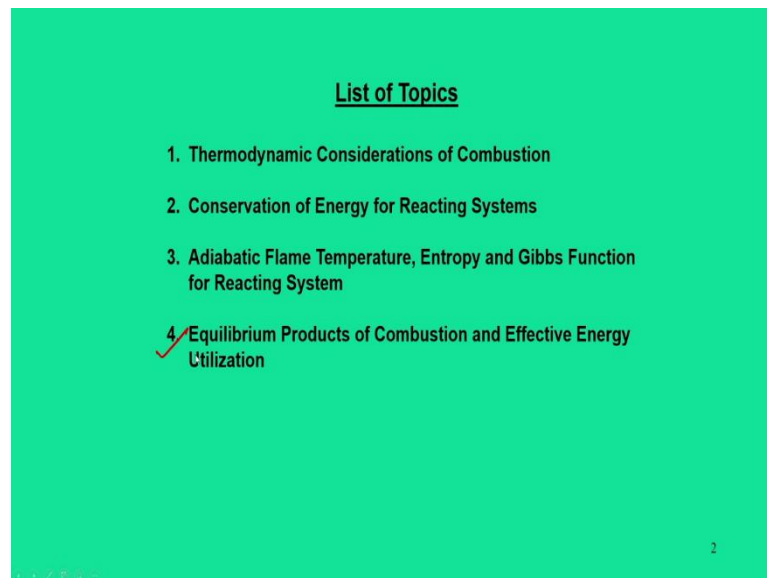


Advanced Thermodynamics and Combustion
Prof. Niranjana Sahoo
Department of Mechanical Engineering
Indian Institute of Technology, Guwahati

Module – V
Combustion and Thermochemistry
Lecture – 22
Equilibrium Products of Combustion and Effective Energy Utilization

Dear learners, greetings from IIT, Guwahati. We are in the MOOCs course, Advanced Thermodynamics and Combustion; Module V, Combustion and Thermochemistry.

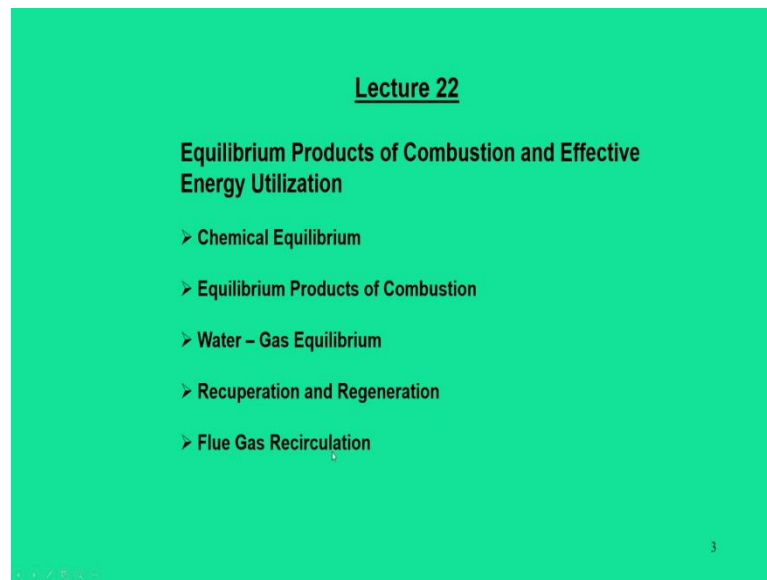
(Refer Slide Time: 00:50)



So, in this module we have covered a majority of the lectures that is thermodynamic consideration of combustion; conservation of energy for reacting systems; we also introduced adiabatic flame temperatures, Gibbs functions, entropy calculations for reacting systems.

