Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 13 Combining Chemical and Thermal Processes 3

Prof. S R Chakravarthy Dept. of Aerospace Engineering IIT Madras

Now today look at the constant volume fixed mass reactor we littered the constant pressure fixed mass reactor earlier will follow pretty much the same approach, except that we now notice the volume is going to be fixed and instead the pressure is going to vary and correspondingly the analysis is going to change a little bit and we let us see how that changes, going to go through this a little bit faster when compared to what we did earlier, so that we just look at the modifications that we have done the will do now.

(Refer Slide Time: 00:41)



So the first law of thermodynamics applied here would be to start with we have the same equation but right away we can now say this is = zero because you do not have any Pv work pv work okay and nothing else okay so you just say there is no work done by the system we just have only a heat interaction and obviously then any change in the internal energy of the system directly comes from the heat or vice versa okay or the heat that is released goes to changing the internal energy directly. So here you now have d you over dt = Q. / M so all heat goes to.

(Refer Slide Time: 01:45)



Changing the internal energy because it is constant volume and then we have a similar situation like what we had before the rest we will now say we have a u this is a total specific internal energy this is now capital U / M this is now total internal energy right previously we had a small H is ω capital H / M your instead of tap you are now looking at internal energy, so this is σ i ω 1 to n ni capital UI / M now capital UI is a molar specific molar specific internal energy of speech is i, ni of course continues to be the number of moles of species i.

So if you are now looking for d you over dt right so du over dt now changes because of two things one is the number of moles that changes with respect to time, as well as the internal energy of species I that changes with respect to time, so this is 1 over m σ i capital UI dni over dt + σ overall i ni d capital UI / dt there are two contributions here again we notice that.



(Refer Slide Time: 04:17)

The molar specific internal energy is a function of temperature alone, so perfect gas for gases therefore d_{UI} over dt is = at constant volume here dt over dt. Now this is = capital Cv i dt over dt, so this is a molar specific heat of speech is I at constant volume.

(Refer Slide Time: 05:06)



Now we can make a now plug du dts Cv idt but then what about dni over dt we can do the same thing is what we did before again 1 over V dni over dt = ω I so this implies dni over dt is ω V times ω i therefore plugging all these back in the first law the means we say we recognize that d you over dt is Q.by M we recognize that the du I over dt is = Cv dt and we look at DNI over dt is = V ω i you plug all these three back in the original equation and you can now get a q . / m = 1 over m σ I capital UI ω I times V + Σ i ni capital C VI d capital t / d small t.

Notice here again as before that V does not have an India index i so that is a common that is common for all the species and similarly dt over dt is independent of species they can be pulled out of their respective Σ , so and then m gets cancelled for non 0m for those of you very picky about these, so we get Q = V times Σ Capital you i ω i + dt over dt Σ over i ni capital C V I so from here we can rearrange to get finally I am going to skip a couple of steps which are just algebraic and get this as Q. over V - Σ over I capital uI ω i / σ over i CI capital CI which I want you to understand is now a function of CVC I and T okay. Why because ω i depends on c in temperature and you also have an explicit presence of Ci.

(Refer Slide Time: 08:16)

Constant Vol	ume Fixed Mass Reactor		
• We have	$\frac{1}{V}\frac{dn_{i}}{dt} = \frac{dc_{i}}{dt} = \omega_{i}\left(c_{i}, T\right) \Rightarrow \frac{dn_{i}}{dt} = V\omega_{i}$	(150)	
 Using the a 	bove equations		
	$\frac{\dot{Q}}{m} = \frac{1}{m} \left[\sum_{i=1}^{N} U_i V \omega_i + \sum_{i=1}^{N} n_i C_{\mathbf{v},i} \frac{dT}{dt} \right] =$	(151)	
	$\dot{Q} = V \left[\sum_{i=1}^{N} U_i \omega_i + rac{dT}{dt} \sum_{i=1}^{N} rac{n_i}{V} C_{\mu,i} ight]$	(152)	
	$\frac{dT}{dt} = \frac{\frac{Q}{V} - \sum U_{i}\omega_{i}}{\sum c_{i}C_{v,i}} = f(c_{i}, T)$	(153)	
NPTEL	121101111	1 040	

Showing up here therefore this is a function of the concentrations and temperature of course you can know we typically do not deal with specific molar internal energies, we typically deal with specific molar enthalpies you look at these tables like John of tables and so on it typically lists enthalpies rather than internal energies, so you could now convert that.



