ENZYME SCIENCE AND ENGINEERING

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LECTURE–25

NON – IDEAL FLOW IN CONTINUOUS IMMOBILIZED ENZYME REACTORS

So far the analysis of continuous immobilized enzyme reactors interms of their performance has been based on the kinetics of the enzyme reactions.

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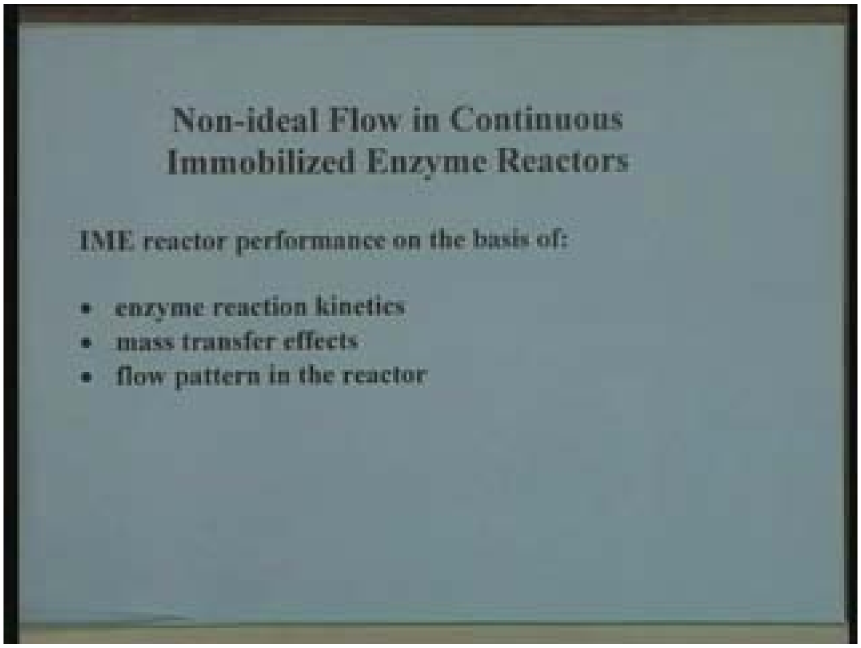

Non-ideal Flow in Continuous Immobilized Enzyme Reactors

IME reactor performance on the basis of:

- enzyme reaction kinetics
- mass transfer effects
- flow pattern in the reactor

We have considered the reactions that follow Michaelis Menten kinetics, the reactions that follows substrate inhibition or product inhibition; we also considered approximation with respect to zero order and first order reaction regimes in the case of enzyme catalyzed reactions. Then we have looked at the effect of mass transfer on the reactor performance by virtue of steady state analysis of mass transfer and biochemical reaction taking place simultaneously in an enzyme reactor.

In all these analyses we have assumed that the flow pattern in the reactor is either perfectly mixed that is the contents of the reactor are homogeneously mixed without any stagnant …….. or without any dead pockets in the reactor or alternatively in the case of plug flow reactor the velocity profile of all the fluid streams are flat and it can be described by a ideal plug flow behavior. Although this kind of situation is practically feasible in a laboratory experiment where you can have a very high height to diameter ratio and have a very uniform packing in the reactor so that the plug flow characteristics are realized in the laboratory but on a large scale reactor which are real industrial reactors the possibility of achieving the ideal flow patterns that means either a complete perfect back mix or a perfect plug flow reactor are usually far from reality and most of the reactors operate closer to the one of the regimes but also have a partly mixed behavior.

Today we will like to look as at how this deviation in the ideal flow behavior influences the reactor performance. How to approach the situation incase if the flow behavior is not ideal interms of perfectly well back mix or a plug flow behavior. Very often we must realize that the causes of deviation from the ideality are because of certain stagnant reasons in the case of reactor. For example if you consider a plugflow reactor which has been separated by certain horizontal ….. (4:08) just to allow a proper mass transfer there might be certain stagnant reason from the corners or in the case of back mix reactors if the impeller is not properly designed or the mixing pattern is not properly designed there might be some region in the whole reactor where the mixing is not uniform and the idea of completely back mix is not realized.

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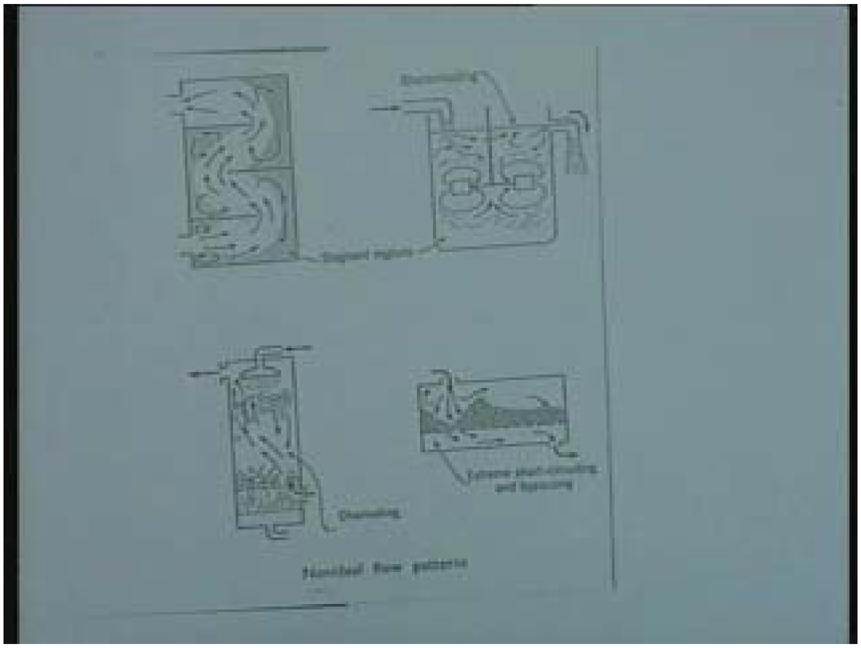

Alternatively there might be some channeling effect. For example in the packed bed reactor if the particles are not of uniform size and the packing is not uniform there might be some channeling with the result that a part of the fluid stream which is getting into the reactor passes through unreacted and therefore the performance can deteriorate. Then there might be short circuiting, something like channeling or bypassing also can take place in the case of a stirred vessel. In all the situations the performance of the reactor is lowered compared to what we look for by analysis in the case of an ideal fluid flow pattern.

