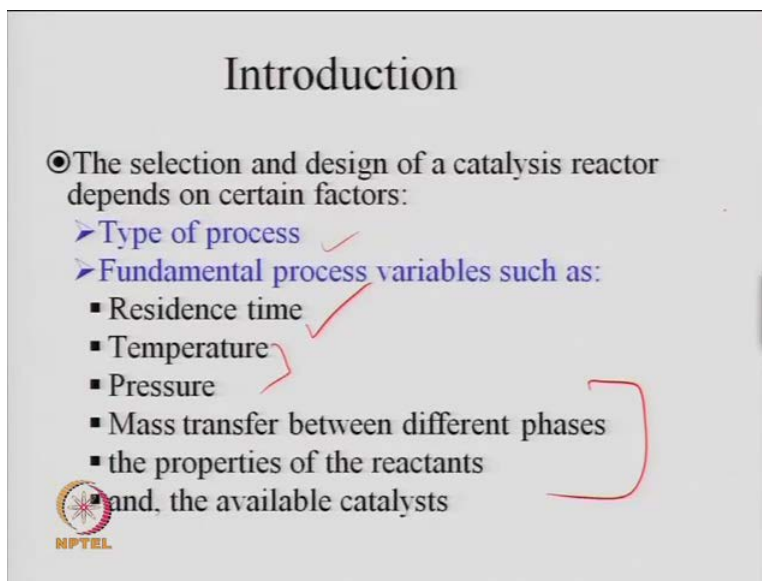


Heterogeneous Catalysis and Catalytic Processes
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Indian Institute of Technology, Delhi

Lecture - 34


Good afternoon, so in the last lecture I was talking about catalyst deactivation and then we were talking about the regeneration of the catalyst which is also very important. And, depending upon the catalyst which is used for the reaction type of reaction and the activity of a catalyst we need to identify a reactor a suitable reactor for the process, or for the commercialization of the process for the product formation. So, in this lecture I will just talk briefly on the introduction about the various reactors which are generally used for the catalytic reactions.

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Introduction

- The selection and design of a catalysis reactor depends on certain factors:
 - Type of process ✓
 - Fundamental process variables such as:
 - Residence time ✓
 - Temperature ✓
 - Pressure ✓
 - Mass transfer between different phases
 - the properties of the reactants
 - and, the available catalysts



So, basically the fundamentals of the reactor design depends on the various aspects of heat transfer, mass transfer, then reaction in fundamentals. And then based on that we select a suitable reactor for a given catalytic reaction so selection and design of a, catalytic process and the reactor that depends on process type of process that is whether it is a batch process or continuous process. So, generally if the small scale production is required then batch process can be used but if the production is required requirement is large. Then, either we need to use a CSTR type which is a tank type reactor or a tubular type a packed bed type reactor but both are the

continuous operation. So, in the batch the conditions may change inside the reactor with time so it is a kind of unsteady reactor whereas, the plug flow or the CSTR these are the continuous type of reactor. So, if the catalyst does not decay during the reaction then we expect that the productivity should not change during the course of reaction.

So, that is one of the basic fundamental either in a homogeneous reactions when you do not have the catalyst or a heterogeneous catalytic system where the catalyst is used in the process the reactors may be a batch or a continuous type. So, type of process is one then fundamental process variables like Residence time which is very important. So, residence time inside a reactor when you talk of flow reactor.

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$$\frac{W}{F_{A_0}}$$

$$\frac{\text{Kg of Cat}}{\text{Kg feed/time}} \sim \text{time}$$

$$\frac{F_{A_0}}{W} \rightarrow \text{WHSV}$$

$W \rightarrow$ mass of the catalyst
 $F_{A_0} \rightarrow$ feed rate
 Weight Hourly space time

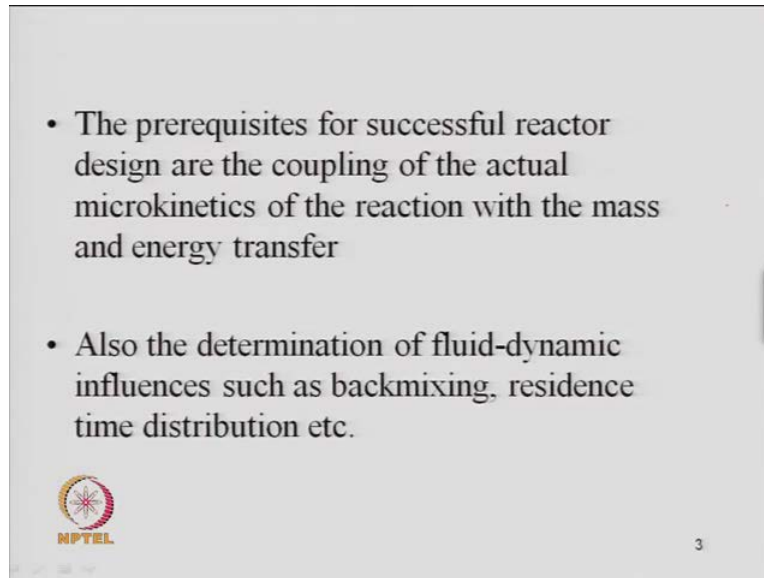
So, generally in the case of catalytic reactor we talk in terms of W by F_{A_0} so this is discussed during the design also when we have the fundamentals of a plug flow design or, a CSTR design then we call this term as Weight Hourly Space time. So, this is a factor related to residence time known as weight hourly space time and a very important factor in the design of a reactor or scalar in the scalar process. So, W by F_{A_0} which is basically W is the mass of the catalyst in the bed so this is mass of catalyst and F_{A_0} is the feed rate of the limiting component. So, this is the molar feed rate or mass feed rate so basically the units of this you can see here Kg of catalyst per Kg mass of the feed which is being fed continuously per unit time.

So, ultimately it has the unit of time so that is why we call it a residence time or weight hourly space time. Sometimes the inverse unit is also used which is known as FA naught divided by W and called as Weight Hourly Space Velocity. So, this is also an important design parameter and especially used in the trickle bed reactor so our hydro carbon process when the superficial gas velocity is used. And, based on that the residence time can be calculated or the space velocity can be calculated which, is known as either gas hourly space velocity or liquid hourly space velocity.

Or if you define in terms of mass of the catalyst in the bed then this is known as weight hourly space velocity. So, this becomes a very important parameter in terms of the scale up of a reactor or design of a heterogeneous catalytic reactor or even in a homogeneous catalytic reaction. Then of course, the Temperature Pressure because, these are the kinetic requirements and depending upon the reaction conditions you need to identify a definite temperature pressure. And accordingly the reactor selection becomes important or it is a design becomes important.


Then, of course as I said that during the catalytic reactions we need to consider or we cannot eliminate the mass transfer between the different phases and the properties of reactant is also equally important. So, these resistances which, is because of the diffusion external mass transfer, internal mass transfer that needs to be considered and that will also depend on the property of the reactant. So, we need to consider then also for the reactor design and finally which catalyst is being selected that is again in what shape in what size and what are the properties of that catalyst in terms of the porosity and other structural geometrical properties that also becomes very important for selection of the reactor.

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• The prerequisites for successful reactor design are the coupling of the actual microkinetics of the reaction with the mass and energy transfer

• Also the determination of fluid-dynamic influences such as backmixing, residence time distribution etc.

