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Lecture - 31 Illustrative Example: Temperature Effects on rate & Euillibria

Today, we looking at some practice problems concerned with non cathletic gas solid reactions.

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First one is on fluidized bed quickly draw, what fluidized bed looks like.

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So, let us look at example using zinc sulphide plus oxygen giving you zincoxide plus sulphur dioxide. The context is that zinc sulphide is available in the polar region of this country and fluid bed is the contacting that is used for making molten I mean metal zinc by first roasting of zinc sulphide. Now, why is that they use fluidized bed? Why they would use a fluidized bed? The reason is this reaction is hexothermic and generates a lot of heat and you can get that heat out by putting a coil in which you put water through and steam out. So, it is 1 way by which you can recover heat of the reaction quite effectively. So, this is 1 of the major reasons why people would use fluidized bed now, just put it in the context. Let me do a small calculation as to what the numbers look like I will do a small calculation.

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Let us say you have sulphur plus oxide giving you sulphur dioxide. Let us look at a plant producing 1000 tons per day of sulphur dioxide which means roughly I am putting just some rough numbers 500 tons per day of sulphur is what is consumed roughly we all agree? Now, the amount of steam that can be produced from 500 tons of sulphur that is I mean if you look at the heat of combusting and so on. You will find that you can produce about 2000 tons of steam. On other words for every ton of sulphur that you burnt about 4 tons of steam can be produced therefore, a 1000 tons per day sulphur dioxide plant will produce about 2000 tons of steam. Now, if you put this steam through a turbine and produce electricity about 0.25 megawatt hour per ton of steam is what you will generally get 0.25 mega watt hour so, 0.25 megawatt hour from 2000 tons of steam.

So, what is the total amount of power that you can produce is about 500 megawatt hour per day correct. Or if you talk about 25 hours in a day just for calculation sake this is about 20 megawatt hour of electricity. What can be produced in a 1000 tons per day sulphur dioxide plant and this is what they do also this is what is done. Now, what the fluid bed becomes quite effective, because the heat transuca efficient here is typically about 200 kilo calories per meter square per hour degree c fairly large heat transuca efficient. That is 1 of the reasons why fluid beds are preferred particularly if you want to recover heat from the chemical reaction or if you want to provide heat to a chemical reaction. Then also fluid bed becomes very useful because heat transuca efficient are quite good it is in that context this particular problem is has been taken.

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So, let us look at this problem the problem says you have a fluid bed I will draw it in the form of STED tank easier too you have gas coming in and then solids coming in. So, you have solids I will draw it from here. So, the gas and our reaction is a gas plus B solid gives you R gas plus s solid. What it says is that this reaction is under reaction control. And it also says that the time required for complete consumption is 1 hour. And what else does it says and you have fluid bed in which solids are fed at 1 ton per hour. And then the solids are taken out through a this front solids are fed this is I will put this solids feet here solids 1 ton per hour. The question is find the weight of solids in the reactive gas and solids are in mixed flow.

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Gas and solids are in mixed flow means what if this is x a is the conversion here and this is the solids coming in x B and x b. And x a are related by their psychometry which you have studied already it is a mixed flow that is important point. How do you do this problem? Solids are going in solids are coming out gas is going in gas is coming out and it says he wants 90 percent gas conversion this should be 0.9 how do we do this problem?

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So, do this first let us recognize that the solid these solids that are coming in it reacts by the shrinking core model something that we have learnt already. And the shrinking core model under reaction control that we have learnt already. It says what d by dt of nb is a single particle I am not talking about fluid bed. Now, is a single particle reacting this reacts as per some in this particular case it is some minus of ks times C A g and it does not say it is irreversible. So, and then a psychometric coefficient is 1 so that also is ks times C A g and what is the surface area of interest? If it is reaction control we said it should be 4 pi R c square is it this is something that we have said before. And we are illustrating what we know already the left hand side we said that d by dt of 4 by 3 pie R c cube times row b. This is what and this is minus of ks C A g times 4 pie R c square is this alright now this we are integrated and then expressed we have done it in class. So, we do not do it again so we have integrated this.

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And finally, we got a result something like this just state the result rc by R equal to t by tough R a tough R is given as row B times R divided by ks times C A g and psychometric factor in this case is 1 is it alright? Now, let us look at the problem now problem says the time for complete consumption of the particle with concentration of gas with ca 0 is 1 hour the time for complete consumption of the particle at ca 0. If it is 1 hour what happens in our fluid bed? What is the concentration of gas in contact with the solid? In the fluid bed we have done the experiment the data given is that the concentration of gas is going in. It is ca 0 the data given is that if it is at ca 0 the time for

complete consumption is 1 hour it is undergoing 90 percent reaction. So, what is coming out what is the concentration of gas coming out? It will be 0.1 ca 0. So, this is 0.1 c a 0 so if the gas is coming out from 0.1 c a 0 what is the time for complete consumption? If the gas concentration is 0.1 c a 0 in contact with the solid if it is ca 0 it is 1 hour. If it is 0.1 c a 0 what time for complete consumption is 10 hours correct is it with all of us therefore, tau are at 0.1 ca 0 is 10 hours do you agree with this all of us?