An alternative situation in enzyme reactor is that sometimes we tend to develop reactor designs for various reasons because of the requirement of the reactions. In the case of recycle reactor as you notice here although it's a packed bed reactor but just to increase the linear flow velocity to overcome the external film diffusion we may like to have a recycle stream so that the linear flow velocity is increased but ultimately it will end up in non-ideality from the plug flow behavior. Similarly in the case of a fluidized bed reactor, we also have the same thing just to improve the mass transfer and heat transfer effects in the case of a reactor, the particles are fluidized by the substrate to the extent that the particles are not thrown out of the reactor; they are retained in the reactor but the voidage increases to a level that they remain fluidized in the reactor and even in this case in terms of flow behavior, the flow behavior will be some where in between the plug flow as well as the packed bed reactor.

In another case if you look at the combined CSTR and ultra filtration reactor which is one of the model system which has been used for substrate which are solid in nature and where enzyme is required to be used in soluble form one can carry out the reaction in stirred reactor, in a CSTR, with the possibility of the product stream passing through a ultra filtration chamber where by the enzyme is the recycled back and the product is withdrawn from the permeate stream.

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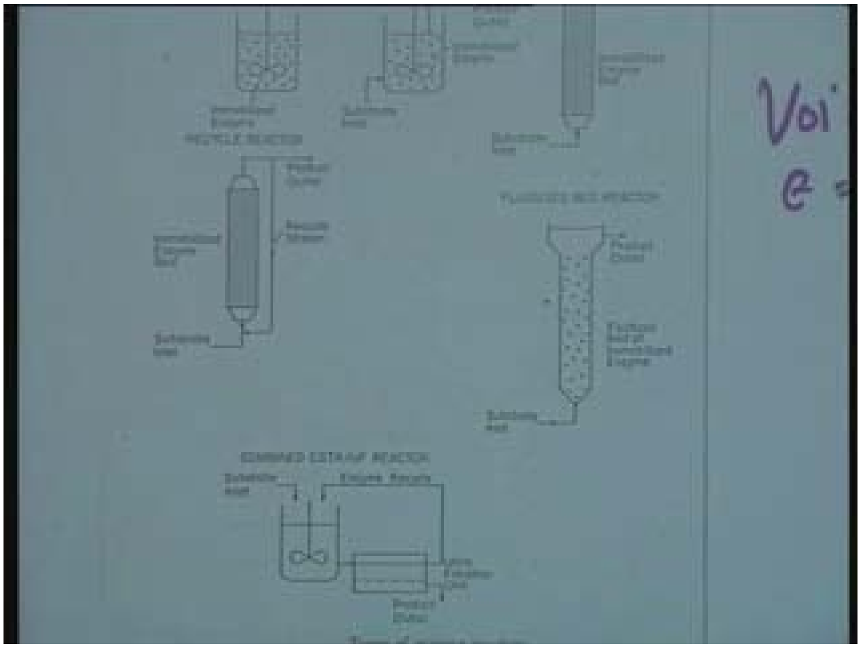

In this case also the reactor although theoretically one has to consider it closer to CSTR, but in performance if you look at, it has revelation from the CSTR because the concentration profile in the whole reactor does not remain ideally perfect.

Similarly we have systems like hollow fiber reactor, as we discussed earlier, in which case the enzyme is entrapped in one of the side of the tubes and substrate is passed from the other side and the two sides are permeable that means they are separated by semi-permeable membrane and the reaction can take place and the product stream can go.

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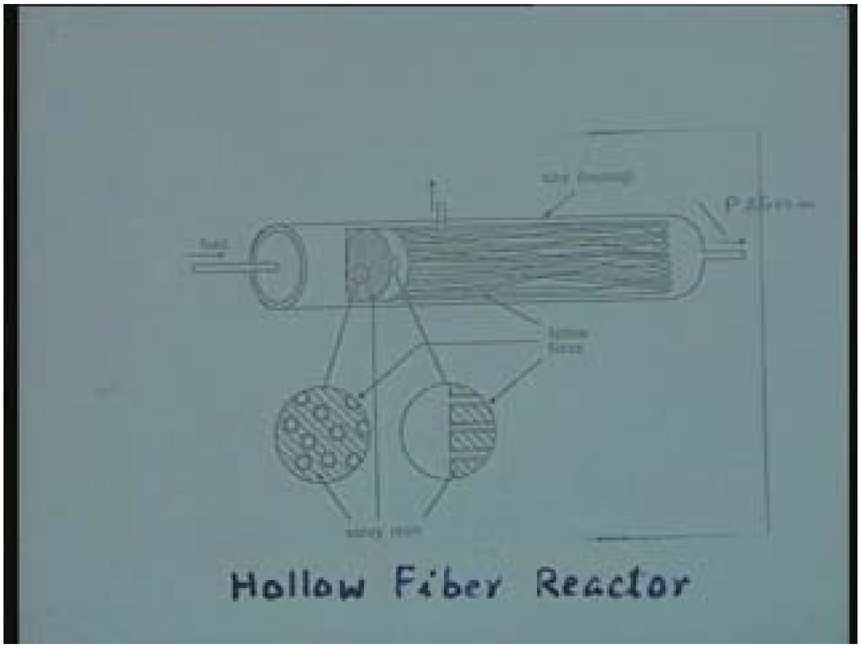

Hollow Fiber Reactor

Although the system is designed to mimic or at least operate closely to a plug flow reactor, still the actual performance may be slightly inferior than a plugflow behavior and it might have some kind of a back mixing, partly back mixing.

Another very important industrial reactor which has been used is a spiral wound, multipore, biocatalytic module. If you recall that the immobilized enzyme preparation is in the form of a thin long membrane film which is wrapped around a central core and the enzyme membrane is also separated by a wire mesh or some kind of a solid support so that the mechanical strength improves and this spiral wound module is then instead into the column whereby the substrate is fed from one of the end and the reactor can be operated as in a packed bed mode.

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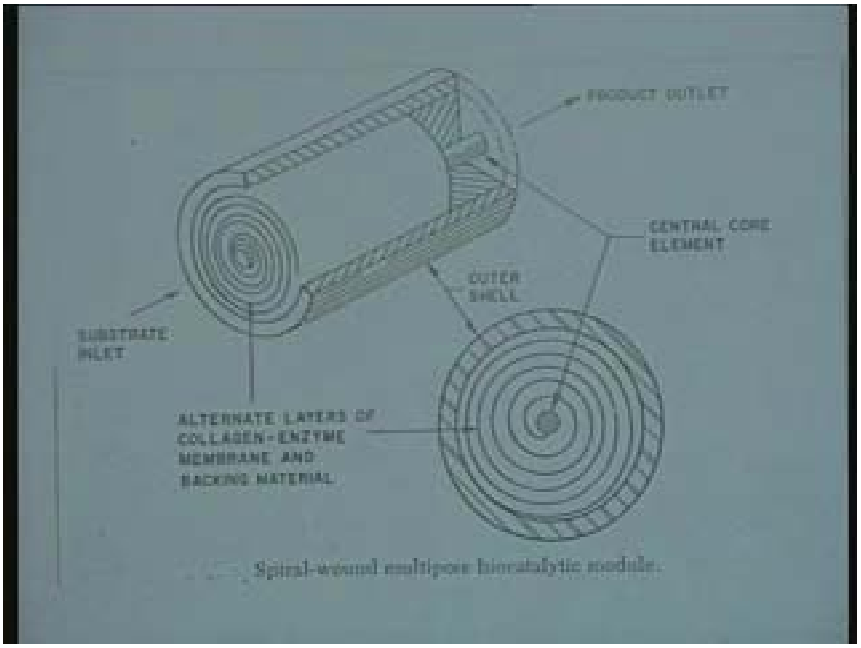

Spiral-wound multipore biocatalytic module.

