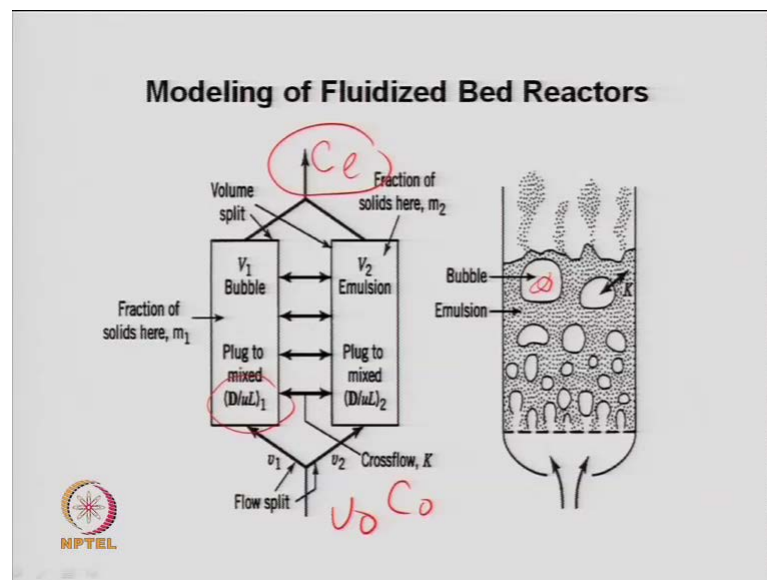


**Heterogeneous Catalysis and Catalytic Processes**  
**Prof. K. K. Pant**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Delhi**

**Lecture - 40**

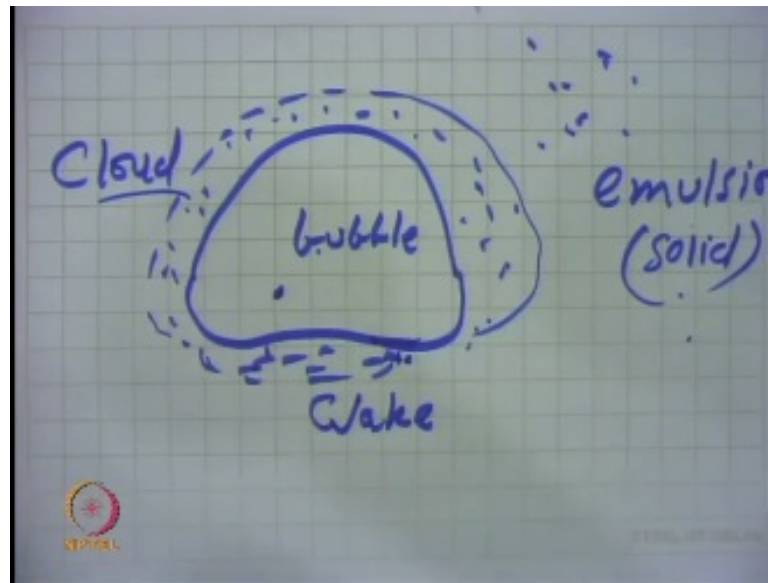
Good afternoon. In my last lecture, I was talking about fluidized bed reactor and I was discussing some design concepts of a fluidized bed reactor. And, I told you that, there are two kind of models available. One is Davidson model, which is known as two-phase model. So, we assume that, there is a bubble phase and then there is an emulsion phase.

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So, the reaction takes place between bubble phase and emulsion phase. And, there is some kind of transfer of mass from bubble to emulsion. And, that is a simplest model if you look at the actual hydrodynamics of a fluidized bed reactor. There is another model, which is known as three-phase model. So, in the three phase model, as I was discussing yesterday also; so bubbles are covered by solids. So, if you look at the fraction of the solids in bubble phase; so if I talk it  $f_b$ , which is in terms of the volume of the solid in the bubble phase divided by the total volume of the bed; that is the fraction of the solid in the bubble phase. So, that is a very low number; say 0.001 or it may be 0.001 to 0.01 – low number. So, there is a very low chances of reaction, because reaction needs a solid surface or catalyst surface. So, the chemical reaction will be low. So, this is one.

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And then at the lower side of the bubble, which I was talking last time also; so this is a kind of the shape if you look at a gas bubble, which is moving. So, this is surrounded by a solid particle; and this is the cloud phase here. So, these are the particles – solid particles. So, this is the cloud of the solid; and this is the gas bubble. And, in between lower portion, you will have some more concentration of the solid here. And, this is known as a wake phase. So, you have a cloud phase; you have a wake phase; and then far away from this, you have a solid particle and that is known as emulsion phase. So, in the emulsion phase, you have more solid. So, here you will have more solid material, catalyst material and less gas. Here you have more gas and less solid in the bubble phase.

And, we are talking a transfer; that is, mass transfer and chemical reaction depending upon the type of the kinetics of the reaction. So, this is what has been shown here that, a fraction of the solid mass, which is present in the bubble phase; and there is a volume  $v_1$  of the bubble. So, when you have a superficial gas velocity  $u_0$ ; and in model, it is splitted like this. So, there is a kind of bubble phase; there is an emulsion phase; and there is a transform – mixing. So, that is known as cross-flow coefficient; that is, from bubble to emulsion when you have just a two-phase model. And then at the exit, these two merge; and we have some average conversion or  $c_e$ ; and here you have some inlet concentration  $c_0$ . So, basically, it is a kind of a combination of a plug flow reactor with certain degree of mixing. So, you can see here the plug to mix flow. So, you will require a term like a dispersion number  $D$  upon  $uL$ , which is in the bubble phase. And, same

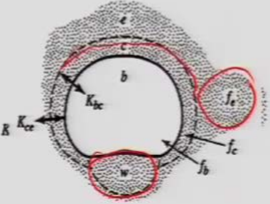
thing again, here is a kind of the plug flow and the mixing that is the CSTR; so some kind of degree of back mixing. So, this is  $D$  upon  $uL$  to, that is, the dispersion number in the emulsion phase.

So, these are the volumetric flow rates, that is, in terms of the bubble, volume of the bubble and volume of the emulsion. So, we are talking the concentration of the gas in bubble phase and concentration of gas in the emulsion phase. And then there is an average concentration of gas in the exit. So, how the concentration of the reactant species change, as it moves from this point to this point in a fluidized bed reactor? So, this will tell you the conversion or the productivity in a process. So, accordingly, you need to size this reactor; that is, the height of the fluidized bed reactor is to be decided. So, this is what you can see here the actual condition. So, you have an emulsion phase, which is shown by the dot of particle; this is the bubble, which is just like this; this is the bubble phase; and there is a cross flow, that is, the mass transfer.

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**THE K-L MODEL FOR BFB (Three Phase model)**

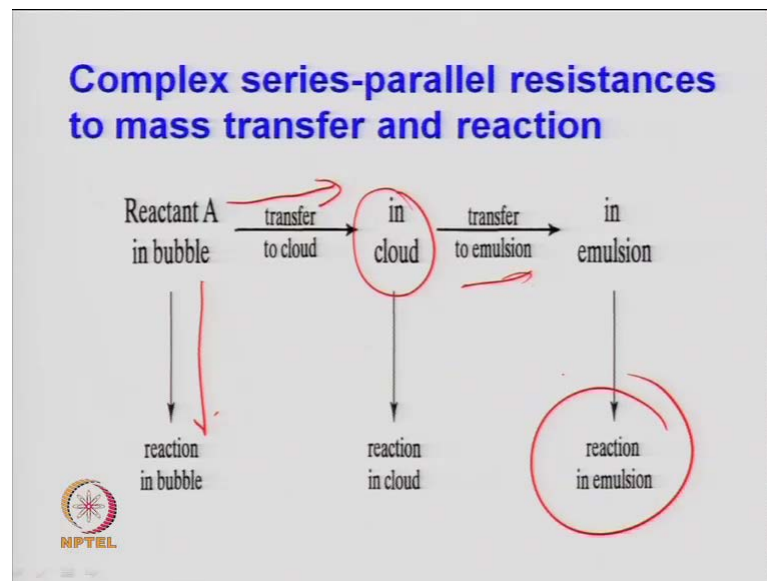
Assumptions:  
 The bubbles are all spherical, all of the same size  $d_b$ , and all follow the two phase model. The bed contains bubbles surrounded by thin clouds rising through an emulsion.



And, this is what I was talking here that, you have a three-phase system now actually. So, the bubbles are... So, when we write a three phase model, which is known as a Kunii-Levenspiel model – K-L model. So, there is a bubble; there is a cloud phase, which is shown by this dot line like this. So, this is the cloud phase and this is the wake here at the lower portion of the bubble. And, this is the fraction of the solid in emulsion. So,  $f_e$ . So, that is the volume of the solid in emulsion phase per unit volume of the bed;

or, in terms of mass also, mass of the solid in emulsion divided by the mass of the bed. Same thing – this is the cloud phase. So, mass of the solid in cloud phase divided by the mass of the bed; and this is the bubble phase. So, definitely the concentration of solid in the bubble phase will be very low. So, chemical reaction in the bubble phase is low. So, the reaction is in bubble phase; reaction is in the cloud and wake phase; and reaction is in the emulsion phase. But, there the degree of contribution is different.

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So, this is what the very complex series-parallel resistance because of all this mass transfer and chemical reaction. So, as I said that, the gas is entering like this. So, this is the entrant point and then this is the exit point. So, during this, when you look at a model – a three-phase model, we have something like this. So, you have a reactant A, which is in the bubble. So, concentration of the reactant in the bubble or transport or mass of the reactant in the bubble. So, partly, it transfers to the cloud phase and partly it reacts here. So, reacts... So, total mass balance if you look at; so moles of A or reactant A, which is transferring partly to the cloud phase; and rest is reacted there. So, since the concentration of the solid here is low; so this reaction will be low. So, this is what is here, what discussed in this that there is a transfer. So, this is the cross flow transfer to bubble to emulsion, which is in the two-phase.

