Combustion in Air Breathing Aero Engines

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Lecture - 10
Oxidation Mechanism of Fuels III

Welcome back. So, we just talked about details of the hydrogen oxidant; oxygen reactions and the explosive limits of hydrogen oxygen mixtures and the details of hydrogen oxidation essentially and then we discussed about carbon monoxide oxidation and now we will consider general considerations of hydrocarbon oxidation.

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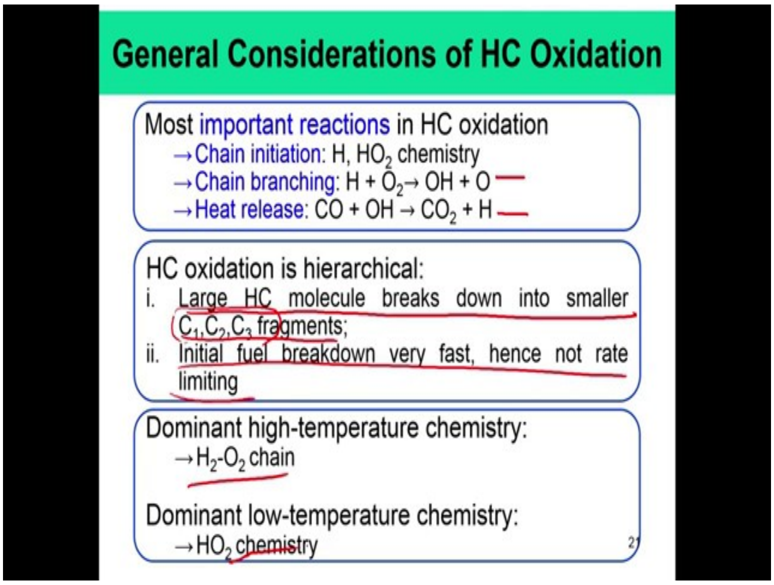

General Considerations of HC Oxidation

Most important reactions in HC oxidation
- →Chain initiation: H, HO_2 chemistry
- →Chain branching: $H + O_2 \rightarrow OH + O$
- →Heat release: $CO + OH \rightarrow CO_2 + H$

HC oxidation is hierarchical:
1. Large HC molecule breaks down into smaller C_1,C_2,C_3 fragments;
2. Initial fuel breakdown very fast, hence not rate limiting

Dominant high-temperature chemistry:
- →H_2-O_2 chain

Dominant low-temperature chemistry:
- →HO_2 chemistry

Now, the most important reactions in our hydrocarbon oxidation is as we have discussed that is of course, the chain initiation that is the formation of H, HO2, H is as we discussed is a very active radical and its formation is intrinsic and it is very very important towards further propagation of the reaction because these active radicals attack further incoming fuel molecules and oxygen etcetera and then this is these 2 are the most important reactions this H plus O2 going to OH plus O and of course, that is the key chain branching step and the key heat release step is the CO plus OH going to CO2 plus H.

Now, hydrogen carbon oxidation is hierarchical what; that means, is that that whatever large your fuel molecule is suppose you are talking about butane propane methane octane and dodecane which as we discussed is essentially a surrogate for or a representative fuel of jet fuels. So, nevertheless these fuels does not react with oxygen in its does not directly go undergo oxidation.

What they do is that these large hydrocarbon molecules they breakdown into smaller C 1 C 2 C 3 fragments this now this initial fuel breakdown is very fast hence these are not rate limiting and, but the important thing is that it essentially than no matter how large the fuel is of course, there are complex species formed, but essentially the most important part is essentially the reaction of this C 1 C 2 C 3 fragments and reaction of HO2 OH plus and so on and so forth.

So, in a very large complex fuel for example, with n dodecane the methane chemistry is still very important because methane chemistry is essentially governed by the C 1 chemistry and also like hydrogen chemistry is very important because these kind of hydro this H will be formed and those will react with O2 to form OH plus 1 plus so on and so forth.

So, when you want to construct a big reaction mechanism of a or the or reaction mechanism of a big fuel we first need to understand the reaction mechanism of the small fuel there is why hydrogen oxidation is very important C oxidation is very important and then next we will study methane oxidation which is also very important.

Of course methane is an important fuel in natural gas as you know and of course, hydrogen is also a very clean fuel and the hydrogen is even more important because you see it does not produce CO2 which is a important greenhouse gas and which is believed to be which is of course, known to be important for climate change. So, because hydrogen does not produce CO2 it is very important as a clean fuel, but of course it has as you see it behaves it is a explosive and its very strong in a diffusive and explosive over large range of temperature and pressures and that is the its habits its large scale use actually.