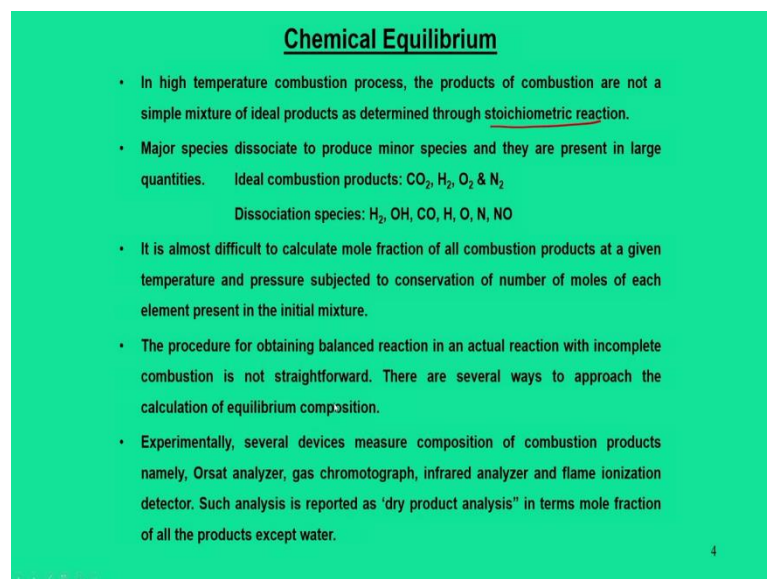
Today we will focus on some of the practical aspects that is Equilibrium Products of Combustion and Effective Energy Utilizations. So, it means that by looking at the combustion products which is mainly dependent on the equivalence ratio, we can say that we have properly utilize the a fuel energy or not. Now, if not, what is the mechanism that can be incorporated to improve the effective energy of the fuel.

(Refer Slide Time: 01:38)



So, in this lecture that is Lecture number 22, we will be touching upon the following topics like chemical equilibrium, equilibrium products of combustions, water-gas equilibrium, recuperation and regeneration, flue gas recirculation.

(Refer Slide Time: 01:56)



So, let me start the first segment of this lecture that is Chemical Equilibrium. Prior to this, we all know that a thermodynamic system is in complete equilibrium when it is physical equilibrium, chemical equilibrium and it is equilibrium in terms of temperature, thermal equilibrium.

So, we have covered the other aspects, but when you dealt with combustion process, we must know that under what circumstances the equilibrium of reaction happens, what is the criteria for deciding that the system has already achieved the equilibrium situation or not. So, this is all about we are going to study with a very important prospective or viewpoint by incorporating the laws of thermodynamics.

So, we will see how you are going to use this thermodynamic laws in down the slides. If I give some introduction, then I can say that always in high temperature combustion products, the products of combustion are not simple mixture, rather they have many complicated species that forms and what we have dealt with so far is the stoichiometric reactions; that means, what is the exact amount of oxidizer requirement for one unit of fuel.

So, that condition we call this as a stoichiometric conditions. Now, if the reactions are not in the stoichiometric situations and in fact, it is the majority of the cases then we will have combustion species and that they will appear. And, there are two types of species one is major species, other is minor species and this control of major and minor species is mainly governed whether the fuel is lean or rich.

Now, ideally if at all the combustion has to happen as a complete combustion; so, the ideal product should be carbon dioxide, hydrogen, oxygen, and nitrogen. But, in most of the situations we do not have this occurrence, we have dissociation species that are formed which are mainly for combustion reactions are hydrogen, OH radical. OH is a hydroxyl radical, carbon monoxide, hydrogen atom, oxygen atom, nitrogen atom, NO nitric oxide.

So, these formations are very similar for hydrocarbon combustions. It is almost difficult to calculate the fraction of all these combustion products at a given temperature and pressure subjected to conservation of moles of each element present in the initial mixtures. So, that is ideal calculation is not straight forward.

So, we have to rely on the experiments or observing the combustion products and taking the samples and then analyzing we can report some of the combustion products analysis or composition analysis. And that will tell whether we have achieved the equilibrium or not.

