Combustion in Air Breathing Aero Engines

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Lecture - 08
Oxidation Mechanism of Fuels I

Hello everybody. Welcome back to this course on combustion in air breathing aero engines. Now last class we have seen that you have seen details of chemical kinetics from a generalised view point. We have introduced the concepts of a generalised reaction then we have introduced law of mass action and then we introduced the reaction rate constant or the reaction rate coefficient and the concepts of activation energies, etcetera. And then we discussed how we can describe a explosion that is fast reactions, which release which leads to rapid release of energy due to the chain branching steps; chain branching which is an essential reaction that is involving the chain carriers.

So, this we have seen, but that was as you have seen that that specifically and of course, we have also looked into the different theories of reaction rates, the namely the collusion rate theory and the transition state theory. But as we have seen this was done for generalised reaction and we did not discuss specific reactions that is specific to combustion in air breathing engines as such, but that; so what we will do in this class is that we will use that generalised framework that was introduced in last class, and here in this class we look into specific reactions that are of interest in an actual practical combustor ok.

So, that is what we will do here.

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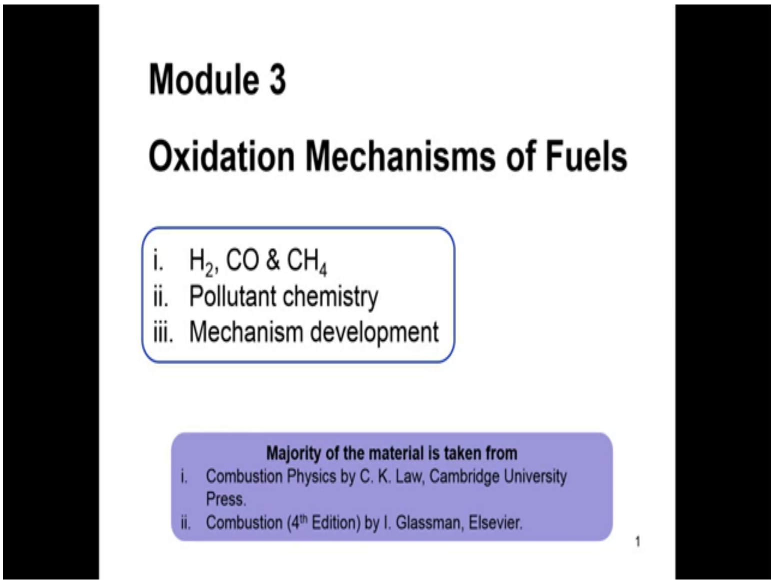

Module 3

Oxidation Mechanisms of Fuels

i. H_2, CO & CH_4
ii. Pollutant chemistry
iii. Mechanism development

Majority of the material is taken from
i. Combustion Physics by C. K. Law, Cambridge University Press.
ii. Combustion (4th Edition) by I. Glassman, Elsevier.

So, what we will do is that as you see here we will talk about the reactions involving hydrogen carbon monoxide methane, and not only because these are important fuels, but these are these if your idea is that if you understand the reaction mechanism of this, the reaction mechanisms through which the hydrogen combusts or hydrogen oxidises in presence of oxidiser, how carbon monoxide oxidises, how methane oxidises these reaction mechanism form integral parts of reaction mechanisms of complex fuels that are used in actual air breathing engines, alright.

So, that is the idea and then we will look into pollutant chemistry of course, when you design a combustor you have ensure two things; basically that number one it should be producing the required amount of power that it should burn the fuel air mixture that you are sending in and it should burn cleanly it should not produce too much of nox and too much of soot.

So, soot and nox are two major polluting major pollutants that are result of hydro carbon combustion, and we will try to understand the reaction mechanisms of the formation of those pollutants. And then we will go into mechanism we will go into mechanism development. So, mechanism development and also mechanism reduction that is we will often see that the reaction mechanisms that are of interest that is for example, involving a combustion of larger hydro carbon those are often involved too many species and too many reactions, and as a result of that it often becomes prohibitively expensive for their use in a given CFD code, suppose you want to do the computation of fluid dynamics simulation of actual combustor. So, then you want these realistic mechanisms, but then this realistic mechanisms are so large that you cannot use it for practical simulation.