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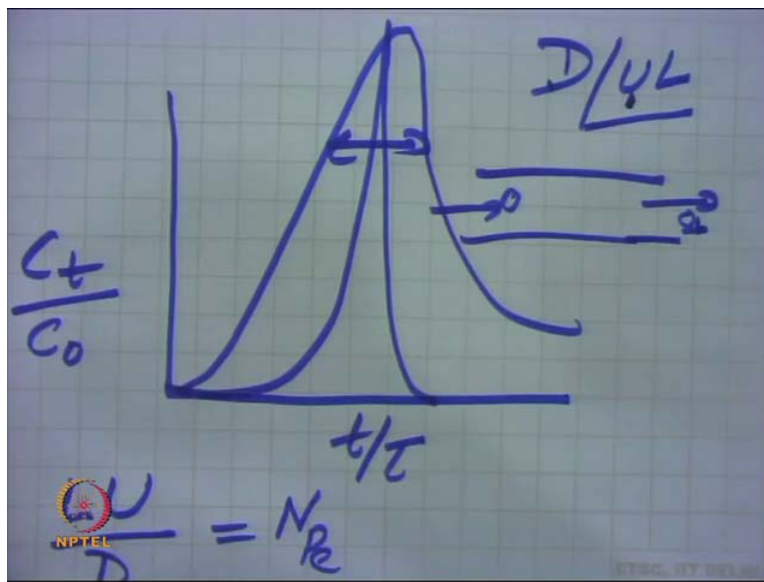
So, the prerequisite if you look at for a successful reactor design are coupling of the actual micro kinetics of the reaction with the mass and energy transfer. So, high micro kinetics because the mechanism of a catalytic reaction is very important so micro kinetics when we look at a molecular scale or, something like a radicals which form during the reaction or the intermediate which, form during the reaction that should be known other in order to optimize the process or a catalytic process this micro kinetic is also very important.

So, one thing is that when you get the overall rate of reaction but, when you look at the fundamentals in terms of the design to actually how a reaction takes place on the surface of the catalyst, which is helpful in a scale up or in order to remove the undesired product of the reaction the temperature that is very important parameter. And, other conditions also which can control the product formation or one can maximize the selectivity of a desired product if that kinetics or micro kinetics of the reaction is well known. And, simultaneously the dynamics fluid dynamics that also influence like back mixing in the reactor. So when you, look at a plug flow reactor and we avoid that kind of back mixing but in the case of actual reactor you cannot avoid the back mixing.

So, we need to find out the residence time distribution of terms of the flow numbers like pick let number or dispersion number which talks in terms of the degree of back mixing. And, that term

which is a kind of axial dispersion or radial dispersion term which are especially in the packed bed reactor. And, when you have the length to diameter ratio of the reactor is to be decided in order to avoid these kind of dispersion we need to identify it, which depends that is depending upon the size of the particle, depending upon the diameter, depending upon the length of the reactor L by D ratio can be fixed. And, we can minimize these kind of numbers which is dispersion that is the coefficient a kind of known ideal parameter introduced under the into the reactor design.

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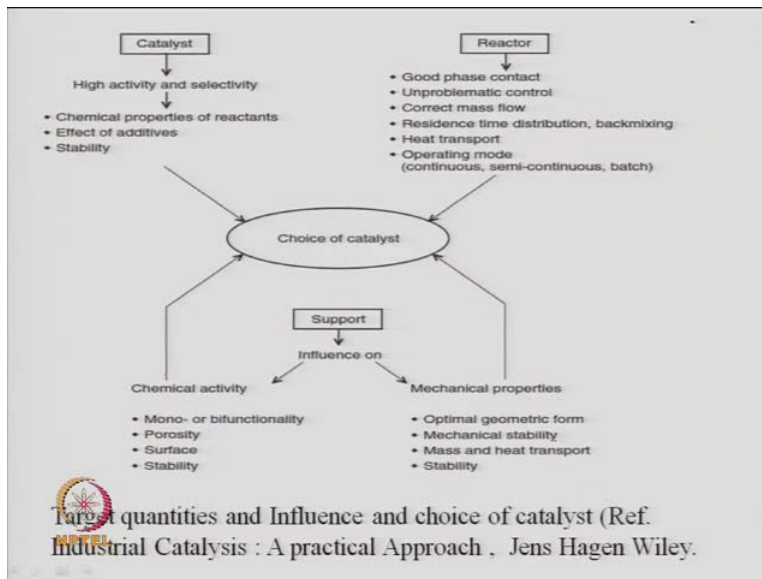


So, basically what is this if you just talk in terms of C_t by C_0 for a tracer input so for an ideal plug flow reactor the everything should come at the same time. So, this is your t by τ if I just plot this where τ is the actual space time or residence time and this t is the time inside the reactor. So, when the so some tracer input is given in the reactor in terms of pulse input and then the concentration is measured. So, if this ideal reactor means everything should come at the same time so if the everything does not come at the same time so it is kind of dispersion. So, that is a kind of known ideal term here and this is measured in terms of dispersion number.

So, this is known as dispersion number but this is dispersion coefficient and this is the velocity which is superficial velocity and L is the length of the reactor. So, this number becomes important so for a suppose if I say plug flow reactor then this dispersion number should approach

to 0. So, our pick let number which is LU by D so LU by D is known as pick let number. So, this gives some idea about the degree of dispersion or back mixing in the case of a plug flow reactor. So, we need to consider these studies also or hydrodesulphurization dynamic studies and residence time distribution in a reactor in order to understand the flow behavior inside a reactor even under the cold conditions.

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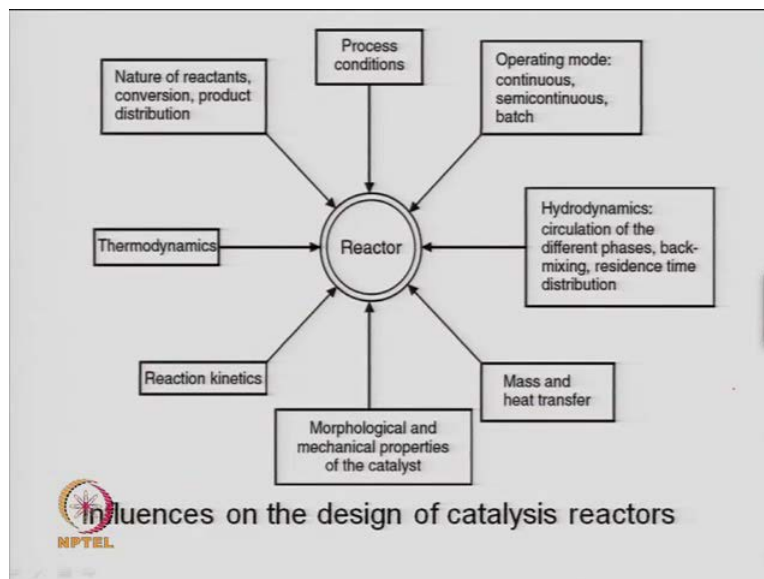


So, this is just an schematic if you look at here the target quantities and influence of choice of catalyst which, can affect the reactor so we have a catalyst here we have reactor system. So what we aspect in the reactor? A, good face contact we expect un problematic control in the reactor the mass flow should be good residence time distribution should be known. Degree of back mixing should be known heat transfer should be known that is transfer property should be well known. And operation mode whether it is continuous semi batch or semi continuous or batch that is again important. In the case of catalyst as we discussed we expect high activity of a catalyst and selectivity towards a desired product. So, high activity high selectivity is desired. So, chemical properties of the reactants are very important so we need to understand their viscosity surface tension not only these properties. But, other chemical properties also should be known t and there the effect in terms of the temperature pressure thermodynamic property.

So, everything should be known additive effects on the catalyst should be known stability should be known of that catalyst so all this terms and then based on those we select a choice. So, this choice of catalyst will depend on all these activity and stability and other properties during the catalytic reaction. Then, we have to look the chemical activity also which is mono or bi functional catalyst, porosity of a catalyst, surface property stability of the catalyst which will depend on the type of support.

