Advanced Thermodynamics and Combustion

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Module - VII
Thermodynamics of Reactive Systems
Lecture - 26
Chemical and Thermal Analysis of Reacting Systems

Dear learner's greetings from IIT Guwahati we are in the course Advanced Thermodynamics and Combustions, today we are going to start module 7 that is Thermodynamics of Reactive Systems.

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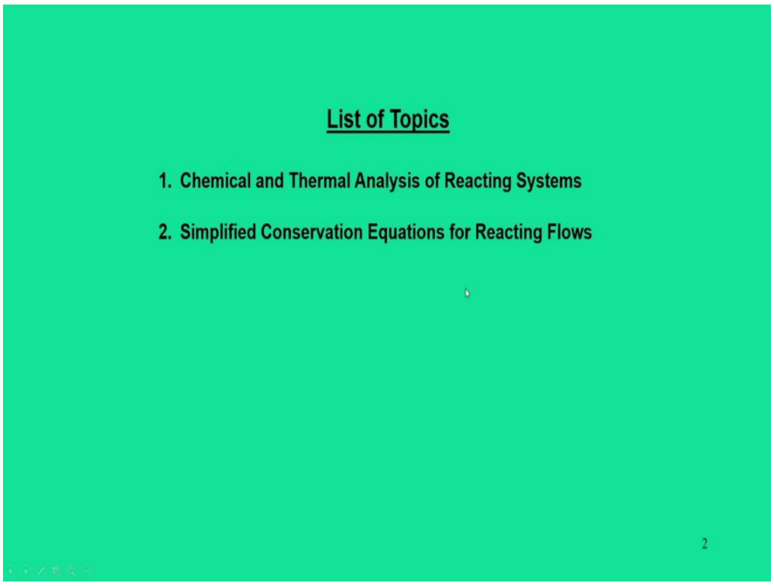

List of Topics

1. Chemical and Thermal Analysis of Reacting Systems
2. Simplified Conservation Equations for Reacting Flows

So, in this module we will cover 2 important lectures first one is Chemical and Thermal Analysis of Reacting Systems, second one is Simplified Conservation of Equations for Reacting Flows.

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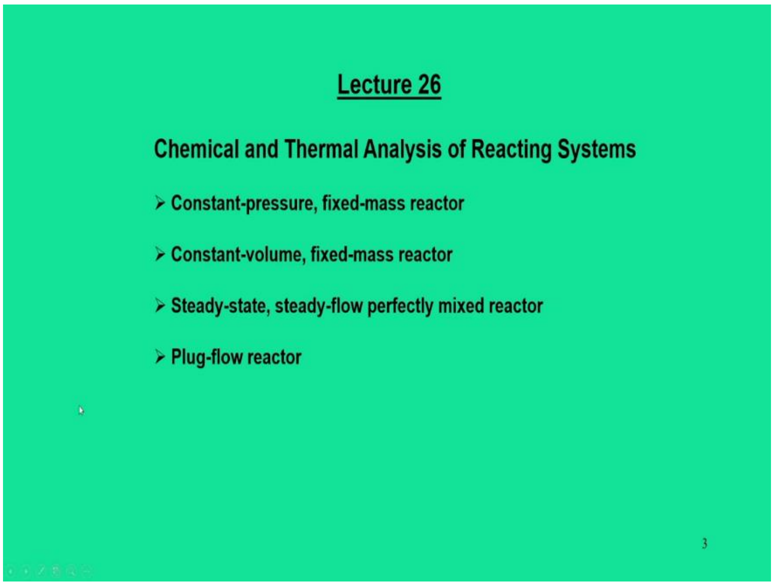

Lecture 26

Chemical and Thermal Analysis of Reacting Systems

- Constant-pressure, fixed-mass reactor
- Constant-volume, fixed-mass reactor
- Steady-state, steady-flow perfectly mixed reactor
- Plug-flow reactor

So, we will start the first lecture on this module that is chemical and thermal analysis of reacting systems, lecture number 26 and in this lecture we are going to touch upon the following topics that is constant pressure fixed mass reactor, constant volume fixed mass reactor, steady state steady flow perfectly mixed reactor and plug flow reactor. So, basically the entire idea or learning components for this module is the reacting systems.

So, what does this mean is that in an combustion process, the reactants vanishes the products are formed. The conventional thermodynamic equations based on mass, energy, entropy all these equations are true as long as the system is in steady state or in a transient state.

But on top of that when you think about a reacting system, in fact in a reacting system some of the species they form and some of the species also vanishes. Side by side there are some intermediate species they are formed, but they initiate the chain reactions. But subsequently when you look at the overall reactions, they are not present. Another important segment is that the rate coefficient that generally governs the directionality of this chemical reaction also plays a crucial role.

So, overall, the chemical kinetics and the formation of different species plays an important role in the analysis of reacting systems. Now, to have such kind of systems in place we are going to couple the governing equations of mass, energy and momentum equations; with respect to chemical kinetics. That means, we will superimpose the chemical kinetics equation into this. So, this will give a complete overall picture of the reacting systems.

With this viewpoint four simplified models are framed which are like constant pressure fixed mass, constant volume fixed mass, steady state steady flow and plug flow reactors. So, our entire intention or will be to discuss some of the important aspects of this reacting systems.

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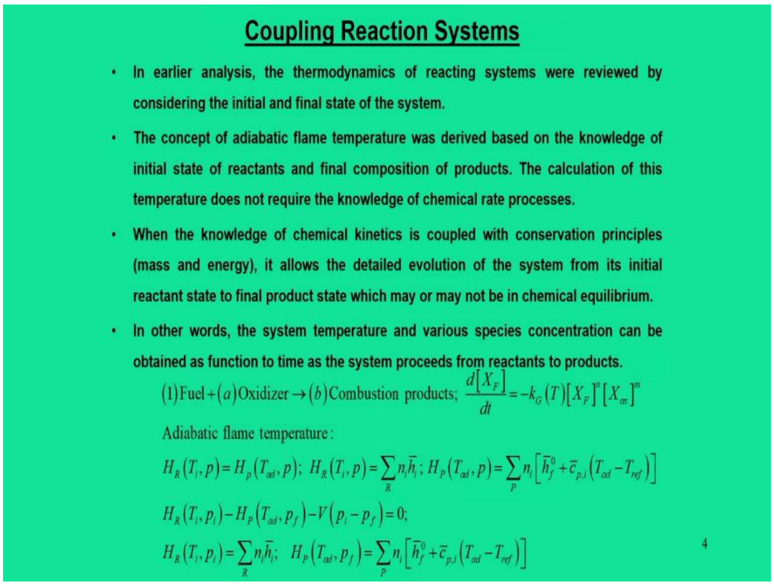

Coupling Reaction Systems

- In earlier analysis, the thermodynamics of reacting systems were reviewed by considering the initial and final state of the system.
- The concept of adiabatic flame temperature was derived based on the knowledge of initial state of reactants and final composition of products. The calculation of this temperature does not require the knowledge of chemical rate processes.
- When the knowledge of chemical kinetics is coupled with conservation principles (mass and energy), it allows the detailed evolution of the system from its initial reactant state to final product state which may or may not be in chemical equilibrium.
- In other words, the system temperature and various species concentration can be obtained as function to time as the system proceeds from reactants to products.

$$(1)\text{Fuel}+(a)\text{Oxidizer}\rightarrow(b)\text{Combustion products};\ \frac{d[X_F]}{dt}=-k_G(T)[X_F]^n[X_{ox}]^m$$

Adiabatic flame temperature:

$$H_R(T_i,p)=H_p(T_{ad},p);\ H_R(T_i,p)=\sum_R n_i\bar{h}_i;\ H_p(T_{ad},p)=\sum_P n_i\left[\bar{h}_f^0+\bar{c}_{p,i}\left(T_{ad}-T_{ref}\right)\right]$$

$$H_R(T_i,p_i)-H_p(T_{ad},p_f)-V(p_i-p_f)=0;$$

$$H_R(T_i,p_i)=\sum_R n_i\bar{h}_i;\quad H_p(T_{ad},p_f)=\sum_P n_i\left[\bar{h}_f^0+\bar{c}_{p,i}\left(T_{ad}-T_{ref}\right)\right]$$

So, before we start let us give some introduction to that what do you mean by Coupling Reacting Systems. If you look at the combustion situations that is fuel mixes with oxidizer, it gives the combustion products and with time if you look at the concentration of fuel it keeps on decreasing.

And the rate at which the combustion products are formed, it depends on the global rate coefficient k_G. And the maximum temperature that can be achieved during a combustion process is defined through adiabatic flame temperatures and these adiabatic conditions can be ascertained by assuming a constant pressure model or constant volume model.

So, through this process we can say that when you define this adiabatic flame temperatures, we say that there is no enthalpy of combustion term. So, basically difference between enthalpy of reactants and products they should equalize, when did they equalize the equilibrium temperature what we say is that adiabatic flame temperatures.

Now until this point of time when we have model this kind of systems, it all depends on the equilibrium conditions, that is reactants where they stand products where they stands. That means, all the thermodynamic parameters are estimated based on the reactant operating conditions in terms of pressure and temperature or product conditions in terms of pressure and temperatures.

And we really do not bother how the chemical reaction proceeds, as per the chemical reaction proceeds through chemical kinetics mechanisms; formation of different species like elementary reactions, formation of radicals through another elementary reactions all those things.

So, when you deal with a couple systems, we try to mix both chemical kinetics as well as the conservation of principles and by conservation principle we mean mass, energy. So, when we couple them then we can say that the detailed evolution for this entire combustion phenomena can be formulated.