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Now, the question in front of this is we have the solids it is reacting as per shrinking core model where the R t d of the system is given by the R t d of stirred tank ((Refer Time: 11:01). The average conversion from a reactor where the R t d specified by the given 0 to infinity and we said we integrate this 0 to tau tau to infinity we have done that So, we can integrate this 0 to tau of 1 minus x B E t of dt plus tau to infinity 1 minus x B E t of d t we said this term disappears. Because 1 minus x B is identically 0 in the range of tau to infinity the reason is the time is greater than tau the particle reacts completely that is why x B is 1. Therefore, 1 minus 1 is 0 therefore, this term disappears. So, you only have to integrate 1 minus x B E t of dt given when what is the value of 1 minus x B. Let me write it down here from here we get R c by R is 1 minus t by tau R this is 1 minus x B is it right is what 1 minus x B power of 1 by 3 is it. So, 1 minus x B is equal to 1 minus t by tau R power of 3 and E function for stirred tank is this is alright this is. So, this is the answer we are

looking for is it alright. Now, can you integrate this can this be integrated can right hand side integrated or not?

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Let me just expand this and see whether it is looks or it looks complicated let me expand this minus t by tau R minus 3 plus 3 t by tau R minus whole cube alright. So, it is 1 by t bar E to the power of t by t bar of dt integral 0 to tau tau R actually is it. This can be done by all of us difficult complicated take too long it may take little while. So, save some time you can do this at home it simplifies like this just put this final form we can do it ideally it is not it is difficulty do this home we just get this. So, where alpha is tau R by t R alpha is tau R by t R. So, what is given problem specifies this we need 90 percent of solid what 90 percent of solid needs to be converted. So, what is x B 0.9 so x B given as 0.9 is equal to thrice alpha minus 6 alpha square plus 6 alpha cube minus 6 E to the power minus alpha by alpha cube. Can we solve this? The way to solve this take some values take some values 3 or 4 values all they are required to get a answer 3 or 4 numbers we take let us do some calculation.

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Let us say alpha equal to 10 quickly. So, what is the right hand side? I will just writing it down you tell me whether I write correctly or not alpha equal to 10 ((Refer Time: 15:54)). So, what is the value right hand side? 0.24 do we all get this 0.24. So, alpha equal to 10 is the not the answer let us try alpha equal to 5 3 by 5 minus 6 by 25 plus 6 by 1 25 minus 6 E to the power minus 5 by 1 25 is it all right? what is it now, so, right hand side is 0 point we all get this is with everyone even it is no good alpha equal to 5 also not a good answer.

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Let us try what? alpha equal to 1 alpha is 1 3 by alpha so RHS 3 by alpha minus 6 by 3 by 1 simple 6 by 1 plus 6 by 1 minus 6 E to the power minus of 1 by 1. So, what is it become? Point RHS is equal to 0.7 nine I have made some mistakes we are closer So, shall we now try 0 point five; 0.5 is point 8 9 we almost got it good So, it is 3 by alpha sorry alpha is 0.5 and there is 6 by 0.25 plus 6 divided by 0.1 2 5 minus 6 E to the power of minus 0.5 divided by 0.125. So, that according to my friend is 0.89 so this is about this is RHS so LHS is 0.9. So, our answer is probably around 0.5.

Student: ((Refer Time: 18:07))

So, 0.4 is the answer is not it so alpha is equal to 0.4 my friend says x B becomes 0.9. I think you can directly solve this is very good then let us go with alpha equal to 0.4. Because it is neat number now, I ask you what is the hold up of solids in the fluid bed? Alpha is 0.4 alpha is 0.4 what is the hold up?

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Now, the question is question says find the weights of solids in the reactor weights of solids means what hold up of solids. So, W divided by F s is equal to t bar yes or no? And alpha equal to tau by t bar now do we know alpha? It is 0.4 do we know tau? What is it? What is tau? It is 10 hours why it is 10 hours? Because the gas is in contact with the gas of a concentration which is only 10 percent of the data that is given to us that is why tau is not 10 hours, but it is 10 hours. So, tau is 10 divided by t bar so t bar is how much? 10 divided by 0.4 that is equal to 25 hours now what is F s? It says treating at the rate of

1 ton per hour correct. So, F s is 1 ton per hour therefore, W divided by 1 equal to 25 therefore, W equal to 25 tons. So, the hold up of solids is 25 tons is this clear? What we are trying to get across here is in gas solid reaction single pen ((refer time: 19:57)) experiments we do experiments with a given concentration of gas in the equipment. The actual concentration is very different from in which you are done in your experiments you must correct. The time required for complete consumption by appropriately accounting for the gas concentration which is responsible for the reaction.

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Alright we go to the next question.

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Here we have a rotary kiln in the hand out I give you that is read as l n of beta minus x a by beta is equal to minus tau g times of alpha here we have rotary kiln. So, we have solids gas this is gas; this is solids and the products are coming out. The rotary kiln is every popular device particularly in the lime calcinations. Lime calcination will use probably 15 percent of the carbondioxide that goes into the atmosphere comes from lime calcination about 25 tons of the carbon dioxide throughout into the atmosphere. In that 15 percent comes from lime klin it is not a small quantity now, why rotary kiln for lime calcination why rotary kiln for lime calcinations? Why rotary kiln for soda ash manufacture? If you go to factory making soda ash you will see rotary kiln. How do you supply the heat to rotary kiln? In rotary kiln the heat that is required is supplied along with the raw material.