And, same thing here in between, because there are solids present – fraction of the solids present. So, there will be a reaction – catalytic reaction. So, partly it is reacted and partly

it is transferred. So, this is equal to this plus this basically. And, when it is reached into the cloud phase, then again there is a reaction in the cloud depending upon the concentration of the catalyst present. So, there is a reaction in the cloud. And, the rest is transferred into the emulsion phase. And, again when it reaches to the emulsion phase; so because there is no zone for further mass transfer, it is reacting in the emulsion. And finally, it will leave the bed.

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Let  $u_0$  = superficial gas velocity in the bed,  $m^3$  gas/ $m^2$  bed .s,  $d$  = diameter,  $\epsilon$  (epsilon) = fraction of voids in the bed,  
 Subscripts  $b, c, e, w$  refer to *bubble, cloud, emulsion, and wake*, respectively. subscripts  $m, m_f$ , and  $f$  refer to *packed bed, minimum fluidization, and bubbling fluidized bed conditions*, respectively.

The diagram illustrates a cross-section of a fluidized bed reactor. It shows a central bubble (labeled 'b') surrounded by a cloud (labeled 'c'), an emulsion (labeled 'e'), and a wake (labeled 'w'). Arrows indicate mass transfer coefficients:  $K_{bc}$  and  $K_{cb}$  between the bubble and cloud, and  $K_{ce}$  between the cloud and emulsion. A red checkmark is visible next to the diagram.

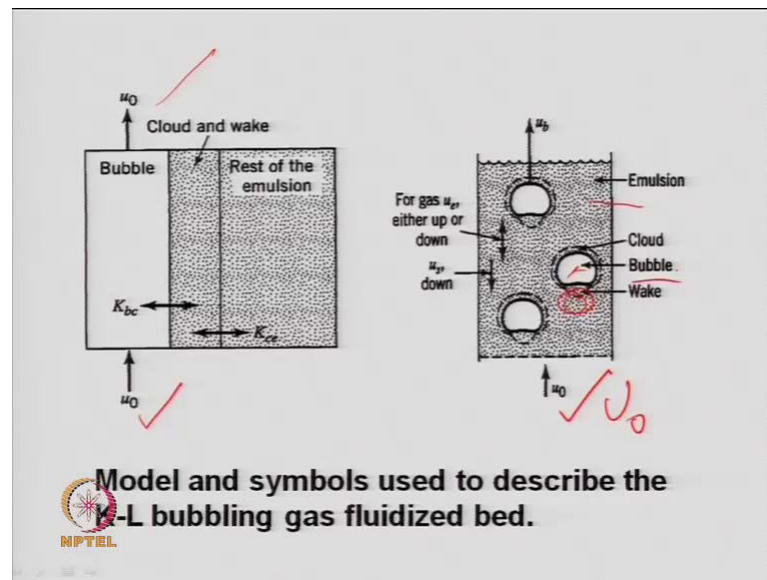
So, just very briefly, I will talk about the design concept, because that is a design of fluidized bed reactor, which is a separate course; where, you understand the hydrodynamics; calculate all the parameters – hydrodynamic parameters; calculate the RTD model using to calculate the dispersion number; and then correlate for the exit-age conversion. So, here in this, I am very briefly talking about that, when you use a catalyst in the fluidized bed reactor, what are the parameters required to design a fluidized-bed reactor; or, what is the basic approach to design a fluidized-bed reactor.

So, I have just defined certain parameters here. So,  $u_0$  is the superficial gas velocity in the bed; that is depending upon the volumetric flow rate divided by the area of the cross section based on empty bed. So, that is known to you. So, this is nothing but in terms of meter cube of gas per unit area of the bed per unit time. So, basically, flow rate, which is volumetric flow rate divided by the area of cross section, which is  $\pi d^2$  by 4; where,  $d$  is the diameter of the bed. Epsilon – we are defining the void fractions in the

bed. So, that is the fraction of the solid if you know in the bed; so 1 minus that solid fraction is the total void fraction in the bed. So, basically, it is a bed porosity. And, we represent the subscripts like b – representing a bubble phase; c is representing the cloud phase; e is representing the emulsion form phase; and w is representing a wake phase. So, generally, the cloud and wake phase are combined together, which is in the model. So, this defines the different phase in terms of subscripts.

m and m f – they are referring basically the minimum fluidized bed condition. When I write b, it is a bubbling fluidized bed reactor and condition. And, f is just... Basically, the f is representing the bubbling fluidized bed condition. And, this m f is representing a minimum fluidized bed condition. And, when it is m, it is just representing a packed bed. So, when there is no velocity of the gas or very low velocity of the gas, that is stagnant – solid particle. There is no bubbling. But, when you have increased the velocity, now bed starts bubbling. So, there will be more and more void in the bed. So, that is what these are the different terms used. And, when you have increased the velocity to a extreme high; so that becomes a bubbling fluidized bed. And, if you have even high, it will reach to turbulent conditions or fast fluidized bed conditions. So, we are not talking that part here. So, this is what the subscripts written. So, when it is written k c e; so basically, it is representing a cross flow coefficient or transferred coefficient, which is representing c e. So, cloud and emulsion – between cloud and emulsion. Same thing here – this e is representing an emulsion phase; this c is representing a cloud phase; f e – I told you it is the fraction of the solid in emulsion phase; f c – fraction of the solid in cloud phase; f b – fraction of the solid in bubble phase; and w is representing a wake phase.

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So, in order to understand the transport property as I said that, there is a reaction and there is a mass transfer. So, this is what here; you have a gas at superficial velocity  $u_0$ . So, this is representing the superficial velocity of the gas and passes through the bubble. So, total volumetric flow rate is constant. So,  $u_0$  is again the superficial gas velocity in the exit. So, there is a transport. But, the three-phase model we have said now – that has been shown now; there is a bubble; there is a cloud and wake, which is combined now  $c$   $w$ . And then there is other phase, which is where you have more solids.

So, that is known as emulsion phase. So, rest of the emulsion. So, there is a transfer from cloud to emulsion. So, this is what is shown here; transfer from bubble to cloud. So, that is shown here. And, this is the actual picture in a bed. So, you have a superficial gas velocity  $u_0$ . So, this is superficial gas velocity meter per second; this is what the bubble is moving up. So, this is basically a bubble velocity, which can be calculated from the mass balance. And, this is what for gas, which is either up or down, because there is the movement of the solid particles or circulation here. So, it is moving up and down. So, this is the emulsion phase. This is the cloud here in the bubble; this is wake here; this is the bubble here. All these terminologies had been discussed. So, this is basically a Kunii-Levenspiel bubbling gas fluidized bed model.

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**Steps:**

1. Mass transfer from the bubble to the cloud-wake phase. There is possible chemical reaction in the bubble phase, but will be small in size since **amount of catalyst in bubble phase is negligible**.
2. Mass transfer of reactant into the cloud-wake(c-w) phase from bubble phase, and from there into emulsion phase (e). There is chemical reaction in cloud phase.



So, what happens? Whatever we have seen, the mass transfer is taking place; chemical reaction is taking place. So, that steps during a three-phase model or steps, which have been discussed here in this; the same things have been defined here. So, first step is the mass transfer from the bubble to cloud-wake phase, that is, the mass transfer. So, one can calculate from the mass transfer coefficient and the concentration difference in the two phase; that is, concentration of gas in cloud and in the wake phase. So, bubble... That concentration gas in bubble phase; and concentration of gas in cloud and wake phase. So, that is first thing – a mass transfer.

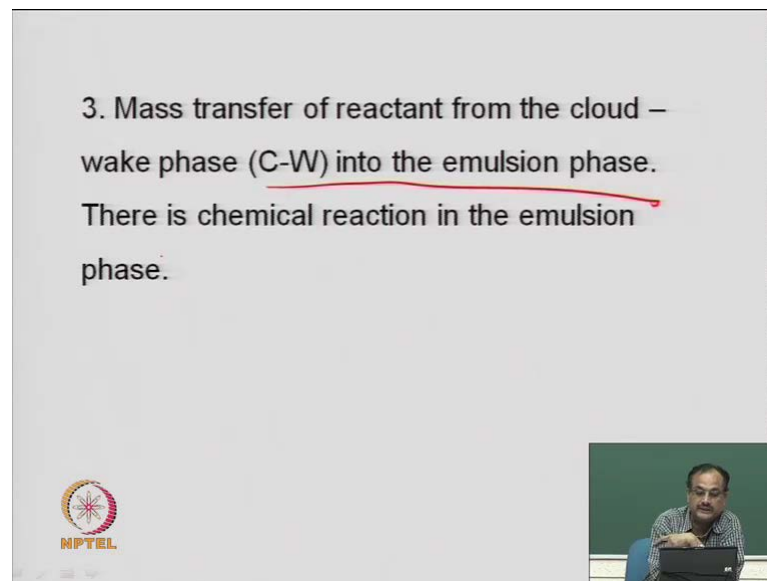
So, there is a possible chemical reaction in the bubble phase also. So, that is the... We said that, there is a chemical reaction. But, since concentration of the catalyst in this phase is low; so this amount of reaction will be negligible, because amount of catalyst in the bubble phase is low. So, their reaction possibility or the rate of reaction or the moles transport because of chemical reaction will be low. So, ultimately, the transfer is because of the mass transfer and because of chemical reaction. So, this is the first step.

Second step – when it reaches to the cloud and wake; so mass transfer of reactant into cloud and wake, which is c-w phase from bubble phase; and from there into the emulsion phase. So, again now, there is a cloud and wake. So, there is enough concentration of the catalyst. So, there will be a chemical reaction also in the cloud phase. So, this is this step here. So, first is this one; which is transferred from this to cloud and wake now; which is



combined cloud-wake. And, from there, it is transferring into emulsion. So, this is transfer into the emulsion and also there is a chemical reaction, because it has the catalyst there. Here also there is a reaction, but this contribution will be low, because the catalyst concentration is low in this zone. So, this is the second step, where the transfer from cloud-wake to the emulsion phase, and there is a chemical reaction.

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3. Mass transfer of reactant from the cloud – wake phase (C-W) into the emulsion phase. There is chemical reaction in the emulsion phase.


The slide features the NPTEL logo in the bottom left corner. A small inset video in the bottom right corner shows a man with glasses sitting at a desk with a laptop, presenting the slide.