So for ideal get ideal gases ideal gases $U_I = hi - Ru t$ and CvI equals $C_{PI} - Ru$ okay so dt over dt is = Q. over $B + Rut \sigma i \omega I - \sigma$ over i h i $\omega i / \sigma i C_I$ capital Cbi - Rut he reason why we are actually having a universal gas constant show up here is because we are dealing with things on a molar basis okay. So you would have a specific gas constant only if you are using things on a mass basis therefore this is appropriate I would like to make a few comments we will we will in the future look at these kinds of expressions or terms but I want you not to get confused at that time.

 σ i ω i is non zero primarily because the number of moles in a chemical reaction is not necessarily conserved, it is a mass that gets conserved so if we were to actually look at ω I as the amount of mass that is produced per unit volume per unit time okay for which we will assign a symbol WI later on okay then Σ overall I of WI will be = 0 because you don't have any net mass that is produced or consumed if you, now try to sum over all the chemical reactions so a chemical species that are produced and consumed on their mass basis okay.

But that is not true when you are now trying to have ω keep this in mind because later on we will be looking for a σ WI and plug in a zero you should not get confused okay the English

alphabet gives you zero the Roman does not give you zero, so if you want to quickly remember that way that is also fine Roman is smaller English is mass, this you can now write H_I s hf hif 0 I okay + sensible enthalpy okay the catch if not I times ∞ RI that combination Σ iH if not i will be the net heat release rate in the chemical reaction okay.

So it is finally coming from the standard heat of formation times the rate at which it is formed for every species add it all together is the total heat that is released in the chemical reaction okay. So and then you will have a sensible enthalpy part that will stay, so these things will show up as we go along more explicitly we will just do not worry about it now just disused. So this as before is a function of Ci , T keep that in mind now here since the volume is constant one over we d&i over dt is = ω I can be directly written as dc_i over dt is = ω i.

Previously we could not do this okay previously we had to notice that ni developed by V is = C_I and we will change with time, so we had two terms for contributing to the rate of change of concentration okay, one because of the chemical reactions the other because the pressure was constant the volume was changing and since the volume was changing the concentration was changing, but since the volume here is constant we do not have to worry about that effect okay.

So the concentration changes one lead you to the chemical reactions here okay or in other words you could take the V directly within the derivative without any effect and get the concentration right there and that is what we are looking for we are looking for a time derivative of concentration as a 0e so this is again a function of Ci and T this is because of the chemical kinetic equations that we saw earlier on, so this is like a fairly large expression for each of those and n equations there okay.

And this is like typically what you would get solved in liquid with the package to okay so you are you advance in time and see what happens but now what is that that is with a constant temperature but now what you are saying is we will now have this effect the temperature ok and then the temperature will change that is essentially the idea that we are talking about and so here dp over dt is of interest. As I derived quantity that means we now have these two as a closed set

of equations you have n + 1 equations in n + 1unknowns where n unknowns are CI + n equations of these okay.

So this is the you should say really is i = 1 to N and t is the n + 1 are known and this first equation here is the equation corresponding to that but they are all coupled all of them are coupled, so once you do this you should be able to find out dp over dt which is of interest here. So the way we do this is to go back and say pv is $= \Sigma$ over ni or U_T so V DP over DT is = or UT d by dt of σ n i + or u σ n i dt over dt, that means there is a contribution because of change in the number of moles and a contribution in because of change in temperature with respect to time towards a rate of change of pressure.

