can see here two things. Number 1, as we are increasing the partial pressure of ethylene, the rate initially increases reaches a peak value and then starts decreasing. That is one characteristic of this behavior. Or in other words, our typical power law kinetics that we saw first order, second order or any fraction thereof. Rate increases as concentration increases. But here is a situation, where rate increases as concentration increases, but only up to a certain point. Beyond this particular concentration for example, the rates starts decreasing, so this is an unusual kinetics. That is number 1. Number 2, now here does this peak in concentration occurs that is ethylene peak occurring at this concentration, when depends on what is the oxygen partial pressure. It is determined by the concentration of the second reactant. For example, for partial pressure of 0.526 of oxygen, this is where the peak is occurring. But if the partial pressure is 0.06, this is where the peak is occurring. So, this peak itself is also shifting, where the rate is maximum that is an interesting kinetics. We will try to find out, how does this kinetic effect come about.

(Refer Slide Time: 23:46)



Here is another example of what happens, when you have complex reactions. this is a this is a example of running a stir tank reactor **running a stir tank reactor** for oxidation of sodium sulphite, which is an exothermic reaction. And what we have here is on the X axis is our residence time and on y axis is the temperature of the reactor. This is the adiabatic reactor, so depending upon how far reaction proceeds, since it is an exothermic reaction, as reaction proceeds temperature tends to increase. Now, as we are increasing the residence times **as we are increasing the residence times**, you can expect that more and more reactions take place.

At low residence time, the temperatures are fairly low **at low residence time temperatures are fairly low**. At high residence times **at high residence times**, temperatures are fairly high. And this is to be expected, because high residence time is reactants on an average have spend more amount of time in the reactor. So more conversion, more conversion means more liberation of energy, because it is an exothermic reaction. And hence, we have high temperatures, but look at how this behavior changes, as we change the residence time. Let us say that we started our experiments with very high residence time and we progressively decrease the residence time. So, what we are doing? Is we have a reactor; residence time as you will recall is a ratio of volume of the reactor to volumetric flow rate.

If you want to change the residence time, easiest way of doing is to change the volumetric flow rate. That is our residence time, is volume divided by volumetric flow rate. So, it is difficult to change the volume of the reactor. That means, you will have to change the liquid level, but easy to change the volumetric flow rate small v and thereby we can increase or decrease the residence time. What we are saying is, we start with certain residence time and let's decrease the residence time. So, if we decrease the residence time, the reaction extend will decrease and the temperatures will also decrease, because now less and less reaction is taking place. Let just stop here for a minute.

Let's do another set of experiment, where we increase the temperature or increase the residence time. Let us say that we start our experiments over here. And progressively increase the residence time, we will find that if we increase the residence time temperatures increase. But, now let us say that we keep on increasing the residence time. If we keep on increasing the residence time, we find that the temperature that you get is actually now a higher branch.

On this end, if we keep on decreasing the temperature **if you keep on decreasing the temperature** beyond this temperature, the temperatures are actually on this line. So to complete this experiment, if we keep on changing the residence time, we will get temperatures at different residence times, which will have this kind of behavior.

And this is an interesting behavior for a following reason. You choose a residence time, such as 12 seconds, such as this particular value. Reactor is operating under exactly identical conditions, but depending upon how we achieve this residence time of 12 seconds. We could get steady state temperature in a reactor either this value, which I denote it by number 1 over here or this value number 2 or some value over here number 3. That is what I am doing is, I am just drawing a straight line and these are the three possible temperatures that I could get.

So, three difference steady state temperature values for a same residence time, or in other words, we have what we call multiplicity of steady states. Now, you may ask the question, if I am given a reactor and if I am going to run it at 12 second residence time. How do I know, which steady state will I reach? Will I go to number 1, number 2 or number 3.

So, that depends on where you start your, how you start your reaction. So, two lessons here; one, because of these complex kinetics and we will see why these occurs. Because of this kinetics, there is a possibility forced of multiple steady states. And number 2 which of this steady state we will reach depends on, how we start the reaction? For example, in this particular case, if you achieved 12 second residence time by increasing the residence time from a low value to high value, we will go to steady state 1.

If you achieve the same residence time of 12 seconds by decreasing the residence time, we will go to steady state 3. But what about 2, now it turns out that steady state 2 is an ignorantly unstable system. So no matter what you try to do, if we do not have any additional help in the form of a controller to control the reaction, you will never reach this steady state whereas, 1 or 3 are perfectly possible. So, these are what we call stable steady states and 1 and 3 and number 2 is an unstable steady state.