So, once again the dominant or we can say that the dominant hydro high temperature chemistry is essentially governed by this H2 O2 chain and this dominant low temperature chemistry is governed by the HO2 is governed by this HO2 chemistry. So, that is the idea that we will follow.

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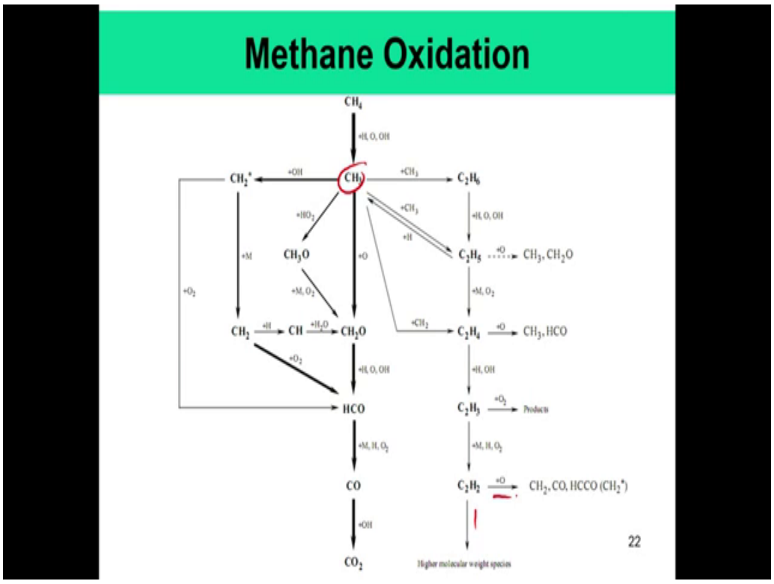

Methane Oxidation

So, methane oxidation can be schematically represented in this diagram where methane essentially goes to form (Refer Time: 03:50). So, this diagram is essentially that these arrows indicate the process that is more important these thick arrows indicate a process which is more important, whereas these thin arrows these indicator process which is less important, but we can will discuss this in more detail when we go into schematic.

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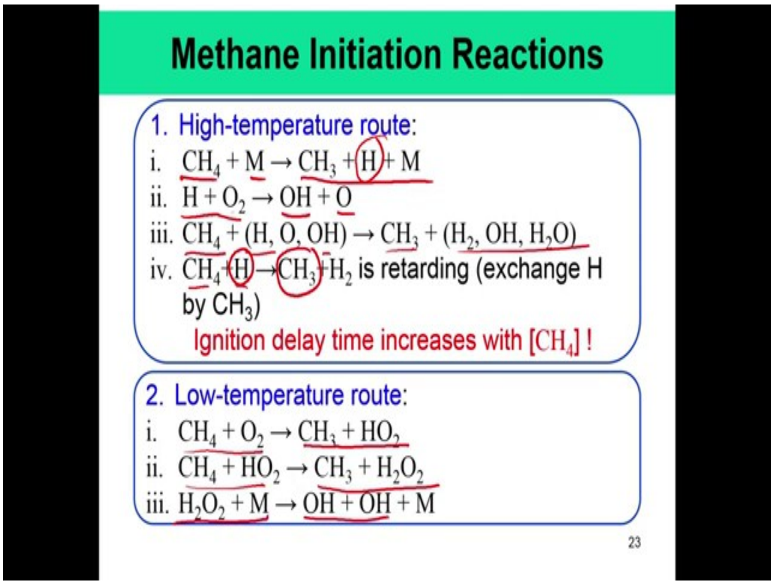

Methane Initiation Reactions

1. High-temperature route:
   - i. $CH_4 + M \rightarrow CH_3 + H + M$
   - ii. $H + O_2 \rightarrow OH + O$
   - iii. $CH_4 + (H, O, OH) \rightarrow CH_3 + (H_2, OH, H_2O)$
   - iv. $CH_4 + H \rightarrow CH_3 + H_2$ is retarding (exchange H by CH_3)

   Ignition delay time increases with $[CH_4]$!

2. Low-temperature route:
   - i. $CH_4 + O_2 \rightarrow CH_3 + HO_2$
   - ii. $CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$
   - iii. $H_2O_2 + M \rightarrow OH + OH + M$

So, first important thing is that how does CH4 essentially breaks down number one is once again is the most important step is initiation, but before that we should say that there are 2 initiation routes. So, these we will first talk about the initiation reactions. So, the first is the high temperate route for the methane breakdown. So, methane breaks down essentially by CH4 plus M goes to CH3 plus H plus M once again the formation of this H radical is very important as we discussed because as soon as the H radical is formed the key chain branching step that we saw this H 1 reaction in hydrogen oxygen. So, immediately that can happen and that can attack the fuel the oxygen molecule and it can form OH and O.