So this gives you dp u /dt ω to r U_T take this V over here right and then get this derivative inside the summation also the volume inside the summation, you will now have a σ over i won over we dn i over dt which is nothing but ω Ri okay, so this you this gives you a σ over I ω i + you can pull out the dt over dt from the summation get this volume over here and then that becomes a concentration, so you get are you dt over dt σ c i right so that is that s a function of Ci and T which can be evaluated once you have solved for Ci and T. This is not coupled with the other okay so you can get this so this again formulates the constant pressure. (Refer Slide Time: 17:00)

constant forante finea mass freactor	
• For ideal gas	
$U_i = H_i - R_w T, C_{v,i} = C_{p,i} - R_w$	(154)
$\frac{dT}{dt} = \frac{\frac{\dot{Q}}{V} + RT \sum \omega_i - \sum H_i \omega_i}{\sum c_i \left(C_{p,i} - R_u\right)}$	(155)
• Since volume is constant $\frac{dc_i}{dt} = \omega_i$	(156)
 From equation of state 	
$pV = \sum n_i R_u T$	(157)
$V\frac{dP}{dt} = R_{w}T\frac{d}{dt}\left(\sum n_{i}\right) + R_{w}\sum n_{i}\frac{dT}{dt}$	(158)
$\frac{dP}{dt} = R_u T \sum \omega_i + R_u \frac{dT}{dt} \sum c_i$	(159)

Sorry constant volume fixed mass reactor dissolve this is not a joke okay if your n is say fairly large number should not say Farley should not even say fairly large even this modestly large it is going to be complicated, you got a pray to pray do God's that n is like one okay then you are in decent shape but even then it is difficult because this term here thus showing up here and here is to be, so huge you are going to have the temperature sitting on top of a tree like an exponent to the e- e over RT there okay.

So that is very difficult to handle there are numerical techniques for these ok so you have to use like some stiff reaction solvers so stiff equation solvers, so there are there are special numerical techniques that can handle these simultaneous equations. (Refer Slide Time: 18:07)

So let us now look at the other two ideas that we had on open flow systems, so the first of those is the well stir red reactor which is typically abreacted as we saw it is also called as perfectly stirred reactor many times okay and of course that could be abbreviated as PSR and that would that would kind of like Ryan with the next one which is a plug flow reactor AB revealed as PFR so you could think about PS all versus PFR and so on if you do not hear me right then you could get confused between the two, so we want to get into all that.

So we will just use WSR okay for the well stirred reactor so or perfectly stirred reactor just use some space below PS are sometimes historically it is also referred to as long will reactor because of the person who came up with this it turns out apparently that Zelda which actually came up with this ten years earlier in Russia, so whatever you can think of during the time that Zelda which loved you have done it before other people that there is elder which for you is like a father figure in combustion.

So here what we are talking about is right, so you have an inlet and you have an outlet and so you have a m . mi in when a corresponding why I in and a hitch in a Hi and you can say hi in there is a mass specific enthalpy of species I at the inlet and correspondingly we now say you

have a m.i out Yi out, Mi out and so on but all these things of course you now have a control volume that is that you apply within this reactor just pairing the inlet and outlet okay and consider a Q. that would that would get out of this reactor with a with the following characteristics.

So it has a fixed mass flow more mass flow rate so that means Σ mi in is = Σ mi out = I am sorry Σ M i .in = σ m i . out = σ so = m. okay so you have an m. we did not use m. here that is the reason why i was apologetic there is a fixed mass system okay this is a fixed mass flow rate system, so when you say fixed mass flow rate implicit in it is that we are looking at steady state you do not have any accumulation of mass or depletion of mass. So then course you are now looking at the reactor having species all species with concentrations whose spatial variation we will not worry about okay.

There is a steady state that means we are not looking at any template total variations as well the means it is not supposed to bury right, so if it is not supposed to very well the beans you do not you do not have to look for differential equations of evolution of these with respect either space or time okay, but they will depend on parameters what parameters typically we are looking at what is the size?



Of the reactor that you want to work with okay and what is the heat out that you want to get out of this reactor. So depending upon these and the input conditions you will get the corresponding output or you will now get the composition inside the reactor and the temperature to attain based on what is the size at which you want to operate this reactor size is given by m. okay that is like the throughput and what is the heat that you want to get out of this. So these are now like the key parameters in the problem yeah okay.

So then of course it has a certain temperature pressure and volume okay and of course you could you could ultimately we will see this there is there is a relationship between these it is like you are handling a certain m. at a certain pressure and volume okay that will relate to certain density alright and with that density for these mass fractions you will now get the partial densities of each of those species to be fixed correspondingly and so on so, there are relationships that we will be working out among these okay.