(Refer Slide Time: 05:16)

Chemical Equilibrium

- In order to be consistent with treatment of equilibrium, the approach is limited to obtain equilibrium constant with ideal gas approximation for combustion products.
- The concept of chemical equilibrium has its roots in the second law of thermodynamics.
- Consider a fixed-volume adiabatic reaction vessel with fixed mass reactants (CO and O₂) that form the products (CO₂). As the reaction proceeds, both pressure and temperature rise till final equilibrium condition is reached.
- The final state is solely governed by second law of thermodynamics. If the final temperature is high enough, CO₂ will dissociate the product will have components of CO₂, CO and O₂.
- A dissociation fraction (α) is introduced that can be treated as a function of adiabatic flame temperature.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$\left[CO + \frac{1}{2}O_2 \right]_{in,R} \rightarrow \left[(1-\alpha)CO_2 + \alpha CO + \frac{1}{2}O_2 \right]_{out,P}$$

5

But, when we want to see the theoretical viewpoint that whether by looking at the sample of data or the experimentally measured data, we can at least predict whether these products are equilibrium products of combustion or not. But, to say or to justify this fact we have to rely on the theory of chemical equilibrium and this chemical equilibrium has its roots with respect to second law of thermodynamics.

Now, to demonstrate this fact let us consider a fixed volume adiabatic reaction vessel with fixed mass reactant CO and O₂. So, that is a reactor in which there are reactants like CO and O₂, they are entering to this reactor at reference pressure and temperatures and side by side they are producing the CO₂ at same reference pressure and temperature.

So, as the reaction proceeds both pressure and temperature will rise till the final equilibrium condition is reached and but the final state is solely determined by the second law of thermodynamics. And, that second law of thermodynamics what parameter we are going to find is nothing but your entropy. So, if the final temperature is not high enough then CO₂ will dissociate and the products will have components CO₂, CO and O₂.

So, basically if it has not achieved this equilibrium conditions, the product will have some intermediate components. Now, to account this fact let us introduce parameter α and we call this as a dissociation fraction and this can be treated as a function of adiabatic flame temperatures means that what is the effect of this α when there is a change in the adiabatic flame temperature.

Why I say adiabatic flame temperature because it is the theoretical thermodynamic estimates that is the upper limit of reaction temperature. So, if you say that the reaction in a balanced form like $CO + \frac{1}{2}O_2 \rightarrow CO_2$. Now, always what we look at this reaction is with final state, but what the intermediate step would have followed that when this reactions proceeds, at any intermediate situations when the temperature is high the species could have $(1 - \alpha)CO_2 + \alpha CO + \frac{1}{2}O_2$.

So, at any time instant we when you look at this chemical equation we can find this.

(Refer Slide Time: 08:11)

Chemical Equilibrium

- By assuming ideal gas behavior, the individual species entropies can be obtained.
- Thus, for constant U, V, m and no work interaction, the second law imposes that the entropy change internal to the system should be greater than or equal to zero.
- The composition of system will simultaneously shift towards the point of maximum entropy when approaching either side since dS is positive.

$$\left[CO + \frac{1}{2}O_2 \right]_{\text{ref}, R} \rightarrow \left[(1-\alpha)CO_2 + \alpha CO + \frac{\alpha}{2}O_2 \right]_{\text{ref}, P}$$

$\alpha = 0 \Rightarrow$ Maximum heat release (Highest possible pressure and temperature allowed by first law)
 $\alpha = 1 \Rightarrow$ No heat release (Mixture temperature remains unchanged)

Entropy of product mixture: n_i : Number of moles of species 'i' in the mixture

$$S_{\text{mix}}(T, p) = \sum_{i=1}^3 n_i \bar{s}_i(T, p) = (1-\alpha)\bar{s}_{CO_2} + \alpha\bar{s}_{CO} + \frac{\alpha}{2}\bar{s}_{O_2}; \bar{s}_i = \bar{s}_i(T_{\text{ref}}) + \int_{T_{\text{ref}}}^T \frac{dT}{T} - \bar{R} \ln \left(\frac{p_i}{P_{\text{ref}}} \right)$$

By second law, entropy change internal to the system, $(dS)_{U, V, m} \geq 0; dS = S_P - S_R$

In terms of Gibbs function, second law expression: $(dG)_{T, p, m} \leq 0; G = H - TS$

Equilibrium condition for reaction: $(dS)_{U, V, m} = 0; (dG)_{T, p, m} = 0$

6

So, we have to say that ideal gas behaviour for individual species is assumed and since there is no work interactions internal energies remains constant, say fixed volume and mass. So, what else parameter that is required is nothing but your entropy.