For example, you go to lime kiln they will add lime and also coal as the coal burns. The heat of the reaction is used for the decomposition the take care is that whatever you add to the raw material that does not add or benefits to the final product example. Coal combustion is the part of the final product itself it does not affect the quality of the final product. So, in rotary kiln you generally put your fuel so along with the raw material. It is not very easy to provide heat from the walls of the rotary skill or it is rotating is very convenient it is nicely insulated. We do not lose too much of heat, but all the heat of the combustion is added along with the raw material. So, we have c a C o 3 plus heat giving

you C o plus C o 2, but in this case that is not a problem that a gas plus B solid equal to c gas plus d gas. So, it is not quite not similar to line calcinations can we think of any other example of process industry (Refer Time: 24.00) where gas and solid react to give you gas and solid. As an example zinc sulphide to an zinc oxide zinc sulphide to zinc oxide do not use rotary kiln why zinc sulphide to zinc oxide?

Rotary kiln is not common if you go in Udaipur it is an fluid bed quality of product no in zinc sulphide combustion or rusty will gives you lot of heat. So, there is no need to provide external heat source so that is why indeed what we do zinc sulphide to zinc oxide rusty. That is why rotary kiln are not suitable for heat recovery suitable for heat recovery rotary kiln are very good for (Ref time 25.00) very large throughputs large throughputs are soda hash for example, large throughputs are very useful. What is closest example for a gas plus B solid giving you c gas plus d gas what is the closest we think off in process industry cement? What they will do in cement industry? What happens there we have lime and we have coal and all the fluxes actual the clinker forms inside the kiln what is the product gas is C o 2? What is the feed gas is air? Air burns that is required for the cement take place very good example of cement manufacture is an excellent example for the reaction.

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Now, it is says the reaction says that it is under shrinking coal under external diffusion control.

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Now, how do we justify in cement manufacture? How do we justify in external diffusion control? The thing is justiful assumption cement manufacture ((Refer Time: 26:25)) some of you seen in the cement industry what comes out is a clinker. The clinker is a typically about 7 8 centimeter not small may be 5 6 centimeter which is clinker is powder and they sold now as cement. So, what you make is clinker so clinker has in large size now here it says external mass transfer control. So, would you think that cement manufacture would be an example of external mass transfer control? What is your perception I hope you understand if you are working in plasters and builders ic 1 of the l and t built many of this plants. You might be involved in designed in these things is this example correct or not a good example. Now, the answer is like this you will find that the reaction there is a solid product for machine external machine internal reaction and diffusion all are important.

We are talked about it when the temperature is very high the reaction cannot take is not a important reaction cannot take is not a important. It is external diffusion or diffusion through the product layer these are 2 important what seems to happen in the cement industry what you add is actually powdered of lime stone powdered coal. So, as it is going through because of the temperature forms a clinker. So, a substantial part is only a heat transfer to the particle is very important only in the latest stage because of these glassy things forms a solid. So, substantial part of this is controlled by external transfer that is the example we are taken better example. We can take it is not a bad example

although it is not a best example, we have done all the mathematics, but we have to put it in the context what is the context? It is a gas let me quickly write down put it in our F a 0 times 1 minus x a we have F B is F B 0 minus F a 0 x a. We have c F c 0 plus F a 0 x a then we have d F d 0 plus F a 0 x a then that our constant k p is given by gas is p c divided by p a I put a star to indicate it is equilibrium. So, we express all these things p c in terms of concentration we would not do it again.

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So, k p is p c star divided by p a star equal to in our stoichiometry we get something like this correct we have done this. So, I would not go this again so the equilibrium is given by k p minua theta c divided by 1 plus k p this we have done this your don. So, we know what is the equilibria an how it is determine by the composition of for choice? Is it what we have done. So, this reforestation consultations stoichiometry we are done this before we are done this here and directly follow from stoichiometry. We are done this class now rated which the reaction takes place the rate we say this is ra dash divided by while ra dash is a reaction rate per unit surface area. And as is a surface area per unit volume this what do way said and you foodie s he for reactions is what external diffusion control kg times ca minus ca star times our surface area per unit volume is it. (Refer Slide Time: 30:55)

So, now, we can convert this you have d fa 0 dxa divided by dv minus nor for guard nor minus am sorry minus. So, it is minus minus of kg ca 1 minus or x a ca star it is 1 minus there x a star it is times as alright. So, this simply as dxa by be of gas residential kg times x a star minus of x a cans us of on this our as is it all right? Why this x a star what we a got here are x a star is this we the contact of your said this early Roswell. They contact steers is that this value of theta c theta c is the product in the feed and this as a bad effect on the rate of the chemical reaction. Because it effect x a star and many in casus be may not have great choice, because you have to expected fat that this amount you expected. For example, calcium carbonate decompositions be said we have to expect the theta c to be about a significated value other total resistant all right.

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What is as surface area per unit volume? What to be say external diffusion times number of particles divided by volume and then we said our experimentally mash ruble quantity is this. That means the old poufs of solid in the equipment older be actually data that readily available for all equipment given they had we dynamics people will be tellers what is the old up so the old up solid epsilon r. This readily available there for we are able to deter mean as has s equal to 3 epsilon are divided by R something like this. So, that our he question describe our process is this 3 epsilon here by R kg within in brackets x a star minus or x a. Now, if he look at this question we find it is this terms which is deter mean this eyes the equipments if we can do something about this terms. The size can be reduce if this terms is poor sizes very large let us integrated what we integrated this what do we get ln of actually we are denoted x a star it is a denoted x a as beta. Therefore when we integrated this idle come out be to what to let be ln of beta minus of x a divided by beta. (Refer Slide Time: 34:03)

So, ln of beta minus of x a divided by beta equal to minus of towage call this as alpha. We this alpha we becomes something like this is it now for this data given for the quickly calculate what is the value? All of you please calculate what is alpha? Alpha is rice epsilon R kg divided by R this is alpha and then beta is pirates kp minus of theta c divided by 1 plus kp please calculate and tell me this number please.