So, what you need to do is that you need to reduce it is size make them compact so the number of species and number of reactions used are of are practical the numbers are less. So, that we can do this simulation with required amount of computational power and of course, it compromises on the accuracy, but we have to ensure that we desire some kind of properties and desire some kind of accuracies so that, those are compromises at a minimum level.

So, we need to understand mechanisms the oxidisation mechanism of fuels basically to basically without that we do not we have no idea about how the products are being formed and as a result of which even which products will be formed and what we can do how we can engineer. So, that we can desire we can make sure certain properties are certain desired properties are maintained inside the combustor for example, you can have a always a flame stabilise inside the combustor whereas, certain undesired properties like pollutants and emissions those are mitigated ok.

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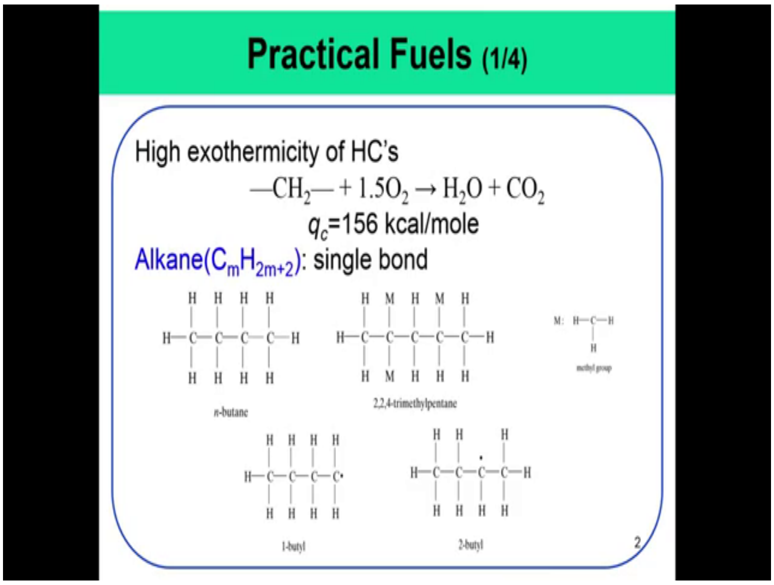

Practical Fuels (1/4)

High exothermicity of HC's

$$—CH_2— + 1.5O_2 \rightarrow H_2O + CO_2$$

$$q_c = 156 \text{ kcal/mole}$$

Alkane(C_mH_{2m+2}): single bond

So, first now thing is that; so before we go into the details of the oxidisation mechanisms what we will study here is that we will go into the practical fuels, just to as a as a reminder of what the practical fuels are, what those names are what their nomenclature is and how their structures look like. Now first of all we will see that in most of these practical fuels the this becomes the CH 2 and of course, this CH this this this portion of CH 2 forms an integral part of all practical fuels and there is of interest because if you just consider this just that reaction of this CH 2 with a with this hypothetical of this CH 2 with oxygen this oxidisation, what we will see is that the heat release is huge 156 kilo calorie per mole and this kind of you do not encounter this kind of very large heat release in any other any other reactions in chemistry.

So, this is this large heat release in a small molecule and as a result small mass and small volume that is very high energy density. Once again this very high density of the hydro carbon fuels is what makes them very attractive for air breathing aerospace propulsion. Now, let us look into some of the typical fuels you see that these are the typical fuels. For example, this can be alkanes H Cm H 2 m plus 2 where m can be anything from one to many many large number of course, this is as you see this is n butane this a normal butane and straight chain alkanes you can have this trimethylpentane where methyl group can be attached to this second carbon atom.

These are the radicals one butane radical two butane radical which will encounter in different oxidisation mechanisms, but not all alkanes are straight chain, alkanes we can have cyclo alkanes ok.