Now, by looking at this equation, we need to calculate the mixture entropy and we already explained that how for a ideal gas mixture, we are going to calculate the mixture entropy at a given temperature and pressure. And, this is nothing but summation of their molar enthalpies.

And in this case, we can find out at any arbitrary instant what is the component or mole fraction of CO_2 and corresponding molar enthalpy, and what is the mole fraction of CO corresponding its molar enthalpy and same for oxygen as well. And, also from the data sheet or data table, one can find out the entropy of formation at reference temperature and

subsequently knowing their respective mole fractions and partial pressures, one can determine the mixture entropy.

Now, if you look at this particular equation, now let us try to find out or let us try to evolve what the first law of thermodynamics tells and what the second law of thermodynamic tells. So, if you just look at the equations, when α is 0 which means it is a complete balanced equation; that means, reaction has taken place, maximum heat has been released. And, when maximum heat is released as per that evaluation, we can do with respect to first law.

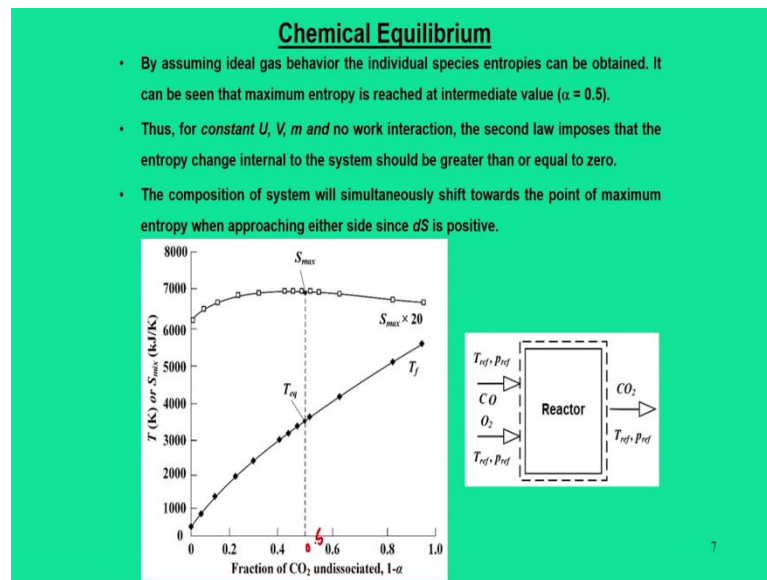
Now, when α is 1, the mixture temperature remains unchanged because there is no heat release. So, α is 1 means CO_2 is 0 that is we have $\text{CO} + \frac{1}{2}\text{O}_2$. When same reactants and products, they remain as it is, reaction has not happened. But that is not the case, what we need to have? We need to find out the entropy.

Now, what this second law imposes that when you calculate the entropy change internal to the systems. So, for a fixed internal energy volume and mass systems, the second law imposes the conditions that this change in entropy must be greater than or equal to 0; $(dS)_{U,V,m} \geq 0$. That means this $dS = S_P - S_R$ and this condition needs to be satisfied and since this Gibbs function has another link with respect to enthalpy, temperature, entropy.

So, this gives a reverse expressions like one can also find out the Gibbs function from the second law expressions and this tells that Gibbs function at a given temperature, pressure and mass system is always less than or equal to 0; $(dG)_{T,p,m} \leq 0$. Why I say because when I say Gibbs function, it is measured with respect to temperature and pressure when I say internal energy with measured with respect to volume and mass.