And now this OH and O this CH4 can react with H OH and O or H and OH and O and form C H and 3 to this thing and again, but we see that that the parallelly if you just consider this reaction CH4 plus H becomes CH3 plus H2. So, this very energetic hydrogen radical is leads to the formation of a less energetic methyl radical CH3 as a result if there is too much if you see the ignition delay co relations of methane.

You see that the methane comes with a with a positive exponent that is the more methane is produced the larger is the ignition the more there is more for the larger the concentration of methane the larger is the ignition delay which is counter intuitive, because methane is a fuel, but because this the hydrogen atom this hydrogen very energetic hydrogen radical that is produced that reacts with methane to form to form this less energetic CH3 this becomes the deter deterring step, but these are the initiation reactions.

The low temperature route is that the CH4 which reacts witHO2 to form this CH3 plus HO2 CH4 plus HO2 goes to form CH3 plus H2 O2 hydrogen peroxide and hydrogen peroxide plus M goes to form this chain branching OH plus OH plus M. So, this is the low temperature route.

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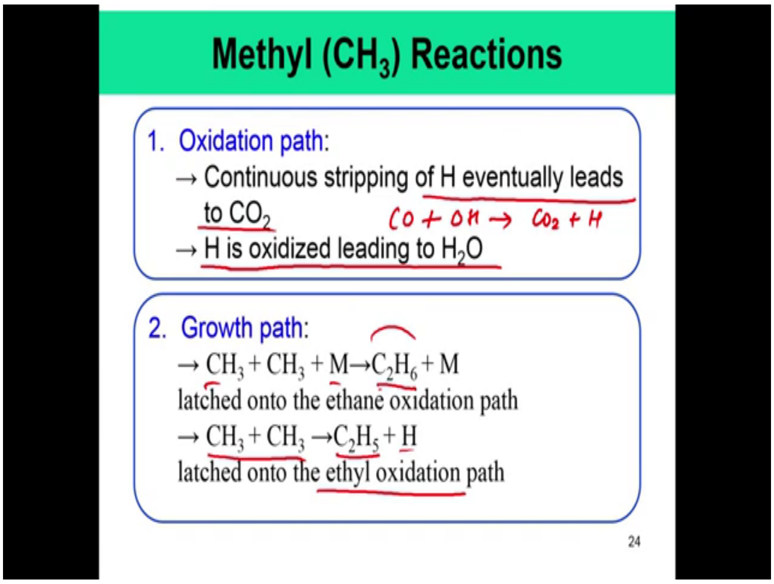

Methyl (CH_3) Reactions

1. Oxidation path:

→ Continuous stripping of H eventually leads to CO_2 $CO + OH \rightarrow CO_2 + H$

→ H is oxidized leading to H_2O

2. Growth path:

→ $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$

latched onto the ethane oxidation path

→ $CH_3 + CH_3 \rightarrow C_2H_5 + H$

latched onto the ethyl oxidation path

Oxidation path, now what happens then is that within there is continuous stripping of hydrogen from this C methane from this as you see here this CH3 is formed and with this is essentially from CH4 it forms CH3 and from CH3 it forms OH 2. And there is this continuous stripping of hydrogen and eventually it will be oxidized with by CO by the CO will be formed CO plus OH will go to react and will go to form CO2 plus H, we know.

So, these steps will continue to basically strip the C-H the CH4 to CH3 and CH3 to essentially CO and then to CO2 and this is the oxidation path and of course, any hydrogen that is the H atom that is formed will oxidized leading to HO2.

So, this is continuous stripping path, but then there is also a growth path because this you will see that if you consider this GRI methane reaction mechanism that is pretty big in size. So, what happens is that the CH3 CH3 can also combine and it can in the presence of a third body it can form C2H6? So, from 1 carbon it forms 2 carbons.

So, in methane reaction mechanism these larger molecules of this C2H6 these are also important and this becomes essentially a part of the ethane oxidation path and it can also form CH3 plus CH3 and it can also form C2H5 plus H and it can go latched on to the ethyl oxidation path. So, as a result these re hydrocarbon reaction mechanisms are pretty complex because on one hand you see the stripping of H from CO2 plus H.

