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Module No. # 02 Lecture No. # 07 Chemical Reactor Design

Friends, let us continue our discussion on, design equations for ideal reactors. But, before we continue I just want to once again reiterate, what is ideal reactor? The reactor, ideality is determined by the conditions of flow inside the reactor; and it has nothing to do with what size, shape or color that reactor or material for that matter that reactor is made up of. So, it all depends on what kind of flow is going through the reactor or what flow conditions exist in the in the in the reactor.

So, we have two extremes of flow conditions, ideal flow conditions. One in which, we have a good way of mixing the entire contents of the reactor, so that there are no heterogeneity in the reactor. Or in other words, the reactant concentrations temperature or any other condition, that matters for the reaction are uniformed throughout the throughout the reactor.

Just imagine the room in which you are sitting right now as your reactor and if you look at the right corner, left corner, middle, top, bottom anywhere you look, if the conditions are same; that is this room is your reactor and concentrations of various species are same for example, in right corner, left corner, top, middle wherever you look, then we call such reactors as well mixed reactors.

Of course, you have to have some physical provision inside reactor to achieve this condition. And one good way of doing that is having an impeller that is, you have a stirrer mountained on some shaft, which is connected to a power source and you turn this shaft, so that impeller rotates and it causes uniform uniform mixing. I should also point out that, there are various different ways of achieving mixing, if not uniform at least partially, but we will talk about them when we talk about some some special reactors towards the end of this course.

So, we have stirred-tank reactors and that is one extreme, where all contents are uniformly uniformly mixed. The other extreme of flow condition is no mixing, no mixing in an axial direction. And what I mean by that, let us let us consider a reactor and we consider a tubular reactor, but it need not be tubular, it could be any other reactor.

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So, let us say that, this is our reactor let me make this little darker. So, this is our reactor let us say and there is an entry point everything we denote with subscript o and there is a there is a exit point. Now, in this tubular reactor, there are two directions, one is the axial direction and other is the radial direction. The axial direction is the direction of the flow, so material is flowing in from this entry point upto the exit point. So, in a plug flow reactor, it is as good as saying that, liquid moves like a plug.

So, imagine a thin plate or imagine thin planer fluid, it enters **into the** into the reactor, so we have we have let say one thin plane over here, then following this, another fluid element moves in; then we have yet another fluid plane moving in, and these fluid elements in these axial plan in this plan, they do not interact with each other.

So, for example, in this pictorial cartoon these blue and green fluids do not mix with each other, they continuously move from this particular end to the exit of the reactor. So, that is to say that, there is no axial mixing. So, the concentrations or fluid properties or reacting mixture properties with temperature or any other property is continuously changing as we are moving along the direction of the flow and this is what is an ideal plug flow reactor.

But, I should also point out that, in case of plug flow, there is a complete mixing along the radial direction. Along the radial direction there is a complete mixing, what it means is that? If you look at this particular plane, then the fluid properties at this radial point this, this, they are all same (Refer Slide Time: 05:37). And $($ ()) case in case of green fluid, so along the radial plane, there is a complete mixing. So, properties are uniform, but along the axial flow direction, there is no **mixing of** mixing of fluids and this is what the ideal **ideal** flow behavior is.

And we consider the mass balance for this in the last class and it worked out to be d F j d t equal to r j. Let us, rework this mass balance once again, so that we we follow this development clearly.

(Refer Slide Time: 06:33)

So, let us say that, we have our reactor and in this particular case, what we are going to say is the reactor volume at the entry point is V is equal to 0 and reactor volume at the exit point is, reactor volume is some V R. Now, let us consider a small element of this reactor at some location V equal to V, and V equal to V plus delta V. Remember, along this axial direction, properties are changing, but along radial direction, properties are uniform, that is what is our plug flow reactor reactor.

So, now let us write down our mass balance equation for this particular particular reactor saying that, the concentration of the species which enters at this particular plane of a given species is C j; and let us consider a small volume delta V and small time interval delta t, so what happens in this particular particular segment? There is first of all, accumulation, the mass balance is same as before, that is accumulation is in minus out plus generated. So, there is a accumulation.

So, let us say that, concentration at time t plus delta t minus concentration at time t multiplied by the volume of this element, is how much the mass has accumulated in this small element delta V. Now, this has accumulated as result of three different things as I just now said, so this is equal to the concentration is C j prime let say that, V is the V is the volume volumetric flow rates small V, small V is a volumetric flow rate coming in going out.