So, influence of these chemical activity, that is the type of support catalyst then it is clubbed in the reactor and along with the mechanical property of the catalyst which is also important for the stability of the catalyst. So, it means the optimal geometrical form for high activity because the mass transfer control reaction the geometry of the catalyst is also equally important, mechanical stability of the catalyst especially when it is a high pressure reactor system that is important mass and heat transfer properties should be known. Or we should do that study in terms of the energy balance and material balance in terms of the mass transfer and diffusion limitations and finally the stability of the catalyst. So, all these things should be clubbed together for a suitable reactor design.

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What we look in a design of a catalytic reactor again? That is whether it is a homogeneous or heterogeneous system so the reactor design depends on the process condition that is the first

thing in terms of the temperature pressure, which, is required nature of the reactant the conversion which is expected product distribution that is important. Thermo dynamics of the process should be known reaction kinetics in terms of the micro reaction kinetics well known. Then, we need to understand the morphologically and mechanical properties of the catalyst which will be placed inside the reactor. Hydrodynamics not as becomes very important which is now days the CFD tools are available in order to understand the radial and axial profile and to look at the behavior under the cold conditions.

So, flow behaviors during the actual reactor condition may be a temperature and pressure condition with some say simple cold air water system. Or a similar system like hydro carbons which is kerosene if it is used for hydrodesulphurization so similar properties can be used in the to study the hydro dynamics under that cold flow conditions. So, physical chemical properties of the systems should be same and one can do the CFD of that and look at the behavior or flow behavior in terms of the known ideal parameters and that helps in terms of improving the efficiency of the reactor. So, all these terms are important when we look at the reactor design.

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Reaction Phase	Reactor Model
Homogeneous	Plug flow , CSTR, bATCH
Heterogeneous Catalytic Two Phase : Gas or Liquid catalyst	Packed bed or Fluidized bed
Three Phase : Liquid, Solid catalyts	Trickle bed, CSTR Slurry bed, bubble slurry , bubble



In general if, I if you look at a broader classification for a process so we talk a catalytic reaction based on Homogeneous catalysis and Heterogeneous catalysis. So, Homogeneous catalysis when I say so of course the node is it is a new trend that homogeneous catalyts are preferred, because

the mass transfer limitation or diffusion limitations are minimum in the case of homogeneous catalysis. So, that is why they are preferred but as I said that separation of a catalyst is difficult so still lot of r and d is to be done to develop these kinds of homogeneous catalysis systems.


But, once the catalyst is being operated in a homogeneous system one can very easily use these kinds of plug flow reactors CSTR or a Batch kind batch type of reactor depends whether, it is a continuous operation or a unsteady state type of operation. So, small scale operation or large scale operation and accordingly the reactor can be selected. Heterogeneous catalysts I just said that still widely common and most of the process industry they are using the heterogeneous catalyst and for that it can be a Two Phase type. Where, the catalyst is in Liquid Phase or catalyst can be in gas phase or it can be three phase where the catalyst is the liquid or a solid or a gas also. So, in the case of two phase pack bed of fluidized bed type of reactors just like in the fluid catalytic cracking I told the fluid catalytic cracking the gas and solid system is used and the catalyst a kind of zeolite type of catalyst that is used.

So, that is a two phase type of system. And if, you look at three phase of kind of system then the trickle bed reactor especially used for hydro desulfurization reaction removal of sulfur from hydro carbon fraction which, is important for the refinery to reduce the sulfur to certain level. And, in that case the trickle bed reaction which they are kind of pack bed reactor at low gas and liquid flow rate I will talk on that later. It can be kind of CSTR Slurry bubble column reactor slurry reactor or, it can be just a bubble column reactor if it is just a two phase system. So, different kind of reactor systems can be used for heterogeneous catalytic reactions.

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Reactors for Homogeneously Catalyzed Reactions

- Homogeneously catalyzed reactions with dissolved transition metal complexes are generally carried out in the usual two-phase reactors for gas-liquid systems.
- The standard reactor is the batch or continuous stirred tank
- Since diffusion problems are rarely encountered in homogeneous catalysis, the reaction engineering is much simpler than for heterogeneously catalyzed reactions



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So, briefly I will talk some expect some fundamentals of these reactors so homogeneously catalyzed reaction as I said. So, Homogeneously catalyzed reaction this is something like a catalyst which is present in the liquid phase if the reaction is in liquid phase. So, these can be some metal complex, organo metal complex, or something which is in gel form or hydro gel form that itself acts as a catalyst. So, the idea of nano particles or when we look at a better dispersion of a metal during the catalytic reaction, so there we get the during the homogeneous reaction we do not have any mass transfer limitation or diffusion limitation into the pore of a catalyst which is the problem in the case of heterogeneous catalyst.

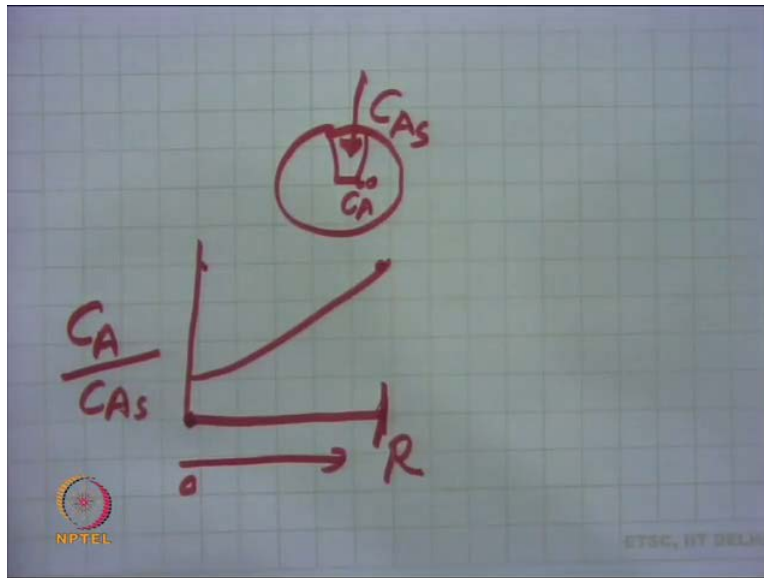
So, in that case these kinds of transition metal complex which are basically in the liquid phase and they are generally a two phase type of gas solid or, gas liquid reaction systems. So, gas liquid or liquid reaction system so they act as a homogeneous catalysis the standard reactors again in this case can be a bubble column type or a CSTR type of reactor or it can be done in a batch reactor also, as I said the, because the diffusion problem is just avoided and diffusion is a severe problem which because of which the effectiveness factor decreases.

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$$r_A = \eta r_{int}$$
$$\eta \sim \frac{1}{\phi}$$
$$\phi = R \sqrt{\frac{k}{D}} \quad \phi > 10$$

So, I was discussing this before that when we have a diffusion we were introducing a term rate at any time. Or, rate in the catalyst is some factor effectiveness factor times the rate when there is no influence of diffusion resistance so that I called intrinsic rate. So, we defined effectiveness factor which is a contribution of diffusion resistance. So, as I told eta can be something if there is a strong diffusion it is something like phi. And, phi was defined something like $R \sqrt{\frac{k}{D}}$ if I talk of first order reaction, so just for a first order reaction if you look at this diffusion coefficient of this trilomodus and generally this is large number. So, it may be 10 it may be 20 like that. And, because of this your effectiveness factor if you look at the eta decreases like this as a function of phi. So, when you have a high value of phi so effectiveness factor goes down like this. So, in this case your actual rate which is your observed rate basically will reduce drastically compared to the rate where there is no diffusion resistance. So, intrinsic rate means rate when there is no diffusion resistance.