And on the other hand you will there is also continuously there is also a growth path in which larger; larger molecules are important eventually these larger molecules will be broken down into smaller fragments and then it will again go to CO plus OH and CO2 plus H.

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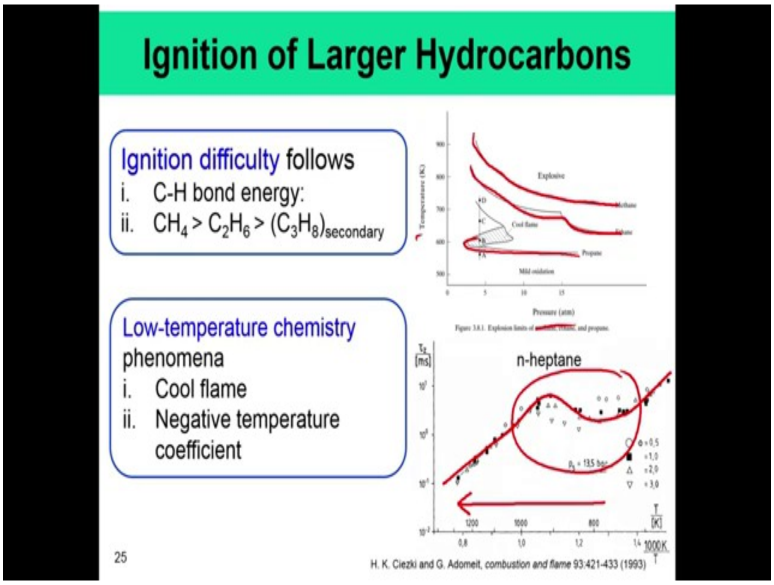

Ignition of Larger Hydrocarbons

Ignition difficulty follows
i. C-H bond energy:
ii. $CH_4 > C_2H_6 > (C_3H_8)_{secondary}$

Low-temperature chemistry phenomena
i. Cool flame
ii. Negative temperature coefficient

Figure 3.8.1. Explosion limits of methane, ethane, and propane.

H. K. Ciezki and G. Adomeit, combustion and flame 93:421-433 (1993)

Now that goes about that is about methane oxidation. What about oxidation of larger or ignition of larger hydrocarbons now we discussed what ignition delay time is and that is a very important process and, but the if you see the ignition difficulty it essentially depends on 2 things that is the C-H bond energy and you will find that methane is the hardest to ignite followed by ethane followed by propane and this is what is shown here in this temperature pressure curve that methane is methane becomes explosive only in this regime at very high temperature and high pressure whereas, propane is ethane is then follows then and then propane is this shows a very complicated behavior.

The complicated behavior of propane essentially comes from this can be characterized by 2 things; one is called the cool flame and another is the negative temperature coefficient both are very interesting things and we will discuss a little bit about that.

And known as this region of cool flame where essentially we will see that instead of a bright blue flame the normal flame you will see a blue in color if it is a (Refer Time: 09:26) flame which essentially comes from the hydroxyl and C2 radicals, but in the cool flame you will see there is a lot of emission where these formaldehyde radicals and which gives a very pale blue color and this is different from the normal; normal high temperature flames as we will discuss later.

And also the corresponding phenomenon in ignition delay is that this ignition delay of heptane where you see this negative temperature coefficient that is if you increase temperature; temperature is increased in this direction. So, in this direction temperature, temperature increases 800, 1000, 1200 plus, so, if you see that normally we think that if temperature increases this ignition delay time will be just like this that is often temperature increases ignition delay time also increases because it is clear that the chain branching reactions are promoted.

But you see in these kinds of comp larger fuels like heptane etcetera; this ignition delay first; first decreases then again it increases or it has a plateau region then it decreases. So, this is called the negative temperature coefficient phenomena, but it happens at a very interesting range you see this 700 to 1000 Kelvin which is often the inlet often the temperature at which fuel and air mixes in practical air breathing propulsion engines like in a gas turbulent engine or in a scramjet combustor.