But the spiral wound module operates some where closer to only closer to plug flow behavior reactor and not exactly as a plug flow reactor.

The extent of non-ideality in the case of a flow pattern, the first parameter is that we must be able to identify the extent of non-ideality in the case of an enzyme reactor. If we can understand or arrive by some means the distribution of the residence times of the various element of a fluid which is passing through a reactor with respect to time and that distribution can give us an idea about the extent of flow pattern. That means if the distribution, if it passes almost like a plug flow behavior or like a CSTR one can then compare the two patterns and see whether the flow pattern in the actual reactor is ideal or what is the extent of ideality. This analysis to monitor the deviation from the ideality for enzyme reactor in flow pattern is mediated by what we call as residence time distribution. It gives you the distribution of the various elements of the fluid passing through a reactor. That means the age of various elements in a fluid stream from the reactor interms of age distribution that means what is the duration of the time which each element of the fluid has stayed in the reactor. That is the residence time and this if in all cases same as in the case of a space time then it should be an ideal reactor. If it deviates and the ….. distribution or a residence time distribution is given in the form of ….. verses time distribution and one can say that if this is the total …. distribution for any given fluid element from a reactor then your zero to infinity Edt is equal to one.

If you just consider a very small element in this distribution having the age between t and dt and t and t+dt then the fraction of the exit stream of age between t and t+dt will be Edt and this fraction integrated over infinite time will give you the total fluid which is flowing through the reactor and the ……. distribution is defined that the total area under the curve is unity. If you consider any fraction at time t1, the fraction of the exit stream which has age less than t1 will be zero to t one Edt; the fraction of the exit stream which has age younger than t1. Age means the time spent by an element of the fluid in the reactor vessel. On the other hand the fraction of the exit stream which is older than the t1 will be t one to infinity Edt or this will be one minus zero to t1 Edt because the total zero order infinity is one.

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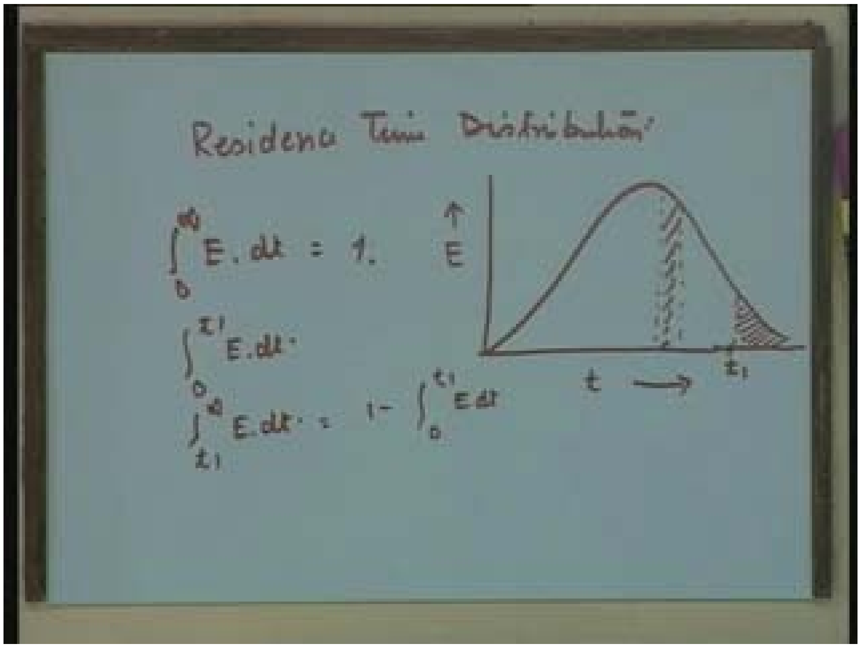

Residence Time Distribution

$$\int_0^\infty E.dt = 1.$$

$$\int_0^{t_1} E.dt.$$

$$\int_{t_1}^\infty E.dt. = 1 - \int_0^{t_1} E\,dt$$

This residence time distribution experimentally for a given reactor system can give you an idea about the nature of non-ideality of a reactor system in terms of flow behavior. Mind it that non-ideality may also be caused by other reasons like mass transfer, partitioning or variety of other reasons that we have discussed but this non-ideality we are talking exclusively in terms of the flow behavior. This residence time distribution is usually determined in the experimental reactors by what we know as stimulus response techniques.

In this technique usually a tracer which is an inert material is put along with the feed stream. Mind the word that you need an inert tracer which can be detected. Detection is important because if you cannot detect this inert tracer, it doesn’t serve any purpose. Very often a dye can be used provided the dye does not interfere in the reaction or it doesn’t get adsorbed in the carrier material.

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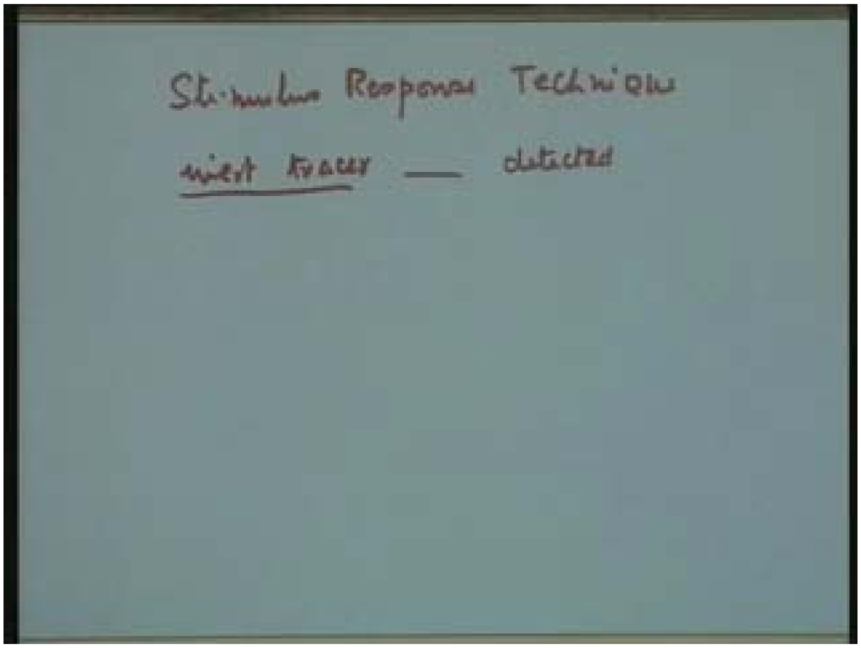