And then third step – when it reaches to the cloud and wake, there is no mass transfer; mainly, it is a chemical reaction. So, that is basically in the emulsion phase. So, mass transfer of reactant from cloud-wake phase to the emulsion phase – that we already talked. And now, there is a chemical reaction in the emulsion phase; and there is no further transfer.

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**Material Balances:**

1. Disappearance in bubble = reaction in bubble + transfer to cloud-wake.
2. Transfer to cloud-wake = reaction in cloud-wake + transfer to emulsion.
3. Transfer to emulsion = reaction in emulsion  
fb = vol. fraction of solid in bed, fc in cloud and fe in emulsion.



So, all these steps can be written mathematically in terms of material balance; which has been discussed and should be clear now that, whatever the disappearance in the bubble phase; so whatever the gas, which is present in the bubble phase – that has gone to the cloud and wake phase and that has partly reacted. So, it means the transfer, that is, the loss in the bubble phase for gas is equal to reaction in the bubble phase plus transfer to the cloud wake phase. So, that is the material, which has been disappeared from the bubble phase; that has partly reacted chemically transformed into the product; and partly it is transferred to the cloud and wake phase. So, that is the first one, which is step.

Second one – whatever the material, which is transferred or lost from the cloud-wake now, or whatever material, which has come to this transfer cloud-wake phase – that is partly reacted in and transformed into the product; and whatever which could not react is transferred into the emulsion phase. So, again, there is a mass balance here. And, the third one in the emulsion phase, whatever the material which is transferred to the emulsion – that is equal to the reaction in the emulsion phase.

So, that is a chemical reaction in the emulsion. If you define this  $f_b$ , which is the volume fraction of the solid in the bed; we have already defined.  $f_c$  as subscript –  $f_c$  is the volume fraction of the solid in the cloud phase; and  $f_e$  is the volume fraction of the solid in the emulsion phase. So, these are the terms, which we have defined earlier; that is, the volume of solid in the bubble divided by the volume of the bed. So, that is  $f_b$ .

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$$1. -dC_b/dt = -u_b dc_b/dy = f_b k_r C_b + K_{bc}(C_b - C_c)$$

(reaction in bubble) (mass transfer to cloud)

$$2. K_{bc}(C_b - C_c) = f_c k_r C_c + K_{ce}(C_c - C_e)$$

(Transfer to cloud reaction in cloud-wake + transfer to emulsion)


$$3. K_{ce}(C_c - C_e) = f_e k_r C_e$$

(mass transfer to emulsion) = (Reaction in emulsion)

Eliminating  $C_c$  and  $C_e$ ,

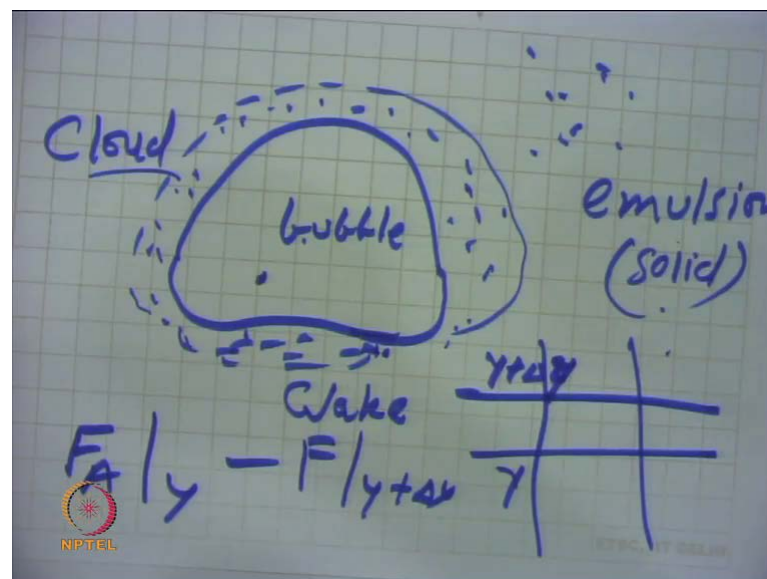
$$-u_b dC_b/dy = K_f C_b$$

$u_b = u_0 - u_{mf}$ ,  
 (Overall rate constant) =  $f_b k_r + 1/\beta$



So, you can very easily write down the rate of disappearance of b; which you write minus d C b by d t; that is, change in concentration of b with respect to time rate. And, you know now that, f a naught d x a is equal to minus r a. And, that is here mentioned in terms of this convective term, which is f a z, which is loss; and between f a at y, which is written in terms of C a into u times e. So, basically, it is a mole balance.

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If I write  $F_A$ , which is at  $y$ ; same thing at  $y$  plus  $\Delta y$ ; something like this; and this is happening in a column, where this is  $y$  and this is  $y$  plus  $\Delta y$ . So, basically, this  $y$  is

the height of the column. So, we can find out to achieve a given conversion, what should be the height of the column if you know how the concentration changes between two sections, between  $y$  and  $y + \Delta y$ . And, this is what we are writing in material balance simply. So,  $F A$  is what? Concentration into volumetric flow rate; a volumetric flow rate is area of cross section multiplied by velocity. So, this is what is written here. And, when you write a differential, then this thing we have already done. So, minus  $u_b$ , that is, the bubble velocity;  $u_b$  is the bubble velocity – and  $dc_b$  by  $dy$ ; that is now the change in concentration with respect to  $y$ . So, this is equal to...

Now, this is transport basically  $df_a$  by  $dy$ ; change in moles of  $a$  per unit depth. So, that is the reaction; that is, this is a chemical reaction in the bubble phase. And, that will depend on the concentration of the solid, which is present in the bubble phase. So, that is why  $f_b$ , because we are writing per unit mass of the catalyst there. And, we have reported it  $f_b$  is a fraction of the solid or volume fraction of the solid in the bubble phase although it is a low number – 0.01 or 0.001 as I said; so times the chemical reaction rate constant times the concentration. So, minus  $r_a$  is equal to  $k C_a$  – something like that. So, we are assuming a first order.

So, that is written a chemical reaction term here – plus there is a transfer – mass transfer, which is from bubble to cloud and wake phase. So, this is the overall cross-flow coefficient. This is a kind of cross-flow coefficient between bubble and cloud. So, one can determine it experimentally or based on the hydrodynamic steady, because it will depend on the diameter of the bubble, velocity – so many other parameters. So,  $k_{bc}$  and times concentration of gas  $a$  in bubble phase minus concentration of gas  $a$  in cloud phase. So, this is the mass transfer to cloud. So, the first step, which I said is that, the transfer or disappearance in the bubble phase is equal to transfer to the cloud and wake phase plus the chemical reaction, which is here; so chemical reaction plus mass transfer.

And now, this whatever you got in this cloud phase – this one –  $k_{ce} C_b$  minus  $C_b$ , because this is the material, which is available in cloud and wake phase. And, that is again partly reacted. So, will depend on the concentration of solid in cloud-wake phase times the chemical reaction rate constant times the concentration of gas  $a$  in the cloud phase – plus there is a transfer also, that is, mass transfer. So, again this is a cross-flow coefficient  $k_{ce}$  in cloud to emulsion times the concentration different. So, this is a mass

transfer rate  $C_c - C_e$  – concentration of gas in the cloud phase minus concentration of gas in emulsion phase. So, this is the second step what we discussed in the earlier slide.

Now, this thing is reached into the emulsion phase and that will react chemically; which is here. So, this is  $k_c(C_c - C_e)$ , which is the material available in the emulsion phase is reacting chemically; which is the mass fraction of the solid in the emulsion phase times again the kinetic and times the concentration, which is available in the emulsion phase. So, this is what the simple material balance for this kind of situation. So, now, you can eliminate them; easily you can add them or these all can be eliminated and you have the concentration expression in terms of bubble phase concentration. So, you have... Now, just simplify it.

So, you have  $-u_b dC_b/dy = K_f C_b$ ; which is here is equal to some overall constant, because you will have... This, this cancels; this, this cancels. So, remaining terms are in terms of this – kinetics – this and this term. So, overall some constant, which we call  $K_f$  – overall rate constant; which will have some contributions of the resistance. So,  $K_f$  times  $C_b$ . So, now, this is a function of  $C_b$ . So, one can integrate this equation easily and find out how the concentration changes down the or to in a fluidized bed reactor. So, this  $K_f$  is represented something like  $f_b k_r + 1/\beta$ ; which is nothing but the constants obtained from this.

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$-u_b dC_b/dy = K_f C_b$ ,  $u_b = u_0 - u_{mf}$ ,  $K_f$  (Overall rate constant) =  $f_b k_r + 1/\beta$   
 where,  $\beta = 1/K_{bc} + 1/(f_c k_r + 1/\alpha)$ ,  $\alpha = 1/K_{ce} + 1/f_e k_r$   
**Integrating for bubble conc. At any height:**  
 $C_b/C_0 = \exp(-K_f(y/u_b))$   
 Overall Conversion  $1-X = \exp(-K_f(L/u_b))$   
 Solid balance  $L_0(1-\epsilon_m) = L_{fluidised}(1-\epsilon_f)$   
 ( $\epsilon_f$  = porosity of fluidised bed)  
 $\Rightarrow 1-\epsilon_f = \text{solid fraction} = (f_b + f_c + f_e)\delta$   
 Where,  $\delta$  = volume fraction of the bed taken by bubbles

So,  $f_b$  times  $k_r$  plus  $1$  by  $\beta$ . So,  $f_b$  times  $k_r$  – you have already seen here. And, these are the rest of the terms mentioned here. So,  $\beta$  is defined by  $1$  by  $K_{bc}$  plus  $1$  by  $f_c k_r$  plus  $1$  by  $\alpha$ . So, again,  $\alpha$  is  $1$  by  $K_{ce}$  plus  $1$  by  $f k_r$ . So, thus, you do the exercise here; how did you get it? So, you can do it because it is not difficult; just you have to add all these terms and eliminate it; eliminate the intermediates. So, you can find out the overall rate in terms of the bulk  $C_b$  – bubble concentration. And, the other terms are nothing but the contribution of chemical reaction resistance and the mass transfer resistance; that is, the cross-flow coefficients what we are talking. So, this is what the different terms defined. So,  $K_{bc}$ , which is the cross-flow coefficient from bubble to cloud; and this is the kinetic term.