Before we move away from this example, just look at what happens to the reaction. Let us go back to our experiment of increasing the residence times. If you increase beyond this, this is my temperature at this particular residence time. Any small increase beyond that my temperature suddenly increases to this particular value. Or in other words, there is a sudden increase in temperature at this particular point.

So, it is almost like igniting the reaction. From a very low temperature value, you will suddenly experience very high temperatures in your reactor. A phenomenon, which is similar to when what happens, when you ignite a process or ignite a candle from darkness to sudden light. In fact, the term ignition is always this kind of behavior is always referred to as ignition. So, somehow the process has got ignited.

Ignition now let us reverse the reverse the phenomena. If we are coming from a high residence time you are getting very high temperatures. But if you decrease the temperatures marginally, you suddenly come to the lower branch that means temperatures decrease suddenly. Reverse of ignition, an ignited candle suddenly blown off or extinguished and there is darkness in a reaction. For our reactions a high temperature, suddenly becomes a low temperature scenario. So, this is often referred to as the process what is referred to as extinction.

Let me process referred to as extinction of a behavior. So, we have ignition, we have extinctions associated. Now imagine, this kind of scenario happening in a real reactor, where you were trying to operate your reactor at this particular point. And for some reason your residence time increase and how could that happen? The flow rate would suddenly decrease. So, what would happen? Suddenly, you would have reaction temperatures becoming very high, a possible cause of an accident.

If it is a reverse process, suddenly reaction getting extinguished not as much a problem. You probably may not have accident, but still it is a loss, because whatever you wanted to do at high temperature reaction, now suddenly you have low temperatures. While designing reactors, one must be aware of conditions like this, so that proper safety norms are developed and followed vigorously. Otherwise, you know what happens, you have Bhopal's, you have tens see valleys referring to all kinds of accidents that one has witnessed in the past leading to unnecessary loss of property, but more importantly life.

As a reactor design engineers, it is our responsibility to make sure that, you one is aware firstly of likely situations and have the alternate strategies of controlling effect, all such situations arise. So, that we do not have sudden ignitions or extinctions in our reaction. Now, let us come back to analyzing this kind of reactions. And we will start with simple examples.

(Refer Slide Time: 35:55)

Cracking of ethane to ethylene

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

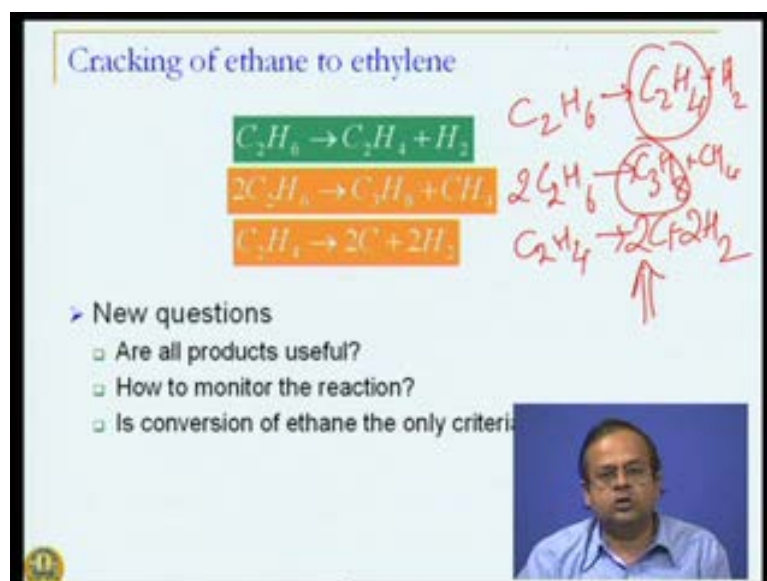
$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$C_2H_6 \rightarrow 2C + 2H_2$$

$C_2H_6 \rightarrow C_2H_4 + H_2$
 $2C_2H_6 \rightarrow C_3H_8 + CH_4$
 $C_2H_6 \rightarrow 2C + 2H_2$

> New questions

- Are all products useful?
- How to monitor the reaction?
- Is conversion of ethane the only criteria



Now, let us take this example of cracking of ethane to ethylene. We in fact, discuss this example in the very first or second lecture, saying that reactors are designed to achieve certain conversions, certain 60 percent conversion and so on and so forth.