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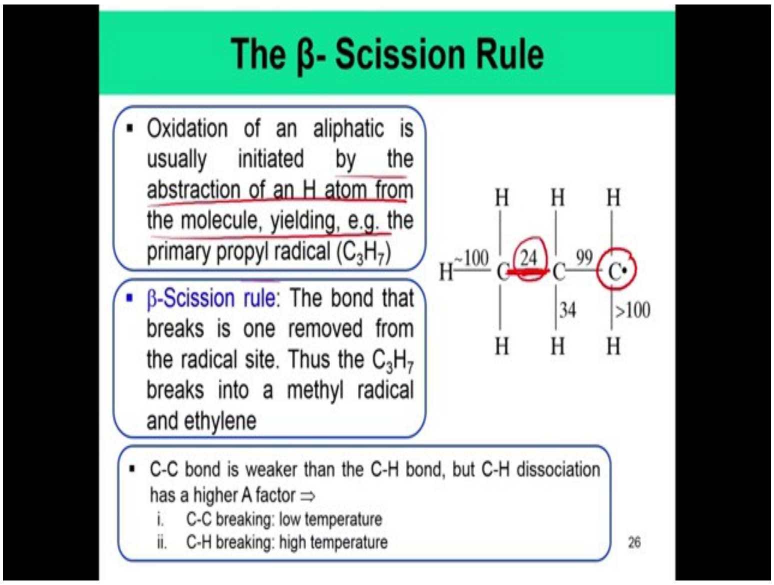

The β- Scission Rule

- Oxidation of an aliphatic is usually initiated by the abstraction of an H atom from the molecule, yielding, e.g. the primary propyl radical (C_3H_7)
- β-Scission rule: The bond that breaks is one removed from the radical site. Thus the C_3H_7 breaks into a methyl radical and ethylene

- C-C bond is weaker than the C-H bond, but C-H dissociation has a higher A factor ⇒
  i. C-C breaking: low temperature
  ii. C-H breaking: high temperature

Now, we need to know some rules about of essentially which bonds we are talking about bond energy that is we said that methane is most least explosive at a given temperature pressure and propane is the most explosive because of the C-H bond energy the bond energy of CH4 is highest and then it is less is you have C2H6 has less bond energy and then the C3H has even lesser bond energy. So, there propane is more easy to break and easy to ignite.

Now, the (Refer Time: 11:29) beta scission rule we need to understand is that in the beta scission rule tells us that the oxidation of an aliphatic that is this straight chain alkenes is usually initiated by the abstraction of a hydrogen atom as you see that what the stripping down of this hydrocarbons means essentially the hydrogen atoms is essentially by this hydrogen abstraction process, so, CH4 plus if you go into this reaction CH4 plus M becomes CH3 plus H plus M. So, this is the hydrogen abstraction reaction where CH4 is stripped off from its hydrogen and this hydrogen becomes a free radical and. So, that it becomes free to react and free to attack other fuel molecules.

So, the oxidation of an aliphatic, so, then the question is that now if you have a this kind of an methyl or a butyl group where you have a this unpaired electron this is a propyl group then this propyl radical then which C; C bond is the weakest.

The rules says is that the beta scission rule is says that the oxidation of aliphatic is usually initiated by the abstraction of an hydrogen atom of the molecule yielding at primary propyl radical and the beta scission rule tells that the bond that breaks the bond that will break is usually the one that is one his breaks is one that is removed from the radical side. So, this is the radical side. So, the most the bond that is most prone to break up is initially the one that is one removed that is not this one this one removed from the radical side which is this one.

Now, why because you see that in invariably this we are presence of this unpaired electron essentially strengthens these bonds this C C bonds which is about hundred these are in arbitrary units, but then in comparison then this; this is bond becomes weaker and as a result this is bound to break and that is the beta scission rule.

So, a C C bond is essentially weaker than a C-H bond, but C-H dissociation has a harder a factor and as a result this C C breaking happens at a low temperature whereas, C-H breaking happens at a high temperature.

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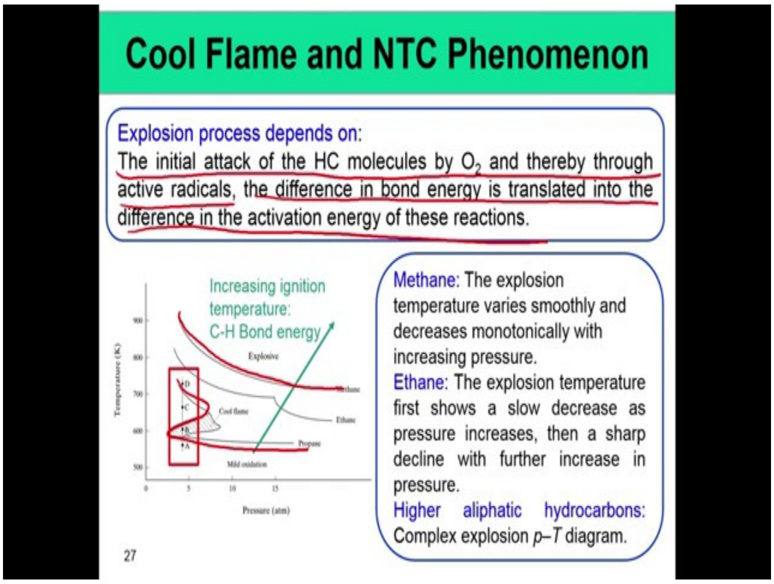

Cool Flame and NTC Phenomenon

Explosion process depends on:
The initial attack of the HC molecules by O_2 and thereby through active radicals, the difference in bond energy is translated into the difference in the activation energy of these reactions.