So, v into C $\dot{\rm j}$ is the rate at which the moles are coming in recall that, v into C $\dot{\rm j}$ or if you do not like v into C j let us let us keep it as in terms of our earlier notation of F j, that is the number of moles that are that are coming in at this particular volume at this particular volume minus the flow rate at that is going out. So, in minus out let me write it more clearly, V plus delta V at this in small time interval delta t, so this is how much has **how** much has coming.

Remember, we are writing balance for mass. So, everything has to be in terms of moles. So, this is what is coming in $F \nvert$ at volume V minus $F \nvert$ at V plus delta V into time interval delta t, that short time interval is what is coming in and out plus let say, the rate of change of generation of species is r j. So, r j into delta V into delta t is how much moles of j has been generated in this interval.

Once again we have a simple mass balance, accumulation in out plus generation. So, now, if we divide this a whole quantity by delta V delta t and take limit as delta V goes to 0, delta t goes to 0, this mass balance equation now becomes del del t of C j divide by delta V delta t, so and take limits equal to minus del F j del V plus r j. So, this is our unsteady state mass balance equation for a plug flow reactor (Refer Slide Time: 11:08), ideal plug flow reactor; that is the accumulation the change of moles plus in and out plus generated. How do we go from this equation to this equation?

(Refer Slide Time: 11:48)

If we say that, we are looking at steady state, if you are looking at steady state, then del del t of C j, this term drops out, we have only this two terms. So, if we now rearrange them, we get d F j d V equal to r j that is our mass balance equation for a plug flow plug flow reactor. Now, there are few points which I want to mention while we are at mass balance equation for plug flow reactor and this is the following.

Now remember, particularly if you are looking at **if you are looking at** a situation, where which involves a gas phase reaction and a gas phase reaction in which there is a change in number of moles and this requires some consideration. For example, we $(())$ this reaction of ethane undergoing dehydrogenation to ethylene plus H2, we had earlier spend some time on how we calculate the flow rates and so on or how they are dependent on temperature and pressure and so on.

But let us, reiterate this example once again and how it affects the design equation for a plug flow reactor. Now, what is happening here is, one mole is giving rise to two moles. So, without going into details we have delta change in number of moles, then epsilon as delta y 10 that is initial moles, all these things we had considered earlier. So, I am not going to repeat once again, but the idea is the following.

Now if you remember our discussion on kinetics we said that, r j is a function of concentration of the species and temperature \bf{r} *i* is a function of concentration of the species and temperature. This mass balance equation does not have concentration in it, remember the mass balance is on mass, that is on moles. So, how do we now relate this two? So, we know by our definition, F j by volumetric flow rate is our concentration C j.

So, there are two ways of relating this this condition, one is you put this value of C_i in this rate expression, so r j now becomes function of F j. So, how do we how do we link this two equations? C j can be expressed in terms of F j by v. So, plug that in into this rate expression, so we have $d F j d V$ as equal to r j, r j which is if we if we plug it for C j we have F i by y volumetric flow rate.

So, that in $\frac{\ln x}{\ln x}$ such case, we now have the mass balance equations which are which are consistent, but there is one more thing that we need to we need to worry about particularly, when you are change in number of moles. Recall that, we have our equation of state, if we say we follow ideal gas law, then P into volumetric flow rate is F T into R T and we can write the same thing at inlet conditions.

And this now has flow rate F T and flow rate F T is nothing but, summation F j. So, the flow rate, molar flow rate $F \in \mathfrak{g}$ not only appears over here as $F \in \mathfrak{g}$, but also in the volumetric flow rate (Refer Slide Time: 16:20). So, all these will help to be considered together if $\frac{1}{1}$ we have reaction in which, there is a change in number of number of moles, so this is one way.

Let me recap, our mass balance equation is $d F j d V$ equal to r j, rate of generation of species $\mathbf i$ is a function of concentration, which is now expressed as $\mathbf F$ j by v, and v in turn is dependent on the molar flow rates, $F T$ which has also $F i$ in it. And therefore, this complete the this completes the discussion. The second approach of dealing with this is as follows, we work with concentrations.