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So, effectively this is a kind of rate when you have pellet and you say that diffusion into the pore of the pellet. And because, of this the rate so here it is some concentration which is C_{AS} and here it is some concentration like C_A . So, when you have a diffusion resistance then your concentration profile in a centre of the pellet if I write here 0, which is your something like if I say 0 here which is the centre so your concentration profile will drop drastically. So, this is your C_A divide by C_{AS} if I say and 0 is at the center so your C_{AS} is one here something like here. So, this is your r capital R radius so here the concentration is C_{AS} and here it is low like this. So, the concentration if you look at here from centre of the pellet to this is going like this. Or, if I just show that I mean to say there is a drastic drop in concentration from the external surface to the centre of the pellet.

And, if the diffusion resistance is more then your concentration will be very low and this is the reason where you get a low effectors factor here. So, it means this when you have a kind of homogenous catalyst then you will not face this problem. Because, in homogeneous catalyst there are no pore no question of internal diffusion resistance. So, this is the important issues here that in the case of homogeneous catalyst there are no complexity compared to the heterogeneous catalyst so no diffusion problem. So, it may rate will be higher and that is again that we have a kind of micro Milson where the rates the catalyst is well dispersed. Dispersion is not an issue in

the case of homogeneous catalyst because it is a kind of micro structure a gel kind of where the particles are well dispersed in the liquid.

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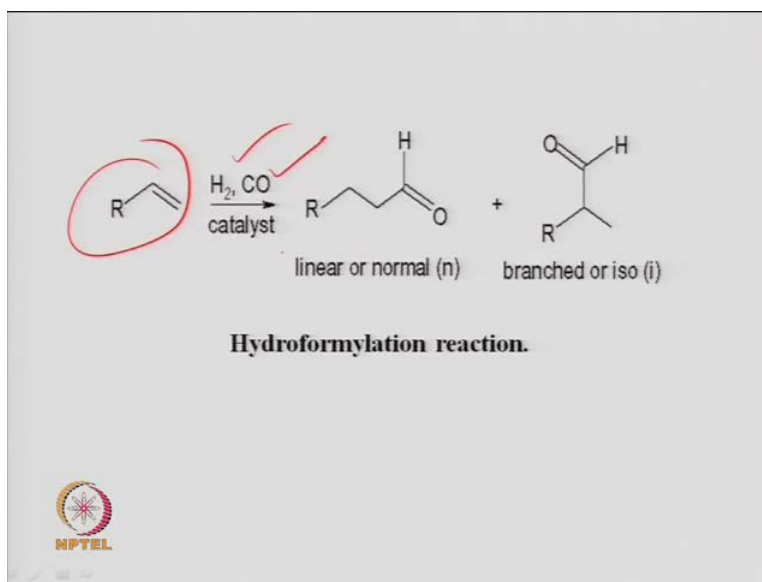
- *Stirred Tanks:*
 - Hydroformylation of olefins with Co or Rh catalysts.
 - Hydroformylation is the simultaneous addition of one mole each of hydrogen and carbon monoxide across a carbon-carbon double bond of alkene to produce linear and branched aldehydes having one more carbon atom than the original compound (Scheme 1).



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So, some of the example if you look at the homogenous catalyst is that hydro formulation of olefins in the presence of say cobalt or rhodium catalyst. So, cobalt rhodium complex basically it is a lot of solid here it is a kind of complex which is in solution and reacts during the catalytic reaction. So, what is hydro formation? Actually, it is nothing but simultaneous addition of one mole of hydrogen and carbon monoxide across a carbon doubled bond that is olefin. So, simultaneous say basically propile reaction with carbon monoxide and hydrogen to produce a linear and branch aldehydes having one or more carbon atom then original compound. So, basically it is a kind of where the isomers can also be formed aldehydes can be formed and this is very important petro chemical reaction if you look at and there the homogeneous catalysts are used.

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So, this is the kind of reaction where any olefin reacts in the presence of hydrogen and carbon monoxide in the presence of catalyst which is a liquid phase catalyst. And, the process is basically known as Oxo process so here you have one linear or normal compound alkyne and aldehyde and then another can be in the form of iso say butane, butanone alcohol compounds.

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- Low-pressure hydroformylation of propene to butanals with water-soluble Rh phosphine complexes: 50–150°C, 10–100 bar, 10–100 ppm Rh.
- Polymerization of ethylene with $\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ at 70–160°C and 2–25 bar

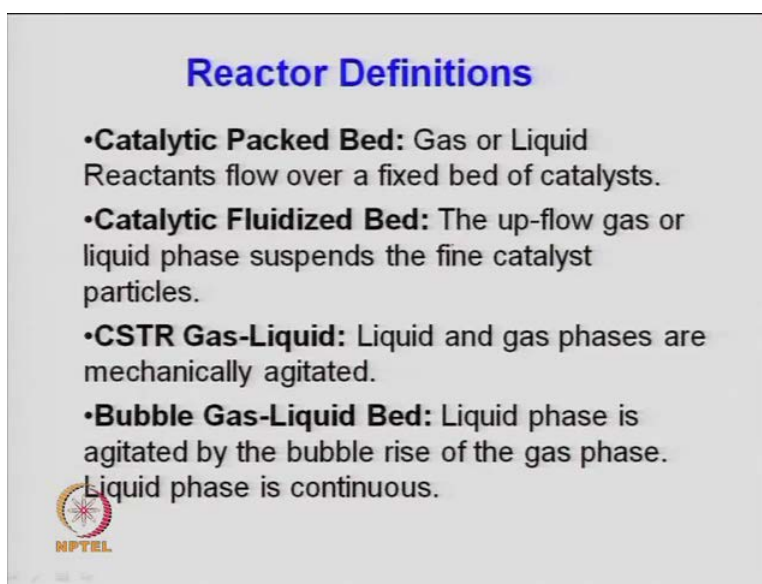
A generic rhodium catalyst, where PAr_3 = triphenylphosphine or its sulfonated analogue.

So, it can be High pressure it can be Low pressure, so Hydroformylation of propene to butanal with water soluble rhodium phosphine complexes, so this is the catalyst which is soluble in water. So, the reaction takes place in the liquid phase and temperature is 50 and 150 degree centigrade pressure is between 10 to 100 bar 1 bar is one atmosphere and the concentration of the catalyst the between 10 and 100 PPM of rhodium.

So, this is a kind of catalyst which you can see here so it is an liquid phase so water soluble compound. So, this can also be used for polymerization of ethylene where the titanium chloride and this aluminum ethyl tri aluminate aluminum compounds of ethylene which is a kind of at a type of catalyst. So, they have been used and that is again a kind of homogenous catalyst so these kind of catalyst are used in the petrochemical industry for homogeneous and the activity of this catalyst is very high compared to the heterogeneous catalyst.


So, this is a kind of the catalyst where the generic rhodium catalyst where PAr 3 that is nothing but triphenylphosphine or it is sulfonated analog which is used for this reaction. And, this is a kind of catalyst where the aluminum halides and tite can be used titanium halides aluminum alkides these kind of compounds are used. And, they are used for the formation of the HDP and LDP type of compounds ethylene polymerization, high density polyethylene, low density poly ethylene. So, these types of compound are produced by using that is polymerization of ethylene.

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Reactor Definitions

- Catalytic Packed Bed:** Gas or Liquid Reactants flow over a fixed bed of catalysts.
- Catalytic Fluidized Bed:** The up-flow gas or liquid phase suspends the fine catalyst particles.
- CSTR Gas-Liquid:** Liquid and gas phases are mechanically agitated.
- Bubble Gas-Liquid Bed:** Liquid phase is agitated by the bubble rise of the gas phase. Liquid phase is continuous.