Again, this is the mass transfer coefficient basically – a cross-flow coefficient in the emulsion side – cloud to emulsion. So, this is representing a kind of resistance offered in the cloud emulsion phase. And, this is representing a kinetic resistance. So, it is basically the number of resistances, which are present during the fluidized bed reactor. And, you have to minimize those resistances. So, you have to do the hydrodynamics; you have to look at the effect of particle size, gas velocity, and then try to design the fluidized bed reactor.

So, if you integrate this expression from  $C_0$  to  $C_b$  inlet is  $C_0$ . So, you have  $c_b$  divided by  $C_0$  is equal to exponent of minus  $K_f y$  divided by  $u_b$ . So, this is this expression. You have this expression here. So, just integrate  $d C_b$  divided by  $C_b$  is equal to  $K_f$  divided by  $u_b$  minus and  $d y$ . So, integrate it when  $y$  is equal to  $0$ ; concentration is  $C_0$ ; and at any value of  $y$ , concentration reached to  $C_b$ . So, integration of this, which is  $\ln$  of  $C_b$ ; and that can be substituted now in terms of limits. So,  $C_b$  by  $C_0$  is equal to exponent of minus  $K_f y$  upon  $u_b$ . So, this is how do you find out that...

Suppose if I now have a  $C_b$  value, which can be written in terms of  $C_0$   $1 - x$  bar basically, because you can have different residence time for each sized particle. So, some mean conversion of the solid. Same thing in  $C_b$  is also for a given size of particles; mean conversion or mean concentration in the bubble phase. So, one can find out this value or conversion value; and one can correlate that with the height of the fluidized bed reactor. So,  $y$ . And, this is how we proceed for the design. So, one can find out the overall conversion. As I said,  $C_a$  is equal to  $C_a$  naught  $1 - x$ . So,  $1 - x$  is equal

to exponent of minus  $K_f L$  upon  $u_b$ . So,  $y$  is now defined by  $L$ ; where,  $L$  is the height of the fluidized bed.

And, there is always a material balance. So, either you write in terms of height – initial height into  $1 - \epsilon_m$ ; that is, the  $\epsilon_m$  is the packed bed void fraction. So, this is representing  $L_0$  into  $1 - \epsilon_m$  is representing... because  $1 - \epsilon_m$  is representing the fraction of the solid in the bed. So,  $L_0$  into  $1 - \epsilon_m$  is representing mass of the solid. And, that any height it will remain same; mass will not change – catalyst mass. So, that is in the fluidized bed times the bed fraction or void fraction when it is fluidized.

So,  $1 - \epsilon_f$  is again the solid fraction. So, this is simply material balance, which can correlate the initial height of the bed and height when the bed is fluidized. And,  $\epsilon_f$  is the porosity of the fluidized bed. So, one can very easily write, because  $\epsilon_f$  is the...  $1 - \epsilon_f$  means solid fraction. And, that will be related to the bubble – solid in bubbles plus solid in clouds plus solid in emulsion. So, fraction of the solids, which is present in the bed and multiplied by the  $\Delta$ . So,  $\Delta$  is the volume fraction of the bed, which is taken by the bubbles. So, that is the volume of bubble divided by the volume of the bed; that is  $\Delta$ .


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**$f_{total}$  = total fraction of solid in bed**

$$f_b + f_c + f_e = f_{total} = 1 - \epsilon_f$$

$$H_{BFB} = H_f = \frac{W}{\rho_s A} (1 - \epsilon_f)$$

For given  $u_{mf}$ ,  $\epsilon_{mf}$ ,  $u_o$ ,  $\alpha$ , and the effective bubble size in the bed  $d_b$ , this model explains all the properties of the bed-flows, region volumes, interchange rates, and consequently reactor behaviour.



So, this is what the expression –  $f_b$  plus  $f_c$  plus  $f_e$  is total fraction of the solid, which is representing from or which can be correlated with the  $1 - \epsilon_f$ . This is the solid

fraction, because  $\epsilon_f$  is the void fraction in the fluidized bed. And, same thing in terms of the height of a bubbling fluidized bed, which is written in terms of mass of the catalyst divided by density of the solid. This is density times  $A$  times  $1 - \epsilon_f$ . So, simple mass balance basically. You have done this that, how to calculate the height of a bubble fluidized bed; which will relate to the mass of the catalyst in the bed divided by the density of the solid. So, this is basically the volume of the catalyst in the bed.

And, you know volume divided by area of cross section; that will be equal to height. And, since this height is related to the fraction of the solid fraction; so  $1 - \epsilon_f$  representing the fraction of the solid, because actual height is low; but since now, solid is covered in between in the interstitial space of the solid, you have a gas. So, what will happen? The height will increase. So, the total height... If you have a packed bed reactor, the height will be lower. So, if you have a fluidized bed reactor, the height will be increased by what fraction? That will depend what is the volume of the gas in that section. And, this is the volume of the gas, which we are representing in this form. So, either you write a solid balance or you write it in terms of the volume of the gas, which is in the bed between the particles – something like the gas, which is in the pockets between the particles. So, that volume plus the volume of the bed, that is, catalyst volume; that is the total volume; relate it with the height.

So, all these parameters like the minimum fluidized bed velocity, which you do from the experiment; minimum bed porosity –  $\epsilon_f$ ; superficial gas velocity required;  $\alpha$ , which we have defined in terms of the resistance; and effective bubble size  $d_b$  in the bed. So, these are known basically in the model – a property. And, once you know this, then you can very easily define the hydrodynamics, bed-flow, flow regime, interchange rate, that is, mass transfer rate. And then finally, you can correlate it with the height of the bubbling fluidized bed.

So, that is a fluidized bed reactor design. But, there are lot of further complication when you look at the hydrodynamics. You have to study RTD to get the mean conversion. For different sized particles, you have to find out their average length of the stay. And then there may be elutriation; some of the particles may leave the bed. So, all these complications will be there when you look at a fluidized bed reactor design. But, once you have efficient design for better heat controlled when the reaction is highly



exothermic, it is a good type of reactor system, because it has the combination of a mixed flow and a plug flow.

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**Material Balance for Gas and for Solids**


Material balance for the bed materials yields:

$$U_{br} = 0.711(gd_b)^{1/2}$$

(acceleration of gravity =  $9.8\text{m/s}^2$ ) m/s rise velocity of a single bubble in a Bed otherwise at  $u_{mf}$ .

$$U_b = U_o - U_{mf} + U_{br}, \text{m/s}$$

Rise velocity of Bubble in bed




So, I am not going in detail of rest of the things, because this is simply a material balance; and one can write the buoyant force, viscous force, react force – all these, which are read in the particle mechanics or fluid mechanics. So, one can... What I mean to say is that, the bubble rise velocity is a function of the diameter of the bubble. So, one can correlate it; can find out at velocity the bubble is rising. And, the bubble velocity is related to  $u_0$ . So,  $u_0$  minus  $u_{mf}$  is basically the effective velocity, which is required for fluidizing, because up to  $u_{mf}$ , it is packed bed. So, you have to give above  $u_{mf}$  if you want to make it a bubble bed. And then bubbles are rising in the bed. So, actually, the bubble velocity is related to the  $u_0$  minus  $u_{mf}$  plus some bubble rise velocity.

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$$\delta = \frac{\text{bed fraction in bubbles, } m^3 \text{ bubbles}}{m^3 \text{ bed}}$$
$$\delta = \frac{u_0 - u_{mf}}{u_b} = 1 - \frac{u_{br}}{u_b}, \text{ and for } u_b \gg u_{mf}$$

we can use  $\delta = \frac{u_0}{u_b}$



Delta – I told you it is the bed fraction in bubbles. So, volume of the bubbles in bed, that is, gas volume – gas bubbles divided by the volume of the bed – delta. And, delta is related to now... because... What is delta? It is related to the volume of the gas, which is in the interstitial space. So, when it is  $u_{mf}$ , the particles are closed together, packed together. When you have put the gas above  $u_{mf}$ , now, particles are moving up – bubbling in the bed; and in between, you have pockets of the gas. So, that can be correlated with this  $u_0$  and  $u_{mf}$ . So, delta is effectively 0 when it is a packed bed; no gas in that. And, this is  $u_0$  minus  $u_{mf}$  divided by  $u_b$  – bubble velocity. So, one can find out all these parameters and then design a fluidized bed reactor.

So, this is about the reactors, which we were talking in the say multi-phase reactor. So, we were talking about a trickle-bed reactor – very effective reactor in the petroleum refinery. Same thing – the fluidized bed reactor is very important when you have the fluid catalytic cracking; and then design is easy in order to say that, you can regenerate the catalyst although design is not simple; but reactor and regeneration combination is possible in these kind of reactors. Then, there are slurry bubble column reactor, suspension reactor. So, different kind of reactor system can be used for a given catalytic system. So, if one has to identify a process, one has to look at the hydrodynamics; one has to look at the experimental conditions required in order to achieve the high conversion and high productivity; and then need to select a design – good design or good kind of reactor and then design of that reactor.

So, again, very quickly, I will just go to some of the processes, which are very widely used or very important – refinery process or petrochemical process. And, say hydrogen production, which is very important in the fertilizer as well as in the refinery, because the hydrogen consumption, huge amount of hydrogen is consumed in the refinery as well as in the fertilizer. Fertilizer industry – generally for the urea products and they use a large amount of hydrogen.

And similarly, in the case of petroleum refinery, hydro cracking, hydro desulfurization, hydro isomerization. So, a large amount of hydrogen is required. And so hydrogen production becomes very important issue nowadays that, how to enhance and to get it from the renewable sources. That is very important with respect to the current scenario. So, lot of catalysts are being developed and lot of the processes are being developed in order to just develop efficient hydrogen products and methods.