(Refer Slide Time: 17:26)

There is $($ ()) r j as a function of $($ ()) r j as a function of C j and T and instead, express F j as volumetric flow rate times C j and then write this equation as (No audio from 17:52 to 18:00). Now, I will also bring your attention to a more common form which you might have seen earlier that, this is our now mass mass balance equation (Refer Slide Time: 18:07), this mass balance equation can be further simplified. And what are the conditions under which it can be further simplified? The conditions are as follows.

If if and only if, v the volumetric flow rate is not changing along the axial direction, that is v is constant that is that is condition condition one, then the diameter of this tubular reactor is constant; that means, cross sectional area is constant and mind you, that is not necessary we may have reactors, which will look something like this (Refer Slide Time: 19:05), where the diameter changes along the axial direction of flow. There are situations where reactors look something like this. So, we are not considering those reactors.

So, if diameter is constant as is the assumption that we have made, then the volume V is nothing but, the cross section area A into whatever distance along the axial direction that we have travelled let say, that this V corresponds to actual direction of z, and this is z plus d z, so this is A into z (Refer Slide Time: 19:50). So, if that is the case, then we get we can simplify this mass balance equation further, what is that simplification? v is constant, so we can take out v from this mass balance equation common outside, so we have v and instead of d V we will put A dou dou z of C j equal to r j.

What is what is v ? v is is the volumetric flow rate divide by the cross section area, so that is nothing but, the velocity the superficial velocity in the of the fluid in the reactor. And in that case, we get our mass balance equation which simplifies to u d C d z equal to rj, this is the equation (Refer Slide Time: 20:53), which you have probably seen as a design equation earlier.

But, this equation is applicable only under specific case, the general mass balance equation is, this particular form $d F j d V$ equal to r j, which under the conditions that volumetric flow rate is constant through the entire reactor; that means, there are no change in number of moles for a gaseous reaction or if it is a liquid phase reaction, that is a reasonable **reasonable** assumption, both these things $((\))$ down to constant density along the length of the reactor and under those conditions plus the radius of the or the diameter of the tubular reactor is constant along the flow direction, then we get our mass balance equation, which looks \overline{u} equal to \overline{d} \overline{c} \overline{d} \overline{z} u d \overline{c} d \overline{z} equal to r j.

(Refer Slide Time: 22:11)

So, now let us go back to our mass balance equation for stirred-tank reactor and that for earlier we had seen that, this is our mass balance equation for a well mixed continuous stirred-tank reactor. The volume of the reactor equal to $F \, \mathrm{i} \, 0$ minus $F \, \mathrm{i} \, \mathrm{divided}$ by minus r j and this is our mass balance equation for plug flow reactor (Refer Slide Time: 22:34), $d F j d V$ equal to equal to r j. Now, one question that we may want to ask ourselves is, how does these two reactors compare with each other, when it comes to performance of this reactor for certain chemical reactions, when reactions are taking place?

(Refer Slide Time: 22:59)

So, let us let us consider an simple example of reaction A 1 going to products. I am considering simple reaction A 1 going to $\frac{1}{2}$ going to products and for this particular reaction we can write, so this is a simple reaction in a single $single$ reactant, so my r 1 that is the rate of, rate of generation of species 1 which is nothing but, nu j into r, if the r is the rate of this reaction; so r is the rate of this reaction times are stoichiometric coefficient.

And for this particular **particular** example, nu j or nu 1 is minus 1. So, r 1 is minus r. So, if we consider this (Refer Slide Time: 24:03), and our assumption that, v is constant, cross sectional area is constant, then by writing F 1 as volumetric flow rate times C 1 and the cross sectional area A being constant.

Remember our our our design equation d r under this simplifying condition, our design equation was u d C 1 d r equal d g equal to r 1. So, you substitute r 1 as minus r, and we normalize this by $\frac{by}{by}$ or rather rearrange this. So, take d z on one side bring r 1 and do the rearrangement, we will get we will get if we rearrange this we will get C 10 to C 1 d C one d \overline{d} C 1 divided by r or 1 over r d C 1 equal to L by u. L is the length of our tubular reactor, u is the superficial velocity.

So, this is in centimeters divided by centimeters per second and this is nothing but, the residence time in the reactor tau, so that is how, how long on an average the reacting fluid has spent in the reactor, from this entry point to the exit point. So, this has units of time, so this is called this as residence time.