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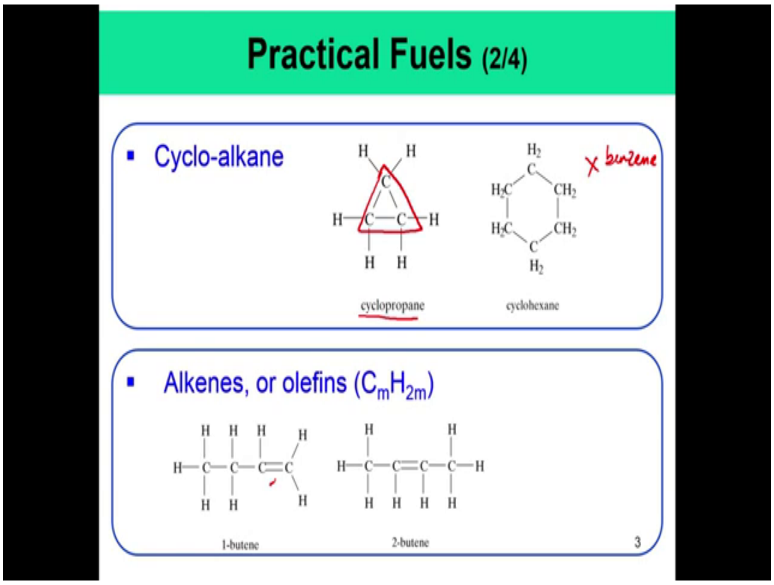

Practical Fuels (2/4)

- Cyclo-alkane

- Alkenes, or olefins (C_mH_{2m})

And for example, this is a cyclo propane, this this is the cyclic structure which makes gives that main is the cyclo propane and you can have the cyclo hexane right, but remember that this is not this is different this is not benzene because in benzene you have this double bonds (Refer Time: 08:06) places, right.

So, but the properties of course, cyclo alkane hexane and benzene are very different and then you can have alkenes, which is represented by this double bond here CmH2m and then you can have two butane alkanes, alkynes is essentially the involving triple bonds propane.

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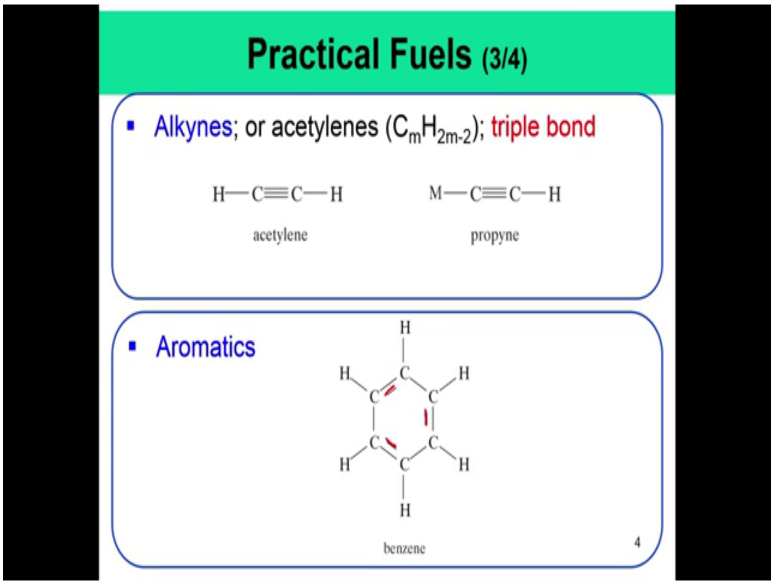

Practical Fuels (3/4)

- Alkynes; or acetylenes (C_mH_{2m-2}); triple bond
- Aromatics

These kind of things and of course, you can have aromatics which we are talking about that is benzene which is gives this double bonds at alternate locations and this gives cyclic structures. Now it will you will soon realise that aromatics even if you start with simple molecules like alkanes like this one, n butane in under different because of the complexity of the reactions different species will be formed different species different radicals even in some cases the aromatics will be formed.

And when you will go into soot chemistry formation of soot you will see that these aromatics play a very important role in the soot chemistry ok.

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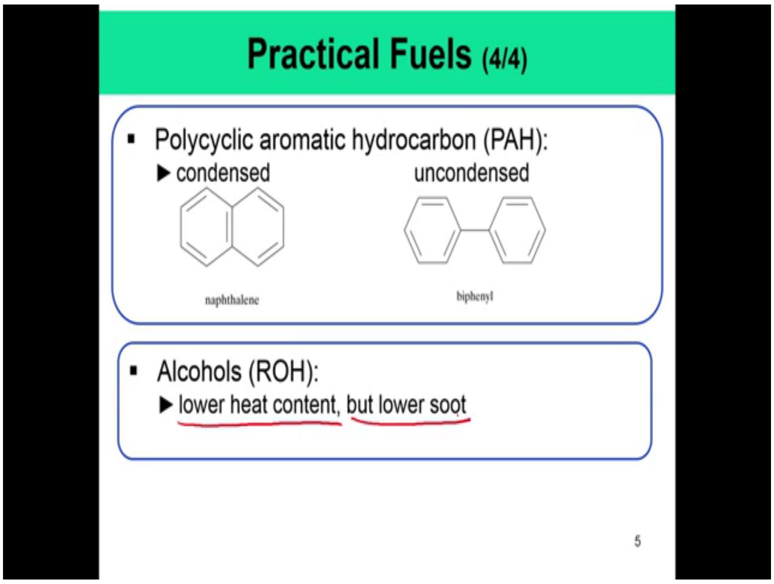