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What is alpha in what is beta alpha is how much?

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Epsilon where is epsilon R somewhere where is the, this 1 this is symbol wrongly return please make it change hold up is 0.0015 this epsilon acutely is not please make that correction yes this is a epsilon. So, this 0.1 5 so 3 times 0.1 5 and kg how much is kg where have the point 01.01 and what is R point 0 5. So, how much is this? He could 0.09 units at the units alpha is in what units units per seconds what is beta what is kp where are we kp is 5 and theta c is 1; this is theta B. Please make that corrections so teta c is 1 and then 5 plus 1 6 of 4 by 6 equal to 0.67. So, you what is problem specifies that we quire what the extended of reaction of the mention some way it not mention.

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What is they conversion require x a desired 0.8 xe 0.8 xe.

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What is the xe is what 0.67 therefore, x a is 0.67 times 0.8 how much is that 0.5 3 6 is it all right. So, xenon so we can find out what is gas resident time tell me ln of beta 0.67 minus of 0.536 divided by 0.67 equal to minus towage times alpha is how much 0.09. So, towage equal to 17.8 seconds. So, what this saying is that the reactions that is control by gas film does not require much resident time. So, this is point that we all should appreciate so it is something age is require last more resident time they for you. If you design on the basis of the gases resident time in parables get I kiln which is quite small, but that would not do your job. Because the kiln has do lot more job, because the clinker as to form the cement as been form, but it is be converted to clinker that may be much slower process. That is why kiln is much match long kiln at the point there hares across to you all right.

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Let us go forward what is solid resident time?

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Solid resident time tau yes is what hold up solid which is v times epsilon R divided by the flow of solid what solid is B correct fb the volumetric solid the volumes solid. And may not change fb 0 divided by row be me not change very much solid density at the feed and solid density exit me not very different this case data is not be given. We take volumetric flow of volumetric solid equals to that the feet solid 0 what is the volumetric flow what is fb 0 divided by 50 what is the volumetric flow what is the volumetric flow

and what is fb? 3.6 multiplied 0.7 divided by 15 is it allright everybody are it is epsilon R 0.15.

And then divided by 3.6 multiplied 0.7 divided by 15 is it is it all right everybody all right 0.15 and divided by 3.6 multiplied by 0.7 divided by 15. We still do not now volume gas residence and multiply the gas flow v naught times tau ggi is what is v naught fa 0 divided by ca 0 fa 0 is 3.6 0.06 0.02 multiplied by tau ggi tau ggi is what 17 second you told me 17.8. So, how much is volume what is the volume how many cubic meters. So, we divide with that 3600 so how much does it now looks much better now what is the answer 0.89 alright 0.89. So, what is these solids 2.67 volt. So, what we are trying t put across is that the gas controlled phenomena whatever is does not occupied much better that is the point what we are trying to get.

Student: ((Refer Time: 40:50))

It does not see, because that reaction is not occupied into much overview all the rest is for converting the cement into clinker that is what takes most ((refer:41:04)) it is alright can we go forward.

Student: ((Refer Time: 41:13))

That is what we are saying man the, what we have looked at only the part that is controlled by gas external firm. There is the fact that we provide a much more volume, because the format the clinker have been it have been converted to clinker. It has to that is what takes a lot of place that is what I am trying to say that is not in this problem. We will put another problem to take care of that in this 1 we are only looking at a small part of the ((Refer TIme: 41:50)) showing that the gas will control will not such an important thing as far as this particular problem is concerned. So, that is the number that comes out the this particular problem we will do that also a little later

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So, this is exercise is c plus H 2 0 give you C o pus H 2 this is q 3. So, all of you have seen this I am sure ((Refer Time: 42:22)). So much talk about gasification of biomass and what happens in gasification of biomass is that you expose the carbonizes material to a high temperature with steel. You exposed to high temperature with steel you get carbon monoxide and hydrogen. Both carbon monoxide and hydrogen are very valuables materials. In fact, there is still lot of work goes around the world to some have the perfect reaction this reaction is endothermic; this is an endothermic reaction. And the thermal is about 25 kilo calories per mole is a kind of energy that is associated with this reaction So, it not small the heat effects are not small, but the products are very valuable products are extremely valuable both carbon monoxide and hydrogen are very valuable products. And therefore, this is great interest around the world people are trying to look for various kinds of catalysts to enhance the and so on. Nothing much was really happened from biomass if you look at coal; coal is not just carbon it also has hydrogen.

If you look at coal I mean at the situations are slightly better situations are much better for a number of ((Refer Time: 43:53)). What happens is that 25 kilo calories per mole is the energy that is required for this reaction and you have to get this ((Refer Time: 44:01))energy from somewhere. Then only you can drive this reaction you will ask yourself how you provide this energy? Yesterday we looked at what is called as a reactor and regenerated system in fact the context of that. And we said solids of that between the two we mentioned that yesterday we did a problem also to illustrate now looking at this looking at this problem of coal gasification. Can you think of a way by which we can do this coal gasification a little better coal gasification is really was really not taken off all over the world 80s and 50 years later you know we still struggling with coal gasification technology what you do? Do you see some solution by this in a two reactor system ((Refer Time: 45:00)). See in the petroleum industry all have you has seen there is a cad cracker what happens in a cad cracker.