So, we get our mass balance equation, which for a plug flow reactor for this reaction, A 1 going to products under this simplifying assumptions as, tau equal to C 1 from the integral of 1 over r d C 1 limits being C 10 to C 1. Now, if we do the same simplifications for a mass balance on stirred-tank reactor, we get this particular particular design equation (Refer Slide Time: 27:03), this is for Stirred-Tank Reactor, C S T R as we refer to it, this is for Plug Flow Reactor or PFR (Refer Slide Time: 27:09). So, these are two mass balance equations and we would like to see, which of these two reactors give you better performance.

Now, what is a better performance? There are two ways of looking at better performance, one is we say that our reactor length and velocities are fixed; it means we have the same residence time in a plug flow reactor and stirred-tank reactor, which of these two reactors give us higher conversion of A 1, so that is one way of comparing. And whichever gives higher conversion that is a better of the two reactors.

The other way of comparing this two would be, we say that we want certain conversion of A 1, that is we are going to design our reactor for 90 percent conversion of A 1, then whichever of the two reactor achieves this 90 percent conversion with a smaller residence time will be the better of the two reactors, it is it is two different ways of looking at the same thing.

Whether stirred-tank reactors is better than plug flow reactor or vice versa, but let us let us look at how do we compare this and of course, one can put in some kinetics computes some numbers and so on. But, let us try to first get a field in a graphical way of, how this two reactors can be can be compare?

(Refer Slide Time: 28:57)

To do that, we need certain certain kinetics and what we see here in this particular plot is the on x-axis or rather on y-axis we have rate as a function of concentration of C 1 and we are going to assume that, rate follows a power law kinetics. So, we have r equal to k into C 1 raise to raise to n. On the x-axis instead of plotting this rate as function of C 1, I have plotted it as a function of C 10 minus C 1 and the reason for this will become operand when we go to the next line.

But for time being, let us take it that this is the function of C 1 and what we see, different colored lines are for different values of n starting with n equal to minus 1 to n equal to 0, 1, 2 and so on. Now, let us start with the simplest case that we (0) that is n equal to 1, now we know for r equal to k C 1, rate verses C 1 is a simple straight line, right that is a linear law.

Now, how does this (0) converted into this violet line, when we plot C 1 minus C 10. What is this particular point (Refer Slide Time: 30:36)? This is a point, when C 1 minus C 10 is 0; that means, this is C 1 equal to C 10. So, this is a point in our regular curve, this is that point rate equal at C 1 equal to C 10, which is this particular point.

And as on this plot of C 1 minus C 10 as we are travelling here, what is happening at this particular point, this is with C 10 minus C 1 is equal to some value of C 10; that means, this is a point, C 10 equal to equal to 0, so that is this particular point (Refer Slide Time: 31:23). So, as we go from concentration of 0 to C 10, the rate increases, but the same thing is happening as we are going from concentration of C 1 equal to 0 in this bigger plot to C 1 equal to C 10, the rate is increasing along this violet line $\frac{right}{right}$. So, this is this is a same rate plot, but slightly in a different manner. In the similar manner, we can plot for n equal to minus 1, 0, 0 where rate is independent of concentration, 1 and 2, this is the blue line is for n equal to 2. So, $kC1$ square $kC1$ k and $kC1$ raise to minus 1.

(Refer Slide Time: 32:24)

So, now let us try to compare this two reactors by by looking at this particular plot. Again going back to our design equation, this is the deign equation for C S T R (Refer Slide Time: 32:33), and this is a design equation for Plug Flow Reactor (Refer Slide Time: 32:41). Now firstly, we notice in both these design equations, there is 1 over r, here 1 over r as well as over here.

So, instead of plotting r the same plot now are converted into 1 over r on the y-axis and verses C 10 minus C 1 on the on the x-axis. Now, let us look at what is the what is the performance of these two reactors? Let us, take the case of n equal to 1. So, this violet line, now you know what is integral 1 over r d C 1 from C 10 to C 1, where is our where is our C 10? Our C 10 is over here, C 1 equal to C 10 is over here and some value of C 1 let us say, this particular point (Refer Slide Time: 33:48).

So, what is this integral? This integral is nothing but, the area under the curve of this violet line at value, $(())$ this area under the curve that is the area of this integral or that is a value of this integral. So, what is this shaded area now? The shaded area is nothing but, the residence time required for plug flow reactor.