Practical Fuels (4/4)

- Polycyclic aromatic hydrocarbon (PAH):
  - condensed
  - uncondensed

naphthalene

biphenyl

- Alcohols (ROH):
  - lower heat content, but lower soot

And then of course, this as we discussed as you said that this poly aromatic hydrocarbons are PAH which is in it is condensed form is called alkaline, in some condensed form it essentially a biphenyl molecule and this forms important a very important soot precursors that is before soot forms these things form and this forms an integral part of the soot reaction mechanisms.

And of course, we can have alcohols as you know that it is lot of interest in making methanol, butanol these things ethanol work in engines car engines and they can also emerge as useful in for future aircrafts so, but they have because of the large water content, they are they have lower heat content, but they also produce lower soot.

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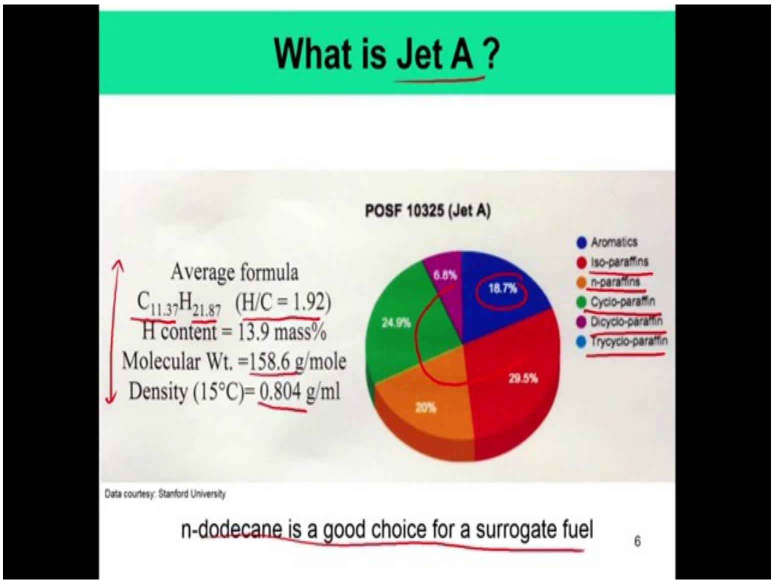

What is Jet A ?

Average formula

$C_{11.37}H_{21.87}$ (H/C = 1.92)

H content = 13.9 mass%

Molecular Wt. =158.6 g/mole

Density (15°C)= 0.804 g/ml

Data courtesy: Stanford University

n-dodecane is a good choice for a surrogate fuel

So, it is beneficial they are less polluting. Now the course is as you know as we know it is combustion in air breathing aero engines. Now what is the most important fuel used in aero engines for example, aviation gas turbine engine what does it use it uses some variants of kerosene, which is called aviation jet fuel or jet A jet A 1 known as slightly variation in composition and these names come from their use in different countries.

So, what is jet A here you can see the composition of jet A, it is as in continent what we just discussed of a normal alkanes cyclo alkanes etcetera it is not a single fuel, it is essentially a combination of this different kind of alkanes aromatics etcetera. So, as you see here this jet A contains about 19 percents of aromatics, that is benzene phenol etcetera mainly benzene type of species, but the rest is like iso-paraffin paraffins are but nothing but alkanes iso is a position of the methyl radical carbon atom normal paraffins normal alkanes cyclo, alkanes tricycle, paraffins tricycle, paraffins. So, the rest 81 percent is nothing but alkanes now of course, do a fundamental study or a CFD simulation it is very difficult to use all these kinds of different species (Refer Time: 11:37) at the starting point.