So this has a and inlet and outlet out let for steady stream steady stream of reactants and products respectively the reactants get into the inlet and products get out of the outlet, now when you get this kind of situation where you do not worry about this details is when you now have high velocity jets of reactants coming in and then getting into like a tumble or a huge swirl or something of the sort okay, so and then finally something that comes out so it is so chaotic inside you do not want to worry about it right.

So experimental reactors employing a high-velocity jets okay, offer this situation ideally okay, the interesting thing as we will see is what we are interested in we are now looking for algebraic equations without any derivatives right in concentrations and temperature again those are the ones that we are interested in, so the concentrations obviously depend on the reaction rates and the reaction rates depend on what are the reactions? So in principle you could actually use a reaction scheme of large set of reactions detailed elementary reaction steps involving whatever species that you are interested in keeping track off.

That there are that are going to happen and this reactor on come out of there right and typically this is good for doing relatively quick actually, I say relatively because it is not quick to start with okay you still have like a huge set of algebraic equations to solve which is not easy okay but you are not bothered about the spatial distribution the temporal evolution and all those things you are not really worried about the geometry and all that stuff right. So relatively quickly you can get things like pollutant formations.

Like for example you are interested in Knox okay, so you can actually get a fairly good handle of what would be the Knox production from pushing in so much amount of air and so much amount of fuel into a reactor that is going to be operating at this particular pressure this bigger reactor and so on okay or maybe carbon monoxide production. Why carbon monoxide production let us suppose that you are now trying to push lot of fuel in there and maybe also corresponding amount of fog air okay for complete oxidation but this volume is not good big enough for complete oxidation to happen.

And before complete oxidation can happen you now have products coming out you are going to be primarily looking at incomplete combustion products right that means you are going to have some carbon monoxide that is a pollutant you see. So you the volume available is going to also constrain how much reaction can happen and therefore you can you can estimate pollutants based on that as well okay. What we will also see is typically this is used to design reactor sizes like the volumes okay based on another idea of what is called as residence time okay.

So essentially what happens is you now have a reactor and you want to have a through put of reactants coming in reacting and producing products and that go out you want to first of all decide, what how big this reactor should be? Right for this you have to have a notion of what is the residence time of these species inside this reactor by the time they could actually go through all the chemical reactions and come out as complete products. So for complete products we will now use the concept of residence time that will be related to the volume okay.

So that is another way of doing this the third and very interesting idea that with which you can actually use this is something like flame blow out all right and how does that work? So it is like let us suppose that I have a reactor okay and then I am now trying to pump in more and more and more of the reactants in and at steady state, we are now expecting a the same mass flow rate of products out all right and of course for a given volume you are not going to have incomplete combustion progressively.

But at some stage it is simply not possible for you to combust at all okay as you now throw in more and more reactants at it, that makes sense but how are you going to get this out of a model like this. The answer is you now have a set of nonlinear algebraic equations that you are looking for which may not have a solution at all for certain values of m. or q. okay. Let us suppose that you are trying to extract lot of heat out of the system as well you can crunch right, so for the set of parameters that you are employing you may actually get into a no solution region which now begins to can correspond to a flame low out situation.

So yes the other thing is anyone at reactions are occurring all the time, so whatever you are talking about everything is happening all the time that sets a fake a dynamic process a, as you speak right you have now reactants coming in react and produce products or intermediates and products everything is happening. So you know we are not in we are not bothered about the spatial variation okay, so in reality what might happen is as you come in you have more of reactants here okay more of intermediates here and mode of products there as they go out but we are not worried about that distribution.

So if you are not worried about that you all you have to say is you have in this reactor for a given set of reactant inputs right you are going to get infact the question that you are asking has to be approximated this way we are looking for this output of products okay but we do not resolve the spatial we do not spatially resolved between somewhere here and somewhere inside okay. So in that sense it is like saying it is all perfectly mixed all right and you are now going to get out these species okay.