So, with the knowledge of chemical kinetics coupled through the conservation of principle allows us for detail evolution of the systems from its initial reactant state to the final product state which may or may not be in chemical equilibrium. So, in other words we can say system temperature various species consent concentrations has to be obtained with respect to time, as the systems proceeds from reactants to products.

Of course, this reaction time scale is a very short duration events and we can say it is something like in millisecond durations and in these durations many species are formed and many species also vanishes. So, the chemical kinetics through estimation of rate coefficient will allow us to model such kind of simulations, when you go from reactants to products.

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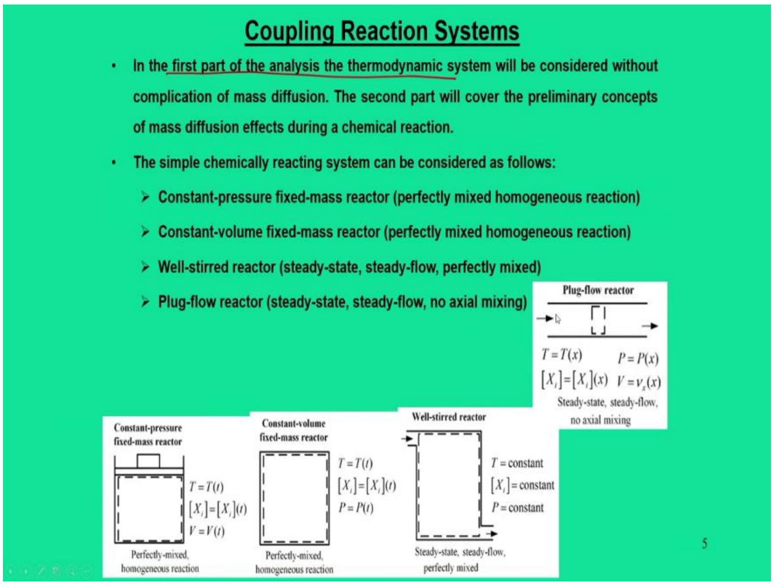

Coupling Reaction Systems

- In the first part of the analysis the thermodynamic system will be considered without complication of mass diffusion. The second part will cover the preliminary concepts of mass diffusion effects during a chemical reaction.
- The simple chemically reacting system can be considered as follows:
  - Constant-pressure fixed-mass reactor (perfectly mixed homogeneous reaction)
  - Constant-volume fixed-mass reactor (perfectly mixed homogeneous reaction)
  - Well-stirred reactor (steady-state, steady-flow, perfectly mixed)
  - Plug-flow reactor (steady-state, steady-flow, no axial mixing)

Now, to do that there are 2 approaches that one can design in the first one or the first analysis the thermodynamic system is considered without complications of mass diffusion. So, mass diffusion term where the species diffuses into other and through this, mass diffusion does not arise in this case. That means, in our conservation equations we will not look into the mass diffusion terms, the second part of the analysis will cover the some of the preliminary mass diffusion effects into the chemical reactions.

So, for the simplicity we will now consider the first part where the thermodynamic systems are analyzed without mass diffusion. There are 4 models that are possible first one is constant pressure fixed mass reactor. So, it is a perfectly mixed homogeneous reactor. So, as you see in this picture. So, it is a constant pressure, so we have a piston cylinder, then this particular system is viewed in this manner. So, thermodynamically we can say the fixed mass reactor is modeled by putting a certain mass on to a piston.

And entire system or gaseous medium is within this cylinder that is reactants as well as the products and this mass allows us that piston does not move, that means a fixed mass is experienced by this species. And all these species and these reactants and products in this domain they are perfectly mixed and homogeneous.

Other type of situation can be modeled that instead of fixed mass we can ascertain that we have a fixed volume system, but in this fixed volume systems the pressure can vary with time. So, as the reaction evolution starts, the pressure can vary with time. But when we say constant pressure reactor, volume can change, but mass remains same. Another model is that well stirred reactor.

So, when you deal with the constant pressure or constant volume reactor, we try to see how temperature changes with time, how concentration changes with time and in a constant pressure reactor, we see that how volume changes with time and in a constant volume reactor we have same thing like temperature and concentration that changes with time.

But at the same time, we will look into how pressure changes with time. But in a well stirred reactors we assume that all these things that mean temperature is always constant, concentration is constant, pressure is also constant. But what happens is that it is a steady state steady flow analysis and in a perfectly mixed. Another kind of reaction is a plug flow reactor that is a steady state steady flow, but no axial mixings. So, basically this is a kind of a duct in which certain gas is passing.

So, something like in an aerospace propulsion system like ramjet combustion or scramjet combustions, some high-speed air that enters and fuel is injected into it. So, we can say that we can arrest the flow mixing in one particular directions. So, like in a plug flow reactor we can model this as a steady state steady flow, but we do not allow any kind of axial mixing, there is no axial mixing but there can be lateral mixing.

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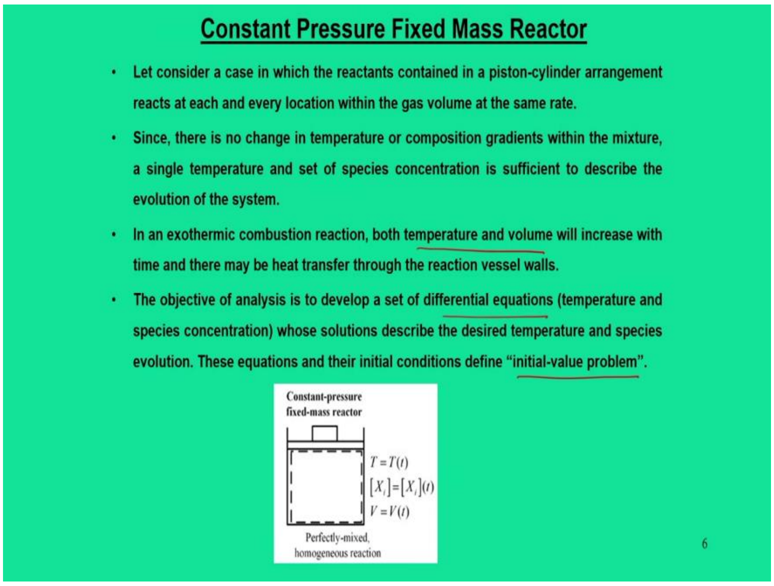

Constant Pressure Fixed Mass Reactor

- Let consider a case in which the reactants contained in a piston-cylinder arrangement reacts at each and every location within the gas volume at the same rate.
- Since, there is no change in temperature or composition gradients within the mixture, a single temperature and set of species concentration is sufficient to describe the evolution of the system.
- In an exothermic combustion reaction, both temperature and volume will increase with time and there may be heat transfer through the reaction vessel walls.
- The objective of analysis is to develop a set of differential equations (temperature and species concentration) whose solutions describe the desired temperature and species evolution. These equations and their initial conditions define "initial-value problem".

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Now, out of all these 4 models we will analyze one by one, but we will give more emphasis the emphasis to the first model and other models will just give some glimpses that how they are modeled. So, in the first model what we see is that is a Constant Pressure Fixed Mass Reactor. So, we consider the case in which reactants are contained in a piston cylinder arrangement and when they react and they react at each and every location within the gas volume at same rate.

That means, reaction takes place in this entire space at same rate; that means, every mass or every specific species sees similar reaction coefficients or kinetics at every location. Since there is no change in the temperature or composition gradient within the mixture, a single temperature and set of specific concentration is sufficient to describe the evolution of the systems.

Now if you say that the reaction is exothermic, then both temperature and volume will increase with time and there may be heat transfer through the reaction vessel as well. Now our objective is that how we want to model this temperature volume or species evolutions when the reaction proceeds.

So, towards the end of the things we will see that we need to find some differential equations and those equations can be modeled through initial value problem; that means, with the initial conditions they can be modeled.

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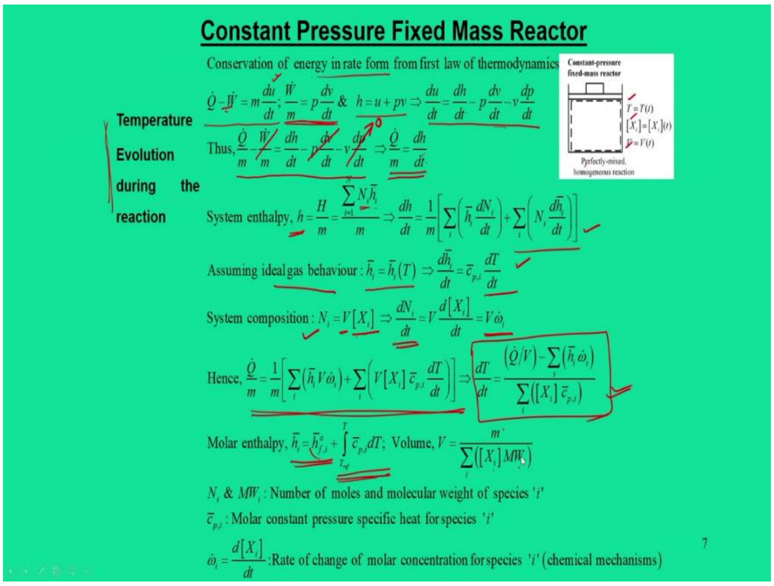