So, what we do is that we use something like a surrogate fuel, which is a representative fuel which represents the properties of jet A very well. So, how do you get such a representative fuel? So, you find out this what are the compositions of jet A, and you come up with an average formula of jet A which is given by cs this is a C11.37, H 21.87

and the hydrogen to carbon ratio is 1.92 as you see the hydrogen content is 1.39 percent by mass molecular weight is about 158.6 gram per mole and it is density is less than water at 0.804 gram per millilitre, and we said that depending on these things n-dodecane that is C21H24 is becomes a good choice for the surrogate fuel for jet A. This is the typically the composition of fuel that use in aviation gas turbines ok.

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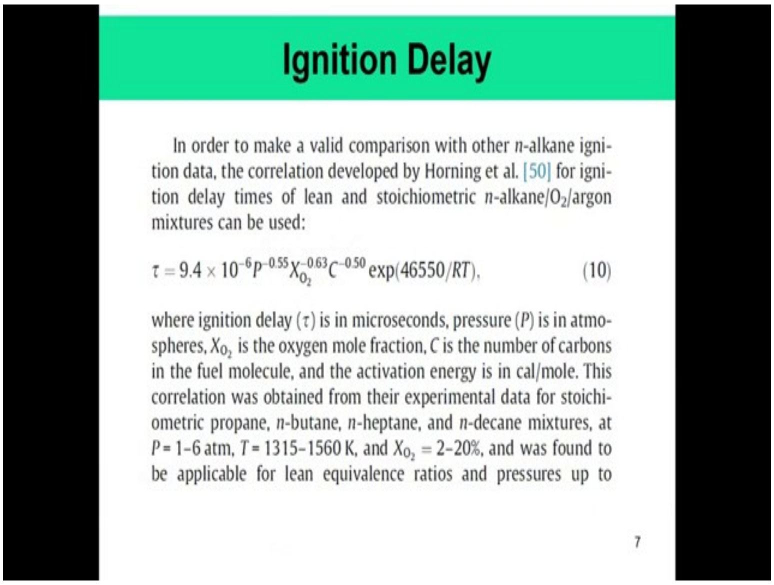

Ignition Delay

In order to make a valid comparison with other *n*-alkane ignition data, the correlation developed by Horning et al. [50] for ignition delay times of lean and stoichiometric *n*-alkane/O_2/argon mixtures can be used:

$$\tau = 9.4 \times 10^{-6} P^{-0.55} X_{O_2}^{-0.63} C^{-0.50} \exp(46550/RT), \qquad (10)$$

where ignition delay (τ) is in microseconds, pressure (P) is in atmospheres, X_{O_2} is the oxygen mole fraction, C is the number of carbons in the fuel molecule, and the activation energy is in cal/mole. This correlation was obtained from their experimental data for stoichiometric propane, *n*-butane, *n*-heptane, and *n*-decane mixtures, at $P = 1$–6 atm, $T = 1315$–1560 K, and $X_{O_2} = 2$–20%, and was found to be applicable for lean equivalence ratios and pressures up to

Now, why are we talking about this? We are talking about this for example, we will just we will just discuss something here now how to characterise this fuel properties. Now one important property of fuels is basically what is it is ignition delay; what is ignition delay? Now suppose if you take the fuel and air you take the fuel air mixture in a container in a close container which is adiabatic ok.

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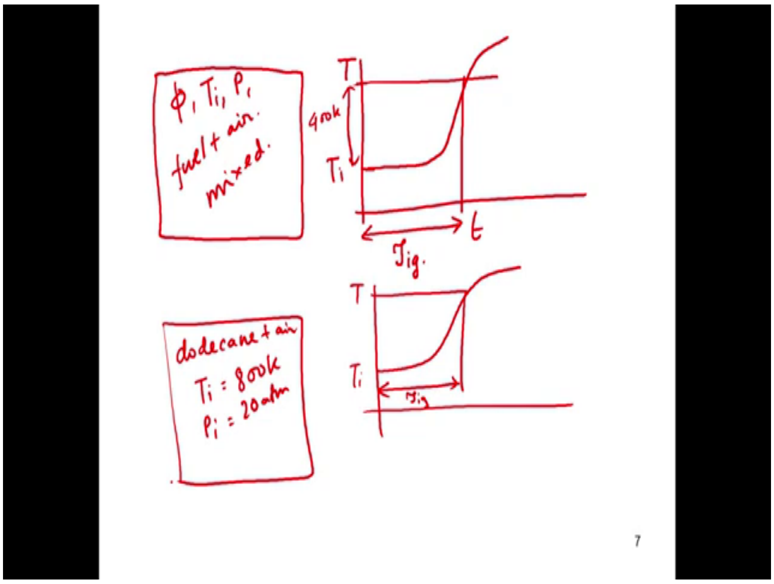