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Cad cracker; there is this reactor and there is this regenerator from the reactor the solid send by the gravity from the regenerator. It goes by ((Refer Time: 45:15)) what happens is this is the reactor this is the regenerator here catalyst gets deactivated here catalyst is regenerated. So, this is the regenerator this is the reactor correct now we have to conceptualize the same thing for the case of gasification of coal what is the object here? The object here is gasification of coal in this reactor gasification should occur which means c plus H 2 o should go to C o plus H 2 o for this u need heat. So, what do you want? We like to do you want to burn coal here to burn coal and because of that heat this solid heat you want to take it there. So, that the heat solid serve as the heat carrier for the gasification reaction do you understand. Now, this technology itself does not really taken out it is not ((Refer Time: 46:24)) think of whole classification, but if you can do this if you can separate these generation of heat and supply the heat of process.

Then the advantage of this gas the ((Refer Time: 46:38)) is very high because you do not allow the combustion this is A I this is lot of nitrogen here this nitrogen does not get in otherwise lot of nitrogen gets in to the combustion this gases. And your thermal values is very low see most of this what is called biomass gasifier that is running around the world the thermal value will be around 800 to 900 kilocalories for cubic meter 800 not sometime even less and very lean gas you see. And therefore, it is not very suitable for various types of engines unless you have a substantial amount of additional fuel like diesel. You have to put some diesel then only it will work or it will not work by itself you are not able to do use these gases in combustion IC engines. Because it is just to lead this is where the technology is stuck for a large number of years do not have a way by reach to produce a gas which got sufficient ((Refer Time: 47:45)) that is why coal gasification programs have more or less sort of going forward.

Now, recently thanks to a huge increase in the cost of you know crude oil the interest has come back again ((Refer Time: 48:00)) in India for example, I mean when I join this department 30 years ago not very important. Now, it may depends up on the cost of fuel oil correct what is called crude oil now the crude oil cost is so high the tremendous ((Refer Time: 48:19)) in the world. But still we do not seem to have to a good way to carry the solids and heat ((Refer Time: 48:29)) that is the problem you are facing. Now, the question now what is the question? The non react catalytic reaction is carried out enclosure ((Refer Time: 48:40)) last at temperature T the reaction endothermic and ((Refer Time: 48:45)) setup of module x plus conversion time relationship for the shrinking part. Now the other shrinking what do we have?

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We have a particle we start with this particle and now this particle becomes this as the reactions proceeds how do you handle this problem? We write this d by dt of N B equal to what? Sum R B dash S ((Refer Time: 49:22)) what is this S? S will be the reacting surface. What is the reacting surface? Then we start this radius is R as a reaction produce it becomes R c on other words the reacting surface. It is always exposed to the gas the shrinking particle the reacting surface is always exposed this is c a j and ((Refer Time: 49:49)) a there is no external gas under the reaction control it is not mentioned. So, at least hash is not there. There is no product layer correct either or is controlled by chemical reaction or it is controlled by external mass transfer or both we do not know.

Since nothing is specified we should consider both and bring it together we have done that also correct let us first look at reaction control. So, what is our n B 4 by 3 pie R c cube time row B right hand side is what if it is reaction control case time C A g our strike metric factor. If it is there it probably 1 I will put negative sign to show it is being consumed multiplied by 4 pie R c square is this all right. Now, let us recognize this situation is very different from situation consider earlier situation was there was unreacted core here. And the gases were diffusing there was not resistance in the product layer that was situation considered earlier here situation is particle every instance of time the unreacting surfaces of the particle are exposed to the gas that is the difference between to the situations. So, can we take this forward now. (Refer Slide Time: 51:46)

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So, the left hand side is 4 pie R c square row B d R c by dt on the left hand side the right hand side is minus B times k s times cag. So, this we can integrate and we will get something similar to what we have got before rc by R equal to t by tau. I put s to indicate the shrinking part of the particle where t rs is row B times R divided B times k s times C A g is it all alright? Now, we have been talking about shrinking core models then just now about shrinking particle. Now, we would like to look at this whole issue of shrinking particle ((Refer Time: 52:48)) instead of external diffusion control. Now, why are we looking at eternal diffusion control? Because this could be one of the mechanism you should encounter. So, we should have appropriate formulations.

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Shrinking Porticle

So, what we have got here is particle of radius R which is undergoing part of burning let say and as shrinking proceeds the particle is shrinking the combustion. So, we want to see how we can delay how combustion can takes place for fundamental process the rate at which particle is shrinking. If it is an external diffusion control C A g rate supply of material takes place and gas plus B b solid equal to B is symmetric. This is the representation of particle and how it can be related to composition in the external combustions. And this is the 4 pie R c square is the surface area over which the reaction takes place correct in other words are over which diffusion takes place is 4 pie R c square as particle shrinking this rc keeps decreasing. So, we have to take into account the amount of decreasing surface area in the proves we know the nb is 4 pie R c square. We can differentiate the left hand side the R c square gets cancelled row B drc by dt.

Notice that when you differentiate the left hand side R c square gets cancelled so that you get row B drc by dt. This concentration of C A g should not be changed as the reaction proceeds. So, that we do not have to worry about the changes. So, we consider situation as we take these changes into account shortly for the moment. We are formulating for the case where the combustion to the gas is external to the gas is not changing some points bear in my mind area also this particle is burning surface is decreasing in size in many textbooks. Because how it is described with that because core shrinking is correct. Therefore, we call rc k some please do not put k just call it rc show it as particle shrinking any instance the particle burning call it rc the term is rc used for unchanging size when changing size use r. I have written the same subscript rc. So, we can continue with the same nomenclature. So, what we have for the shrinking particle for the external diffusion control row B drc by dt on the left hand side. So, this describes how the size of the particle is changing kg is the transformation constant C A g is composition of the gas external to the solid assuming not to change as the reaction proceeds. Now, what we know from our basic mass transfer studies is Sherwood number which is defined as kg rc by R where kg is mass transfer.