Stimulus Response Technique

inert tracer — detected

An inert dye can be used as a tracer system and by calorimetry it can be estimated or alternatively in the case of enzyme catalyzed reaction any other reactant or any other sugar or any other material, chemical species which will not take part in the reaction can be inserted or which should be possible to analyze at the ….. (15:44). Very often some time one ends up in a difficult situation in choosing a good tracer. Then in that case radioactive material could be also used as tracers so that they can be monitored at the exit stream by measurement of simple radioactivity by the counters. After inserting you can insert any kind of feed stimulus; it can be a step input, it can be a delta input or it can be even a random input, doesn't make a difference. Various types of inputs can be given and ultimately at the end of it we need to monitor the response of the tracer in the exit stream mid (16:30) time and the record of this gives you a picture of the residence time distribution. That is what usually is followed.

A variety of types of tracer inputs are inserted into the vessel. Consider this is a vessel. We put a tracer input signal or what we call as a stimulus. It can be a random input in any fashion; you allow some quantity of tracer to be inserted randomly and notice the output which will also be random depending on the flow profile. Then it can be a cyclic input in the waveform and then output also will be some type of a cyclic output. Then we can have a step input that means initially the tracer concentration is set at zero and then it is raised or suddenly after a time t, after some time it is in the feed stream continuously you supply a tracer let us say concentration one, hundred percent and then this input again in the reaction vessel will come out in the case of a exponential behavior.

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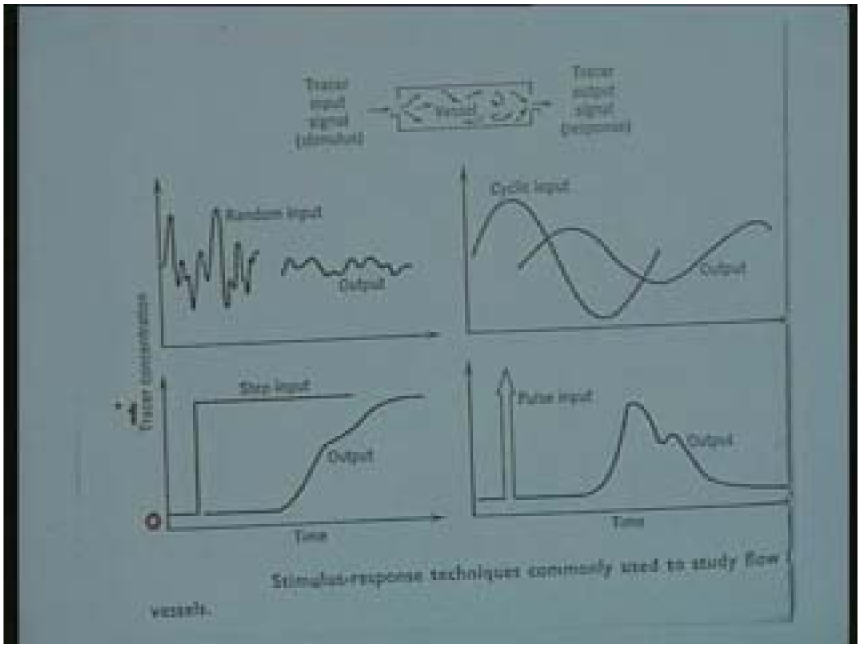

Stimulus-response techniques commonly used to study flow vessels.

Alternatively you can also give a pulse input also called as delta input where over a very short period of time that means your Δt approaching zero you provide a small quantity of a tracer and then monitor the output. Theoretically the product in a plug flow reactor must come out exactly after the residence time of the feed stream but very often because of the deviation from the ideality of plug flow behavior it might come out almost in a slightly broad zone. Some of you must have done chromatographic experiments. Very often broadening of the output is one of the major problems. The theoretical chromatographic adsorption column must operate as a plug flow column but ultimately because of certain non-ideality there is some kind of broadening. That means the fraction which you are interested is distributed over a period of time. Ideally it should come out in a very short period of time like we have put it here but it comes out in a broadened fashion.

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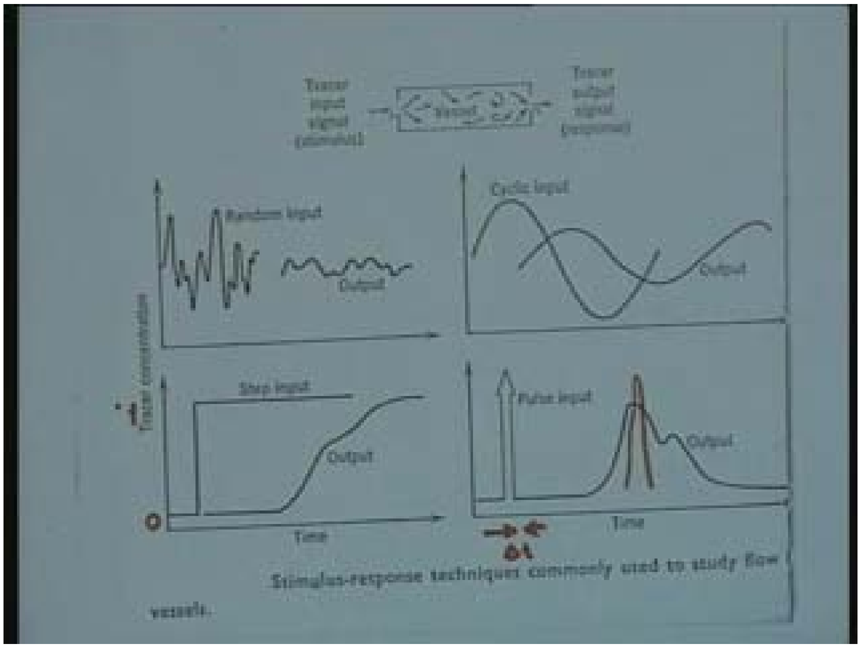

Stimulus-response techniques commonly used to study flow vessels.

Although I have mentioned that any kind of input can be given but for analytical convenience we often resort to either a step input or a pulse input because ultimate analytical solutions might be difficult and the step input and pulse input are commonly used technique for analyzing or getting the residence time distribution.