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If, Reactant Definitions the basically the in common as I said that batch CSTR or a pack bed reactor where two blood type reactor and catalyst is placed in between in the center and then depends on the mass of the catalyst. So, we have a kind of distributors when the top depending upon the liquid and gas and to have a better distribution and need to design the distributor. So, you combined if you look at the reactor design is very complete complex it is a complicated process. But, in general or when you look at just for the catalytic reaction how much mass is required that simple design we write for the say pluck flow reactant design.

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$$\frac{W}{F_{A0}} = \int_0^x \frac{dx}{(-r_A)}$$

$$\frac{W}{F_{A0}} = \frac{x}{(-r_A)} \quad \text{CSTR}$$

As, I discussed this W by F_{A0} naught is equal to x_A something like this dx upon minus r_A something like this. So, this a kind of say rate equation which you get from the writing a mechanism or micro kinetic reaction or one can simply write for simple design kC to the power n . And, find out the mass of the catalyst for a given production or for the conversion given conversion. Say 90 percent conversion with how much feed been used and what will be the productivity of one can write these expression and this is a kind of pluck flow reactor design. If, it is CSTR or 10 type reactor then one write simply W by F_{A0} naught is equal to simply x_A upon minus r_A dash.

So, one can very easily find this is for a CSTR or ten times. So, even if you write a bubble column or fluidized bed reactor under simplest condition one can assume it like a CSTR. But, if

you look at the actual design for a fluidized bed reactor you need to look at the three phase model or two phase model to find out these rate equations. Because, there will be a limitation of mass transfer accordingly one needs to consider the overall rate of reaction which includes the resistances for mass transfer also in different phases.


So, these are the very common design expression for a ideal pluck flow reactor and this is for this CSTR reaction. And, similarly in the batch reactor one can find out the time for a given conversion and which is again time for given conversion is equal to $N_A \int_0^x \frac{dx}{-r_A}$ upon minus r_A into r_A dash if I write so into W . So, one can write the expression like this which is similar to a pluck flow reactor expression. Where, only W by F_A naught is replaced by something like a t_{batch} which is your fluoride. So, here T is written in terms of that, because the batch is unsteadies operation and condition change with time on stream.

So, this is the time required for a given conversion in a batch with this the moles which have already been cap. Because, in the batch there is nothing like a continuous flow the reactant are fed inside and then after certain time we get the product and we measure the conversion by analyzing the components. So, these are simple design expression but when you look at the actual design reactor design you need to correlate these in terms if the hydro dynamics, that is as I told CFD type expression or look at the cold flow conditions and then evaluate the mass transfer effects also and then include it into an overall rate expression. So, it means the effect of particle size will be important the flow velocity will be important and that needs to be incorporated in the actual reactor design.

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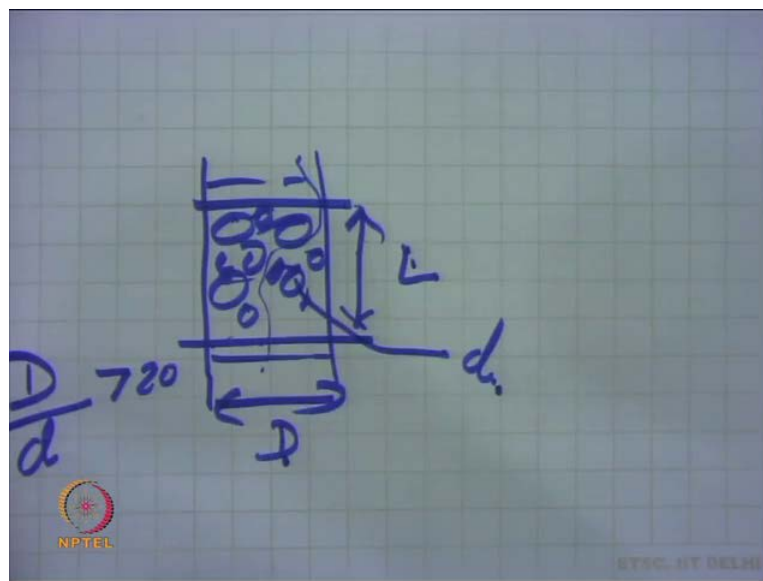
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So, if you look at the Definition wise the Reactors the various reactors which are used in the catalytic process industry. So, pack bed reactor is very common as the name says that something in this tube and you pack it with the catalyst. So, gas or liquid reactants flow over a fix bed of the catalyst. So, you have a bed and you pass the liquid or gas concurrently or counter currently.

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So, something like this there is a bed where you have put the catalyst you have inserted that there is a proper distribution. So, you have to make the condition that there should not be any channeling this may happen that the gas pass through the bed like this so this is to be avoided. So, sufficient amount of inert is to be packed here from top and bottom like this and need to put look at the size of the particles also. And, these catalyst particles should be mixed with sufficient amount of inert also especially when the reactions is endothermic or exothermic. So that the heat transfer heat should be depending upon the type of the reaction one needs to look at this also design. And, again this height of the bed is important which I told L the diameter of the reactor is important the diameter of the catalyst is important size of the catalyst so all this factor should be considered.

You, need to have a large length to diameter ratio a large length to this diameter ratio and a definite d by d ratio also to avoid the channeling that is wall effect. Otherwise, when you have a liquid it has a tendency to move towards wall so there will be more wall flow. So, you need to decide these factors depending upon the hydrodynamic study. And, these are very important when you look at the actual reactor design or when you model the reactor. We, need to introduce those terms or known idiom parameter in terms of the axial dispersion range dispersion like that terms. So, this is one same thing can be done in a fluidized bed reactor also fluidized bed means something where the solid is acting like a fluid.

So, small particles these are the small particles where which are fluidized or in fluid medium or bubbling media along in the presence of some gas. So, some carrier gas may be required to keep the particles in the suspension form. So, what is the advantage is that every particle is available for reaction catalytic particle is available for reaction. Where, here it may happen that the pressure drop is an issue the particles are packed tightly. So, there may not be any voids between the particle so the pressure drop will increase.

But, in the case of fluidized bed pressure drop is less and you can have better contact between the gas and solid or reactant and that catalyst. So that is some there are some, advantage with this fluidized bed. But, of course because the distribution is poor now there will be more back mixing because when you look at the pack bed reactor we reassemble with plug flow reactor. So, in the plug flow reactor there is no back mixing there is no back mixing at all, so and concentration if you look at in the longitudinal direction that it is decreasing down the length of the reactor. But,


in the radial direction its uniform throughout but in the case of this feudalized bed will be a kind of back mixing. So, it means you need to find out the residence time distribution because it is not like an ideal reaction. Basically, pluck flow reactor compared with feudalized bed reactor feudalized bed reactor is behaving like a CSTR. So, when you have a circulating feudalized bed reactor it gives a higher conversion because it will reassemble to some extent to the pluck flow reactor.

So, this is what the design expect, we have discussed here and CSTR again CSTR can be used just like a bubble column reactor. So, gas liquid contact so liquid and gas pressure are mechanically agitated. So it is a, kind of agitated bubble column reactor also which is again a kind of tank reactor. So, you have a gas or along with the liquid or you can do gas with bubble from the bottom and then liquid is already in the bed in the column. So, that is a bubble gas liquid bed reactor both are similar in one bed.

So, this here the liquid and gas phases are mechanically agitated here the bubble gas liquid bed the liquid phase is agitated by the bubble rise of the gas phase. So, bubble size becomes important here because smaller the bubble size the mass transfer coefficient will be very high. So, it is a, kind of the system where if you have a, solid also it becomes three phase kind of reactor so we need to look at the mass transfer solubility of the gas liquid and then accordingly the design or size or sparser design. So, many things or starrer hesitator speed all these thing should be fixed or identified for the design of the reactor.