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**Steam reforming reactions**

$$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \overset{\text{CO}_2}{\text{CO}} + 3\text{H}_2; \Delta H_{298}^\circ = +206 \text{ kJ mol}^{-1} \quad (1)$$

$$\text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightleftharpoons n\text{CO} + \left(n + \frac{m}{2}\right)\text{H}_2; \Delta H_{298}^\circ > 0 \text{ kJ mol}^{-1} \quad (2)$$

Simultaneously, the so-called water gas shift reaction produces CO<sub>2</sub> as well:

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2; \Delta H_{298}^\circ = -41 \text{ kJ mol}^{-1} \quad (3)$$

**Typical composition of Natural Gas**

Component	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>n</sub>	CO <sub>2</sub>	N <sub>2</sub>	S
	94.9	3.8	0.2	0.1	0.2	0.8	4 ppm

So, this is one steam reforming process. So, all of you know that, steam reforming – generally, naphtha reforming. Naphtha type of reformers are used for hydrogen production. And, nowadays, natural gas is available in plenty. So, a bi-fuel type or naphtha reformer and the natural gas-based fertilizer plants are also available. So, gas plus naphtha in order to balance the amount of carbon dioxide; that is also being practiced. So, generally, reforming – all of you know you have a methane – natural gas reforming. So, this is a natural gas; basically, I am saying here methane plus water; and it

gives you carbon dioxide –  $\text{CO}_2$  and plus hydrogen. So, basically, the other option is syngas also; where, you have the partial reforming and partial oxidation also sometimes. So, that gives you the syngas also; that can be used for liquid fuel production or alcohol production, and widely being practiced Fischer-Tropsch type of reaction, is used here also.


So, any hydrocarbon again here that, not only this methane natural gas. So, what I said, naphtha is also being used. So,  $\text{C}_n\text{H}_m$ , which may be any combination of paraffin, naphthenes and aromatics; and reacts with some water molecule and gives you carbon monoxide and hydrogen. So, this is a kind of syngas production and which can be reformed. Further this syngas can be converted again by water-gas shift reaction, which is shown here. So, you have a carbon monoxide and water and reacts; you get carbon dioxide and hydrogen. So, the contribution is something like this. If you look at here, this reaction is an endothermic reaction. And, here if you look at, this is an exothermic kind of reaction. So, reforming requires a lot of amount of heat during this process; so endothermic reaction, exothermic.

Or, if you have something like a partial oxidation; if you had little bit oxygen; then it can be a kind of autothermal type of reaction also. So, this is what the trend in the refinery, fertilizer and also in petrochemical industry for hydrogen production. So, the typical composition of natural gas, because it is available in plenty nowadays and transported through the pipeline. So, this side becomes one of the reasonably good source of hydrogen production.

So, roughly, it contains more than 90 percent of methane, which is mainly methane. But, besides methane... So, it can be the wet gas something like that. So, it may have the heavier fractions like ethylene, propylene, some  $\text{C}_4$  plus. So, these are known as the heavier fractions on natural gas liquids. So, they may also be present. And then there may be some carbon dioxide and sulfur. This is the problem in fact in natural gas when you have to... We have to remove the sulfur before treatment in order to avoid the deactivation of the catalyst.

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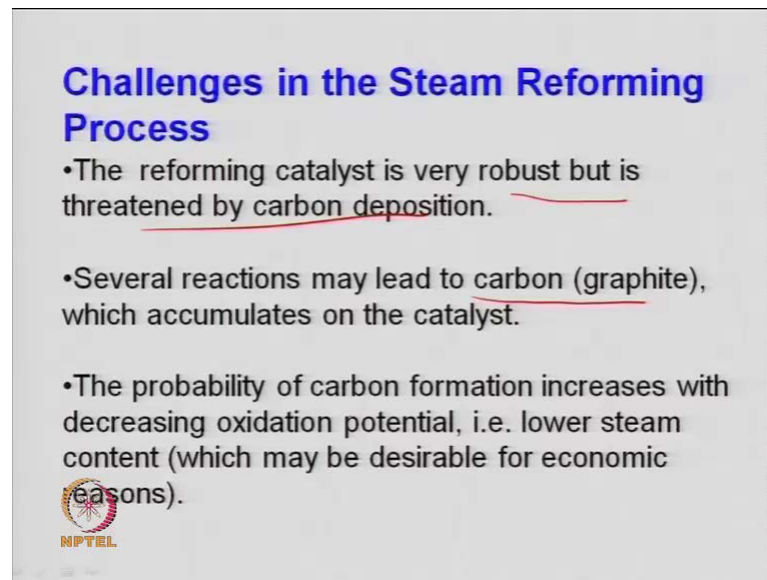
- Transition metals such as Pd, Pt, Ru, Rh, and Ir can be used as catalysts for steam reforming, but **nickel-based catalysts** are, economically, the most feasible.
- More reactive metals such as **iron and cobalt** are in principle active but they oxidize easily under process conditions.



The image shows a slide with two bullet points. The first bullet point discusses transition metals (Pd, Pt, Ru, Rh, Ir) as catalysts for steam reforming, noting that nickel-based catalysts are the most economically feasible. The second bullet point mentions more reactive metals (iron and cobalt) as being active in principle but prone to oxidation under process conditions. The NPTEL logo is located at the bottom left of the slide.


So, now, the most common catalyst used in the reforming is nickel-based catalyst. So, this is what the most common catalyst, because it is economical and available also. But, this palladium, platinum, ruthenium, rhodium, iridium – they can also be used. And, they may be more effective in fact. Even a low concentration of these materials may be good for catalytic activity. And, that is what is being looked nowadays in order to have the highly efficient reactor. Or, if you want to look at a small size reactor, you need a more active catalyst; rather size can or the reactor can be reduced and a kind of micro-reformers. That is the concept, where we need from large scale unit, we want to go in a small or channel type reactors. So, that is one R and D area, where one needs to look at the new kind of reactor design, new kind of novel catalyst, where the system can be smaller and smaller. So, iron and cobalt have also been tested. They are also very active, but they can oxidize easily, because lot of water is present. So, that may not be good for the reforming reaction.

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**Challenges in the Steam Reforming Process**

- The reforming catalyst is very robust but is threatened by carbon deposition.
- Several reactions may lead to carbon (graphite), which accumulates on the catalyst.
- The probability of carbon formation increases with decreasing oxidation potential, i.e. lower steam content (which may be desirable for economic reasons).



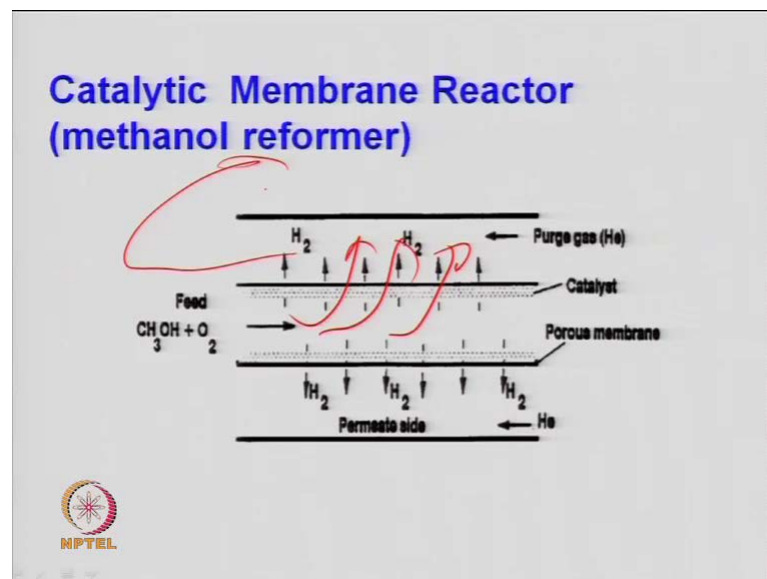
There are lot of challenges in the steam reforming. So, process is available in terms of the reforming as far as the technology known. But, as I said that, nowadays, the trend is different in terms of the E factor, atom efficiency, and highly efficient catalyst and novel reactor design. So, new kind of reactor design is required or new kind of reactors are to be fabricated or designed and order to produce the efficient hydrogen with low carbon dioxide or hydrocarbon monoxide if you have just the hydrogen production. So, the reforming catalyst is very robust, but lot of carbon deposits on the catalyst. So, the deactivation of catalyst is an issue. So, life of the catalyst may be just 1 year or may be up to 3 years.

So, catalysts like say ((Refer Time: 39:26)) lot of licenses are available UOP; they have provided the catalyst and the reactor design for this reforming reaction. But, still one needs to look at the novel approach or new kind of catalyst in order to reduce the deactivation of the catalyst, because every three years, the catalyst is to be replaced after every 3 years. So, it means the solid material, which is now as a waste now the catalyst; that is to be dumped somewhere. So, disposal of these kind of solid waste is again an issue. So, it is a problem. So, we need to find out a different catalyst either a more active catalyst or look at how to reuse the catalyst into the process. So, this is again an issue, where the R and D is required. So, several reactions like this secondary reaction, which happened – they may tend to form carbon. So, lot of secondary reactions also take place

during this. So, it accumulates on the surface of the catalyst. So, life of the catalyst decrease.

So, how to reduce the carbon formation? So, that is again important to give a thought. Then... So, it depends like the probability of carbon formation; this increase with decreasing oxidation potential. So, if you have a lower oxygen steam or oxygen content; so the carbon formation may be more and more. But, again the larger amount of steam is generally used, because lower amount of steam should be used theoretically; but otherwise, you are increasing the loading on the reactor. So, higher the steam, the co-formation will be low, but how much? That is important. So, one needs to check the optimum concentration or steam to hydrocarbon ratio for the process. But, very high amount of steam cannot be used, because it unnecessarily dilutes the reactor and the reactor sizing will increase. So, one needs to check that.

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So, new trends are looked into. So, one thing is that, thermodynamics. So, you know that, when the methane produces or methane reforms or any alcohol reforms or partially oxidize; so we get hydrogen, carbon monoxide, carbon dioxide, and maybe some other unwanted product also. So, there is some kind of equilibrium conversion during the process. So, if somehow, this CO removal system like say for the fuel cell application, where the hydrogen is required; pure hydrogen is required, because the electrodes, which are generally used in the fuel cell – they have the platinum or palladium type electrodes.