Constant Pressure Fixed Mass Reactor

Temperature Evolution during the reaction

Conservation of energy in rate form from first law of thermodynamics

$$\dot{Q}-\dot{W}=m\frac{du}{dt};\ \frac{\dot{W}}{m}=p\frac{dv}{dt}\ \&\ h=u+pv\Rightarrow\frac{du}{dt}=\frac{dh}{dt}-p\frac{dv}{dt}-v\frac{dp}{dt}$$

$$\text{Thus, }\frac{\dot{Q}}{m}-\cancel{\frac{\dot{W}}{m}}=\frac{dh}{dt}-\cancel{p\frac{dv}{dt}}-v\cancel{\frac{dp}{dt}}^{0}\Rightarrow\frac{\dot{Q}}{m}=\frac{dh}{dt}$$

$$\text{System enthalpy, }h=\frac{H}{m}=\frac{\sum_{i=1}^{N}N_i\bar{h}_i}{m}\Rightarrow\frac{dh}{dt}=\frac{1}{m}\left[\sum_i\left(\bar{h}_i\frac{dN_i}{dt}\right)+\sum_i\left(N_i\frac{d\bar{h}_i}{dt}\right)\right]$$

$$\text{Assuming ideal gas behaviour}:\bar{h}_i=\bar{h}_i(T)\Rightarrow\frac{d\bar{h}_i}{dt}=\bar{c}_{p,i}\frac{dT}{dt}$$

$$\text{System composition}:N_i=V[X_i]\Rightarrow\frac{dN_i}{dt}=V\frac{d[X_i]}{dt}=V\dot{\omega}_i$$

$$\text{Hence, }\frac{\dot{Q}}{m}=\frac{1}{m}\left[\sum_i\left(\bar{h}_iV\dot{\omega}_i\right)+\sum_i\left(V[X_i]\,\bar{c}_{p,i}\frac{dT}{dt}\right)\right]\Rightarrow\boxed{\frac{dT}{dt}=\frac{(\dot{Q}/V)-\sum_i\left(\bar{h}_i\dot{\omega}_i\right)}{\sum_i\left([X_i]\,\bar{c}_{p,i}\right)}}$$

$$\text{Molar enthalpy, }\bar{h}_i=\bar{h}^o_{f,i}+\int_{T_{ref}}^{T}\bar{c}_{p,i}dT;\ \text{Volume, }V=\frac{m}{\sum_i\left([X_i]MW_i\right)}$$

N_i & MW_i : Number of moles and molecular weight of species 'i'

$\bar{c}_{p,i}$: Molar constant pressure specific heat for species 'i'

$\dot{\omega}_i=\frac{d[X_i]}{dt}$:Rate of change of molar concentration for species 'i' (chemical mechanisms)

Now let us understand the basic mathematical concept behind the constant pressure fixed mass reactor. The first thing that we are going to analyze is the how temperature evolution takes place during the reactions. So, basically we are looking at temperature concentration and volume, how they changes with time when the reaction proceeds.

So, first equation that we recall is the first conservation of energy from the first law, but here we are looking at this energy equation in the rate form; rate form means we are looking in terms of time. So, that is what rate equations are expressed $\dot{Q} - \dot{W} = m\frac{du}{dt}$ and here u term we express in the form of enthalpy. $h = u - pv; \frac{du}{dt} = \frac{dh}{dt} - \frac{pdv}{dt} - \frac{vdp}{dt}$

Now also the work term that can be expressed in the form of pressure pdv equations. So, $\frac{\dot{W}}{m} = \frac{pdv}{dt}$. Now putting these 2 terms in these equations, we can say the main equation takes in this form, where we can say $\frac{\dot{W}}{m}$ and $\frac{pdv}{dt}$ they vanish, they gets cancelled from the both sides and since it is a constant pressure reactor, we can say $\frac{dp}{dt}$ term goes to 0.

Then $\frac{\dot{Q}}{m} = \frac{dh}{dt}$, now then we need to find out what is this $\frac{dh}{dt}$. So, for that we recall this system enthalpy h specific enthalpy in terms of H/m and in terms of molar form because all our analysis has to be done per mole of the fuel. So, we can write this total enthalpy as $h = \frac{\sum_{i=1}^{N} N_i \overline{h_i}}{m}$.

So, then we can find out what is dh by dt from this equation and you can see that the number each species are formed, enthalpy also changes with time because the temperature also changes with time. So, these two terms are function of time and they are related. So, this differentiation can take place in the manner that we can say $\frac{dh}{dt} = \frac{1}{m}\left[\sum_i \overline{h_i}\frac{dN_i}{dt} + \sum_i N_i \frac{d\overline{h_i}}{dt}\right]$.

Here we are now going to take some approximations, till this point of time we have been considering the ideal gas behavior for this mixing system. So, when you say ideal gas behavior, enthalpy is a function of temperature only and that also can be represented in terms of $C_{p,i}dT$ where here it is a constant pressure. So, I write molar space specific heat for species i. So, this is one part, second part we can also recall the system compositions.

Now try to look into the number of moles of species that is formed and which is nothing but the concentration of respective species multiplied by it is volume. So, from this equation, we can find out how the number of moles in species i changes with time and this is nothing but $\frac{dN_i}{dt} = V\dot{w}_i$ and $\dot{w}_i$ is nothing but concentration of species change with respect to time. So, putting all these things we are now in a position that after simplifications we frame the expression rate of change of temperature change with respect to time and which is nothing but a ratio.

$$\frac{dT}{dt} = \frac{(\dot{Q}/V) - \sum \bar{h}_\iota \dot{w}_i}{\sum_i [X_i]\, \bar{c}_{P,i}}$$

So, here we have to recall our previous concepts how to find out h_i. So, this is nothing but the molar specific heat for species i and it has to be calculated from its enthalpy of formation value through $C_{p,i}T$; Cp is also changing with time and the volume also we can express in terms of mass concentration and molecular weight. So, by putting this we are in a position that we can find an equation in which we can write how the temperature of the reaction changes with respect to time.

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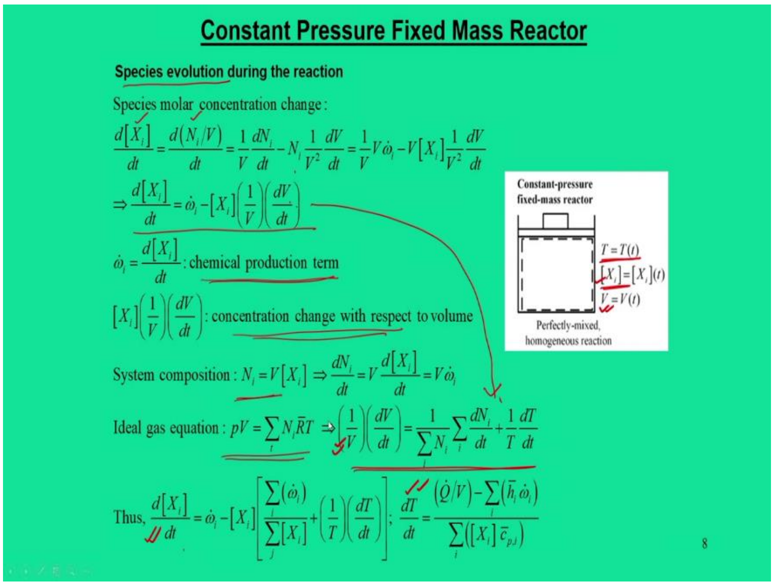

Constant Pressure Fixed Mass Reactor

Species evolution during the reaction

Species molar concentration change:

$$\frac{d[X_i]}{dt} = \frac{d(N_i/V)}{dt} = \frac{1}{V}\frac{dN_i}{dt} - N_i\frac{1}{V^2}\frac{dV}{dt} = \frac{1}{V}V\dot{\omega}_i - V[X_i]\frac{1}{V^2}\frac{dV}{dt}$$

$$\Rightarrow \frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i]\left(\frac{1}{V}\right)\left(\frac{dV}{dt}\right)$$

$\dot{\omega}_i = \frac{d[X_i]}{dt}$: chemical production term

$[X_i]\left(\frac{1}{V}\right)\left(\frac{dV}{dt}\right)$: concentration change with respect to volume

System composition : $N_i = V[X_i] \Rightarrow \frac{dN_i}{dt} = V\frac{d[X_i]}{dt} = V\dot{\omega}_i$

Ideal gas equation : $pV = \sum_i N_i \bar{R} T \Rightarrow \left(\frac{1}{V}\right)\left(\frac{dV}{dt}\right) = \frac{1}{\sum_j N_i}\sum_i \frac{dN_i}{dt} + \frac{1}{T}\frac{dT}{dt}$

Thus, $\frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i]\left[\frac{\sum_i(\dot{\omega}_i)}{\sum_j [X_i]} + \left(\frac{1}{T}\right)\left(\frac{dT}{dt}\right)\right]$; $\frac{dT}{dt} = \frac{(\dot{Q}/V) - \sum_i(\bar{h}_i \dot{\omega}_i)}{\sum_i([X_i]\bar{c}_{p,i})}$

In a similar analogy we can also derive another expression how species evolution takes place during an reactions. So, here we start with is a concentration of species I, $\frac{dX_i}{dt}$ this concentration can be expressed in terms of number of moles by total volume, then we can differentiate after differentiation we arrive at this expression $\frac{dX_i}{dt} = w_i - [X_i]\left(\frac{1}{V}\right)\left(\frac{dV}{dt}\right)$.

So, it means that same concentration of species i changes by 2 terms one is the rate at which it is formed and other is the due to the concentration change with respect to volume. Then further we can write this system equations Ni and we can also make ideal gas expressions and when you do that we can rewrite this particular equations in this manner.