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Constant rc is particle size of any instant of time d is the diffusion constant to the external to the solid surface. Now, this Sherwood number is known to be equal to 1 plus a constant times power of number n critical pointing typical 0.3. This is something we know from the mass transfer showing the kgrc by d is 1 plus constant times of rc to the power on n is typically pointing. Now, if we are looking at the slow over the solid where the Reynolds numbers are slow then we can say that the Sherwood number is kgrc by d is equal to 1. What I am saying is from the shrinking particle Sherwood number is 1 is not bad number if the flow around the particle is slow suppose we look at the situation of lower number. So, the Sherwood number kgrc by d equal to 1 is applicable.

Then what we can do is in this equation row B drc by dt equal to B kg C A g this kg can B E replaced by from this equation kgrc by p equal to 1. What I am saying now is that this equation which tell saying now what is the rate at which it reduces the shrinking particle changing kg appears in the right hand side this kg is actually equal to d by rc kg equal to d by rc therefore, we are able to replace kg as d by rc here in the right side So, row B drc by dt equal to B minus of C A g notice here that the drc by dt now depends upon on cag. This dependence is what interesting when particle is shrinking under external process we just now little while ago derived and show that under shrinking particle and reaction control. And form of the final result is same whether is shrinking particle or unchanging particle both cases the forms are same expression. But in the case of external diffusion control, because of this Sherwood number equal to 1 we have this dependency rc seen from this eqn

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Now, we can integrate this we have done the integration finally, we get this result row B this is the result the result shows that which we can simplify.

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~/R* = 1

What does it say? What it says is rc square is t by tau fs where F refers to fill diffusion s refers to shrinking particle and what is fs? That means the time for complete consumption of the particle is roby r2 divided by twice B times we can see a change now this result is slightly different from the result we got when we talked about unchanging particle size. So, we want to look at that result carefully but before we do that let us also recognize that rc by R is 1minus xb.

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Therefore the same result can be written in this form showing that if there is a shrinking particle and we want to understand the extent of reaction x B. Then we can write our result in this form where x B is the extent of reaction t is the time of reaction tau fs is the time required for complete consumption of the particle. So, for the case of external diffusion control shrinking particle we find that the time required for complete. Consumption of the particle is given by this result this is an interesting result that we must bear in mind, because it is slightly different from the result that we had seen earlier. Just in the since the context is important I am just drawing your attention to what we had done a little earlier.

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What did we do a little earlier we talked about particles of unchanging size where we showed reaction control? Film diffusion control and ash diffusion control and then we derived the time required for complete consumption of the particle for reaction control as roby R by bkcg and film control. We said is ruby R 3b kgcg and then for ash diffusion control roby r2 6 bdcg. Now, moment we went from unchanging particle size this is for unchanging particle size unchanging particle size. Let me write here unchanging particle snow what is a shrinking particle we have shown that also that for reaction control. This is the result for film diffusion control this is the result now frequently our interest is to be able to tell by looking at the results what is the lightly way of discerning the controlling mechanism. We have talked about it I mean as a part of a chemical engineering program but with this draw attention to what we all know. And put it in the context of trying to

understand how these reactions takes place now suppose for example, a reaction is taking place.

And know that if it is a reaction control then if you change the temperature you will find the effect of temperature will be very strong if it is a reaction control. Now, if it is a film diffusion control we said we know that kg the master of the efficient is a very strong function of the velocity or the hydrodynamics of the conditions. And which the reaction mistaking place therefore, is you do a experiment that different flow velocities. We can discern whether the changes are due to external diffusion or due to reaction, because by changing temperature you can determine whether the reaction is the controlling by changing velocity. We can determine whether external master is controlling and since tau d this ash diffusion depends upon square as a particle size. We had said at an earlier time that by changing the particle size like particle twice thrice and so on. We can determine whether ash diffusion is a controlling thing now we know that if it is a shrinking particle. Then there also the dependence of the time for complete consumption depends on square as a particle size.

So, there are 2 kinds of situation 1 ash diffusion also depends on square a particle size the time for complete consumption. Similarly, the time for consumption of a shrinking particle under external diffusion also depends on square as a particle size. Now, the question is how do you distinguish between the 2 mechanisms say ash diffusion control and changing control. And changing particle size film diffusion control and shrinking particle the answer is very simple now you can by looking at the situation itself tell whether it is a shrinking particle. Or whether it is an unchanging particle as an example let us say you are burning biomass now burning of is an shrinking particle. The reason is biomass has very little ash 1 percent 2 percent and so on. Therefore biomass is a good instance of a shrinking particle, because the ash is very low. Therefore, simply by looking at the situation itself we will be able to tell that it is a shrinking particle. And therefore, the question of ash diffusion control does not even arise, because there is no product layer at all.