And of course, say the fuel and the air are mixed at a given field, and this container has a maintainer at temperature T and it contains fuel plus air. Now of course, as you know that our general common sense or intuitions suggest that, if this mixed fuel and air which is perfectly mixed is homogenously mixed and if it is in the mixed state, it is in a perfectly mixed state and now if the temperature and the pressure is sufficiently high you know that for reactions to happen the temperature and pressure needs to be sufficiently high, you know this thing will ignite ok.

So, ignition means it is temperature will rise. So, if you plot the temperature versus time you will see that if this is my initial temperature. So, this was my initial temperature T i and P I when the temperature will rapidly rise after some time. Now we can say that the ignition delay time is the time basically the time it takes for the mixture to rise at a up to a specific temperature which can be like say we will define as like 400 Kelvin difference from the initial temperature to the which we define as the ignition temperature. So, ignition delay is nothing but this time.

So, this is one very important property of that we need to clarify for fuels alright now why do we why are we talking about this we are talking about this because you see you will see that even if the temperature and pressure is sufficiently high, suppose the initial temperature of you are taking say this jet A fuel or it surrogate suppose you are taking n dodecane and the initial temperature and pressure is about the initial temperature is about

800 Kelvin, now we are considering say dodecane and it is T i is equal to say 800 Kelvin, and it is initial pressure is say 20 atmosphere it is a relevant temperature for gas turbine engine right.

So, how long does the fuel air mixture take to ignite of course, this is dodecane plus a. So, then we can what we can do is that once again we can do these two this kind of an experiment and we can find out the how much the temperature rises, this can be done in a shock tube or a homogenous reactor or in a at the any kind of this kind of flow reactors. So, and we find out the ignition delay time, and then we can vary the initial time initial temperature and we can find out a correlation by which as a function of the initial temperature.

That is how much does the ignition delay time is as you change the temperature and when you get this you can from a correlation like this, that your ignition delay time will can depend on pressure; it can depend on the mass mole fraction of oxygen it can depend on the carbon number etcetera ok.

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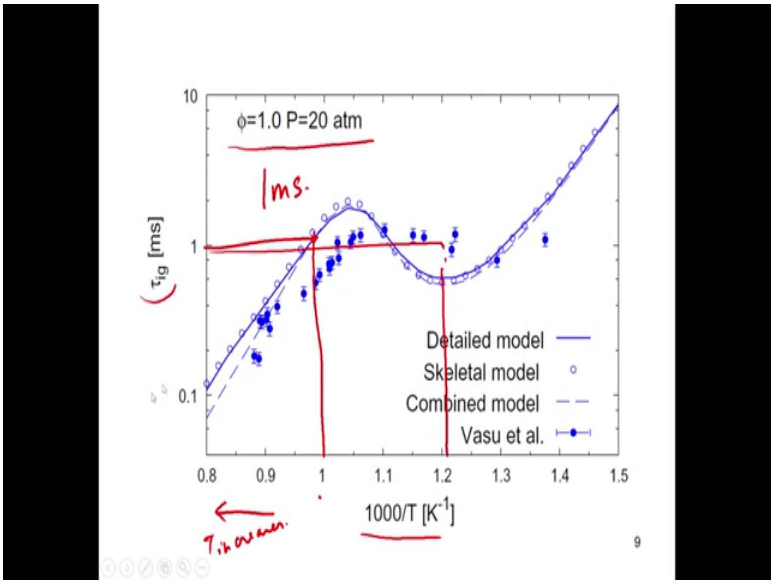

So, this is an n can ignition delay I will not go into the details of this, but we all can find different kinds of correlation and the data will actually look something like this. This is T ignition delay in milliseconds and this is 1000 divided by temperature. So, what we have done is that we have done this experiment in a where we took the fuel air mixture in a perfectly mix state, and then we readied the initial temperature. Now as we vary the initial temperature the ignition delay time changes for example, here you see that initial state of the mixture was phi equal 1.0 and pressure is equal to 20 atmosphere and you see that if it starts what this this tells you that if you start at a say this value of 1 which means 1000 by T is equal to 1 which means T is equal to 1000 Kelvin.