That means, we can find from this equation $\left(\frac{1}{V}\right)\left(\frac{dV}{dt}\right) = \frac{1}{\sum_i N_i}\sum_i \frac{dN_i}{dt} + \frac{1}{T}\frac{dT}{dt}$. So, when this expressions are used in this concentration term we arrive at another expression; that means, how concentration of species i changes with time.

So, if you look at these 2 equations and try to correlate what we are trying to achieve, we are trying to achieve how temperature changes with the time which we get from this expression second one we are trying to see. How the concentration changes with time which we can achieve through this and we also see how volume changes with time this we also can achieve from this equation. So, we have all these three equations which are needs to be solved simultaneously.

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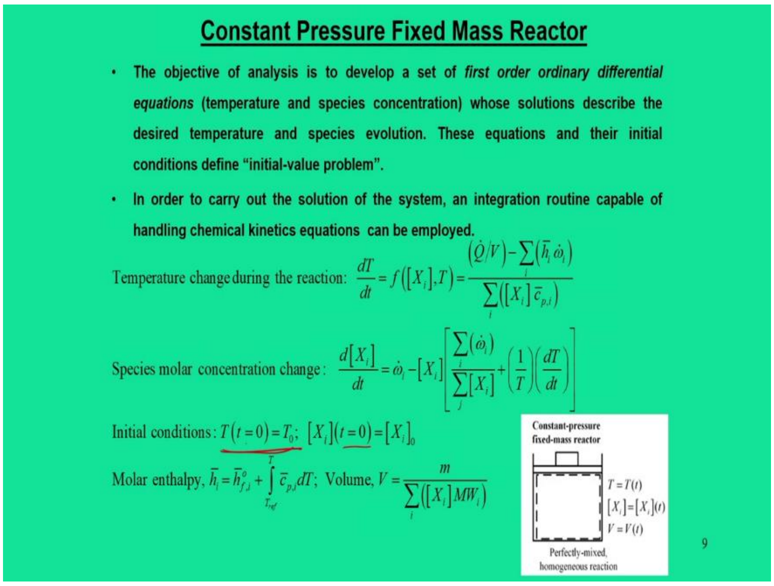

Constant Pressure Fixed Mass Reactor

- The objective of analysis is to develop a set of *first order ordinary differential equations* (temperature and species concentration) whose solutions describe the desired temperature and species evolution. These equations and their initial conditions define "initial-value problem".
- In order to carry out the solution of the system, an integration routine capable of handling chemical kinetics equations can be employed.

Temperature change during the reaction: $\frac{dT}{dt} = f([X_i], T) = \frac{(\dot{Q}/V) - \sum_i(\bar{h}_i\dot{\omega}_i)}{\sum_i([X_i]\bar{c}_{p,i})}$

Species molar concentration change: $\frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i]\left[\frac{\sum_i(\dot{\omega}_i)}{\sum_j[X_j]} + \left(\frac{1}{T}\right)\left(\frac{dT}{dt}\right)\right]$

Initial conditions: $T(t=0) = T_0$; $[X_i](t=0) = [X_i]_0$

Molar enthalpy, $\bar{h}_i = \bar{h}^o_{f,i} + \int_{T_{ref}}^{T} \bar{c}_{p,i}dT$; Volume, $V = \frac{m}{\sum_i([X_i]MW_i)}$

Now, to carry out these equations we require some initial conditions and that initial conditions you can assume some initial temperature $T(t=0)=T_0$. What is this initial value, $[X_i](t=0)=[X_i]_0$.

Now, the solution for this problem requires this new equation is to be solved along with the reaction kinetics, we need to program this or we need some kind of programming which can be coupled with respect to chemical kinetic reactions to solve these equations. We are not going further deep into it because it is a completely different research problems and which are not proper in the purview of this course.

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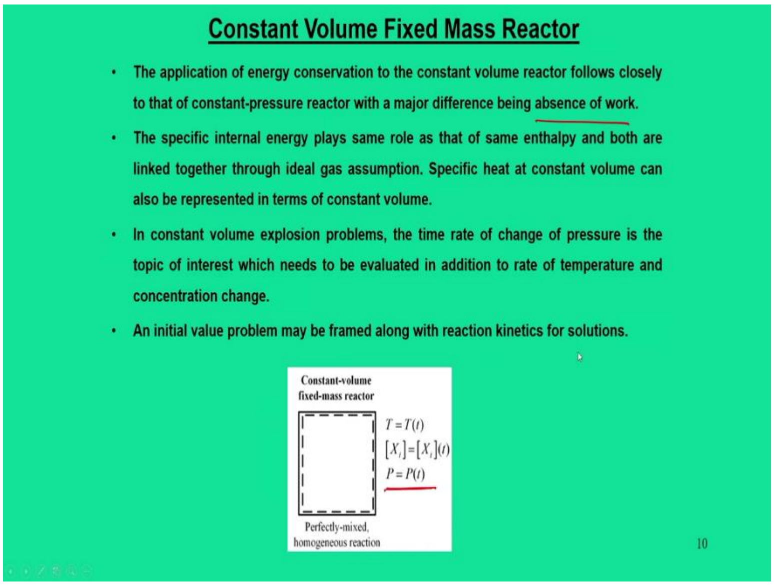

Constant Volume Fixed Mass Reactor

- The application of energy conservation to the constant volume reactor follows closely to that of constant-pressure reactor with a major difference being absence of work.
- The specific internal energy plays same role as that of same enthalpy and both are linked together through ideal gas assumption. Specific heat at constant volume can also be represented in terms of constant volume.
- In constant volume explosion problems, the time rate of change of pressure is the topic of interest which needs to be evaluated in addition to rate of temperature and concentration change.
- An initial value problem may be framed along with reaction kinetics for solutions.

Then we will move on to the constant volume fixed mass reactor, here we are looking at the situation that reaction is taking place in a container which is a fixed volume. And we are trying to see how temperature and concentration of species changes with time, at the same time we also look at how pressure within the container changes with time.

But only difference between the constant volume and constant pressure reactor is that, in a constant volume reactor follows closely with constant pressure. But only with the absence of work because there is no pdV work is involved here, but side by side another important point is that when you look at the constant volume reactor, pressure changes with the time.

So, it may so happen that when the reaction takes place and suddenly, we do not take care the materials in which the reaction is taking place, then it can explode; that means, if the pressure changes with time and it is such that the material is unable to withstand that pressure, in such cases it can explode. So, for such analysis variation of pressure with respect to time is also equally important and again it is an initial value problem which can be coupled with reaction kinetics for the solutions.

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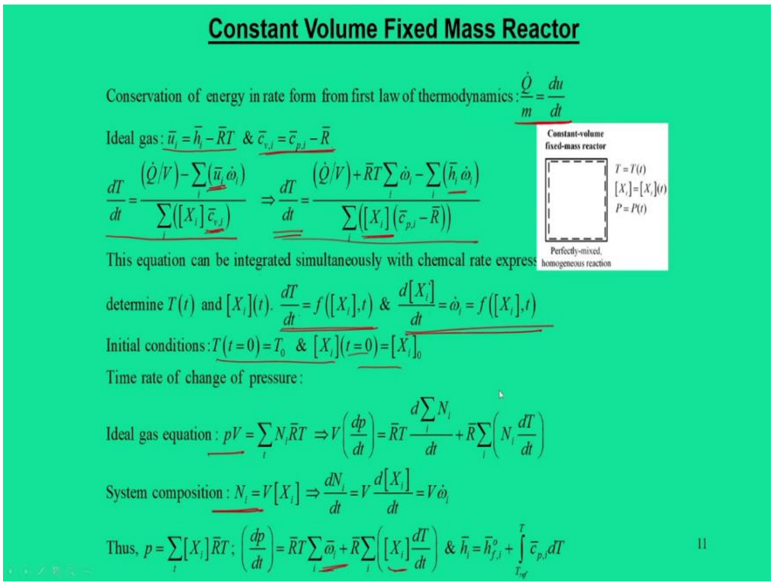

Constant Volume Fixed Mass Reactor

Conservation of energy in rate form from first law of thermodynamics: $\frac{\dot{Q}}{m}=\frac{du}{dt}$

Ideal gas: $\bar{u}_i=\bar{h}_i-\bar{R}T$ & $\bar{c}_{v,i}=\bar{c}_{p,i}-\bar{R}$

$$\frac{dT}{dt}=\frac{(\dot{Q}/V)-\sum_i(\bar{u}_i\dot{\omega}_i)}{\sum_i([X_i]\bar{c}_{v,i})} \Rightarrow \frac{dT}{dt}=\frac{(\dot{Q}/V)+\bar{R}T\sum_i\dot{\omega}_i-\sum_i(\bar{h}_i\dot{\omega}_i)}{\sum_i([X_i](\bar{c}_{p,i}-\bar{R}))}$$

This equation can be integrated simultaneously with chemcal rate express determine $T(t)$ and $[X_i](t)$. $\frac{dT}{dt}=f([X_i],t)$ & $\frac{d[X_i]}{dt}=\dot{\omega}_i=f([X_i],t)$

Initial conditions: $T(t=0)=T_0$ & $[X_i](t=0)=[X_i]_0$

Time rate of change of pressure:

Ideal gas equation: $pV=\sum_i N_i\bar{R}T \Rightarrow V\left(\frac{dp}{dt}\right)=\bar{R}T\frac{d\sum_i N_i}{dt}+\bar{R}\sum_i\left(N_i\frac{dT}{dt}\right)$

System composition: $N_i=V[X_i] \Rightarrow \frac{dN_i}{dt}=V\frac{d[X_i]}{dt}=V\dot{\omega}_i$

Thus, $p=\sum_i[X_i]\bar{R}T$; $\left(\frac{dp}{dt}\right)=\bar{R}T\sum_i\bar{\omega}_i+\bar{R}\sum_i\left([X_i]\frac{dT}{dt}\right)$ & $\bar{h}_i=\bar{h}^o_{f,i}+\int_{T_{ref}}^{T}\bar{c}_{p,i}dT$

So, here we recall the same equations $\frac{\dot{Q}}{m}=\frac{du}{dt}$ and here since it is a constant volume situations we can recall the internal energy and enthalpy can be related through an ideal gas equations also. We have $\bar{c}_{v,i}=\bar{c}_{p,i}-\bar{R}$.