Let us, look at what happens when we have a stirred-tank reactor, for a stirred-tank reactor for a given value of C S T R, for given value of C 1, this is the value of 1 over r and what is this residence time is, 1 over r multiplied by C 10 minus C 1. So now, for a stirred-tank reactor this this particular value which is nothing but, 1 over r at C 1 multiplied by C 10 minus C 1. So, this area of this rectangle area of this rectangle is now the residence time for C S T R.

Once again for plug flow reactor, the area under the curve for for this particular curve of 1 over r verses C 10 minus C 1, area under the curve is the residence time for stirred-tank reactor, area of this rectangle is the residence time for stirred-tank reactor.

So, let us come to our design problem, let us come to our design problem of let say that, I want certain value of C 1 at the exit of my reactor, this particular value what is the reactor which reactor gives me minimum residence time and that would be the better of the two reactors; it is clear from this representation that, plug flow reactor gives us low residence time compared to **compared to** the stirred-tank reactor.

So, for reaction, which is first order kinetics r equal to $k \, C \, 1$, my plug flow reactor results into low residence time as compared to a stirred-tank reactor for achieving the same degree of conversion. Now, this graphically this is all fine, but what is what is actually happening, why is this happening? Let us, try to understand it in a qualitative sense as well, remember in a stirred-tank reactor, our inlet concentration is C 10, our exit concentration is C 1 and because of mixing conditions, the concentration inside the reactor is also C 1.

So, what happens in a stirred-tank reactor, the while concentration value decreases instantaneously that is as soon as, it enters the reactor, concentration drops down from C 10 to C 1 and hence, the rate of reaction also instantaneously drops down from that which one would have achieved at inlet condition to whatever is the exit condition.

Let us compare that with what is happening in the plug flow reactor? In a plug flow reactor, what is happening to my concentration? My concentration is C 10 over here at the entry point and it is gradually decreasing $\frac{1}{x}$ is gradually decreasing to a value C 1 along the length of the reactor.

In a stirred-tank reactor from C 10 to C 1 is instantaneous, because as soon as the fluid element enters the reactor, it mixes uniformly with whatever is there inside the reactor concentration drops down from C 10 to C 1, whereas in this particular case, concentration drops down more uniformly. Now, what happens to the rate? The rate also drops down instantaneously in the stirred-tank reactor, it drops down more gradually in a plug flow reactor.

So, in a plug flow reactor, reactions are occurring at a rate higher than that as the exit for the entire duration of the reactor and therefore, now you can imagine if rates of reaction are higher in a plug flow reactor, the corresponding residence time would be would be lower, because reaction rates are higher, it would take lower residence time to achieve the same degree of conversion.

Hence, for a first order reaction, the plug flow reactor is better than the stirred-tank reactor. Whatever argument we put for right now, can be also turned around and said that, if the residence times are same in stirred-tank reactor and plug flow reactor, we would get higher conversion in a plug flow reactor as compared to a stirred-tank reactor, but is it always the case? No.

(Refer Slide Time: 40:25)

We will go back to our example and see that, that need not always be the case. What we see here with this orange line and let me magnify it, so that it $\frac{d}{dt}$ is clear, this orange line over here (Refer Slide Time: 40:44), this particular line where n is equal to minus 1. So, now our kinetics is r equal to k C raise to minus C 1 raise to minus 1 or k by C 1, for this the plot of 1 over r looks something like this.

Now, remember our design equations are the same, they do not depend on the kinetics of the process, the performance of the reactor depends on the kinetics of the process, but the reactor design equation for say are not dependent on the kinetics of the process. So, they are the same; that means, the residence time for a plug flow reactor is area under the curve, for for stirred-tank reactor, it is the area of the rectangle.

So, let us look at what is the what is the residence time for this particular reaction that is k C 1 raise to minus 1, when n is minus 1 \overline{n} is minus 1 what is a residence time? So, let us say that, this is the C 1 that we are interested in (Refer Slide Time: 41:47), then the residence time would be, all this area under the curve for plug flow reactor.

Now, what about stirred-tank reactor? For stirred-tank reactor, it is the area of the rectangle, but which rectangle now; this is 1 over r at C 1 multiplied by C 10 minus C 1. So, area of this rectangle shown in the blue line is the residence time in a stirred-tank reactor. So, this blue is residence time for stirred-tank reactor.

And now, what do we see, we seen how exactly the opposite phenomena that is area under the curve is larger than the area of the rectangle, which implies that, the residence time for stirred-tank reactor is now lower than the residence time for a plug flow reactor. When did why did this happen? This happened, because the kinetics was of this kind.