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- **Bubble-column Reactors:**
 - Homogeneously catalyzed air oxidation of hydrocarbons (e. g., of toluene to benzoic acid): 130–150 °C, 1–10 bar, Mn or Co salts as catalyst
 - Oxidation of *p*-xylene to terephthalic acid with Co/Mn salts and bromide at 100–180 °C and 1–10 bar
 - Oxidation of ethylene to acetaldehyde : 100–120°C, 1–10 bar, PdCl₂/CuCl₂ catalyst



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Then, we have a Bubble Column Reactors so again if you look at the example here the homogeneously catalyzed air oxidation. So, this is a kind of example of homogeneous catalyst in the bubble column reactor. So, Homogeneously catalyzed air oxidation of hydrocarbon like toluene to benzoic acid. So, basically this process is done for the reduction of the pollutants so it is a kind of wet air oxidation in the presence of some homogeneous oxidizing catalyzing catalyst like hydrogen peroxide. So, toluene to benzoic acid temperature is around 130 to 150 degree centigrade and pressure is around 1 to 10 atmosphere magnesium or cobalt salts are used as a catalyst as they are soluble in that.

So, it becomes the homogeneous system for the same thing heterogeneous catalyst can also be used. So, it is an example of homogeneous catalysis and then in a bubble column reactor but when you have solid catalyst it becomes a kind of trickle bed reactor. So, we will talk on that same thing same thing for oxidation of p-xylene to terephthalic acid over cobalt magnesium salt and bromide at 100 to 180 degree centigrade and 1 to 10. So, these are some example where we can use a bubble column reaction using the homogeneous catalyst again Oxidation of ethylene to acetaldehyde so this can be done in the presence of platinum palladium chloride and copper chloride

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● heterogeneous catalysis the effective reaction rate is usually expressed relative to the catalyst mass m_{cat} (Equation below):

$$m_{cat} / n_{A0} = \int_0^x dx / (-r_A)$$

m_{cat} = catalyst mass, kg
 $n_{A,0}$ = feed rate of starting material A
 XA = conversion of A

● The differential form of the design equation for a heterogeneous catalyzed reaction in a fixed-bed reactor can be described by: $dX_A/dm_{cat} = r_{eff}/n_{A,0}$

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Just if you look at design equation I have already talked a basically this is you are a heterogeneous catalytic reactor design if you have a kind of pack bed reactor. So, this is what the mass of the catalyst divide by the feed rate it can be a molar feed rate or the mass feed rate. So, this is the same expression which I have written in the form of W by FA naught. And, since I told you that pluck flow reactor the condition change down the length.

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F_A → F_A

z $z+dz$

dz

X

$A_c dz S_c = dw$

$F_{A0} \frac{dx}{dw} = -r_A'$

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So, this is our plug flow reactor and we are taking a differential cell element here and for this we are writing our mole balance equation. And, this is the Δz or dz in the reactor which can be written in the form. So, this is your area of cross section into dz so that is your volume of this section and if you multiply with the density of the catalyst which is ρ_c or ρ_{cat} . So that is your mass of the catalyst in the back so this is your w mass of the catalyst which is in differential section in this. So, when you write a mass balance something is going in from here F_A and something is coming here at this distance z plus Δz . So, you know your material balance that input minus output minus because of the chemical reaction within this system.

So, that can be written r_A dash times dW if I write in terms of mass. So, mass in or moles in minus moles out minus because of chemical reaction is equal to 0 because it is your steady state reaction. So, one can easily write this equation that which is simply here dF_A by dW minus dF_A by dW or dF_A by dW is equal to minus r_A dash. Or, that is what I have written F_A naught dx_A by dW is equal to minus r_A dash. So, this is your differential form of reactor design equation and that expression because when you write for whole system. So, here it is 0 to W total mass of the catalyst required to achieve a given conversion x .

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$$F_{A0} dx_A = (-r_A') dW$$

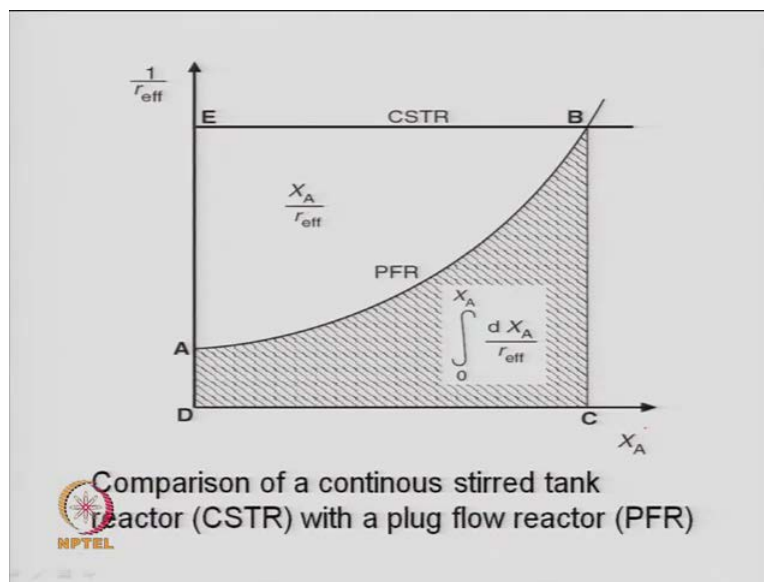
$$F_{A0} \int_0^x \frac{dx}{(-r_A')} = \int_0^W dW = W$$

So, one can easily integrate this because in this case this is simply your integration becomes which is your $F_{A0} dx_A$ is equal to minus r_A dash times dW this equation. So, we have simply integrated this now 0 to x_A because your inlet conversion is 0. And, it will change to final

conversion x for which we are calculating our mass of the catalyst dx . And, since r_A dash will be a function of conversion so we take it here. So, r_A dash is your rate of which will be function of conversion or concentration is equal to 0 to W total mass of the catalyst dW . So, this is simply your W and F_A naught is already here. So, that is what W by F_A naught is equal to 0 to x_A dx_A upon minus r_A a, overall pluck flow reactor design. And, that equation is written here and this is the differential form which I was talking for a differential element.

So, once you are a small reactor a pluck flow reactor in differential form that behaves like a CSTR which is design equation for CSTR when you reported here in this case. So, this is the CSTR design equation total mass if I write it for a differential form this becomes dW/dx . So, it means nothing but the pFr is nothing but infinite number of CSTR placed in series.

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So, this is what the size of the reactor sizing so you can see here that 1 upon minus r_A which is form here in this equation. So, dx_A upon 1 minus r this is your x conversion down the length of the reactor and reported as a function of r_A 1 upon r_A . So, it means for a pluck flow reactor if you take the area under the curve this area this is your integration 0 to x dx_A upon minus r_A . So, minus r_A I am writing because it is disappearance of the reactant. So, this is for a pluck flow reactor that area under the curve is your W by F_A naught. So this, value can you easily the mass of the catalyst required for a given conversion.