And the expression or derivations for $\frac{dT}{dt}$ same as that of constant pressure reactor, but only difference is that in the expressions instead of molar enthalpy we have used molar internal energy here, again we instead of specific heat at constant pressure we have used here specific heated constant volume; with these only changes one can write the equations

$$\frac{dT}{dt}=\frac{\left(\frac{\dot{Q}}{V}\right)+\bar{R}T\sum_i\dot{\omega}_i-\sum_i(\bar{h}_i\dot{\omega}_i)}{\sum_i\left([X_i](\bar{c}_{p,i}-\bar{R})\right)}$$

And since we know that this internal energy and enthalpy are also related. So, another equation can be framed by in including enthalpy terms here. Then now again in this equation also we can look into how the concentration of species i changes.

So, this equation can be integrated simultaneously with rate expressions to find 2 complete expressions that is temperature change with respect to time concentration change with respect to time, with same initial conditions and reaction kinetics, the systems can be modeled with respect to ideal gas frame of equations and system compositions. So, ultimately there are 2 equations that needs to be solved $\frac{dT}{dt}$ and $\frac{d[X_i]}{dt}$ with these initial conditions and chemical kinetics.

Other equations that you require how pressure changes with time which we get from an ideal equation $\left(\frac{dp}{dt}\right) = \bar{R}T\sum_i \bar{\omega}_i + \bar{R}\sum_i \left([X_i]\frac{dT}{dt}\right)$, $\bar{\omega}_i$ is nothing but the change of concentration with respect to time.

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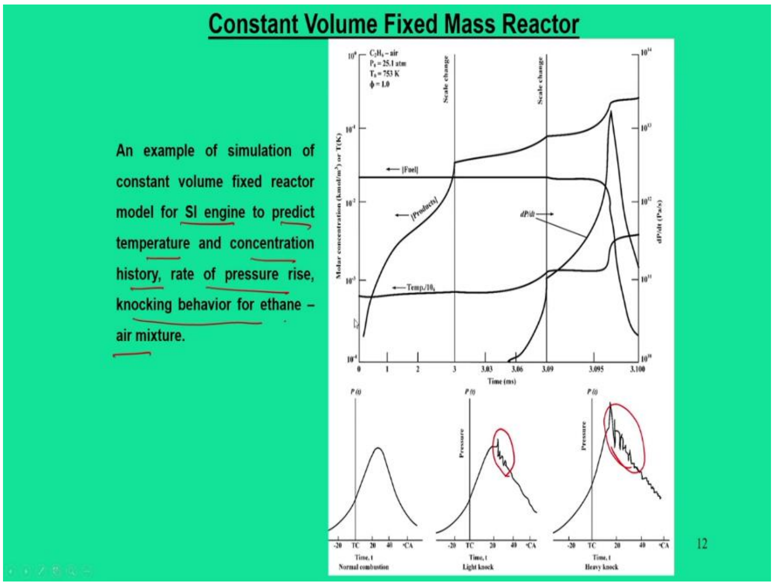

Constant Volume Fixed Mass Reactor

An example of simulation of constant volume fixed reactor model for SI engine to predict temperature and concentration history, rate of pressure rise, knocking behavior for ethane – air mixture.

So, this is how you are going to solve, again we are not going deep into that, but to have some kind of philosophy or glimpses, an example or solutions by solving a constant volume mass reactor, one can achieve some analysis. If you look at this particular plot, it shows the how the reaction evolves in a IC engine and to predict the temperature concentration history, rate of pressure rise, knocking behavior for ethane air mixture. So, you might be knowing about trends of the plots much earlier in the IC engine course in the thermodynamics. But what where we see is that when you look at those things those are major data and during the engine running operations, they are basically experimental data which were acquired during the engine operations.

But what we see here is the model data and in this model data, the fuel that is taken is ethane and it is getting combusted in the air and when it is utilized in an SI engine you can see the fuel with time its concentration suddenly drops up maybe after 3 milliseconds, if you look at the products that are formed its concentration keeps on increasing with time and so on.

So, this is the reactants and when fuel gets oxidized products are formed and initially the temperatures suddenly rises, once rises, after all these things occurs after 3 milliseconds. So, this is temperature rise.

Now if you look at rate of pressure rise, pressure initially you can see, there is a steep rise in the pressure close to about after 3 milliseconds and it goes on and you can have a peak pressure at some point some of the point instantly, so you can say its instantaneous pressure. Now if this pressure is coupled with subsequent operations, you can see some situations if fuels and air are not adequate, combustion takes place in an inadequate manner, we can see the unexpected rise in the pressures with time.

So, this is something like knocking behavior. So, what the significance of these plots is that all these parameters are modeled in a through this constant volume fixed reactor scheme and with this we are trying to predict the different fuel and product concentration as well as the pressure change with time.

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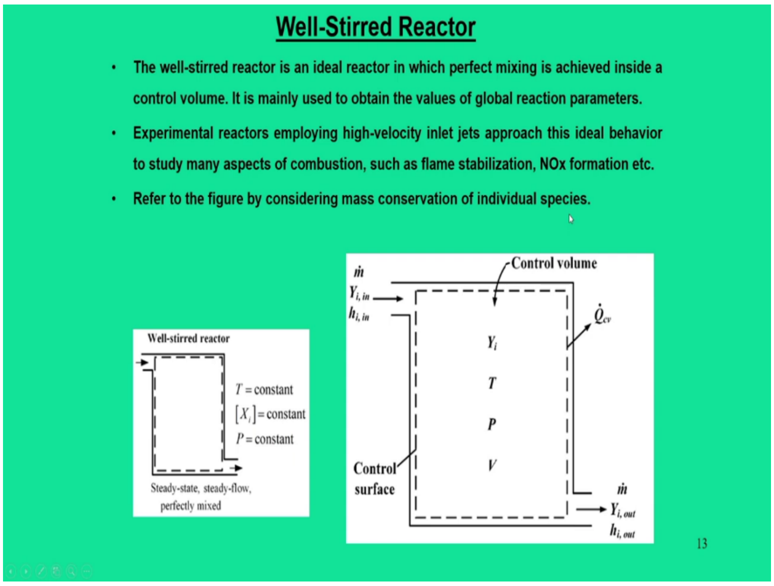

Well-Stirred Reactor

- The well-stirred reactor is an ideal reactor in which perfect mixing is achieved inside a control volume. It is mainly used to obtain the values of global reaction parameters.
- Experimental reactors employing high-velocity inlet jets approach this ideal behavior to study many aspects of combustion, such as flame stabilization, NOx formation etc.
- Refer to the figure by considering mass conservation of individual species.

The next reactor that we are going to analyze is a well stirred reactor. So, till this point of time it is we are looking at how the reaction takes place with respect to time. So, but in a well stirred reactor it is a steady state steady flow perfectly mixed reactor, we can imagine that some fuel is entering continuously and the mixing takes place and products are leaving.

So, after reaction the products are leaving and in this entire model, the temperature remains constant, concentration remains constant and pressure remains constant. But what changes is that the within this control volume we are looking at the mole fractions, temperature pressure and volume.

Or we can say what is this steady state value, when something is coming; that means, in the inlet we have certain mass flow rate, mole fractions, enthalpy; outlet also you have mass flow rate, mole fraction of species and enthalpy. So, it is considered an ideal reactor in which perfect mixing is achieved inside the control volume and it is mainly used to obtain the values of global reaction parameters.

So, basically when it is modeled, it is modeled with the rate chemical kinetics of global reactions not for the elementary reactions; that means, we are not bothered about the elementary species formations. So, typically this kind of reactors are employed to study the NOx formation behavior, flame stabilizations and here we are looking at the mass conservation of individual species.

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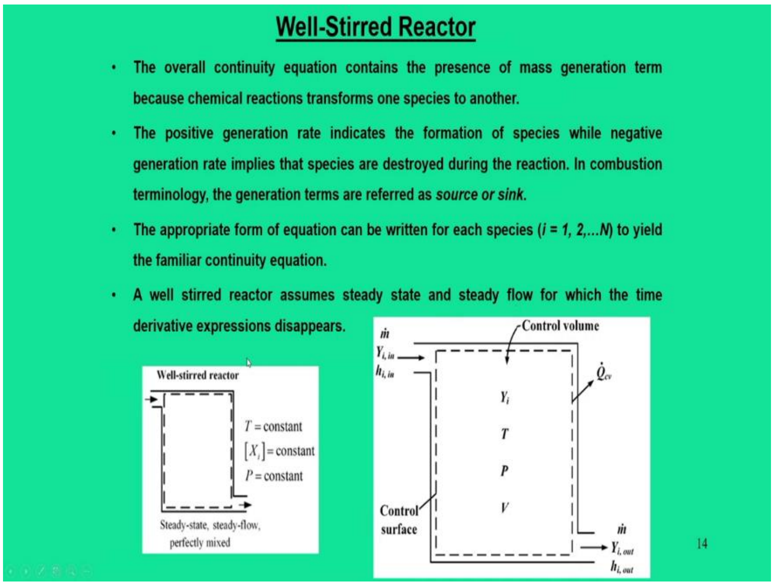

Well-Stirred Reactor

- The overall continuity equation contains the presence of mass generation term because chemical reactions transforms one species to another.
- The positive generation rate indicates the formation of species while negative generation rate implies that species are destroyed during the reaction. In combustion terminology, the generation terms are referred as *source or sink.*
- The appropriate form of equation can be written for each species ($i = 1, 2, \ldots N$) to yield the familiar continuity equation.
- A well stirred reactor assumes steady state and steady flow for which the time derivative expressions disappears.