The response of a step input of the tracer is usually called as F curve. That means the F is equal to C/C_0. If initial concentration is zero and C/C_0 goes to one that means the concentration of the tracer is C_0 and C/C_0 is one and this is given over a period of time. Ultimately its response you get something like this with the average mean residence time of t bar. This is time and F is C/C_0. Here F is equal to zero to t Edt and over a period of time this continues and dF/dt is the …….. (20:58) distribution the differential of the function f C/C_0. On the other hand the response of a delta input is called C curve. In fact we normalize it to get the response. For example normalization in this case is C bar is equal to C/Q if Q is the total quantity of a stimulus given and then its response is monitored over the period of time and Q is the total quantity of the input that is given and therefore zero to infinity C bar dt is equal to zero to infinity C/Q.dt. We plot as C bar is equal to C/Q, the fraction of the total tracer which has been put in which emerges at any time given t and that is equal to C/Q.dt will be equal to one or Q is equal to zero to infinity C bar dt.

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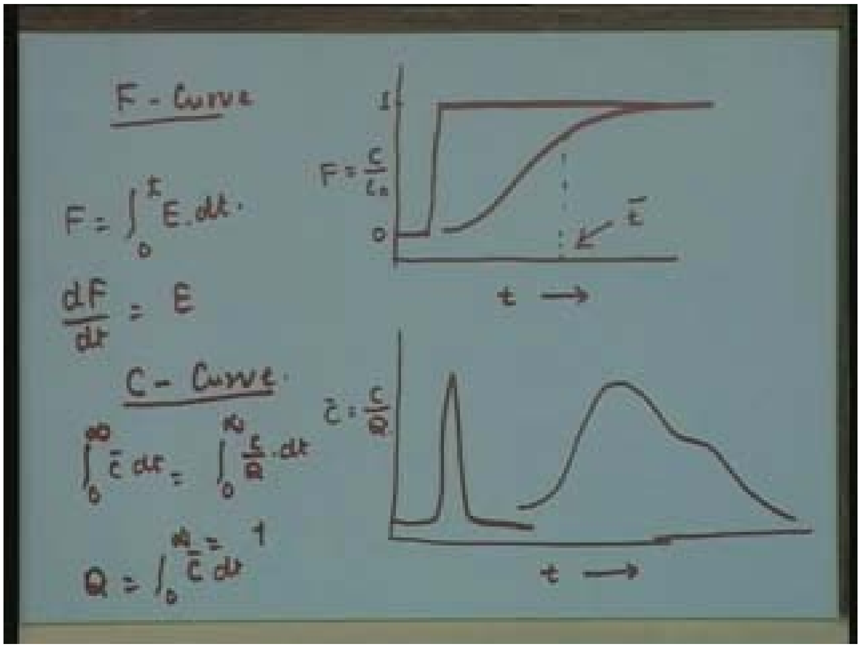

C is the concentration of the tracer which is in the output stream at any given time t and Q is the total quantity of tracer that has been put in. For example here you are not putting continuously you are putting only in one shot. Say for example you are putting one gram of some inert dye into the reactor initially and after that you monitor its output response. This one gram theoretically if it is an ideal plug flow, it should come out in a short period of time in as much time as it has been fed in. But it will not emerge in one go it will come out in small lots. If you analyze the output stream over a period of time and let us say you get such a profile and where this profile interms of the C which is output concentration at any given time t divided by the total quantity which has been fed in a normalized way and that is C bar and C/Q is the normalized concentration of the tracer output in the exit stream and the C/Q verses t gives you a C curve. This shows the performance of a plug flow reactor as a response to a pulse input. In the case of F curve, the C_0 is the maximum concentration and that concentration is reached instantaneously. Up to some time there is no concentration of tracer; suddenly at a given time we start a stream continuing the tracer and so here it becomes C_0. If C/C_0 is one and from then onwards the input is same and the output stream theoretically after a time t it should also come out in a constant stream but it doesn't come out in constant stream. There is a kind of transient phase till it reaches to the constant stream and that is what it defines.

This tracer information can be used directly or in conjunction with the flow model to predict the performance of the real flow reactors. Theoretically the ideal reactor performance we have been looking at interms of the reaction kinetics. That means we develop a mass balance equation for a particular reactor, apply the reaction kinetics and analyze the equation and get the final reactor performance equation interms of tow verses the fractional conversion or the remaining substrate concentration in the reactor. These …… distribution also can be used to determine the reactor performance based on the flow profile along with the reaction kinetics. Reactor performance from RTD also can be obtained and one can compare if you consider the ideal reactor flow profile and also the real reactor flow profile and compare their performance and comparison will give you the deviation from the ideality.

If you look at the C curve which is very commonly used for analysis of packed bed reactor, in the case of a C curve on the basis of the flow pattern the mean concentration of the substrate in the exit stream will be equal to the sum of all this elements of the exit stream for concentration of substrate remaining in an element of age t+dt into the fraction of exit stream which is of age t+dt. That means if you take a differential element of the fluid stream which passes through time dt, whatever the concentration of substrate in that stream which is passing through time dt multiplied by the fraction of the exit stream which is of age between t and dt and t+dt, and sum it over the all the elements. This is the concentration of the substrate in one element of the age dt between t and t+dt and the fraction of the exit stream which is half the age between t+dt that means during the time dt and if you multiply the two you get the mean concentration of substrate in the exit stream and if you sum it up this one over all the elements or integrate it S bar will be equal to t equal to zero to infinity S element into Edt.

This is the fraction of stream Edt; this is the concentration of substrate remaining in the element. This S_{el} is element concentration of substrate remaining in the element which is of age $t+\Delta t$ and this is the fraction Edt. These two terms indicate the concentration term as well as the age term in the reactor. The mean substrate concentration in the reactor will be given by this. If you write for a first order kinetics S_{el} will be equal to

$$S_{el} = S_0 e^{-kt}$$

You can assume this K is V'_m/K'_m, a first order rate constant for the enzyme reaction and you can also write therefore here S bar from the RTD data will be equal to $S_0 \int e^{-Kt}.Edt$