Methane: The explosion temperature varies smoothly and decreases monotonically with increasing pressure.
Ethane: The explosion temperature first shows a slow decrease as pressure increases, then a sharp decline with further increase in pressure.
Higher aliphatic hydrocarbons: Complex explosion *p–T* diagram.

Now, what is cool flame and NTC phenomena as we have seen that when it comes to like propane and higher hydrocarbon it shows something like a there is a regime in which there is which is called a cool flame and this shows the NTC phenomena.

Now, the explosion process if you remember depends on the initial attack of the hydrocarbon molecules by oxygen and thereby through active radicals the difference in the bond energy is translated into the difference in the activation energy of these reactions.

Now, methane as we have seen that previously what we have discussed is that methane very smoothly ethane where is also smoothly, but higher aliphatic hydrocarbons this cool flame it has a complex behavior there is a complex explosion period diagram it is a non monotonic diagram like this.

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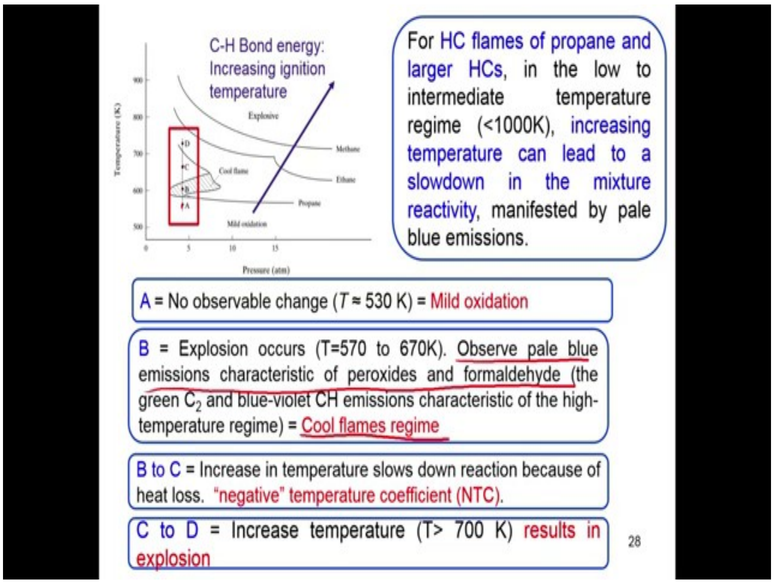

For HC flames of propane and larger HCs, in the low to intermediate temperature regime (<1000K), increasing temperature can lead to a slowdown in the mixture reactivity, manifested by pale blue emissions.

A = No observable change ($T \approx 530$ K) = Mild oxidation

B = Explosion occurs (T=570 to 670K). Observe pale blue emissions characteristic of peroxides and formaldehyde (the green C_2 and blue-violet CH emissions characteristic of the high-temperature regime) = Cool flames regime

B to C = Increase in temperature slows down reaction because of heat loss. "negative" temperature coefficient (NTC).

C to D = Increase temperature (T> 700 K) results in explosion

So, that is what is makes it interesting. So, why does it happen is that for hydrocarbon flames of propane and larger hydrocarbons in the low to intermediate temperature regime increasing temperature can lead to be slow down in the reactivity of the mixture and that is manifested by this pale blue emissions coming from formaldehyde.

So, in this thing if we just take this take at a constant pressure if we just add five stations at different increasing temperature in this regime map what we see is that at point a there is no observational change in temperature there is mild oxidation this is not relevant for combustion then explosion occurs at point b, but it is characterized by this observation of pale blue emission characteristics of peroxides and formaldehyde the green C2 and the blue violet C-H emissions are characteristics of the high temperature regime and this is called the cool flame regime.

And then once we increase it to C increase in temperature slows down the reaction because of heat loss and it is also because of certain production of certain other radicals that will come and this is essentially the negative temperature coefficient regime its essentially the chain branching reactions that will be stopped and as a result of this it becomes a non explosive and then as when we increase it to higher temperature it results to explosion because of the normal promotion of the chain branching reactions at H plus O2 goes to OH plus O at high temperatures.