So, what I am trying to put across you is that by looking at the physical situation by looking at the data that is in front of you carefully you will be able to discern the controlling mechanisms. Of course, the way to do it is that we should do experiment at

different temperature we should do experiments at different flow velocities. And if you do experiments at different particle size therefore, you have to do a number of measurements. And looking at those measurements you will be able to discern where you are what is the extent of control that you have seen from different controlling mechanisms have been said. This we want to draw our attention to some important issue that we will face in days ahead and that is a energy that you. And I require now as you all know that fossil fuel are creating various kinds of difficulties to our global environment the reason being of carbon-dioxide and so on. So, anything that we can do with biomass would be a great value similarly, but biomass is limited by the extent to which can grow biomass, because of limitation in agriculture plantation and so on. Therefore, maybe there is a time may be for a number of years from now may be 20 30 40 50 years. We may have to depend on coal both gasification of coal and gasification of biomass is an area of great interest around the world, because these provide energy for our daily needs.

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Now, whether it is coal or biomass the gasification technology what is the gasification technology? The gasification technology is that you react carbon with steam to give you carbon-monoxide and hydrogen this reaction c plus H20 equals to C0 plus 2 is a well studied reaction. It is endothermic it is heat of reaction is twenty nine 0.9 kilo calories or 1000 Kelvin it is free energy change is condition is minus 1.9 or kp is about 2.6. In other words it is a reaction where the liquid are low it is endothermic and therefore, you must choose reaction conditions which are appropriate for these kinds of thermal dynamic

parameters. But there is a more important feature that we must recognize what seems to happen is that if you try to gasify either coal or biomass using a mixture of steam and air



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In other words you do this reaction just put it down here use this reaction something like this. So, you have an enclosure let us say you have an enclosure and then you have a say biomass or coal is going in via and then you put air and steam at an appropriate temperature. So, that here you get gasses the reaction is c plus h2o giving you co plus h2 and then plus, because it has air this reaction will also takes place. You get co2 this also will happen what seems to have being the major difficulty around the world is about gasification technology is that moment we use air to generate heat this is exothermic correct this endothermic. So, it means you are generating heat by this reaction. So, that it can be supplied to this reaction. That means internally you are using the exothermic heat of this reaction to supply the endothermic heat of reaction for reaction 1 if I call this reaction 1 and reaction 2. But in that process of course, there is a great synergy here understandably but the fact is that since this oxygen is coming from air this gases contains lot of nitrogen and the experience around the world is that 75 percent is nitrogen. Therefore, this is a very lean gas the thermal values are very low may be 6 to 800 kilo calories per cubic meter and it is so low that the thermal dynamic efficiency we can reach in our engines ((Refer Time: 1:10:00))

Now, therefore, the problem that was interest was ((Refer Time: 1:10:14)) that we can have some have separate the exothermic heat generation this is exothermic; this is endothermic. So, if we separate the exothermic reaction and then move the solid to supply heat for the endothermic reaction that means by separating endothermic reaction and making the solids serve as heat carrier and able to achieve high value high caloric value gas. So, they are able to achieve a high caloric value gas by doing this kind of heat supply using the heat carrier that means you are fluid as that. And then the ((Refer Time: 1:11:05)) here this serves as the heat carrier in to the endothermic reaction and this the material comes out by ((Refer Time: 1:11:12)) we have a dramatic transfer ((Refer Time: 1:11:17)) of solid. So, the solid transfer ensure the heat supply and then therefore, ((Refer Time: 1:11:29)) said this whole idea has very very ((Refer Time: 1:11:35)), but in biomass gasification's and coal gasification's. These ideas not very successful ((Refer Time: 1:11:44)) great deal of work experience carried out ((Refer Time: 1:11:59)) have you said this our present interest this exercise is able to setup the ((Refer Time: 1:12:03)) understand the how the equilibria of ((Refer Time: 1:12:11)). Because after all ultimately our 8 functions are required to able to done how these reactions will proceed in the reactions equipment.

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HO: CO+

Now, the example in the we are trying to talking about is that the continuous input of this material it can be code it can be biomass of course, coal means it has. So, many other things as well I am just simplified representation. So, we are talking about a continuous

process in which a material is coming in the reactor with steel at a very high temperature at 1000k. So, that you have carbon monoxide in hydrogen. So, with this problem we want to represent appropriately. So, that we can understand from these stiochometry and how ((Refer Time: 1:12:54)) fixed reaction so on. So, I have written this stochometry here.

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So, you have A B C D are the gases coming A is moisture and sorry steam and B is carbon; carbon we are taking this carbon biomass and now C and D are gases. See now I have written stiochiometry in this form showing that, because the heat of reaction ((Refer Time: 1:13:22)) endothermic is 29.9 kilo calories ((Refer Time: 1:13:27)) is quite low 2.6. Therefore, ((Refer Time: 1:13:35)) the equilibria on the reaction we will do that shortly. Let us write this stiochometry now ((Refer Time: 1:13:38)) we know we can write this stiochiometry table concentrations.

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All these concentrations A C B C C C D can now be written in terms of v extent of reactions which is x. Now, we can do that what we want to understand we have a gas law as per gas law we have written the gas law. We have done this before ((Refer Time: 1:14:00)) gas law is what gas law is v by v c equal to p o by p, T by T o, Z by Z o and F E by F E O we know this is gas law. Therefore, if you want to find concentration you simply had to say what is the molar form of component ((Refer Time: 1:14:30)) and what is the volumetric flow? Because F T by F A O if you can see from here you can add up on this you can say total comes out to be if this total is adding it to 0.