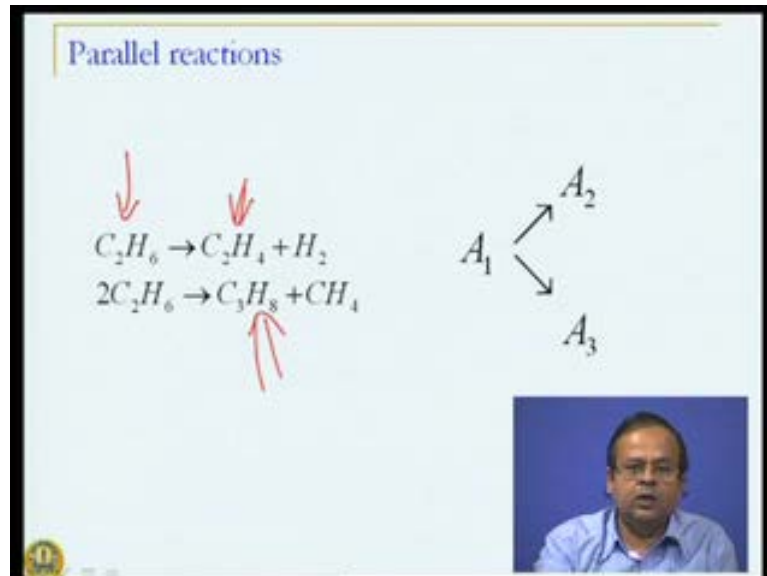
If this is the only reaction that is taking place, conversion is naturally by criteria of a choice for designing the reaction. But we know, from our discussion so far, it is very unlikely that this is the only reaction that will take place. Accompanying this reaction, so we have C_2H_6 going to C_2H_4 plus H_2 that is ethane going to ethylene and liberating hydrogen as one of the reactions. But there is a possibility of another reaction in which two molecules of ethane $2 C_2H_6$ combines with two molecules of ethane combines to give rise to propane and methane. So, while this reaction is what we want, that is our focus is on making lot of ethylene. There is a possibility that second reaction can take place.

Why second? They could be a possibility of worse kind that ethylene completely getting charred. That means ultimate reduced to carbon and hydrogen. So, there is a possibility that we have carbon and hydrogen. So, this carbon will deposit along the walls of the reactor, it will foul the reactor, it will alter the heat transfer ability in the reactor and so on. So, many things can happen or it may even block the entire tube, if this is to be carried in a very small diameter tube. So, these are situations which we certainly we do not want, but they are likely to be present. If that is the case and if I say that I am designing for reactor for 60 percent conversion of ethane or 80 percent conversion of ethane.

How do I ensure that the 60 percent of ethane that has got converted as all gone into making of ethane ethylene, because there is a possibility of second reactions. Of some of this converted ethane could have gone to butane, I mean propane and we certainly would not want that, but conversion alone therefore, is not enough. what it means is, when we come when it comes to complex reactions that are new questions that need to be asked or designs can no longer be focused on getting maximum conversion in a given reactor or designing the smallest reactor for known conversion desired conversion. So, we need to now ask ourselves. Are these all products useful? Certainly, we know that carbon is not going to be of any use. In fact, it is a problem. Now so, how do we monitor such reactions, because monitoring only the concentration of ethane is no longer enough, is conversion of ethane only criteria for design. I think you know answer by now, of course

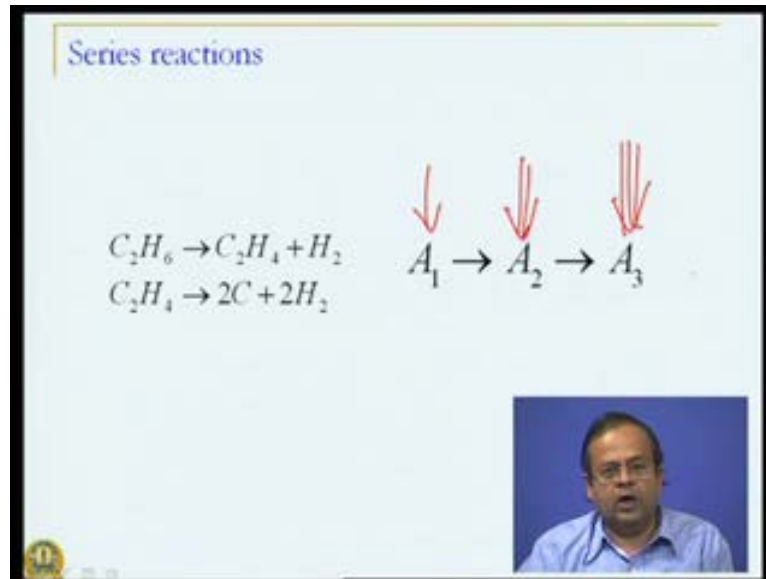
not, there is something else that we need to worry about. So, monitoring of these reactions can no longer be done, in terms of extent of reaction or conversion of key reactant and so on.