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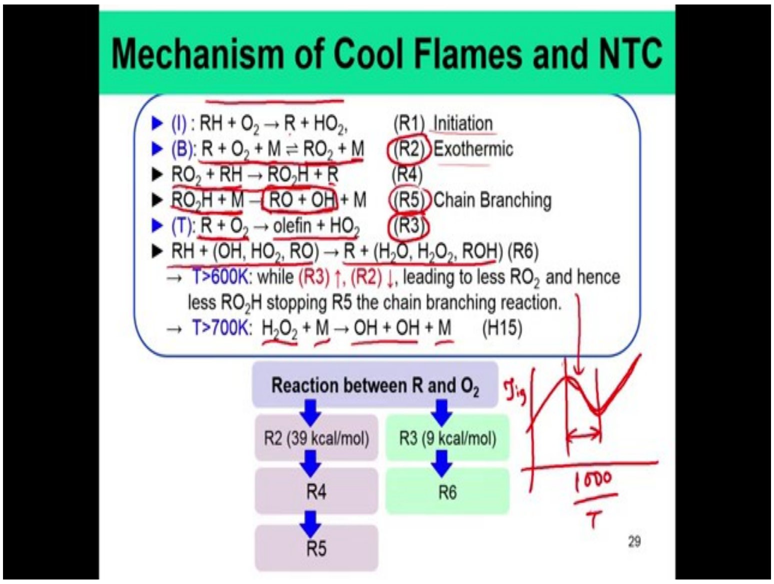

Mechanism of Cool Flames and NTC

- (I) : $RH + O_2 \rightarrow R + HO_2$, (R1) Initiation
- (B): $R + O_2 + M \rightleftharpoons RO_2 + M$ (R2) Exothermic
- $RO_2 + RH \rightarrow RO_2H + R$ (R4)
- $RO_2H + M \rightarrow RO + OH + M$ (R5) Chain Branching
- (T): $R + O_2 \rightarrow \text{olefin} + HO_2$ (R3)
- $RH + (OH, HO_2, RO) \rightarrow R + (H_2O, H_2O_2, ROH)$ (R6)

→ T>600K: while (R3) ↑, (R2) ↓, leading to less RO_2 and hence less RO_2H stopping R5 the chain branching reaction.

→ T>700K: $H_2O_2 + M \rightarrow OH + OH + M$ (H15)

Reaction between R and O_2

R2 (39 kcal/mol) → R4 → R5

R3 (9 kcal/mol) → R6

So, what is the mechanism of this cool flame and this NTC? Now this is important because as we saw that even in the previous slide in the in dodecane slide if we go back?

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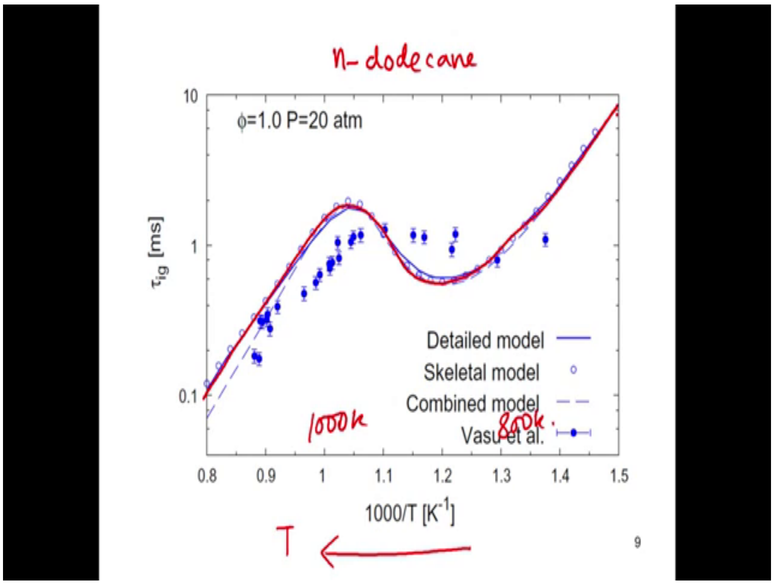

Now, also that that this is the slide that this is the NTC behavior this is for n this was for normal dodecane this as you remember that the dodecane was essentially the surrogate fuel for kerosene and this dodecane shows this interesting negative temperature coefficient. Now that is why it is important to understand the cool flame and this NTC phenomena because this dodecane this large hydrocarbon shows this very interesting negative temperature phenomena at these temperatures of choice which is this is about 1000 Kelvin and this is about say 900, 800 or 700 Kelvin.