So, I will just adding up here ((Refer Time: 1:14:47)) so the total gas coming in the F A O is coming in. And then what is going out going out is F A O times 1 plus x A you can understand all the inputs are F A O ((Refer Time: 1:15:07)) output has F A O. That means there is an increasing 1 v ((Refer Time: 1:15:13)) this is out this is F t a this is F t E so F t by ft 0 is ((Refer Time: 1:15:24)) and this is since F T F F O is 1 plus x A v by v o is equal to ((Refer Time: 1:15:29)) what we have done? We have done is let we have been to able to express concentrations of the gases A B and C the terms of compositions have been left and conversions which is ((Refer Time: 1:15:45)) all these conversions of. So, we have C A C B C D are C A C B and C D in terms of ((Refer Time: 1:15:55)) having done that.

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We can now recognize that the equilibrium constant for this reaction what is the equilibrium constant reaction? ((Refer Time: 1:16:04)) what is k p? K p is p c B g divide by p a denotes and what is the rated chemical reaction takes place. You also know that ((Refer Time: 1:16:16)) chemical reaction takes place under external diffusion control it is k g times the concentration driving force what is the concentration driving force? C A minus C A star what is c a and what is c a star this is the particle which is ((Refer Time: 1:16:28)) C A g which is outside and C A g on the solid surface ((Refer Time: 1:16:33)). And at any instance of time ((Refer Time: 1:16:36)) this is the driving force this is the C A star on the surface and then this C A has said is not going to change. Therefore, we call it as C A g and star C A O I mean here driving force is C A g minus C A star ((Refer Time: 1:16:50)).

And therefore, in terms of our conversion I have written it as C A O x A star x A correct what is C A? We have written C A as. So, we will have to divide this by 1 minus k g C A 0 1 plus X A star. So, is that clear? What are we saying? What are we saying is that our driving ((Refer Time: 1:17:18)) I will just come back what is our driving force? C A g - C A correct and that is what is we have just now we have written here C A g minus C A star is given by this C A 0 1 minus x ((Refer Time: 1:17:31)) which takes place. Therefore, this C A this C A star is known to us because we have written a these things in terms of x. So, what they are trying to say is C A g minus C A star can be written as C

A 0 X A minus X A star this is something you know because C A ((Refer Time: 1:17:50)) are known divided let we put this 1 plus.

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C A equal to C A 0 times 1 minus X A divided by 1 plus X A therefore, C A star equal to C A 0 times 1 minus X A divided by ((Refer Time: 1:18:19)).

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And what is C A? C A equal to it is already mentioned C A 0 1 minus X A divided by 1 plus X A.

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So, what we are saying now is that R B is equal to minus k g times C A g minus C A star now this can be written as in this form. Therefore, it is equal to minus of k g if C A g is changing written as C A minus a C A star where C A is given by this expression C A star if it is not changing then it is ((Refer Time: 1:19:15)). Therefore, we do not have ((Refer Time: 1:19:20)) put across then in the case of a reaction in which thermodynamics effects. The rate of chemical reaction that means this C A star is effected by in fact that k p is of ((Refer Time: 1:19:38)) taking that in account. Then this effect will come of in determination of this driving force C A minus C A star is it clear? Having said this what is the value of k p? (Refer Slide Time: 1:19:53)

The k p from our equation here is written as k p is p c p d divided by p a ((Refer Time: 1:20:03)) p c p d divided by p q. Now, we can write pc and p d in terms of concentrations and so on. Therefore, finally, what you will get is that the X A star is determined by this equation ((Refer Time: 1:20:22)) you determined x a star the k p is known c a is known R t is known ((Refer Time: 1:20:29)). Once we know X A star we can also determine C A star we have done that already therefore, they are now in a position to ((Refer Time: 1:20:42)).

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Now, since C A star is known in terms in x a C A is known in terms of x a therefore, ((Refer Time: 1:20:51)) what is the rate ((Refer Time: 1:16:53)) occur of k p ((Refer Time: 1:21:01)). In this reaction carbon plus hydrogen steel giving you carbon monoxide in hydrogen k p is only 2.6. Therefore, the effect of k p must be taken into account how did you do that? We did that we recognizing that k p is given by p c p d by p a I will put a star here. Therefore, k p can be put in terms of conversion which you have done. Therefore, we find k p and x a star is related by this equation where once k p is known R t is known c a o is known x a star is known in other word we are able to tell what is the driving fusion? Write here that 1 plus wait the defect is wait we are not able to do this point will stop that by saying that k g c a minus c a star c a star is known in terms of k p therefore, we are able to known.

What is the driving force of c a minus c a star? And therefore, we are able to tell what is the effect of the equilibria on the rate of the equilibria what we are trying to say here we put this as C A g minus c a star. This is the value now what we are try to complete here is the time for complete consumption is previously given only in terms of c a g. Because c a star is not important now the driving force is C A g minus c a star now what is c a star and what is c a g? Both we can calculate from our understanding of thermodynamics what we have done here we put it across once again what we are said is important. What we are said is that c a and c a star in this case is given by these 2 equations c a and c a star is given by these 2 equations and if the composition is changing.

The composition is changing the composition is not changing then C A g is remains the same if for some reasons in the flow reactor the composition is changing. We are taking to account of C A g as the composition changes then we are started to use this expression c a star is given by this c a is given by this. So that you can substitute for both C A g and c a star, in this equation and therefore, we know what is the rate function. So, essentially what we are trying to put across this is for a situation of a shrinking part. If the composition is changing along the length of the reactor must take this into account by using this ((Refer Time: 1:23:44)) equation the composition is satisfactory, because we are taken both situations into account.