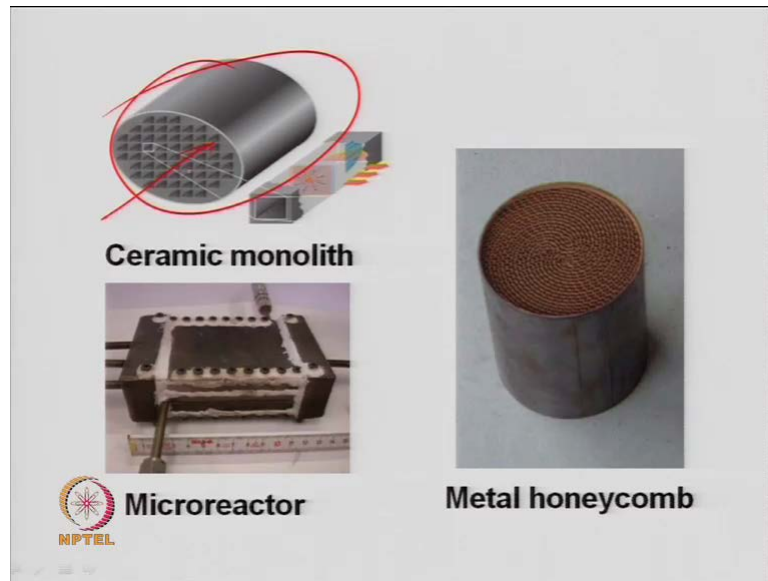
So, small concentration of this carbon monoxide may poison the catalyst. So, it means something is to be done. So, in order to increase the conversion, increase the productivity and also increase the life of the catalyst. So, new concept may be something like this here instead of a packed bed reactor.

So, presently, this reforming is done in the large number of tubes; they are placed there or a just single reactor. So, it is very difficult to dissipate the heat or you need a good kind of heat exchanger. That is a problem. Simultaneously, deactivation of catalyst, is the problem. But, if you have something like this, where you have suppose a methanol reformer or methanol partial oxidation, you are generating the hydrogen. So, if you have a porous membrane, a ceramic type membrane – porous material; so hydrogen will diffuse into this like this. But, larger molecule cannot diffuse. Like  $\text{CO}_2$  – they will remain here; one can recycle it also. So, now you get pure hydrogen here. You purge this gas and take this hydrogen into fuel cell unit and you can have the pure hydrogen required for the fuel cell.

And, here you have disturbed the equilibrium. So, more and more conversion will take place. So, these kind of reactors are nowadays being considered or what is... This is a kind of just an example of methanol reformer; so catalytic membrane reactor. So, membrane type of reactors can be one of the option in the future for the hydrogen production for fuel cell application especially. And then these are the kind of ceramic monoliths – a channel type reactor; where, in this reforming reaction say effectiveness factor, I told the diffusion length. So, that is... which is related to the size of the particles and the resistance, non-porous materials or micro porous materials. So, the effectiveness factor is very low – 1.001. So, it means the actual rate is very low. When rate is very low, the conversion will be very low or you need a large size reactor. So, reformer is one kind, where you have a height – 10 to 15 meters – something like that.

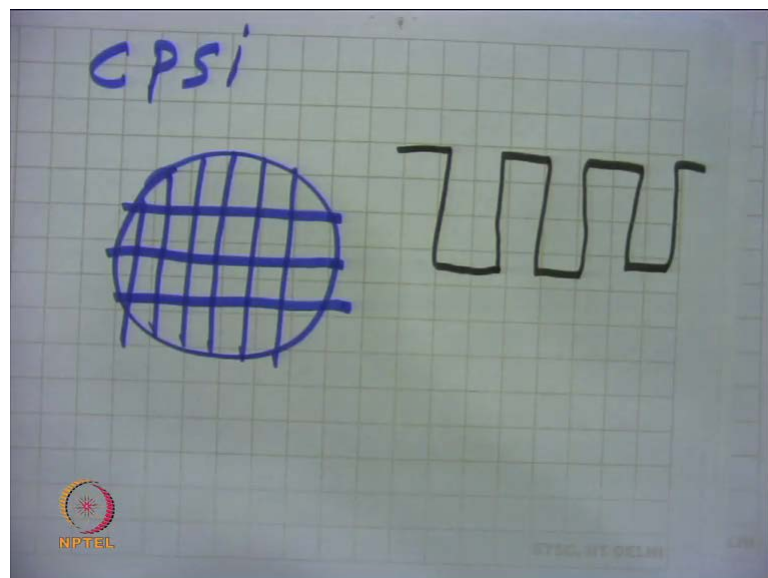


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So, if you need smaller units; so you have to look at those things that, prepare the catalyst in such a way like washcoating of this; where, the diffusion length is very small. So, the resistance for diffusion will be reduced. And, this is what a kind of monolith here; which is shown in the process; it is a kind of channel type reactor. And this is what the actual if you look at here – the model, where you have the small – these are channels here in this reactor... And, this is known as the cells per square inch. So, it can be 200; it can be 100.

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So, this is just like a grid here; if you look at this top section; so it will look like this – just like the sieve like this. So, you have the square openings like this. So, number of... Just like in a mesh you define; so number of cells per square inch – CPSI we call it – cells per square inch. So, this may be 200; this may be 400. If it is 400 means it is still a narrower channel. And, these are known as micro channels. And, in between, we can washcoat the catalyst. So, now, the diffusion length is very small. And, each channel is acting, because it has now large surface area per unit volume. So, this structure. So, it has the channels; it has the openings with different size. So, it will have large surface area per unit volume. So, this is known as a quadrature structure – monolith – a type of structure.


And, this is what here it is shown – a ceramic monolith, where you can see the larger openings here. So, through this, the reaction or the reactant species pass; they diffuse also axially and radially; and then they transfer into the reactor. So, large surface area per unit volume. So, for your automotive exhaust catalyst also, this kind of a structure is used. So, at the exhaust, we put this kind of material, which is coated with the platinum or novel metal. And then it gets all these NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>x</sub>. So, three way type of catalysts; they are reduction, oxidation – all these type of monoliths catalyst are available. And these are now being considered for the reforming.

The same thing is that, just like in a plate and frame heat exchanger; so this is a kind of the system. So, you have something where the fluid goes in path, follows a zigzag path like this. So, this is a channel like this. It will go like this. So, again, you have a large surface area per unit volume and just like in a plate and frames. So, something goes from this side and then comes down like this; flows on this channels – small channels of 0.1 micron. So, small depth channels – they are available. And, this is known as a micro reactor. And, nowadays, widely being considered for the reaction like reforming. So, these are some... Again, there is honeycomb type of structure – metal honeycomb. So, again a curved path is being used here. So, these are some new concepts, which are generally considered especially when the large surface area per unit volume is desired. Again you need to... When you look at a new kind of design, you need to look at the transport properties in that.

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The physical and chemical effects which occur are:

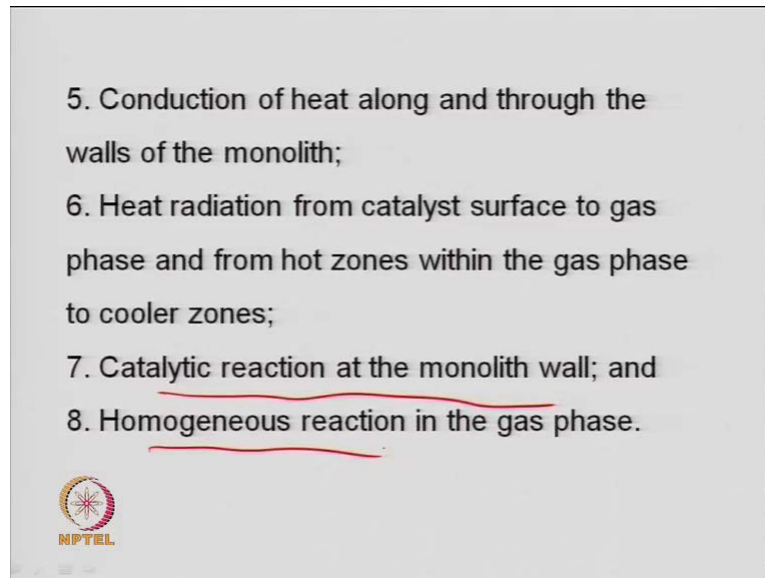
1. Convective flow of reactants and products in the direction of flow through a channel;
2. Diffusion and dispersion of components in both axial and radial directions;
3. Momentum changes resulting from viscous flow;
4. Convective heat transfer in the direction of flow;



So, here again you will have different kinds of transport properties; you need to look at the mass transfer; you need to look at the heat transfer, convective mass transfer, diffusion transfer. So, very quickly, just the... because I am not going to talk on the design of these kind of reactors; but the step – if you look at in terms of transport properties; you have a convective flow of reactant, because of the velocity terms  $C A$  into  $V$ , what we are talking.

So, convective flow of reactants and products in the direction of flow through the channel. This is the convective. Then, second is the diffusion and dispersion of component in axial and radial direction. So, similar steps, what you have seen there; in a pellet also, the approach is similar; there it is a pore; now, we have a channels here in this. Then, momentum changes because of the pressure variation. This is also very important here. You need to check that; transport, viscosity, and all these behavior – pressure drop; convective heat transfer in the direction of flow. So, all these things are required to look at.

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Then, conduction of heat, because it is a metallic monolith; so there will be heat transfer through the conduction also. Then, radiation, because high temperature. So, there may be a radiation also. Then, there is a chemical reaction also, because it is a monolith wall; on that, you have a catalyst. So, there will be a catalytic reaction. And, there are channels to their lot of pores just like pore space of a catalyst – void space. And, in the void space, you do not have any catalyst. So, there will be the thermal reaction also. So, homogeneous reaction. So, you have to look at all these steps when you look at a new kind of monolith design or a kind of honeycomb reactor design. So, these needs to be checked. Similarly... So, the reactors, which are generally used in the refinery, petrochemical; so they are plug flow or mix flow.