Now, these two conditions impose that at equilibrium conditions both the change in the parameter should be 0. So, this is the condition for chemical equilibrium, where for a chemical reactions at which the change in the entropy internal to the system should be 0 and change in the Gibbs function should be also equal to 0.

(Refer Slide Time: 11:58)



Now, by putting this, let us try to analyze these reactions in the graphical form. Now, if you look at this particular figure this is plotted against the fraction of CO_2 dissociated that is $(1 - \alpha)$ versus temperature and entropy of the mixture. What we see when we say these two graphs closely? We have some important points: first thing, that as the reaction proceeds, the entropy of the system gradually decreases and it reaches to a maximum point and then it comes back.

But, we have seen that what is the extreme limit when α is 0 and when α is 1, but that is with the two extreme conditions. But, what we have seen is that the equilibrium temperature is reached when the entropy is maximum because this entropy is maximum at a value of α is close to 0.5. So, if you drop this vertical so, we can find this number to be 0.5.

So, it means not necessarily that we will have maximum entropy when the entire product is formed and not necessarily that the reaction will proceed or what you can say equilibrium condition is achieved only when the maximum entropy condition is reached and corresponding to this maximum entropy conditions, we can find out what is the equilibrium temperatures.

So, based on this what we can say that composition of the system will simultaneously shifts towards the point of maximum entropy, when approaching either side since entropy is a positive number or change in the entropy is positive.

(Refer Slide Time: 13:43)

Chemical Equilibrium

- Once the maximum entropy is reached, no further change in composition is allowed since it requires decrease in entropy (i.e. violation of second law). This state is referred as chemical equilibrium.
- In summary, when the internal energy, volume and mass is fixed for an isolated system, the first law in combination with second law and equation of state, define the equilibrium temperature, pressure and chemical composition.
- Many a times, fixed mass and volume system are not useful for certain applications. So, there is a need to calculate the composition of mixture at a given temperature, pressure and stoichiometry. So, Gibbs free energy (G) replaces the entropy.
- Gibbs function always decreases for a spontaneous isothermal, isobaric change of a fixed-mass system in the absence of all work effects except boundary ($p-dV$) work.
- This principle allows to calculate equilibrium composition of mixture at a given temperature and pressure. The Gibbs function attains a minimum in equilibrium in contrast to the maximum in entropy for a fixed-energy and fixed-volume case.

$$\left[CO + \frac{1}{2} O_2 \right]_{T=2000\text{K}} \rightarrow \left[(1-\alpha) CO_2 + \alpha CO + \frac{\alpha}{2} O_2 \right]_{T=2000\text{K}}$$

8

So, if you can just summarize what we have learnt so far about the chemical equilibriums, so, we can write down like this. So, first one is the maximum entropy condition is reached there is no further change of composition is allowed since it requires the decrease of entropy. So, this is referred as the chemical equilibrium in other words the chemical reaction should proceed in the direction of increase in the entropy.

Now, there are two ways to look at one is fixed internal energy, volume and mass for an isolated system, the first law and second law and equation of state combination decides the equilibrium temperature pressure and chemical composition. But many a times, when the information about volume or mass is not known rather we can have fixed temperature and pressure and stoichiometry, then people use this Gibbs function or Gibbs free energy in place of entropy.

So, this entire message remains same which says that Gibbs function always decreases for a spontaneous isothermal isobaric change of a fixed mass systems in the absence of all work effects except boundary work. So, this principle allows to calculate equilibrium composition of a mixture at a given pressure and temperatures. The Gibbs function attains a minimum value in equilibrium in contrast to entropy which is maximum value for a fixed energy and fixed volume case.

So, this is true for all chemical reactions.