(Refer Slide Time: 40:13)



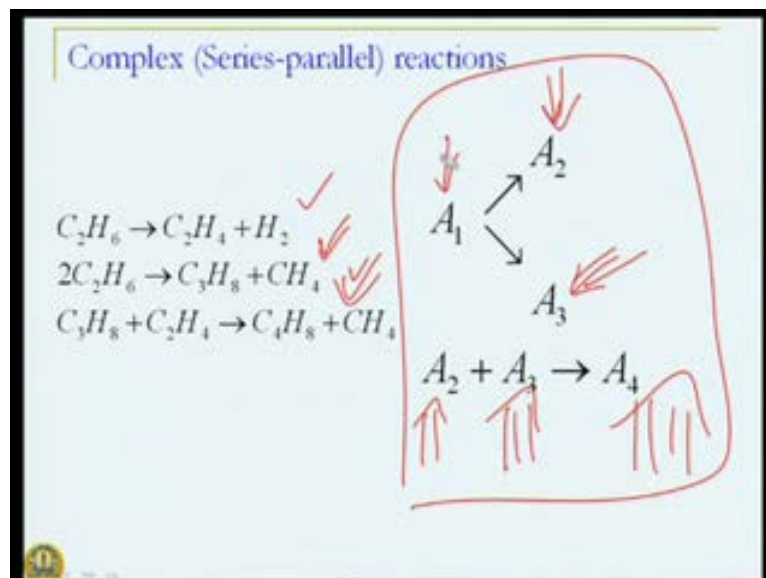
So, let us begin by defining few quantities of interest, but before we do that, just basic kinds of reactions that one encounters, when we have multiple reactions. And first is an example of what we call parallel reactions. So, here is ethane either going to ethylene or to propane. A1 ethane going to either A 2 ethylene or A 3 propane. So, these two reactions are parallel going on, hence the name parallel reaction.

(Refer Slide Time: 40:55)



Then we have what we call series reactions. The same example, ethane going to ethylene and ethylene going to carbon. Ethane going to ethylene **ethane going to ethylene** ethylene going to carbon. So, series kind of kind of reactions.

(Refer Slide Time: 41:25)



And then of course, we could have complex reaction network or series parallel reactions. Ethane going to ethylene, ethane going to propane or propane and ethylene giving rise to butylenes and methane, yet another reaction. So, reaction of the type ethane giving ethylene or ethane giving propane and then ethylene and propane giving rise to yet

another compound. In other words, using only same reactant and few other species, we have now constructed a fairly complex network of reaction.

(Refer Slide Time: 42:37)

Complex (Series-parallel) reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$C_3H_8 + C_2H_4 \rightarrow C_4H_{10} + CH_4$$

Diagram illustrating a reaction network:

- A_1 branches into A_2 and A_3 .
- A_2 and A_3 combine to form A_4 .
- Handwritten red annotations: A_2 is labeled AE_5 and A_3 is labeled A_6 .

Fairly complex network of reaction and you can imagine now, you had more species A 4, A 5, A 6 to this what are all possibilities that can happen among interaction between these 6 species. We are slowly building the complex reaction networks, but how do we analyze such networks?

(Refer Slide Time: 43:03)

Desired and Undesired Reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

Diagram illustrating reaction pathways:

- $A_1 \rightarrow A_2$ (Desired, marked with a red checkmark)
- $A_1 \rightarrow A_3$ (Undesired, marked with a red X)
- $A_1 \rightarrow A_2 \rightarrow A_3$ (Undesired, marked with a red X)

Let us before we do that another example, ethane going to ethylene propane going to propylene independent reactions. So, it is not necessary that all species should interact with each other all the time. Here, may be two reactions almost going on parallel lines, parallel tracks, so independent of each other. We have parallel reaction, independent reactions, series reactions and reactions in which all these reactions are taking place at the same time, in other words, complex reactions. When it comes to these complex reactions, then it is clear that not all products are desired. For example, in this example of ethane going to ethylene, this is my desired reactions. I want this, but I do not want two molecules of ethane give rise to propane. So, this is my undesired reaction.

If we have parallel reactions, may be one of them is desired others are all undesired. And why may be almost invariably when such complex reactions are present. We really do not undesirable reactions, but they are inevitable. So, we have to get a way around, to suppress this undesirable reaction and promote only desirable reactions. The same thing can happen in series reactions. For example, A 1 going to A 2 going to A 3 this may be desirable reaction, but this may be undesirable reaction. So, how do we doubt designed reactors for this?