Again qualitatively we can explain it as follows. Stirred-tank reactor, because of its assumption of well well mixed reactor, the concentrations drop down to a lower value instantaneously whereas, the concentration decrease from the inlet to the exit in a plug flow reactor is more gradual; and this aspect is independent of the kinetics of the process.

But look at the kinetics now, if concentrations are low according to this kinetics r equal to 1 over k over C 1, if concentration is low the rate is high. So now, we are getting higher rates in the stirred-tank reactor, because concentrations are low whereas, concentrations are relatively higher in a plug flow reactor as we move from entry point to the exit point. And hence, the reaction rates are little lower, because higher the value of C 1 lower is the rate of the rate of the reaction or in other words, now the performance of C S T R is better than plug flow reactor.

(Refer Slide Time: 44:40)

We can we can now examine all other kinetics and see what happens. So, for example, we saw that, for this n equal to 1, PFR tau P F R is less than tau C S T R or in other words, plug flow reactor is better than stirred-tank reactor. What about what about n equal to 2? n equal to 2 for n equal to 2 we see that, qualitatively behavior is same; that is 1 over r verses C 10 minus C 1 is increasing is also increasing.

So, we can expect for n equal to 2, this will be the case . What about n equal to 0? The flat line, now if the curve is flat, the area under the curve and area of rectangle will be same or in other words, tau P F R is same as tau C S T R that is both plug flow reactor and stirred-tank reactor will perform equally well.

For n less than 0, 1 over r verses C 1 minus C 10 is a decreasing point. So, what happens for this particular reactor? tau C S T R is less than tau plug flow reactor or residence time in the plug flow reactor. So, C S T R is better than plug flow reactor. So, to recap for all values of n which are greater than 0; that means the rate of reaction increases as concentration increases in which matter whether it is a linear or non-linear is in material, the plug flow reactor will be better than a C S T R.

So, for those reactions, where rate is independent of concentration, the plug flow reactor and C S T R both perform equally well and this is to be expected, because the concentration variation does not change the rate of reaction. So, whether it drops down instantaneously or it decreases gradually both are **both are** same as far as, performance is concerned, but those reactions for which the rate increases as concentration decreases, then C S T R is a better reactor than plug flow reactor.

(Refer Slide Time: 47:36)

So, before we close for the day, this is just a just an illustrative slide we talked about this residence times. So, this plot over here, taken from text from engineering of chemical reactions by $(())$, this shows on the y-axis, the temperature on x-axis, the residence time and various reactions are noted over here. I will start with even though you are not able to read probably this, let me let me say that, ammonia oxidation reaction for example, which is shown here, takes place at around 800 degree centigrade and the residence time is the order of magnitude 10 raise to minus 3 seconds.

So, is the synthesis gas reaction I mean similar order of magnitudes. So, higher temperature lower residence time, because if you look at this plot, even though this not following on a single line, it is obvious that, the trend is in this particular $((\))$ that is higher the temperature, lower is the residence time; and as the temperature of operation decreases, the residence time increases.

For example, a case of bacteria fermentations, bacteria fermentations have residence times of hour's days sometimes and these are carried out at 30 degree. So, on this extreme, we have 30 degrees or upto 40 and residence times, which are 10 raise to 5, 10 raise to 6 seconds you can you can work it out in hours and so on. So, as temperatures are higher, residence times are lower, as temperatures are lower, residence times are higher, with this we will come to the conclusion of our design equations.

(Refer Slide Time: 49:38)

So, essentially what we saw in this particular lecture was, how to do a mole balance on a reactor and we considered only ideal reactors, ideality dependent on the flow pattern inside the reactor that is whether it is a well mixed reactor or whether it is a no mixing in the axial direction or a plug flow reactor. We have different kinds of reactor behaviors; we also have different types of reactor operations, batch continuous. We will come back to semi-batch reactors which fall in between little later on.

Then, we saw the design equations for all these reactors and expressed for simplifying case, residence time tau which is can be expressed in ratio of length of reactor to the velocity or volume of the reactor to volumetric flow rate. And compare the performance of stirred-tank reactor and plug flow reactor, with this we will come to the conclusion of our review of undergraduate material. And from the next session, we will start discussing about complex reactions, some basic aspects of complex reactions and few examples of complex reactions, before we go on to heterogeneous reactions, thank you.