But, if you look at a CSTR in the case of CSTR W by FA_{naught} is not an integration but x divide by $-r_A$ it means the area of this rectangle will be your W by FA_{naught} . So, for same feed rate for identical conversion you can see here the volume of CSTR or the mass of the catalyst required in a CSTR will be much higher compared to a plug flow reactor. So, plug flow reactor is better in that way because the concentration is changing down the length and you are measuring the rate along that. Where, in the case of CSTR the concentration we assume that immediately drops to the final value. So, that is similar to the homogeneous reaction when you studied that we use the same terminology here in the case of heterogeneous catalyst also. That, when you have a CSTR and you want to achieve the same conversion like a plug flow reactor then you need to increase the size of the reactor or you need to use the larger mass of the catalyst in the reactor

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Reactor calculation: Comparison of a fixed-bed reactor with a continuous stirred tank reactor (CSTR)

The gas-phase reaction is to be carried out isothermally according to the equation

$$A + B \longrightarrow R + S$$

M. W	80	20	60	40	g/mol
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Reactants A, B are fed in stoichiometric proportions to the reactor. The rate law for the reaction follows a Langmuir-Hinshelwood mechanism

$$r_{\text{eff}} = \frac{k_1 p_A p_B}{1 + K_2 p_A + K_3 p_R} \quad (\text{kmol h}^{-1} \text{ kg}^{-1})$$


Just as an example for exercise I have just taken a problem here which is nothing but simple design. And, we have said here that there is a reaction between A and B which are in gas phase and transforms into a product R and S. The molecular weight of these reactants are given 80 for A and 20 for B. The molecular weight of the products are given 60 for R and 40 for S. The A and B are fed in stoichiometric proportion that is equivalent to there this 1 mole of A reacts with 1 mole of B and gives 1 mole of R and 1 mole of S. So, this is what given here in this case the product which is formed here. So, this product A plus B gives you R plus S and they are said in the stoichiometric proportion to the reactor. The rate law which

is determined from the mechanism of the reaction and that is given in the form of type mechanism. So, this is given here in the form of mechanism which is k_1 times p_A times p_B divide by $1 + k_2 p_A + k_3 p_R$. So, that has been given because we have discussed this earlier when we write this kind of mechanism. We, say that there is a adsorption of A on the catalyst there is adsorption of B on the catalyst. And, then the transform into some add jobbed R species and S species in the surface reaction. And, then this finally this product dissolves and assuming surface reaction as the rate controlling we write a mechanism.

And, there can be different kind of postulation which we already discussed to derive the rate which is Langmuir Hinshelwood. So, here this has been mentioned that rate is proportional to the partial pressure of A and partial pressure of B. And, species A is add jobbing on the surface but not B so B is in gas phase basically and p_R is add jobbing not the S. So, one can very easily write the mechanism and derive this kind of rate equation which I am not discussing at this point. We, assume that from the rate equation this kind of from the mechanism the rate equation has been obtained and rate parameters have been evaluated like this.

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The reactor is operated at 2 bar and 300 °C, the required an output of 10 t R/ day.

The rate law parameters are :

$$k_1 = 0.6 \text{ kmol l}^{-1} \text{ kg}^{-1} \text{ bar}^{-2}$$
$$K_2 = 4.5 \text{ bar}^{-1}$$
$$K_3 = 41.6 \text{ bar}^{-1}$$

a) Determine the catalyst weight for a conversion of 80% in a packed-bed reactor.

b) Also determine the CSTR catalyst weight necessary to achieve the same conversion as in the packed-bed reactor



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So, the rate parameter which can be determined experimented by regression analysis so k_1 rate constant is given which is this k_2 and k_3 are equilibrium constant. And, they values are given in terms of 4.5 bar inverse and 41.6 bar inverse for the equilibrium constant. So, what you have to

do you have to find out the mass of the catalyst to achieve a conversion of 80 percent in a pack bed reactor and compare the same mass or mass of the catalyst required in a CSTR. So, the same thing which I have discussed here now is given in the form of problem.

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Express the partial pressures p_A , p_B , and p_R as a function of X , combine the partial pressures with the rate law r as a function of conversion, and carry out the integration of the fixed-bed equation.

Reactants	Mol (n_i)	$P_i = \text{total } P \times \text{mole fraction}$
A	$1-X$	$p_A = 1-X$
B	$1-X$	$p_B = 1-X$
R	X	$p_R = X$
S	X	$p_S = X$



So, it is a simple problem and I hope all of you can do because you have to just write down this is the stoichiometric. So, one can say that if 1 mole of this is reacting 1 mole of this will react and 1 mole of this will form and 1 mole of ash will form. So, we need to find out p_A , p_B and p_R in the form of x . Because, our reactant design equation in a plug bed reactor will be this one W by F_A naught is equal to 0 to x dx A , upon minus r_A dash for a plug flow reactor or pack bed reactor assuming plug flow condition.

So, we need to find out the mass of the catalyst F_A naught is the molar feed rate of the limiting component. So, since they are given in their stoichiometric ratio. So, you can take either and A is you let us take A as F_A naught molar flow rate or r_A dash is given only thing that we need to transfer these p_A , p_B in terms of x for integration. So, we made a kind of stoichiometric table here so that is at any time when the conversion is x the moles fractions we can write. So, we have seen that there is no fractional change in the volume.

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$$C_A = \frac{C_{A0}(1-x)}{1+\epsilon x}, \quad C_A = \frac{P_A}{RT}$$

$\epsilon \rightarrow$ fractional change in volume

$$A + B \rightarrow R + S, \quad \delta = 0$$
$$\epsilon = 0$$
$$C_A = Y_{A0} \delta = 0$$

Otherwise, we need to write the expression for concentration in terms of C_A is equal to C_A naught 1 minus x divide by 1 plus ϵx where, ϵ is fractional change in volume. So, fractional change in volume during a reaction that is basically final volume minus initial volume divide by initial volume. So, suppose the reaction is given here in this case A plus B gives you R plus S . So, here 1 mole of this one mole of this so initially 2 moles are reacting because there is no inert and 2 moles of this will form. So, in this case ϵ is 0, because there is δ is 0 δ simultaneous change difference in the stoichiometric coefficient of the product and reactant. So, 1 plus 1 minus her again 1 plus 1, so this is 0, so δ is 0 so ϵ we define based on y_{A0} naught that is mole fraction of the limiting component times δ . So, since δ is 0 so this becomes 0 so in this case your C_A simultaneous simply is C_A naught 1 minus x . And, you know C_A is equal to P_A divide by RT .

So, in some cases you may be given the concentration data so one can substitute either in terms of concentration or in terms of partial pressure of A . And, partial pressure can also be written total pressure multiplied by mole fraction of the component. So, in this case if you look at here we have the stoichiometric table because if 1 mole of A has entered so x mole reactor so at any time T or given conversion it is now 1 minus x . Since, 1 mole of a stoichiometric fed 1 mole of A is fed so one mole of B will be also fed. So, again moles of B left again 1 minus x . Because,

partial pressure at any time when we talk down the length of the reactor here in the case of the time mini at a any length of reactor z 1 mole of a reacts.

So, one mole of R will form so this is x reactor so x will form and similarly 1 mole of a reacted equal number of S will form. So, x moles are also x so this is the total moles. So, partial pressure you know at any time because pA pB is to be substituted so partial pressure is total pressure into mole fraction. So, here you can see that total moles are again the same there is no change in the number of moles. So, this becomes partial pressure of pA which is naught pA so that is again 1 minus x. Otherwise, it is pA naught into 1 minus x you can calculate that, same thing for pB and this is increasing.

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Substituting the partial pressures in the rate law gives

$$r(X) = k_1(1-X)^2 / (1+K_2(1-X)+ K_3 X) \quad r_{at} = \frac{k_1 p_A p_B}{1 + K_2 p_A + K_3 p_X} \quad (\text{kmol h}^{-1} \text{ kg}^{-1})$$

$$= 0.6 (1-X)^2 / (1+4.5(1-X) + 41.6 X)$$

The molar flow rate of A, F_{A0} can be obtained from,

$$F_{A0} = F_p X_A = 10 \text{ t/24} \times 60 \times 0.8 = 8.7 \text{ kmol/h of A.}$$

Design equation of a packed bed reactor ,

$W/F_{A0} = \int_0^X dx/(-r_A)$, Can be solved numerically , ODE Solver using MATLAB, POLYMATH etc. (W= 1615 kg)

For CSTR, $W/FA0 = XA/-r_A$ (evaluated at the exit i.e X= 0.8)

$W/FA0 = 10260 \text{ Kg}$

So, this is x and this is x so these values of pA and pB pR pS will be substituted in this expression. So, this is the rate equation which has been determined so substitute the values of pA pB and pR here. So, now you have k1 pA onto pB so pA is equal to pB here so 1 minus x whole square divide by 1 plus k2 pA is again 1 minus x plus k 3 times pR which is x. So, this is your rate as a function of conversion data.