So, the ignition delay time at this point is about 1 milliseconds, if we increase temperature alright that is if we increase temperature to about to about 1000 about if it was 2000 Kelvin then it would have shifted here. So, when increase if t increases in this direction. So, as we see T when a T increases it ignition delay actually goes, but here is something complicated happening it is actually the ignition delay is instead of it as you as you decrease the temperature. Now here, it actually goes down which is very counter intuitive, but we will go into this later.

But what we want to say is that that even at a temperature as high as 1000 Kelvin or if it is less than 1000 Kelvin if it is at say- this value, when 1000 by T is equal to 1.2 the ignition delay time is a finite number of about 1 millisecond. So, this is a typical number of ignition delay time of 1 milliseconds, alright. Now why are we discussing all these things? The reason is that this ignition delay time of 1 millisecond is the time required for this fuel air mixture to ignite.

So, you must you have to design a combustor in which your flow residence times skills is must be greater than 1 millisecond. So, that is why these things are important; and then if you want to predict the behaviour the actual behaviour in of combustion happening inside a practical combustor you have to capture this ignition delay time properly and this ignition delay time this proper capturing of the ignition delay time can be only done when you have a detailed reaction mechanism.

When you from a given fuel you can break it up you when the fuel breaks up and it becomes small and small molecules, it becomes the product through a series of steps this sort of finite ignition delay times cannot be predicted by global chemistry. So, to predict these kinds of very specific and very important properties like the ignition delay time accurately, you need detailed chemistry. Now under what circumstances do you have to bother about this kind of ignition delay time in terms of a practical engine? Let us consider two cases, like say two combustors one is say a gas turbine combustor, here say you have. So, all are sets etcetera and flow coming in.

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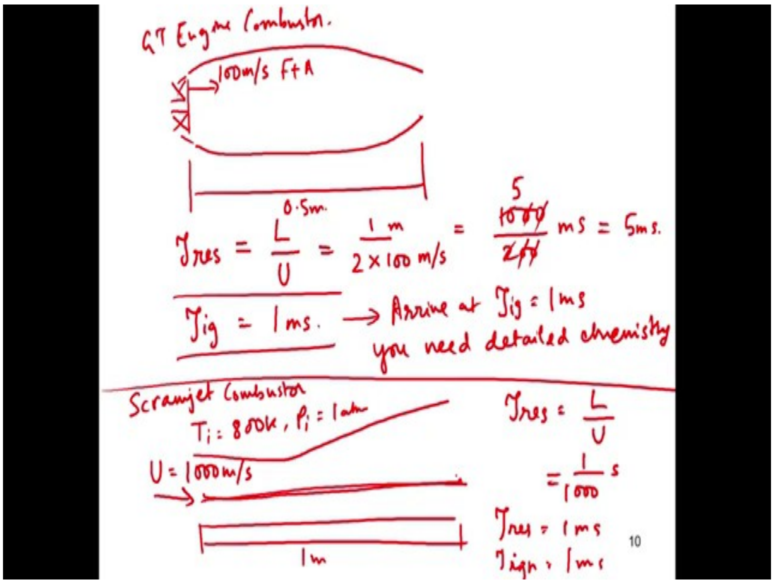

$$\tau_{res} = \frac{L}{U} = \frac{1\,m}{2 \times 100\,m/s} = \frac{\overset{5}{10\cancel{00}}}{2\cancel{00}}\,ms = 5\,ms.$$

$$\tau_{ig} = 1\,ms. \rightarrow \text{Arrive at } \tau_{ig} = 1\,ms \text{ you need detailed chemistry}$$

$$\tau_{res} = \frac{L}{U} = \frac{1}{1000}\,s$$

$$\tau_{res} = 1\,ms$$

$$\tau_{ign} = 1\,ms$$

So, the flow velocity inside is about average velocity is 100meters per second this is a how much? Less than much less than one meter say 0.5 meter length the of the combustor, this is the gas turb engine combustor. So, here the fuel air mixture is coming at a velocity of 100 meters per second, and the length of combustor is 0.5 meter. Now of course, there are many complexities as you know that it is basically in a gas turbine engine we injects the fuel in liquid form.