So, how do you do that? To do that we can say that we have to analyze the overall continuity equations in terms of mass generation terms, because chemical reaction transfers from one species to other. The positive generation rate that means within this control volume, the positive generation rates indicates the formation of species.

And the negative generation rate indicates that species are destroyed and in our combustion term the generator terms are referred as source or sinks; source means it is formed and destroyed means it is a sink. So, it goes to the sink and to do this analysis we need to frame appropriate form of equations for each species, there may be n number of species. The well stirred reactor assumes steady state steady flow for which time derivatives expressions disappears.

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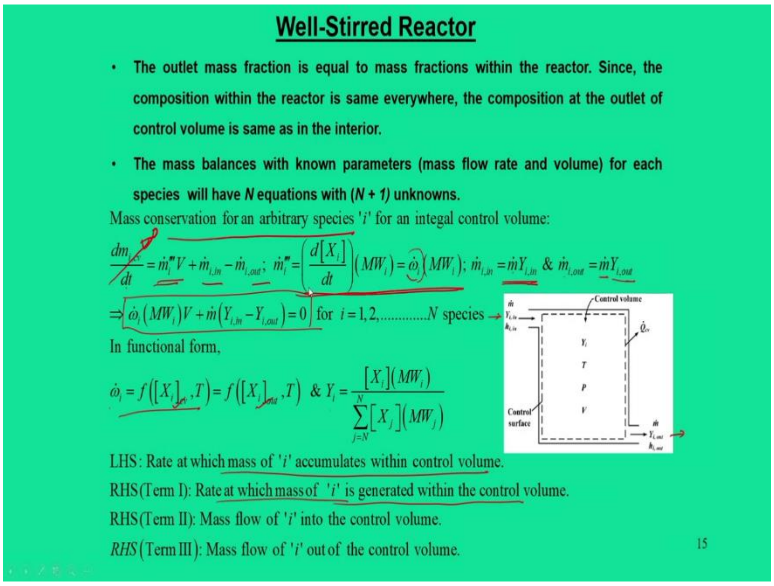

Well-Stirred Reactor

- **The outlet mass fraction is equal to mass fractions within the reactor. Since, the composition within the reactor is same everywhere, the composition at the outlet of control volume is same as in the interior.**
- **The mass balances with known parameters (mass flow rate and volume) for each species will have *N* equations with *(N + 1)* unknowns.**

Mass conservation for an arbitrary species 'i' for an integal control volume:

$$\cancel{\frac{dm_{i,cv}}{dt}} = \dot{m}_i'''V + \dot{m}_{i,in} - \dot{m}_{i,out};\ \dot{m}_i''' = \left(\frac{d[X_i]}{dt}\right)(MW_i) = \dot{\omega}_i(MW_i);\ \dot{m}_{i,in} = \dot{m}Y_{i,in}\ \&\ \dot{m}_{i,out} = \dot{m}Y_{i,out}$$

$$\Rightarrow \boxed{\dot{\omega}_i(MW_i)V + \dot{m}(Y_{i,in} - Y_{i,out}) = 0} \text{ for } i = 1,2,\ldots\ldots\ldots\ldots N \text{ species}$$

In functional form,

$$\dot{\omega}_i = f([X_i]_{cv}, T) = f([X_i]_{out}, T)\ \&\ Y_i = \frac{[X_i](MW_i)}{\sum_{j=N}^{N}[X_j](MW_j)}$$

LHS: Rate at which mass of 'i' accumulates within control volume.

RHS(Term I): Rate at which mass of 'i' is generated within the control volume.

RHS(Term II): Mass flow of 'i' into the control volume.

RHS(Term III): Mass flow of 'i' out of the control volume.

So, how does it look like, we can see here that the outlet mass fraction is equal to mass fractions within the reactor. Since the compositions of the reactor is same everywhere composition of the outlet of the control volume is same as that of interior. So, through this equation one can write mass conservation of arbitrary species, we can write this rate at which the concentration of mass changes with time has 3 terms, one is that is rate at which mass accumulates in the control volume is $\frac{dm_{i,cv}}{dt}$.

Right hand side first term $\dot{m}_i'''V$ is the rate at which mass of i is generated with the control volume; that means, some species are generated, $\dot{m}_{i,in}$ and $\dot{m}_{i,out}$ normally refers to the inlet and exit conditions. The mass flow rate i into the control volume and out of the control volume.

Now this first term $\dot{m}_i'''$ can be correlated in terms of its molecular weight and the rate of change of concentration of species $\dot{\omega}_i$ and this can be written in the functional form and that can be written for inlet as well as out outlet.

And $\dot{m}_{i,in}$ we can find its total mass into its mole fractions, and $\dot{m}_{i,out} = \dot{m}Y_{i,out}$. So, putting these equations and since it is a steady state situation this term vanishes that mean $\frac{dm_{i,cv}}{dt}$ has to be 0.

So, from this equation, we can we arrive at this expression $\dot{\omega}_i(MW_i)V + \dot{m}\left(Y_{i,in} - Y_{i,out}\right) = 0$. And these relations $\dot{\omega}_i$ and Y_i can be expressed in this manner.

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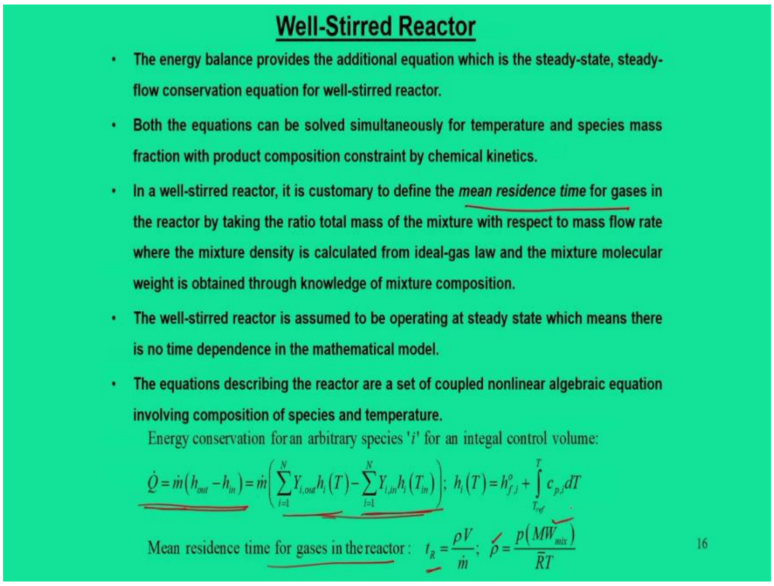

Well-Stirred Reactor

- The energy balance provides the additional equation which is the steady-state, steady-flow conservation equation for well-stirred reactor.
- Both the equations can be solved simultaneously for temperature and species mass fraction with product composition constraint by chemical kinetics.
- In a well-stirred reactor, it is customary to define the *mean residence time* for gases in the reactor by taking the ratio total mass of the mixture with respect to mass flow rate where the mixture density is calculated from ideal-gas law and the mixture molecular weight is obtained through knowledge of mixture composition.
- The well-stirred reactor is assumed to be operating at steady state which means there is no time dependence in the mathematical model.
- The equations describing the reactor are a set of coupled nonlinear algebraic equation involving composition of species and temperature.

Energy conservation for an arbitrary species 'i' for an integal control volume:

$$\dot{Q} = \dot{m}\left(h_{out} - h_{in}\right) = \dot{m}\left(\sum_{i=1}^{N} Y_{i,out} h_i(T) - \sum_{i=1}^{N} Y_{i,in} h_i(T_{in})\right);\ h_i(T) = h_{f,i}^{o} + \int_{T_{ref}}^{T} c_{p,i}\, dT$$

Mean residence time for gases in the reactor: $t_R = \dfrac{\rho V}{\dot{m}};\ \rho = \dfrac{p(MW_{mix})}{\bar{R}T}$

Then moving further, we can also find another equation which is the conservation of energy, involving what is the enthalpy which is going out and what is the enthalpy which is coming in. So, difference in of this enthalpy multiplied with mass will give you the energy conservation equations for each species. So, we have energy conservations we have mass conservations.

So, both the equations can be solved simultaneously for species fractions and product composition constant through chemical kinetics and another important term which is normally defined in a well stirred reactor is the mean residence time for the gases.

So, it is nothing but we say that as the reaction proceed, for the subsequent reactions to allow there is some residence time for each gases that remains at one particular time, so that is called as mean residence time for the reactor in the gases. So, that is defined as $t_R = \frac{\rho V}{\dot{m}}$ and ρ is nothing but the density of the mixture and this can be calculated from the ideal gas relations by knowing the molecular weight of the mixture.

So, the well stirred reactor is assumed to be operating at steady state which means there is no time dependence on the mathematical models. So, equations describing the reactor are a set of non-linear algebraic equations in the form of species and temperatures these are nothing but the algebraic equations.