So, from that point of view it is important to understand why this negative temperature coefficient happens and why this cool flame phenomena happens because this is this regime corresponds to a very interesting regime from a aero propulsion engine aero propulsion combustor point of view. And of course as you know the dodecane is a surrogate of kerosene of jet air and hence we need to understand why what causes this.

So, once again to recapitulate the negative temperature coefficient is that as your temperature increases in this direction in this thousand by T; this kind of representation. So, the temperature increases in this direction. So, it is normal to expect that as temperature increases the ignition delay time reduces right because at high temperature of course, the reaction rates increase and of course, as you have seen the chain branching reactions also increase. So, it is reasonable to expect that at high temperatures your; the ignition delay time will be less and it happens also it reduces as we see here and for normal small hydrocarbons for methane it is like monotonic its goes straight like this.

But you see here that for this dodecane it first decreases and then it increases and then it decreases and this decrease increase and decrease with temperature or this negative temperature coefficient phenomena as we discussed can be only explained by detail reaction mechanisms and cannot be explained by global one step reactions and we need to understand what causes this NTC phenomena because of its relevance to because of its relevance to jet a and the temperature range is relevant in the gas turbine as well as in the scramjet combustors.

This is where we were that the mechanism of cool flames and NTC. So, both are essentially the similar mechanism. So, what happens is that initiation initially of course, this R H then we can represent the R by like if it is dodecane this is essentially formula for dodecane is $C_{12}H_{24}$, but R essentially can be $C_{12}H_{23}$.

H when that RH reacts with is oxygen it becomes R and HO_2. So, this is the initiation step and then this R can now react with oxygen in presence of a third body and not a direct presence the third body comes and hits the molecule slightly afterwards and then it can form this essentially this RO_2 and this M.

Now, this RO2 that is formed can now react with this R H that is actual fuel molecule and from this peroxide molecule that is RO2H plus R this RO2H then can react with M that is the third body to form this RO plus OH plus M the interesting thing is that this reaction this RO plus OH is because one radical gives rise to these 2 radicals essentially a chain branching reaction. So, that is this is very very important.

Of course this is also initiation reaction and this is also exothermic reaction which is also important, but now what happens is that at this is one way of course, now what happens is that if the temperature goes beyond 600 Kelvin instead of this reaction R 2 there is another alternative reaction between R and O2. So, and that alternative reaction is this one that is at beyond at high temperatures beyond not at very high temperatures between 600 and 700 Kelvin this R plus O2 instead of following instead of following this route it can react R plus O2 and it can form an olefin and HO2 and this guy this R H then can essentially react with H plus OH plus OHO2 plus RO and it can form this sort of HO2R OR OH2 etcetera.

Now, the thing is that because instead of because R 3 is promoted and R 2 is diminished let us see what the effect the diminishing of R 2 has now if R 2 is diminished what we see is that if R 2 is diminished because essentially the reaction rate constant of R 2 decreases with temperature its essentially a third body reaction. So, if R 2 is diminished this reaction is diminished RO2 formation of RO2 is diminished a formation of RO2 is diminished you see that the formation of RO2H is diminished the formation of RO2H is diminished the formation of RO plus OH is diminished.

So, the chain branching step the key chain branching step in this reaction mechanism is essentially diminished and as a result if the chain branching reaction is diminished whereas, this R 5 is diminished because of the diminishing of R 2 you see that of course, the reactions stops the chain branching reaction essentially stops and as a result the temperature does not rise.

Or the ignition delays or when the temperature rises between 600 and 700 Kelvin sorry that when the temperature rise is between 600 and 700 Kelvin your ignition delay basically becomes bigger because now you do not have an active chain branching reaction in your reaction mechanism.

Now does it continue forever no because when you increase the temperature to beyond 700 Kelvin you see this H2O2 reacting with in presence of a third body and is forming OH plus OH plus M.

So, this is another chain branching reaction that comes along and as a result of which after 700 Kelvin the ignition delay temperature further can decrease. So, in this intermediate temperature range of 700 to 500 Kelvin you get this thing if you plot it in 1000 by T and this is tau IG you get this kind of a thing. So, this between this range essentially is explained by this thing that is in this range what happens is that up to this range everything was going fine, but after this from this point onwards your reaction 2 is diminished and as a result of the thing that the chain branching reaction is diminished.

But after this point that is after about say 700 Kelvin your there is another alternative chain branching reaction that pops up HO2 plus M OH plus OH plus M. And as a result your T ignition delay further can reduce.