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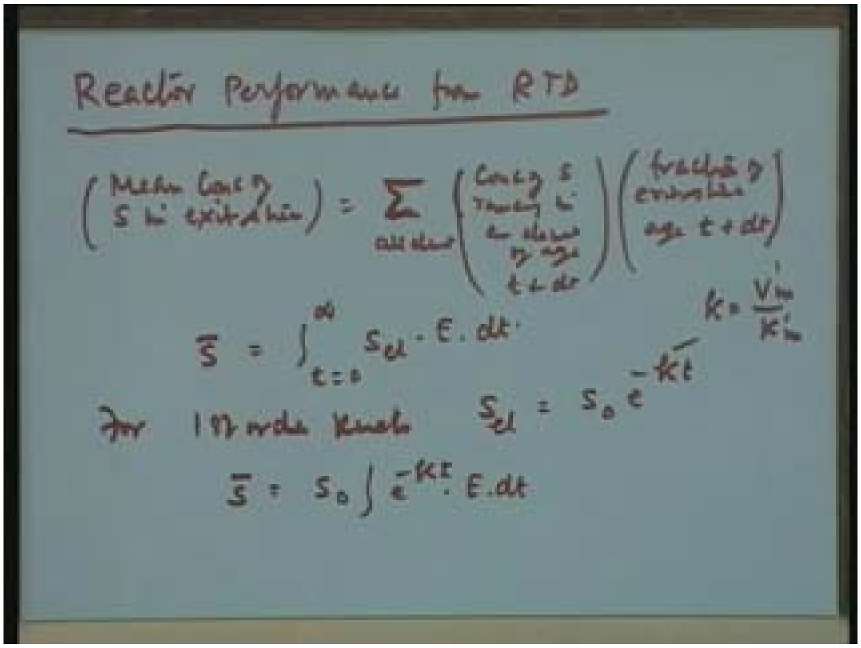

Reactor Performance from RTD

$$\begin{pmatrix}\text{Mean Conc of}\\ \text{S in exit stream}\end{pmatrix} = \sum_{\text{all elements}} \begin{pmatrix}\text{Conc of S}\\ \text{remaining in}\\ \text{an element}\\ \text{of age}\\ t + dt\end{pmatrix}\begin{pmatrix}\text{fraction of}\\ \text{exit stream}\\ \text{age } t + dt\end{pmatrix}$$

$$\bar{S} = \int_{t=0}^{\infty} S_{el} \cdot E \cdot dt$$

$$k = \frac{V_m'}{K_m'}$$

For 1st order kinetics $S_{el} = S_0 e^{-kt}$

$$\bar{S} = S_0 \int e^{-kt} \cdot E . dt$$

What it amounts to is that if you have a residence time distribution for any real reactor in the form of Edt and if you also have the rate constant K, the first order rate constant which can be evaluated for enzyme reaction and you can get all the reaction fraction of the exit stream which has been collected and sum it over, it will give the mean age distribution, the mean substrate concentration in the exit stream. Normally a residence time distribution, a C curve will be of this type. In practice what we do is if we operate a reactor we are making feed from the bottom at some concentration S_0. This is S. Suddenly at any given time t a tracer is inserted into the reactor in the feed stream by short period of time and the concentration is monitored in the exit stream. At time t=0,5 at equidistant time if you determine the concentration of the tracer whatever values come at equidistant time, they are plotted in terms of C/Q. That means you consider the $\Sigma C\Delta t = Q$.

Here is also a check that this $\Sigma C\Delta t = Q$ of all the data must be equal to the actual quantity of tracer which has been put in.

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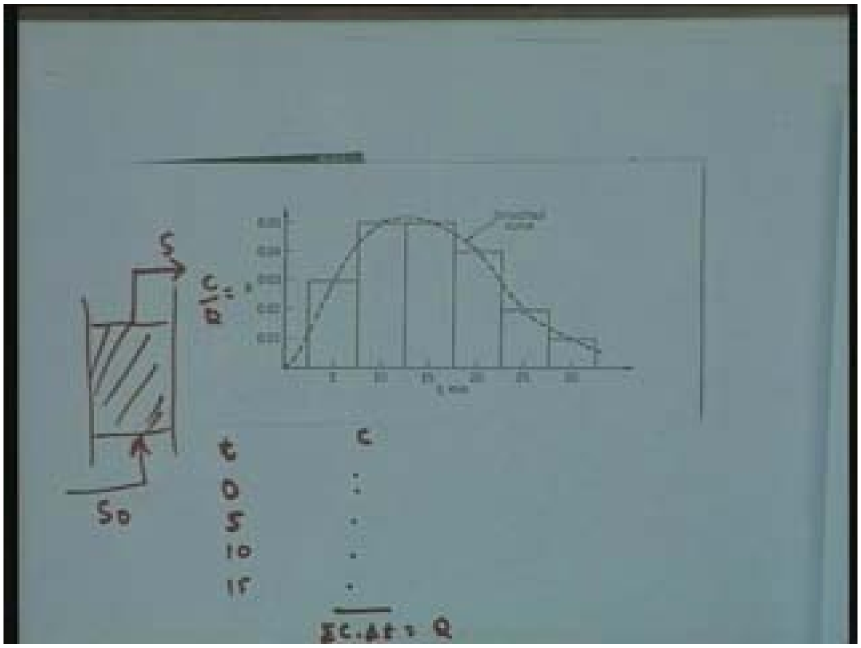

If there is any absorption of some tracer into the system or some reaction taking place or if the tracer is not a good choice that means either it is participating in the reaction. In that case the total amount of tracer which has been put in to the reactor will not be equal to $\Sigma C\Delta t$ and such an analysis is erroneous in nature. It should not be accepted for determining the flow behavior and once you checked that the total quantity of tracer which has been put in matches with the tracer quantity which has come out in the output stream, which is $\Sigma C\Delta t$ and then one can substitute or write down the integration term in terms of $S_0\int e^{-Kt}.Edt$ and sum it over, you will get the concentration of the substrate remaining unreacted in the exit stream as a function of flow behavior and reaction kinetics.

On the other side the same performance can also be judged by purely kinetic analysis. That means in the case of plug flow reactor tow is equal to S_0 0 to x dx/K.S; classical balance equation which gives you the performance of a plug flow reactor and from this one can write $S = S_0e^{-Kt}$. That means because in the case of first order reaction there will be an exponential consumption of substrate with time and therefore if one takes a real data of a particular plug flow reactor based on kinetic analysis and based on experimental value, this will be actually based on the experimental data. Sometime one finds that there is a large deviation. That means this performance will be inferior than this one if the reactor is not an ideal plug flow. If it is an ideal plug flow, the closeness of these values S as well as S bar will indicate the ideality of the reactor flow pattern. But in case there is deviation one will find quite different values and the actual reactor performance will be judged by the reactor performance based on the …… distribution and kinetics.