So it is we will try to relate to what we did for the aerobatic flame temperature well while we do this okay except, we are now going to be able to parametrically very things here so we do not have a spatial variation we do not have a temporal variation. The difference between the aerobatic flame temperature calculations and what we did earlier for the fixed mass systems as well as what we will do later on for the plug flow reactor is we can track variations between the starting point and the ending point which we did not do a layer okay.

Here we are not doing that so the question is for how is it different okay the answer is as far as products are concerned we are going to primarily get something like what we did before and they are like they are not exactly equilibrium products but we will get from similar calculations as we as we will see okay but we will not do the spatial variation right, so in that sense it is difficult for us to understand how it can be steady state okay but in reality this is what we are expecting to have.

So okay so no spatial variation no why I meant to say I meant to write out something that I got distracted from the let us just write out knocks formation incomplete combustion incomplete combustion, can be quantified from combustion efficiency okay. So you can find out how much of the originals field that you put in has been completely oxidized okay so and then that that denotes what is called as combustion efficiency, so that can quantify incomplete combustion and so you can get that kind of quality here incomplete combustion and flame blow out okay.

Flame blow out could be study so considering the complexity of the mechanical process that is happening inside in reality this is a quite powerful idea okay, just use only algebraic equations to do this is actually a fairly powerful idea here for these kinds of complicated situations. So now let us look at the other thing that is that we said no spatial variation no spatial variation of concentration or temperature considered and the steady state assumption for steady state assumed okay no time variation no time variation as well okay. So this should lead to algebraic equations as we will see now.

(Refer Slide Time: 35:36)



So global balance for individual species the reason why I am calling it global mass balance is we are not applying it to any particular point in this reactor it is a it is applied to the entire control volume. When we want to derive a mass balance for each species we will actually take a control volume approach and do like something like a global balance but we will keep in mind we will now make use of the fact that the control volume is arbitrarily shaped and then we will be able to notice then that the equation that you would arrive there is actually valid at any point.

But here it is not really valid at any point because you do not have it you do not have any spatial distinction at all okay. So this is this is still a certainly a global mass balance, so at any at steady

state at steady state for each species iM.i out = m.in + ω I times V oh I am sorry make no mistake we will now use W_I okay so this is this is like this is a this is actually like a verbal equation okay we just put in symbols here but it is essentially like a intuitive idea you think of your back bank balance, for example okay so this is what you had to start with and then you put in some money you get some more some more back the bank balance right.

So anything can be budgeted like this effectively right so whatever you get out is whatever you put in + what you created this now is actually for a particular species, if a species is a reactant and it's going to get consumed this is going to be negative so you are going to get less of it when compared to what went in. So strictly speaking we should say this as i = 1 to N and keep in mind as I say. here that means these are rates so we are looking at something like kilograms per second okay.

Wi then is the okay net rate of production of a mass of species i per unit volume, so long as we were dealing with fixed mass systems we were always handling things on a molar basis okay but the moment we are actually shifting to a open flow system we start dealing with things on a mass basis okay. So here instead of using ω i as we did before we use W_I so we shift from Greek to English okay and this is a mass basis and this is what I was polite riot point out. If you now get a σ WI you should look for it to be zero because mass is neither created or destroyed totally okay.

But so long as you have a $\sigma \, \omega$ i that is all right whatever ok because number of moles is not necessarily concerned, so you look at what is going on this is mass produced / rate of mass produced per unit volume, so this should be kgs per second meter cubed, so times the volume should get you kgs per second okay so these are kgs per second mass flow rates okay. So we know that $W_I = \omega_I$ times capital W_I where capital W_I is the molecular weight molecular weight of a species I okay.

The distinction between my W sin ϖ is you have this little curly thing 4 w that is absent in the ϖ it so you have to you have to look for that little thing they are ok and m.i = m.times why I and this m. is the total mass flow rate which is a constant because we have steady state okay and that is a fair a meter in the problem, that that tells you what is the through put we want to handle in

this system okay. So if you now want to put all these things here we get ω I capital w i v + m. why I out- why I out- why I n = 0 I = 1 to N okay.

Now you could leave it as it is and then say this is given okay this is a parameter that means you can have a set of why I for any M. okay that means you can send in a particular composition of reactants at any level of mass flow rate you, now have a large mass flow rate of the same composition or a small mass flow rate of the same composition Yin for i = 1 to n will refer to the composition that is scented m. will actually refer to the size how much you are trying to push in through this right.