So, k1, k2, k3 all are known so we have substituted these values here. So, now FA naught FA naught is the molar feed rate of A and you know that the production desired is send here is 10 of R per day. So, 10 of R per day is to be produced so in a reactor design produce 10 of R how

many moles of A are required to achieve at a given conversion level one can find out. So, that is written here if the conversion design is x . So, F_p which is the product design in term divide by x will be the moles of A which is to be fed. So, this is the moles of a fed so that is 10 divide by this is given in terms of per day. So, we have converted it in terms of hour so conversion level is given 80 percent. So, x is 0.8, so this is hours in a day and this is day in to multiplied by 60 so total number of hours and this is conversion.


So, roughly it is 8.7 kilo mole per hour of A so now this value will be substituted in this equation which is your W by F_A naught is equal to 0 to x dx upon minus r_A . So, this equation can be solved analytically if not possible then one can use any OD solver also. So, any ordinary differential equation solver or in mat lab polymer it can be solved. And, one can use the numerical methods like sin sins rule which you have read in your homogeneous catalytic reaction also any mathematical course. So, the one can use either mat lab or polymath or any other software for solving this kind of equations or integrating this numerically.

So, this is roughly if you do that you get 1650 and so please check it and you can practice it at home. For, CSTR I told you need not to integrate the conditions will be calculated at the exit of the reactor. So, for CSTR W by F_A naught is equal to simply x_A divide by minus r_A dash calculated at 80 percent conversion. So, this just substitute here x is equal to 0.8 so rate can be calculated and F_A naught you have already calculated here. So, W is equal to F_A naught times x_A divided by minus r_A . So, this comes roughly 1260 kg so one can see that a large amount of mass of the catalyst is required in the case of tank type reactor because there is a degree of back mixing. So, one can compare so pluck flow reactors are always better in terms of better means most of the reaction when you look at smaller mass of the catalyst or smaller size of the reactor.

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Single-Bed Reactor

- The single-bed reactor is the simplest catalysis reactor
- It is completely filled with catalyst and is mainly used for thermally neutral and autothermal gas reactions
- Owing to its design, the pressure drop is high, and the residence-time distribution has a major influence on the selectivity and conversion of the reaction
- Of particular importance is the maintenance of temperature limits, both axially and radially, as heat removal is naturally poor



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So, we quickly the different type of reactors which are used in the process industry if you look at here the one is your just like a pad bed reactor or fix bed reactor so we call it single bed reactor. So, there is only one bed of catalyst so especially the selection depends on the deactivation performance of the catalyst the conversion level which is desired endothermic that is the endo thermicity that is the exothermicity of the reaction. So, which will depends on the heat transfer that will decide the reactor design how the heat can be removed from the process or it can be added by take isothermal non isothermal type of reactor.

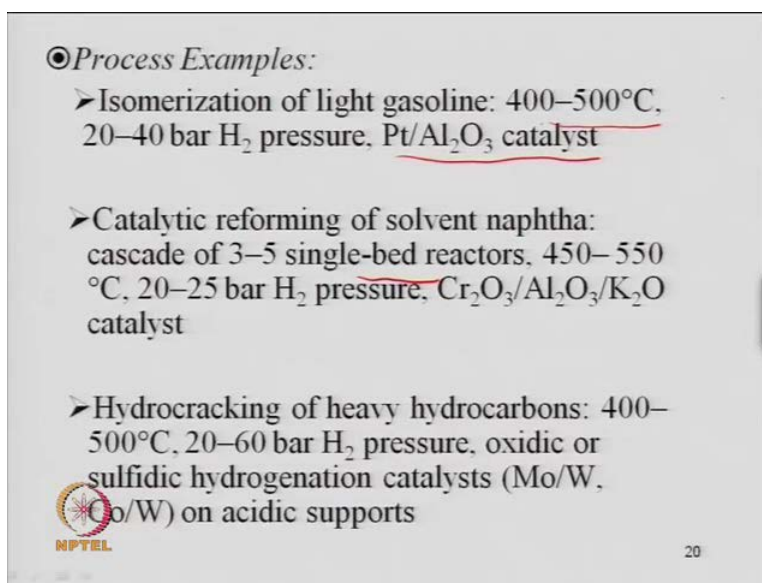
So, though different names have been given different type of design approaches have been given depending upon the heat transfer mass transfer. And, so mass balance in a energy balance momentum balance pressure of calculation so all these thing should be said for the commercial reactor design. So, the Single Bed Reactor if you see here it is a simplistic catalytic reactor because it is a kind of fix bed reactor as I said earlier deactivation should not be a big issue then only it can be used. So, it is completely filled with catalyst and in mainly used for thermally neutral and auto thermal gas reaction.

So, because here in the heat romal should not be an issue otherwise hot spot formation may occur. So, that that time reaction may not good. So those, reaction where the heat generation term negligible we can prefer a pack bed or fix bed type of reactor. So, own to its design the

pressure drop is high so as I said it is a pack bed reactor. So, avoids a particles are fine very small power type particle then the pressure drop will be excessive. So, energy loss will be there so and the residence time distribution has the major influence on the selectivity and conversion. So, RTD becomes very important we need to look at the resistance time distribution sold flow condition co visualization. So, mall distribution we avoided or kind of distributers to be designed so this, things should be looked into. So, that is why the pressure fix bed reactor or single bed reactor may not be very good when the reaction highly exothermic or when the particle or catalyst is in powdered form.


So, a particular importance this type is the maintenance of the temperature limit both axially and radially as heat removal is naturally poor. So, in this case heat removal is an issue if the reaction is endothermic or exothermic this should not be used. So, this reactor is only used when the reactor is ISO thermal and very large particle size large size of catalyst particles are used in the bed. So, the pressure drop should not be the issue but the advantage is that it is a catalyst can be regenerated easily because generally the deactivation is not an issue in this kind of reactor. But, you can shift it to some other reactor and regenerate it and again take it back though the maintenance problems are very low in this kind of reactor or less.

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● *Process Examples:*

- Isomerization of light gasoline: 400–500°C, 20–40 bar H₂ pressure, Pt/Al₂O₃ catalyst
- Catalytic reforming of solvent naphtha: cascade of 3–5 single-bed reactors, 450–550 °C, 20–25 bar H₂ pressure, Cr₂O₃/Al₂O₃/K₂O catalyst
- Hydrocracking of heavy hydrocarbons: 400–500°C, 20–60 bar H₂ pressure, oxidic or sulfidic hydrogenation catalysts (Mo/W, Co/W) on acidic supports

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So, some of the simple reaction like isomerization of like gasoline which is done at 400 to 500 degree centigrade pressure around 20 to 40 atmospheric in the terms of hydrogen pressure. And, catalyst is platinum alumina catalyst so that is done in the kind in this single tube reactor. Catalytic reforming of solvent naphtha which is again a cascade of 3 to 5 single bed reactors the temperature is 440 to 550 degree centigrade pressure is 20 to 25 atmosphere in terms of hydrogen pressure. And, chromia alumina potassium oxide catalyst are used so these are some examples of the catalyst or reactors which where the single bed catalyst can be used. And, say another example is your Hydrocracking of heavy hydrocarbon where again the temperature is around 400 to 500 degree centigrade and the pressure is 20 to 60 bar of hydrogen and oxidic or sulfide hydrogenation catalyst like molybdenum tungsten, cobalt tungsten, or alumina or silica supports are generally used. So, these are some of the reactors some of the reaction where this kind of catalyst can be used in the process.