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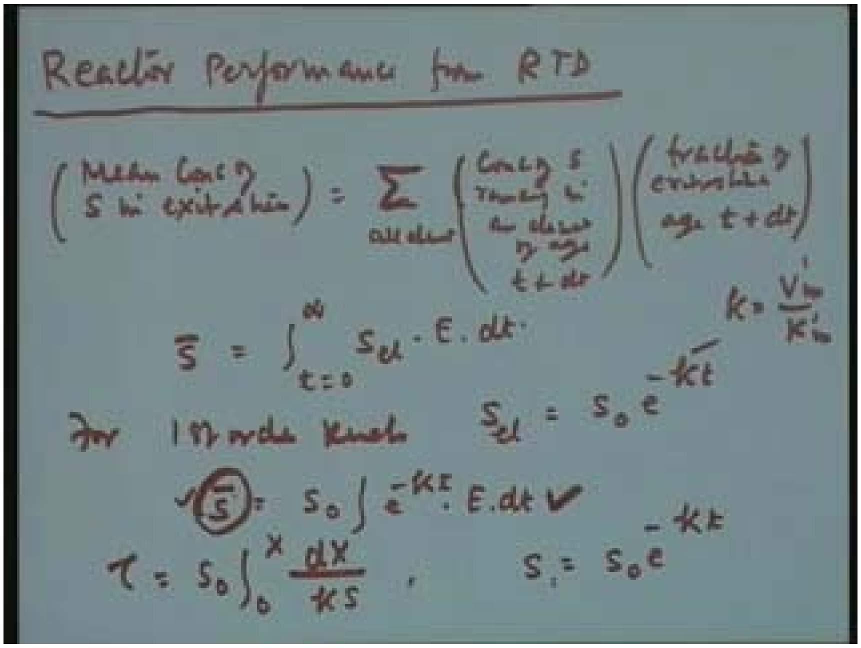

Reactor Performance from RTD

$$\begin{pmatrix}\text{Mean Conc of}\\ S \text{ in exit stream}\end{pmatrix} = \sum_{\text{all elements}} \begin{pmatrix}\text{Conc of } S\\ \text{remaining in}\\ \text{the element}\\ \text{of age}\\ t+dt\end{pmatrix}\begin{pmatrix}\text{fraction of}\\ \text{exit stream}\\ \text{age } t+dt\end{pmatrix}$$

$$\bar{S} = \int_{t=0}^{\infty} S_{el} \cdot E \cdot dt$$

$$k = \frac{V_m'}{K_m'}$$

For 1st order kinetics $S_{el} = S_0 e^{-kt}$

$$✓\ \bar{S} = S_0 \int e^{-kt} \cdot E.dt\ ✓$$

$$\tau = S_0 \int_0^X \frac{dX}{kS}\ , \qquad S_1 = S_0 e^{-kt}$$

If you consider the characteristics F curves for different kinds of flow profiles, in the case of ‘a’ curve you have a typical F curve for a plug flow reactor. That means as soon as the tracer concentration in that plug flow reactor has been inserted after time t or Qt/V or one residence time, the tracer must come out in the same concentration in the case of a step input.

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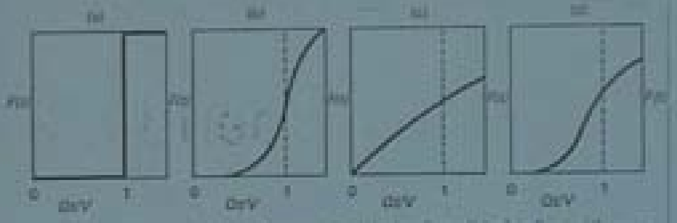

Characteristic F diagrams for (a) plug flow, (b) plug flow with some axial mixing, (c) perfect mixing, (d) mixing with some dead zones.

In the case of a plug flow with some …… mixing that means a non-ideal plug flow, the behavior instead of being like this, it may be something like this. The output becomes instead of vertically …. (34:52) a curved one, the deviation of this from the vertical absorption gives the non-ideality. In the case 'c', this is the performance with the perfect mixing. An exponential output of the tracer from the reactor. After time zero as soon as you put in the tracer, there will be a dilution or mixing taking place and the tracer will get diluted and from zero concentration it will come to a concentration finally all the tracer will come out. On the other hand if there is a mixing with some dead zones, some stagnant zones again the mixing pattern might get unchanged. So these are the two non-ideal flow patterns and these are the two for plug flow as well for well mixed conditions the exit age distribution in terms of F curve.

Earlier we have seen the use of 'C' curve for getting the reactor performance. If you want to identify or detect the deviation from ideality using the 'F' curve then consider a CSTR, a continuous stirred tank reactor and give a step change in the concentration of tracer in the feed stream. Consider a stirred reactor of constant volume V where the substrate is put, the product stream is coming out and the step input is added here at a concentration C_0 and the flow velocity is Q. Therefore the total mass balance that is

$$QC_0 = QC + Vdc/dt$$

That means the C will also start coming out here at a flow rate of Q. There will be some change in the rate of change of concentration of C in the reactor. Therefore this can be integrated to give

$$C/C_0 = 1- \exp(-Qt/V)$$

This is the theoretical output for a step change in a CSTR. If you make a plot of this curve a semi logarithmic plot that means ln C/C_0 or ln $1-C/C_0$ verses time you will end up with a slope of Q/V and intercept of ln 1 that is zero. For an ideal reactor such kind of response is obtainable.

If you assume that there is some kind of deviation from ideality and in the case of CSTR the kind of deviation could be of two types. One is that there is some kind of a non-mixing or part of the stream which is being fed here, Q is going unmixed. This is $1-f_1$, f_1 is going to the reactor for mixing. This is volume V and the fraction $f_1$of the total stream Q is going into the reactor. The $1-f_1$ fraction is getting channeled or bypassed from the mixing pattern and therefore one is losing. Another source of non-ideality could be that the reactor may have some kind of dead zone because of the improper mixing and this dead zone is $V.f_2$. The fraction f_2 of the total volume of the reactor is represented as a dead zone. There mixing is not taking place. If you write a mass balance for such a system then you will get $f_1.Q.C_0$. We are putting C_0 as step input of tracer.

$$f_1.Q.C_0 = f_1.Q.C + f_2.V\ dc/dt$$

$f_1.Q.C$ is the fraction which will come out; $f_2.V$ is the one which is dead zone.