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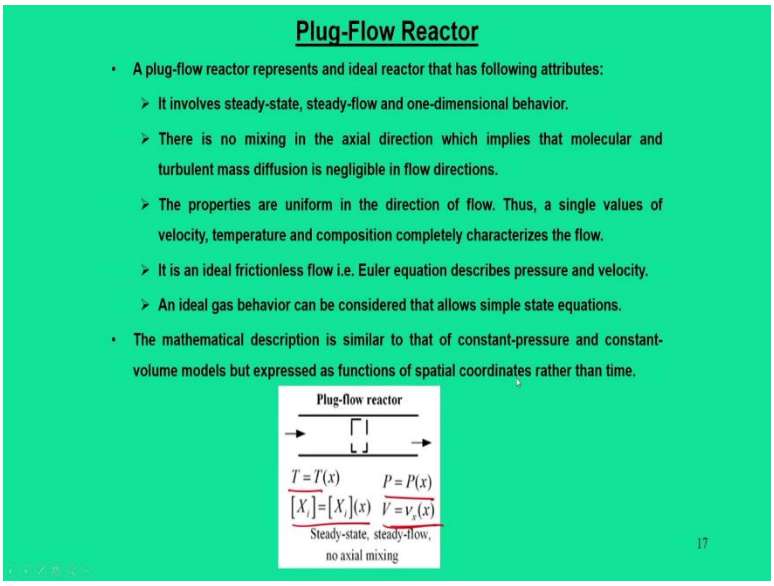

Plug-Flow Reactor

- A plug-flow reactor represents and ideal reactor that has following attributes:
  - ➢ It involves steady-state, steady-flow and one-dimensional behavior.
  - ➢ There is no mixing in the axial direction which implies that molecular and turbulent mass diffusion is negligible in flow directions.
  - ➢ The properties are uniform in the direction of flow. Thus, a single values of velocity, temperature and composition completely characterizes the flow.
  - ➢ It is an ideal frictionless flow i.e. Euler equation describes pressure and velocity.
  - ➢ An ideal gas behavior can be considered that allows simple state equations.
- The mathematical description is similar to that of constant-pressure and constant-volume models but expressed as functions of spatial coordinates rather than time.

Plug-flow reactor

$T = T(x)$

$P = P(x)$

$[X_i] = [X_i](x)$

$V = v_x(x)$

Steady-state, steady-flow, no axial mixing

So, now next reactor which we are going to analyze is a Plug Flow Reactor. The plug flow reactor is another kind of reactor in which we see that the reaction proceeds as and when the flow is happening. You can say that the flow is going from one directions; that means, direction of the flow is fixed either this flow can be mixture of both reactant as well as products or it can be a situation that the air is entering and fuel is being spread into this medium.

So, such kind of situations are model through plug flow reactors. But what assumption is says that the temperature, pressure and concentrations they vary only in one particular direction. Of course, velocity that varies with one particular direction and there is no axial mixing. So, it is a steady flow, so there is no time term steady state steady flow, but no axial mixing. So, the plug flow reactor represents one of the ideal reactors which has following attributes it involves steady state steady flow 1 dimensional behavior there is no mixing in the axial directions, which implies that molecular and turbulent mass diffusion is negligible, the properties are uniform in the direction of the flow. So, thus a single values of velocity temperature and composition allows completely to characterize the flow, it is an ideal frictionless flow.

So that means, we can use Euler equations to describe pressure and velocity, one can assume an ideal gas behavior which allows the steady state equations. So, we can say it is a similar to that of a constant pressure or constant volume models expressed in a spatial coordinates rather than time coordinates.

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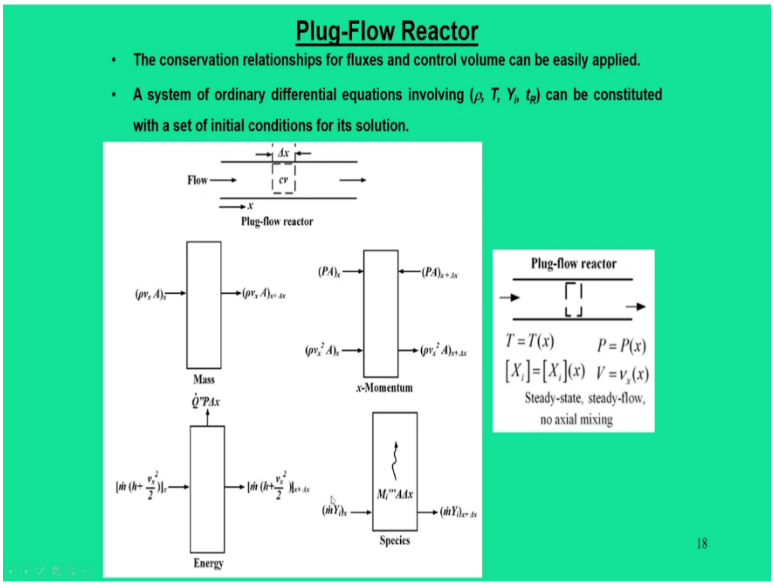

Plug-Flow Reactor

- The conservation relationships for fluxes and control volume can be easily applied.
- A system of ordinary differential equations involving (ρ, T, Y_i, t_R) can be constituted with a set of initial conditions for its solution.

So, I am not going to go deep into details, but just to see that how the 4 governing equations are model one is mass equations. So, we can say there is a flow we can assume some elementally length dx and across that length we can find a control volume, within that control volume we are trying to see what is the fluxes that entering and what is the fluxes are that leaving.

Now when it is entering how much force it carries how much energy it carries and how many species it contains. So, all these things can be equated.

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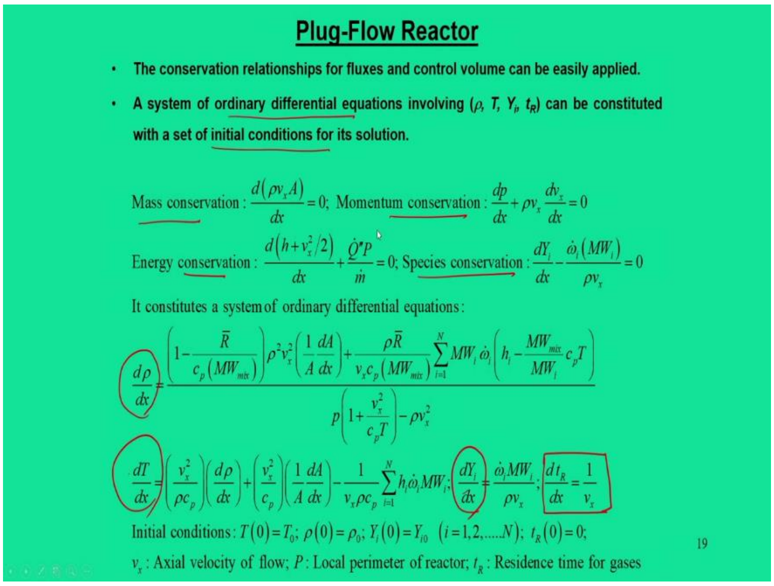

Plug-Flow Reactor

- The conservation relationships for fluxes and control volume can be easily applied.
- A system of ordinary differential equations involving (ρ, T, Y_i, t_R) can be constituted with a set of initial conditions for its solution.

Mass conservation : $\frac{d(\rho v_x A)}{dx} = 0$; Momentum conservation : $\frac{dp}{dx} + \rho v_x \frac{dv_x}{dx} = 0$

Energy conservation : $\frac{d(h + v_x^2/2)}{dx} + \frac{\dot{Q}'' P}{\dot{m}} = 0$; Species conservation : $\frac{dY_i}{dx} - \frac{\dot{\omega}_i (MW_i)}{\rho v_x} = 0$

It constitutes a system of ordinary differential equations:

$$\frac{d\rho}{dx} = \frac{\left(1 - \frac{\bar{R}}{c_p (MW_{mix})}\right) \rho^2 v_x^2 \left(\frac{1}{A}\frac{dA}{dx}\right) + \frac{\rho \bar{R}}{v_x c_p (MW_{mix})} \sum_{i=1}^{N} MW_i \dot{\omega}_i \left(h_i - \frac{MW_{mix}}{MW_i} c_p T\right)}{p\left(1 + \frac{v_x^2}{c_p T}\right) - \rho v_x^2}$$

$$\frac{dT}{dx} = \left(\frac{v_x^2}{\rho c_p}\right)\left(\frac{d\rho}{dx}\right) + \left(\frac{v_x^2}{c_p}\right)\left(\frac{1}{A}\frac{dA}{dx}\right) - \frac{1}{v_x \rho c_p} \sum_{i=1}^{N} h_i \dot{\omega}_i MW_i; \quad \frac{dY_i}{dx} = \frac{\dot{\omega}_i MW_i}{\rho v_x}; \quad \boxed{\frac{dt_R}{dx} = \frac{1}{v_x}}$$

Initial conditions : $T(0) = T_0$; $\rho(0) = \rho_0$; $Y_i(0) = Y_{i0}$ $(i = 1, 2, \ldots N)$; $t_R(0) = 0$;

v_x : Axial velocity of flow; P : Local perimeter of reactor; t_R : Residence time for gases

Now, when you equated, then we can find four in different equations one is mass conservation, momentum conservation, energy conservation and species conservations. And by doing so we can solve for 2 important equations $d\rho/dx$, dT/dx, and dY/dx.

So, these 3 terms needs to be find out and from this equation of course, if you see it is a big equations, but most of the things are known and each equations can be drawn for individual species and we can find out the density change, temperature change and mole fraction change with respect to time.

And of course, here also another term that can be find out what is the residence time for gases with respect to a particular location. But one significant advantage that it contains the ordinary differential equations and which can be solved with some certain initial conditions for its solutions.