So this is given this is what you are trying to look for okay, now since we do not make a distinction between here and here we do not have a special variation that is possible okay what you are looking for is only mainly what is happening inside as like a whole quantity right and therefore you can say because you have to bring in the volume and so on you now say why I out is the same as, whatever is the Yi inside the control volume because he just cannot make the distinction okay especially.

So here we suppose right Yi out is identically the same as Yi Cv where Yi Cv stands for the composition in the control volume okay and of course keep in mind this ω i is going to be a function of concentration of individual species and temperature, so temperature is coming into picture here and we do not know that right so for that we need to solve the global energy balance so you get one more equation for that unknown and that is what we should be pursuing okay.



So global energy balance Q. this = i = 1 to n m. I out a h_I te out - Σ I =1 to n m.i in a h_i t in okay so let us just go back and write Yi Cv as simply why I let us not have any subscripts anymore for what we want to calculate anything that we want we try to not have subscript superscripts primes and all that stuff, that should be like the main quantity. So here what is happening is this is the product enthalpy rate stand corrected this is the rate at which enthalpy is coming out okay this is the rate at which the enthalpy is going in.

The reason why we have a rate is because we now have an m. the. is what is making it a trait okay and this is beginning to look like what we did earlier okay, so when you did the unit body flame temperature calculations, we were looking at energy not the energy rate right not the power rather so here looking at Q. previously we set Q and for adiabatic flame temperature calculations we said we set Q is = 0 and then equated the product in T P not the enthalpy rate = the reactant in T P okay.

And then we try to find out the T out which is what we are going to do, now as well all right so it is an algebraic equation that we had earlier which is also same thing as what we are doing here you see except the in.i out was calculated based on equilibrium calculations earlier on whereas here m.i is nothing but M times why I out and why I is going to be now calculated with this equation taking in it account the chemical kinetics, so this is a difference, so this is the real process that was a hypothetical process you see.

So here so you want to now say this is a parameter and this is what we want to try to find out and we suppose T out is equivalent to identically equivalent to TCv which is the temperature in the control volume because we cannot distinguish and that would be = C this is given you might argue with me that wait a minute we cannot we cannot distinguish between here and here as well do not do not do not off the question okay that is essentially the point.

We are not telling doing anything bad strictly speaking this is out that is okay hey this balance is correct we just drop this drop the subscript that is it okay and so Q. is = we can now pull m. out σ i equals 1 to n why I H i of t - Σ R= one to n why I in H I of TN so here why I n is also given as we said earlier that means we need to know the inlet composition and recall of T is = H if not I so hf0 i + integral trf2 t small CP I DP okay.

So we are we writing everything in small it is small hatch here small H here small cp okay this is because this is on a mass basis the capital CP that we wrote earlier for the fixed mass reactors is on a molar basis okay. So we now have two equations in two unknowns you will perceive this a little bit more on tomorrow this is this is a good time to stop because we are now looking at the picture. (Refer Slide Time: 49:33)



Okay, we will now do some finishing touches tomorrow and then proceed with the plug flow reactor thank you.

Production and Post Production

M V Ramchandran G Ramesh K R Mahendra Babu Soju Francis S Subash R Selvam S Pradeepa Ram Kumar Ram Ganesh Udaya Sankar Robort Joseph Karthi Studio Assistants Krishnakumar Linuselvan Saranraj

NPTEL Web & Faculty Assistance Team

Allen Jacob Dinesh P Banu K M Dinesh Babu G Manikandansivam G Prasanna Kumar G Pradeep Valan C Rekha J Salomi P Santosh Kumar Singh Sridharan P Saravana Kumar S Shobana R Soundhar Raja Pandian K R Vijaya

Administrative Assistant K S Janakrishman

Principal Project Officer Usha Nagarajan

Video Producers

K R Ravindranath

Kannan Krishnamurthy

IIT MADRAS PRODUCTION

Funded by Department of higher Education Ministry of Human Resources Development Government of India <u>www.nptel.iitm.ac.in</u>

Copyrights Reserved