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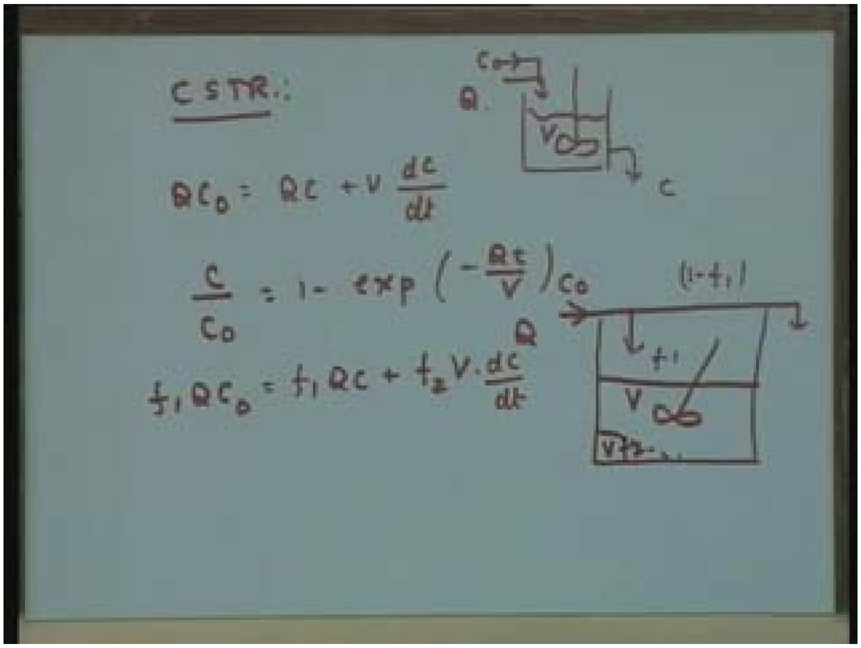


CSTR.:

$$QC_0 = QC + V\frac{dC}{dt}$$

$$\frac{C}{C_0} = 1 - \exp\left(-\frac{Qt}{V}\right)C_0$$

$$f_1 QC_0 = f_1 QC + f_2 V.\frac{dC}{dt}$$

In the case of a non-ideal system which incorporates a fraction of the feed stream which is directly channeled out into the exit stream and another fraction of the total volume of the reactor which is almost like a dead zone and does not participate in the reaction process.

No. This f_2 is the fraction of total volume which is stagnant. Here the f_2 is not of the total feed stream. Of the total feed stream f_1 has come into the reactor and $1\text{-}f_1$ has gone untouched from the reactor. Of the total volume of the reactor V, a fraction f_2 is a dead zone. Yeah we have now because we have a dead zone. Okay. Then we can write probably this is $1\text{-}f_2$ the total of the active volume and this becomes f_2.V. So the total fraction f_2 is well mixed and so $(1\text{-}f_2)$.V is the dead zone. So the rate of concentration will be f_2.V dc/dt. Is that right? f_2 is the fraction which is in the mixed zone as per this mass balance. So $1\text{-}f_2$ is the dead zone and therefore if you integrate this equation you will get

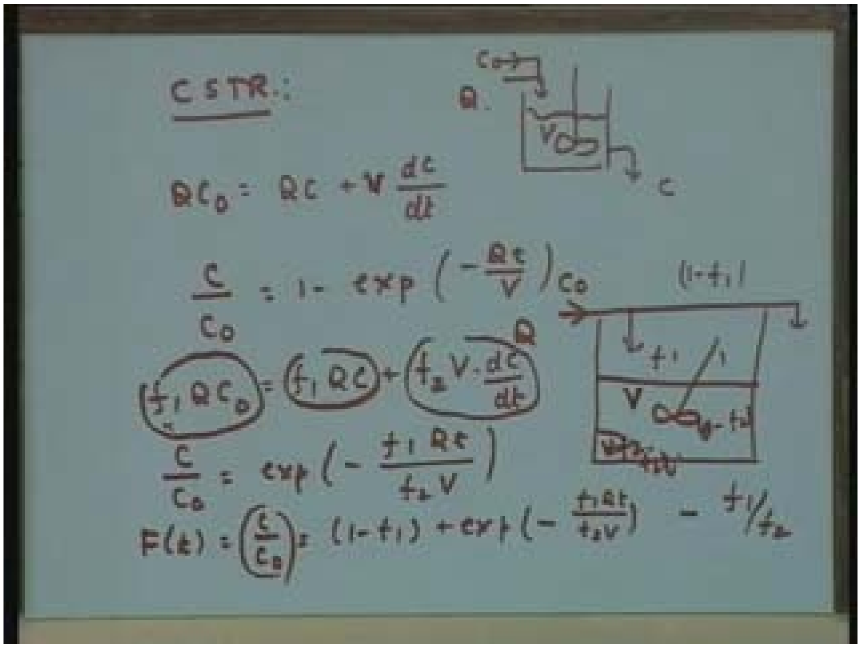
$$C/C0 = \exp(-f_1Qt/\ f_2V)$$

This can be combined with the outflow stirred equation that means the mass balance equation. That is

$$F(t) = C/C0 = (1\text{-}f_1) + \exp(-f_1Qt/\ f_2V)$$

If you plot this profile ……. distribution C/C_0, you will get a different kind of a profile from which the parameters $f_1$and f_2 can be calculated. The slope will be - $f_1/\ f_2$. If you plot Qt/V verses C/C_0 the slope will be $-f_1/f_2$ minus and the intercept will be ln C/C_0. The input in the reactor going is only f_1Q. This is not going to the reactor. This is the actual input to the reactor and this is the exit stream which is going f_1QC and this undergoes change in the concentration. Therefore by comparing the two profiles you can see the order of deviation the dead zone and the mixed stream in the reactor has gone into performance.

[Refer Slide Time: 43:51]



CSTR:

$$QC_0 = QC + V\frac{dc}{dt}$$

$$\frac{C}{C_0} = 1 - \exp\left(-\frac{Qt}{V}\right)$$

$$\boxed{f_1 QC_0} = \boxed{f_1 QC} + \boxed{f_2 V \cdot \frac{dc}{dt}}$$

$$\frac{C}{C_0} = \exp\left(-\frac{f_1 Qt}{f_2 V}\right)$$

$$F(t) = \boxed{\frac{C}{C_0}} = (1-f_1) + \exp\left(-\frac{f_1 Qt}{f_2 V}\right)$$

That is to illustrate the use of residence time distribution in the case of a real reactor which can be used to determine the reactor performance and such a reactor performance then can be used to calculate or correct the actual performance based on the kinetics data. This is one way to account for the non-ideal flow. The other way to handle is to develop the full flow models which can vary in degree of complexity depending upon where you can either consider the dispersion as a parameter and thereby you can write dispersion mass balance equations based on dispersion and finalize the reactor performance equation. Alternatively you can also consider as a like a tangent series model because a plug flow reactor or plug flow pattern can be considered as a infinite number of CSTR in series and plug flow can be considered as a CSTR in series and if you can calculate based on the reactor performance, the number of CSTR in series as equivalent to the plug flow that can quantify the reactor performance. Their order of complexity increases on the basis of the number of parameters considered. But even the residence time distribution can give you reasonably good idea of the non-ideality of the flow based on which one can even monitor the reactor performance and use that information particularly for scaling it up when you want to go on a larger scale reactor. So I think we will stop at this point.