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### Reactor type in Petroleum Refinery

- Reactor may be a plug flow or mixed flow or batch flow reactor or other.
- Contacting pattern of reaction will be known.
- In case of expensive catalyst and high heat transfer rate required, mixed flow (fluidized bed) reactor are used.
- For high mass transfer plug flow (packed bed) reactor will be used.



So, I have already talked on that; a bubble column reactor, slurry bubble column reactor. So, these kind of reactors, which may be a combination of a plug flow reactor or a CSTR type reactor. So, contacting patterns should be known; that is very important we have discussed. And, suppose the catalyst is very expensive; so heat transfer or removal of heat is important; otherwise, the catalyst life will diminish. So, you prefer a fluidized bed reactor, because it is easy to dissipate heat. Then, mass transfer is again an issue. So, for high mass transfer, you prefer a plug flow reactor; that high velocity at high ((Refer Time: 49:49)) So, all these kind of reactors are used in the refinery and petrochemical reaction.

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**Refinery and Petrochemicals : Alkylation Reaction**

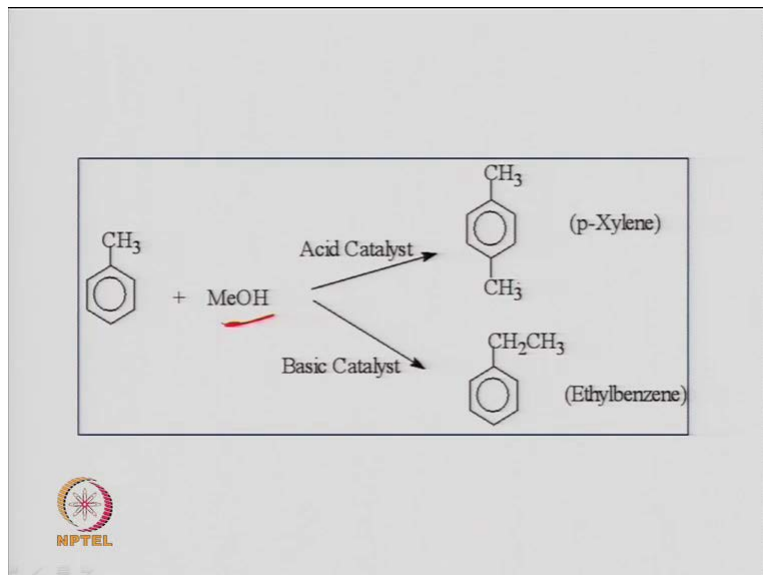
- Alkylation is the introduction of an alkyl group into a molecule.
- Alkylation is catalyzed by **acidic or basic** catalysts.
- Acid catalysts are used mainly in aromatics alkylation at ring.
- Basic catalysts are used in alkylation at side-chain.



The important reaction if you look at the refinery and petrochemical; so there are... So, alkylation, isomerization, cracking, hydro cracking and dewaxing. So, all these kind of reactions are taking place in refinery. And, in the petrochemical reaction also, you have the polymerization reaction for manufacturing the high density polyethylene, low density polyethylene, and different kind of say polypropylene, and then styrene-butadiene rubber. So, lot of... If you look at the refinery, petrochemical, fertilizer; large amount of catalysts are being practiced; and the type of reactor design will depend on the kinetics; it will depend on the hydrodynamics, heat transfer, exothermicity of the or endothermicity of the reaction. So, very quickly, just the alkylation say if you look at; a very important reaction; where you are adding an alkyl group to a molecule. And, this is generally catalysed by either acid catalyst or basic catalyst. So, when you have acid catalyst, they

mainly do the aromatic alkylation in the ring. So, ring is alkylated. And, when you have basic catalyst, then it just prefer the side chain of that reaction.

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So, if you look at that just alkylation; so you have just say a component like this is the toluene. So, a ring compound and you can have any compound here ethylbenzene also. So, it reacts with the methanol. So, you have acid catalyst. So, it makes a paraxylene here. And, if you have a basic catalyst, it makes the ethyl benzene. So, you can see that, depending upon the catalyst – type of catalyst here, concentration of the active side, the product distribution changes. So, this is a kind of alkylation reaction. So, depending upon the acid catalyst or basic catalyst, the product distribution will be different.

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## ALKYLATION REACTIONS

- Typical acid catalysts: Friedel-Crafts catalysts: HF, H<sub>2</sub>SO<sub>4</sub>, HCl-AlCl<sub>3</sub> and (Zeolites)
- Typical alkylating agents: Olefins, alcohols, ethers, alkyl halides, dialkyl carbonates (DMC), etc






So, most of the catalysts, which are acid catalysts used in the case of alkylation; so alkylated gasoline is very important product in the refinery. So, alkylated gasoline, which has higher octane number. So, this is generally HF alkylation I was discussing earlier. So, hydrofluoric acid is used, which is very strong acid. So, nowadays, trend is that, how to replace this hydrofluoric acid or sulfuric acid, because for polymer gasoline again, isobutene ((Refer Time: 52:08)) alkene and alkane can react and you can have higher isooctane type. So, this is again sulfuric acid is used by the catalyst.

So, all these are highly acidic. So, different kind of material of construction is desired. So, new trend is that, use the catalyst something like a solid catalyst. So, although not well-documented or not very popularly commercialized, but new trend is that, one needs to look at the solid catalyst for the process, because they are easy to handle and material of construction is not an issue for them. So, they say these are the catalysts, which are being used. So, typically the alkylating agents or reactants are olefins, alcohols, ethers, alkyl halides, dialkyl carbonates – all these are used for the alkylation.

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**Solid-acid based alkylation reactions in commercial practice**

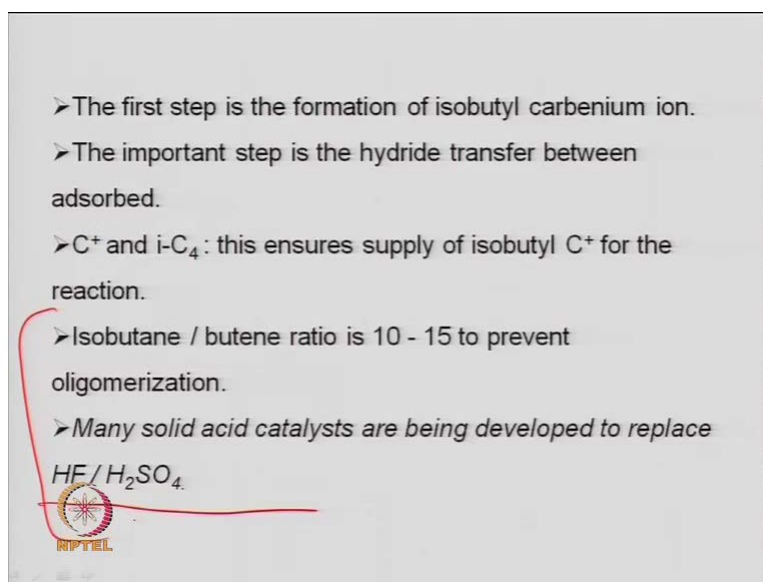
Reactants	Product	Catalyst	Status
Benzene + ethylene	Ethylbenzene	Zeolite (ZSM-5)	Commercial
Toluene + methanol	p- Xylene	ZSM-5 (proprietary)	(Commercial)
Benzene + propylene	Cumene	Solid phosphoric acid / zeolite	Commercial
Benzene + C <sub>10</sub> -C <sub>13</sub> olefins	LAB	Proprietary	Commercial



So, as I said that, it is a very important reaction in the industry. So, benzene and ethylene – the product is ethylbenzene alkylation. ZSM-5 is used as a catalyst; and process is something like a commercial process here. Toluene and methanol – it gives you paraxylene. So, again ZSM-5 type catalysts are used here. Benzene and propylene reacts; isopropyl benzene is the product cumene. Solid phosphoric acid and zeolites are used as

a catalyst. Same thing here – benzene plus C10 to C13 olefins – we get linear alkyl benzene used for making the detergent. And, they have again the proprietary catalyst. So, lot of R and D's again being done here in these areas to develop new catalysts and new process for the reactor – commercialization of the process.

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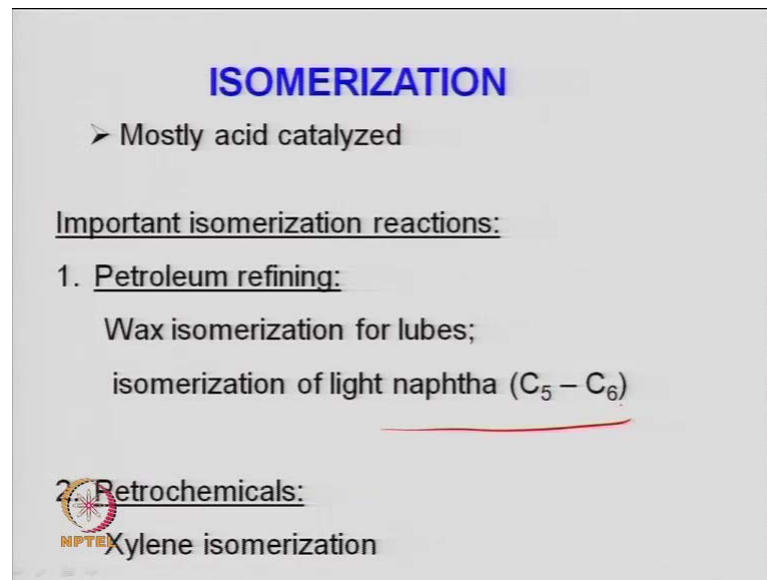


- The first step is the formation of isobutyl carbenium ion.
- The important step is the hydride transfer between adsorbed.
- $C^+$  and  $i-C_4$ : this ensures supply of isobutyl  $C^+$  for the reaction.
- Isobutane / butene ratio is 10 - 15 to prevent oligomerization.
- *Many solid acid catalysts are being developed to replace  $HF / H_2SO_4$ .*

NIPTEL

So, this is just a different kind of isobutane, isobutene, butane, isobutane – these react generally for making the isooctane, which is alkylated gasoline or something a polymerization – polymer gasoline. So, these are the catalyst generally used in the refinery also to make the isooctane or larger molecular weight compound, which can be added to the gasoline. So, these have higher octane number.