(Refer Slide Time: 44:59)

Yield

Desired reaction $A_1 \rightarrow A_2 \quad r_1$

Undesired reaction $A_1 \rightarrow A_3 \quad r_2$

Overall Yield $Y_2 = \frac{\text{Exit molar flowrate of desired product}}{\text{Inlet molar flowrate of reactant}}$

$= \frac{F_2}{F_{10}}$

But before we do that, let us define few quantities of interest when it comes to multiple reactions. Let us say the first quantity of interest is yield. So, let us say that we have these desired reactions A 1 going to A 2 and is undesirable reaction A 1 going to A 3.

This follows rate R 1, second reaction is rate R 2. See how we are bringing together now the concepts that we studied in the first few lectures. We have many species A 1, A 2, A 3. We have many reactions to in this particular case. And we have rates of these two reactions **rates of these two reactions** R 1 and R 2.

And now we are saying there are some desirable undesirable. So, let us define the yield. And let us say that this reaction is taking place in a tubular reactor. the same yield can be defined for batch reactors also, but in a tubular reactor. So, we are feeding a reactant A 1 over here. Let us say concentration is C 1 0 and we are getting C 1, C 2, C 3. That is concentrations of A 1, A 2, A 3 or if you do not like concentrations, the molar flow rate F 1 0 then molar flow rate F 1, F 2, F 3 of a species data is coming out.

We define the overall yield y 2 of; let us say our desired compound A 2, as the exit molar flow rate of desired product. So, in this particular case, it will be F 2. Desired product divided by inlet molar flow rate of the reactant. That is one way of defining the yield. So, of this rate at which A 1 is coming in, how much of A 2 are we getting?

(Refer Slide Time: 47:22)

Selectivity

Desired reaction $A_1 \rightarrow A_2$ r_1 ✓

Undesired reaction $A_1 \rightarrow A_3$ r_2 X

Instantaneous Selectivity $s_2 = \frac{r_1}{r_1 + r_2}$

Overall Selectivity $S_2 = \frac{\text{Exit molar flowrate of desired product}}{\text{Exit molar flowrate of all products}}$

$S_2 = \frac{F_2}{F_2 + F_3}$

So, that is one criteria. There is another criteria, where we have same desired reaction undesired reaction A 1 going to A 2 desired, this is undesired. But we now define selectivity. We define instantaneous selectivity, we define two selectivities actually, instantaneous selectivity and overall selectivity. Let us first define overall selectivity and then we will come back to instantaneous selectivity.

So, we define overall selectivity S_2 , as exit molar flow rate of desired product **exit molar flow rate of desired product**. That is in this particular case, F_2 two exit molar flow rate of all products. So, F_2 plus F_3 . So, what we are now saying, is that of all the products that are coming out at F_1 , F_2 , F_3 , as flow rates, we are feeding in F_1 , of all the products that are coming out. So, what are the products that are coming out? A_2 and A_3 are the main products. So, F_2 and F_3 together is the exit molar flow rate of all products. Of all these products, how much is the actually desired product that is coming out. So, that is our F_2 . The ratio of this two as the selectivity S_2 .

This is while looking at what is the exit condition. But we know our discussion on plug flow reactor. We know that at each point on these along these directions of flow concentrations are changing, rates are changing. So, we can now define what we call instantaneous selectivity that is selectivity at any given location in this reactor. That will be the rate of the desired reaction that is first reaction, to the rate of both desired and undesired reaction r_1 plus r_2 . And why we call these instantaneous? This we call instantaneous, because this selectivity will depend on what is the concentration here. So, this particular value S_2 will be some value at this location, but will be a different value at some other location. In other words, this is not a fixed value or overall value, whereas, this selectivity capital S_2 capital S_2 is overall value. That is what is it that is coming out. Now, if you look at this instantaneous selectivity, what it is doing is the ratio of desired reaction to ratio of desired plus undesired reaction. Overall selectivity, is the ratio of flow rate of desired compound coming out to flow rate of total compounds that are coming out.

Little going ahead little bit, it is not very difficult to now think about this instantaneous selectivity, somehow determining this overall selectivity. That is, whatever comes out of this reactor S_2 , will be determined by what is happening inside the reactor. How far is the first reaction proceeding compared to both the reactions? So, what is happening inside the reactors or this small S_2 will somehow therefore, determine what we see at the exit of the reactor. But this we will pick up in our next class that is, what is the connection between S_2 small S_2 that is instantaneous selectivity and overall selectivity. And this is a matter for discussion in our next lecture. **thank you**