So, it is injected in a spray form. So, the spray must atomise, it must it is the spray must break up it must atomise it must go for it makes and then combust, but let us not go into these things. So, just by these two information that is average velocity is about 100 meters per second and the length of the gas turbine combustor is 0.5 meter, we can find out the tau residence time scale tau res as the length of the combustor divided by the flow velocity. So, then it gives us is basically half a meter times 100 meters per second.

So, this gives you essentially a time of 1 by 2 100 seconds which is nothing but 1000 by 200 milliseconds. So, it is about 5 millisecond; this is one meter this is meter per second yes. So, the time scale available is about 5 milliseconds, whereas you see it is not hugely different from what the ignition delay time of jet A was. So, you have to ensure that that the fuel whereas, ignition delay time as we discussed is a time for the homogenous mixture to go from initial stage of T i to the product state to ignition to at least ignition to a sufficient level. So, you have to design combustors in such a way so that you can have complete combustion and less pollutant emission.

Now if you are doing a CFD calculation of this gas turbine combustor you then it clearly says that to resolve the ignition delay time of about 1 milliseconds, you need to produce you need to put in all the detail reaction mechanisms by which the fuel will go from the large fuel molecule of dodecane through it will break down into smaller and smaller pieces of fuel, it will become methane, methylene. ethane, propane, butane, etcetera. And all these things, and then it will oxidise through different reaction mechanisms there will be chain branch (Refer Time: 23:59) there will be chain initiation mechanisms there will be chain, carrying mechanisms there will be chain branching reactions and then it will go to a complete combustion.

So, to understand this thing and to resolve these kinds of ignition delay to resolve this to arrive at this 1 millisecond, you need detailed chemistry by detailed chemistry what I mean is that you need all these detailed steps and detailed this numerous species by which this can be predicted this situation is even more complex in a scram jet combustor. Let us consider a scram jet combustor, what the flow velocity is about 1000 meters per second and this is about say one meter. Now here your temperature is about 800 Kelvin and your pressure is about 1 atmosphere or 0.5 atmosphere something like that. So, once again we can estimate the residence times scales which is nothing but the length by the average velocity and that comes out to be like 1 by 1000 seconds is equal to 1 millisecond ok.

So, in this scram jet combustor you see the residence time is equal to the ignition delay time of course, this is at high larger pressure, but still this is 1 millisecond right. So, when you are suppose you are doing a simulation of a scram jet combustor for design purposes or for other validation purposes of your scram jet combustor code. So, the thing is that you cannot design it properly, you cannot arrive at proper validation until and unless you have enough reactions in your calculation which can predict this ignition delay time of 1 milliseconds, and then after you do that you have to engineering and that is why CFD calculations are important.

You know today engineering so that you can have a stable combustion. If you do not do anything you see that you cannot have stable combustion because this fuel and air packet is reaching here at 1000 meters per second. So, by the time ignition starts it will all it will already reach the end of the combustor right in 1 milliseconds it will travel this distance, and that is the time it takes for it ignite.

So, it will go out in the outside out of the combustor and then it will get mixed with the outside air and there will be no combustion then there will be no thrust and no pagination. So, to properly design the scram jet combustor you see you feeling it to have detailed reaction mechanisms. So, that is the importance of reaction mechanisms which is clearly understood from our comparison of the residence time and the ignition delay time. Of course, here we have compared very simplified quantities it is a just back of the envelope calculation, your residence time scale is very crude measure here and so, is the ignition delay time cell because the process much more complex.

The most important thing is that it is not in a homogenous state even though it can start from homogenous state the combustion does not happen in a homogenous state, you will see that flames differ from this kind of things because in flames you will diffusion, you have heat conduction and you all have viscous effects. So, this thing is in a actual engine things are more complex nevertheless, this gives a clear idea about that the competition between your flow times skills and the ignition delay times skills. And to resolve this thing properly your CFD code must have some amount of details of the reaction mechanism.

Now, when we mean some amount of details, what are we actually meaning, what details are we putting in what are steps that is required to predict these kind of ignition delay, what is why 1 millisecond time is required why do you see empty this dip in the ignition delay behaviour etcetera. So, to study those we will go into the details of the reaction mechanisms.