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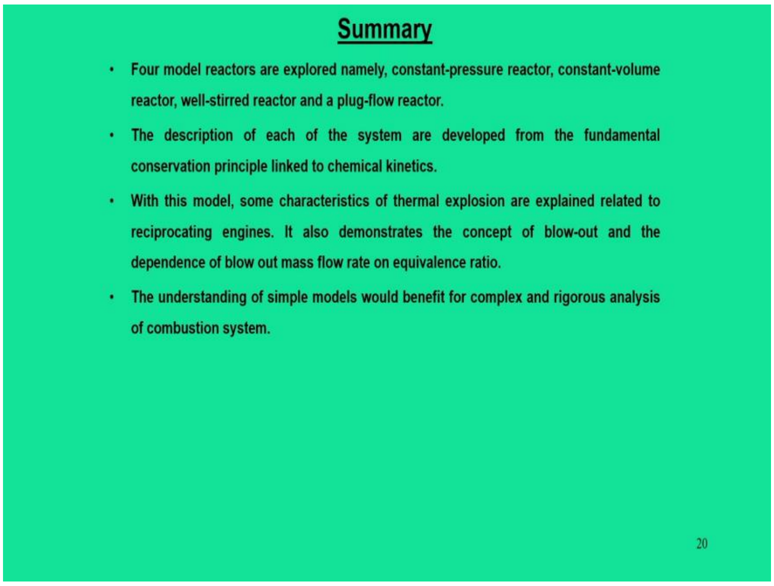

Summary

- Four model reactors are explored namely, constant-pressure reactor, constant-volume reactor, well-stirred reactor and a plug-flow reactor.
- The description of each of the system are developed from the fundamental conservation principle linked to chemical kinetics.
- With this model, some characteristics of thermal explosion are explained related to reciprocating engines. It also demonstrates the concept of blow-out and the dependence of blow out mass flow rate on equivalence ratio.
- The understanding of simple models would benefit for complex and rigorous analysis of combustion system.

So, in summary what i can say that all the reactions models what you have described so far are highly mathematical in natures and there are many number of species means number of reactions also will also be higher. So, if there are n number of species, the number of equations will be also n number of such equations and each equations has to be linked with respect to it is chemical kinetics form, so that to arrive its solutions.

So, 4 models are explored constant pressure, constant volume, well stirred and plug flow reactor and each of them has to be developed with conservation principle linked to chemical kinetics. Through this model some of the characteristics of thermal explosion can be explained related to reciprocating engines, we can also relate the information of how pressure changes with respect to time, so that we can formulate the expression for explosion.

So, the understanding of the simple model will benefit the complex and rigorous analysis of combustion systems. So, we are not going to deep into these models because it is not in the purview of this course. But however, the fundamental concepts of reaction models and it is corresponding chemical kinetics we will help for the learners, so that they can create their own combustion models for different chemical reactions.

Now before we proceed, I will just try to solve a very simple problem we are trying to link this particular concept with compression ignition engine combustion.

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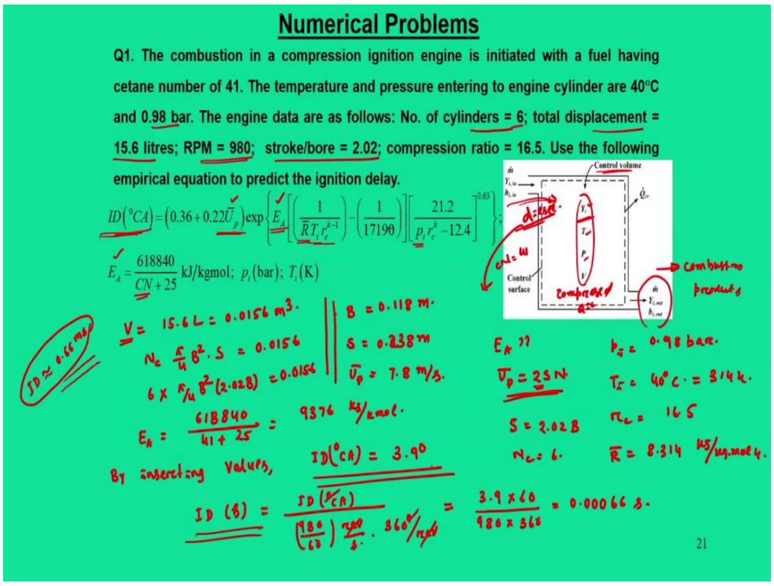

Numerical Problems

Q1. The combustion in a compression ignition engine is initiated with a fuel having cetane number of 41. The temperature and pressure entering to engine cylinder are 40°C and 0.98 bar. The engine data are as follows: No. of cylinders = 6; total displacement = 15.6 litres; RPM = 980; stroke/bore = 2.02; compression ratio = 16.5. Use the following empirical equation to predict the ignition delay.

$$ID(^{\circ}CA) = (0.36 + 0.22\bar{U}_p)\exp\left\{E_A\left[\left(\frac{1}{\bar{R}T_i r_c^{k-1}}\right) - \left(\frac{1}{17190}\right)\right]\left[\frac{21.2}{p_i r_c^k - 12.4}\right]^{0.63}\right\};$$

$$E_A = \frac{618840}{CN + 25}\ \text{kJ/kgmol};\ p_i(\text{bar});\ T_i(\text{K})$$

$V = 15.6\ L = 0.0156\ m^3.$

$N_c\ \frac{\pi}{4}B^2.S = 0.0156$

$6 \times \pi/4\ B^2(2.02B) = 0.0156$

$B = 0.118\ m.$

$S = 0.238\ m$

$\bar{U}_p = 7.8\ m/s.$

$E_A = \frac{618840}{41 + 25} = 9376\ kJ/kmol.$

By inserting values, $ID(^{0}CA) = 3.9^{0}$

$ID\ (s) = \frac{ID\ (^{0}CA)}{\left(\frac{980}{60}\right)\frac{rev}{s}.\ 360^{0}/rev} = \frac{3.9 \times 60}{980 \times 360} = 0.00066\ s.$

$ID \approx 0.66\ ms$

$E_A\ ??$

$\bar{U}_p = 2SN$

$S = 2.02B$

$N_c = 6.$

$p_i = 0.98\ bar.$

$T_i = 40^{\circ}C = 314\ k.$

$r_c = 16.5$

$\bar{R} = 8.314\ kJ/kg.mol\ k.$

What we are looking at in a CI engine combustion, we all know that in a CI engine combustions we have a diesel fuel and fuel and air that mixing takes place in the combustion chamber; in a compressed air medium the fuel is spread. So, you can assume that as if some of the fuel is entering into a combustion model and we can assume this combustion chamber as a control volume.

So, if you look at this things, these are different mole fractions temperature, pressure and volume which changes with pressure and volume and it is a steady state reactor. And here we are seeing that we have fixed air or we say compressed air and fuel is entering into it and in this case, it is diesel and its cetane number is given as 41 and out of this we have some combustion products.

So, there are many models that has been derived. So, when a diesel engine combustion we all know there is a term called as ignition delay, ignition delay is like the at certain time fuel is injected, but the combustion happens after certain period of time.

And this ignition delay is correlated with respect to $\bar{U}_P$ that is average piston speed, activation energy, universal gas constant, initial temperature, compression ratio, initial pressure and this is a semi empirical relation. And with this engine data we are expected to find what is the ignition delay period. So of course, the problem is simple and all the data are given, but only thing is that we need to meticulously find out the different parameters which are appearing in this equation.

So, in this equation what parameter is required is $\overline{U}_P$ average piston speed, E_A needs to be calculated from this equation with the value of cetane number, all other data are given. So, data that are given: $p_i = 0.98\ bar; T_i = 40C = 314K; r_c = 16.5; R = 8.314\ kJ/kg.mol.K$

Now to calculate this $\overline{U}_P$, other engine data is given what is that total number of cylinder is six, total displacement is 15.6 liter.

$$V = 15.6L = 0.0156m^3; N_c \frac{\pi}{4}\ B^2 S = 0.0156\ \Rightarrow 6 \times \frac{\pi}{4} \times B^2 \times 2.02B = 0.0156$$

$$\Rightarrow B = 0.118m; S = 0.238m$$

$$\overline{U}_P = 2Sr_c = 7.8m/s$$

So, that 2 terms comes because it is a 4 stroke engine that is 2 revolutions and 2 power stroke. So, other term that needs to be found what is E_A activation energy for the fuel.

That means, during the reactions when the fuel that is carrying the energy, during the reactions, the chemical bonds needs to be broken. As a result the energy which is going to be released is through its activation energy due to chemical bond.

$$E_A = \frac{618840}{41 + 25} = 9376\ kJ/kmol$$

So, in this equation all the number are known. So, by inserting values one can find out ignition delay in terms of degree crank angle this is 3.9 degree. So, ignition delay can express in terms of 2 things one is in terms of engine view point, we express at what particular locations the fuel needs to be injected and at what point the combustion takes place. So, this is represented in terms of degree crank angle. Now in terms of time this can be converted by knowing engine speed, engine speed is 980 rpm.

$$ID(s) = \frac{ID(\circ/CA)}{\left(\frac{980}{60}\right)\frac{rev}{s} \times 360°/rev} = \frac{3.9 \times 60}{980 \times 360} = 0.00066\ s$$

And the so ideally the ignition delay is can be approximated as 0.66 millisecond. So, when such a model is done for a fuel we can say the ignition delay that defines time at which fuel is ignited and the time difference between the time of injection and the time of combustions and in this case it is 0.66 milliseconds. So, with this I conclude.

Thank you for your attention.