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**ISOMERIZATION**

- Mostly acid catalyzed

Important isomerization reactions:

1. Petroleum refining:
  - Wax isomerization for lubes;
  - isomerization of light naphtha ( $C_5 - C_6$ )
2. Retrochemicals:
  - Xylene isomerization

Similarly, isomerization is also very important process. So, hydro isomerization, isomerization. So, isoparaffins are made in this. Normal paraffins suppose – they are converted to isoparaffin, because it has higher octane number. So, this is again an important process in the refinery. So, wax isomerization for lube also – this is done, because the pour point... that is, if it is a cold country; the material – if it is wax, it gets solidified. So, it will be very difficult to flow. So, flowability will be low; flow index is low. So, one needs to convert this wax material right. So, isomerization is done; which has now... in order to reduce the pour point. So, that is important here. So, light naphtha isomerization to improve the octane number. In petrochemical, the paraxylene is important. So, isomerization is done to get more and more paraxylene.


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Catalysts are usually bifunctional:

- Metal/support type

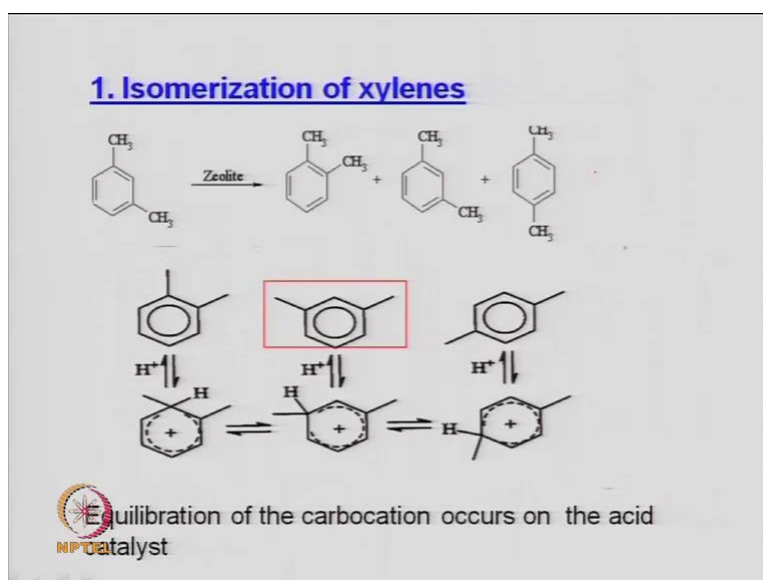
Typical examples:

- Pt-SAPO-11 for wax isomerization
- Pt-Mordenite /acidic-alumina for C<sub>5</sub> – C<sub>6</sub> hydrocarbons
- Pt-ZSM-5 /mordenite/(silica)-alumina for Xylene isomerization



So, again here the catalysts are platinum, which is a metal part on support, which is a kind of silica-alumina phosphate, what I was talking during the zeolite type catalyst. And, something – platinum modernite catalyst, acidic alumina catalyst – these are used in this reaction. Platinum ZSM-5 catalyst on modernite silica. So, all these catalysts are used for the process.

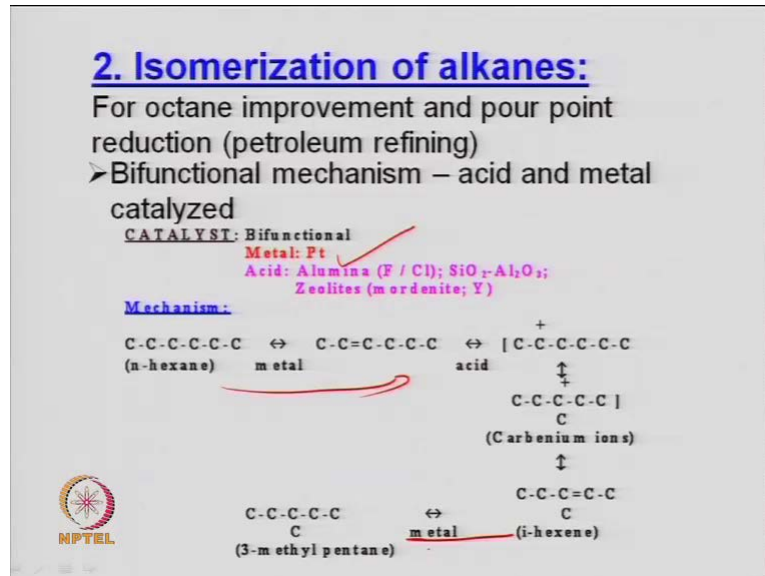
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So, these are some reactions, which are generally shown in the isomerization. And, one can look at and depending upon the catalyst, which is used, one can have the process.

And, that is in terms of the concentration of ortho-meta paraxylene. So, these are a kind of selective. So, shape selective zeolite materials are preferred here.

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So, same thing for isomerization of alkanes. So, we need to look at a higher octane; so in order to produce more and more high octane gasoline. So, here platinum base, which is a bifunctional type catalyst now. So, platinum includes the hydrogenation activity and dehydrogenation activity. Second is the acid function, which is from the support side. So, it promotes the cracking activity like this – hydrocracking activity. So, alumina silica, silica alumina, zeolite – they are used. So, it is a bifunctional, which has the acid and metal catalysts. So, you can see here some reactions are promoted on acid sides and some reactions are promoted on the metal side here. So, depending upon the requirement, a combination of the two catalysts can be taken in this.

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**Cracking reactions**

**Catalytic cracking mechanism – occurs via carbocations**


**A. Carbenium ions are produced mainly by:**

1) Addition of  $H^+$  to an olefin:  
 $CH_3-CH_2-CH_2-CH=CH_2 + H^+ \rightarrow CH_3-CH_2-CH_2-CH^+-CH_3$

2) Addition of  $H^+$  to a paraffin and subsequent loss of  $H_2$ :  
 $R-CH_2-CH_2-CH_3 + H^+ \rightarrow R-CH_2-CH_3^+-CH_3$  (carbonium ion)  
 $\rightarrow R-CH_3-CH^+-CH_3 + H_2$

**B. Beta-fission of the carbenium ion produces the products:**

$R-CH_2-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-CH^+-CH_3 \rightarrow R-CH_2-CH_2^+ + CH_2=CH-CH_3$   
(or)  
 $R-CH=CH_2 + CH_2^+-CH-CH_3$



Similarly, cracking reaction; and where the again the larger molecular weight compounds are cracked into smaller. And, again zeolite or silica alumina type catalysts are used in this process.

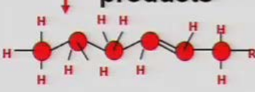
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**How to Maximize Propylene Yield?**

**Feed**

**Primary Cracking**

**Highly olefinic products**




**Gasoline olefin**

**Cracking by ZSM-5**

Favored by:

- Low pressure,
- High temperature
- Fast diffusion of primary cracking products from the catalyst

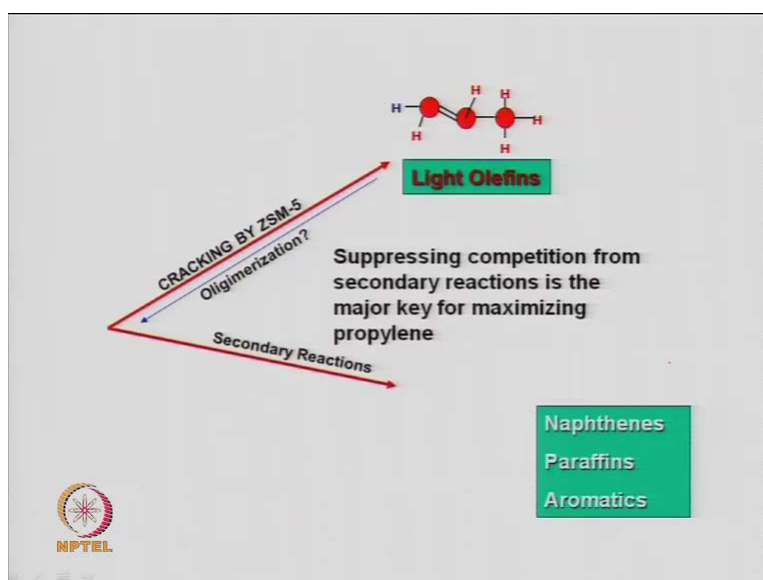


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Propylene is nowadays in the refinery and petrochemical. The high yield of propylene is desired. So, how to improve the propylene unit? So, selective catalysts are required; which can maximize the olefins, especially the propylene. And, that is generally for the petrochemical purpose. So, when you have a pyrolysis type process, where the

hydrocarbon is cracked; and you get more and more olefins in that. When you have a refinery process, you do the cracking; but intention is to get the gasoline range of hydrocarbon. So, for cracking purpose, we use generally in the refinery, a zeolite base material; just what I said FCC gasoline. But, in the case of pyrolysis process, which is for the petrochemical industry, we take something like silica-alumina type catalyst – a different kind of catalyst system; calcium-aluminate type catalyst, magnesium aluminate. So, they enhance these olefin production. So, that is again a challenge that, how to enhance the propylene yield during the operation. So, that is the cracking by ZSM-5. So, operating conditions, temperature, pressure – everything is very important; residence time; so in order to avoid the coke formation. And, that is what I told FCC or fluid catalytic cracking is very important in this case.

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So, cracking – if you have zeolite materials, you get a different kind of combinations here. And, if you have... you do not control that; then secondary reactions also take place. And, that will give you naphthenes, paraffins, aromatics. That is what I told you gasoline range of hydrocarbon. So, oligomerization – that is olefins forms and they oligomerize. And, you will have the larger molecular weight compound. And, that is what the polymer gasoline during the reforming reaction. So, different combinations; and one needs to control for maximization of propylene. The secondary reactions are to be suppressed. And, a new catalyst or a novel catalyst system is to be designed. So, I stop here and... So, thank you for your attention.