(Refer Slide Time: 15:30)

Equilibrium Products of Combustion

- Combustion is the result of series of very complicated and rapid chemical reaction while the formation of products depends on many factors.
- There are several devices that measure composition of combustion products namely, Orsat analyzer, gas chromatograph, infrared analyzer and flame ionization detector. Such analysis is reported as 'dry product analysis' in terms mole fraction.
- In a complete combustion with a specified fuel, products can be determined by applying conservation of mass principle to the chemical equation.
- The procedure for obtaining balanced reaction in an actual reaction with incomplete combustion is not straightforward.
- The equations involving the first law, chemical equilibrium principles, adiabatic flame temperatures and details of combustion are simultaneously solved with appropriate atom-conservation constants, to obtain the equilibrium products of combustion.
- The constant pressure combustion of *propane-air* mixture is considered with intermediate products as, CO_2 , CO , H_2O , H_2 , H , OH , O_2 , O , NO , N_2 and N .

Propane - Air: $C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$

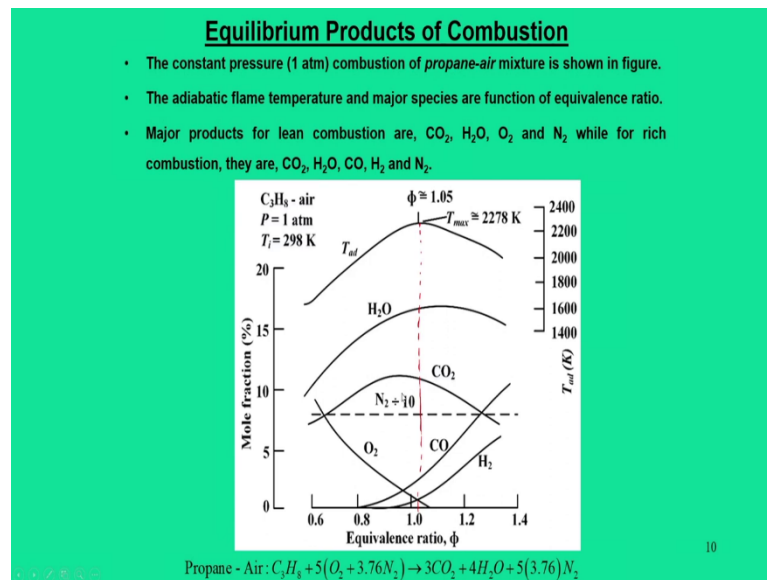
9

Now, having complete understanding of chemical equilibrium, let us see that what are the equilibrium products of combustions. So, you all know that the combustion is the result of series of complicated and rapid chemical reactions, but the formation products depend on many other factors and this combustion product normally is determined through experimental observations by instrument like Orsat analyzer, gas chromatography, infrared analyzer and so on.

So, what we want to find out from our previous study that equilibrium compositions during a combustion phenomenon. So, to have this complete understanding about the equilibrium products of combustions let us take an example may be a one case like propane air mixture. $C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$.

But, what we see is the equilibrium composition, but not necessarily this composition will always come into pictures. So, we may have other components like CO_2 , CO , H_2O , H_2 , OH , O_2 , O , NO , N_2 and N . So many atoms are there. Now, under what circumstances these species will come into pictures?

(Refer Slide Time: 17:04)



So, let us understand here we can have two situations like the mixture can be lean or rich; lean means it is less in fuel more quantity of air, rich means it is rich in fuel and less quantity of air. So, when we have lean combustions, the major product should be CO_2 , H_2O , O_2 , and N_2 , that is quite obvious because we do not have sufficient fuel. So, we will have oxygen as the product.

Now, for rich combustion; that means, fuel is quantity is more. It does not find enough oxygen. So, there cannot be oxygen at the product. So, the major product should be CO_2 , CO , H_2O , H_2 , and N_2 . Now, what we have done is here that in a particular sample cases people have tried to analyse and tried to plot them equivalence ratio which is a non dimensional parameter versus mole fraction; mole fraction of these reactants and products.

And, at the same time people have find out what is the typical adiabatic flame temperature for these conditions. So, what has been observed is that with increase in the equivalence ratio is quite obvious the adiabatic flame temperature increases and it goes to a maximum and then further drops.

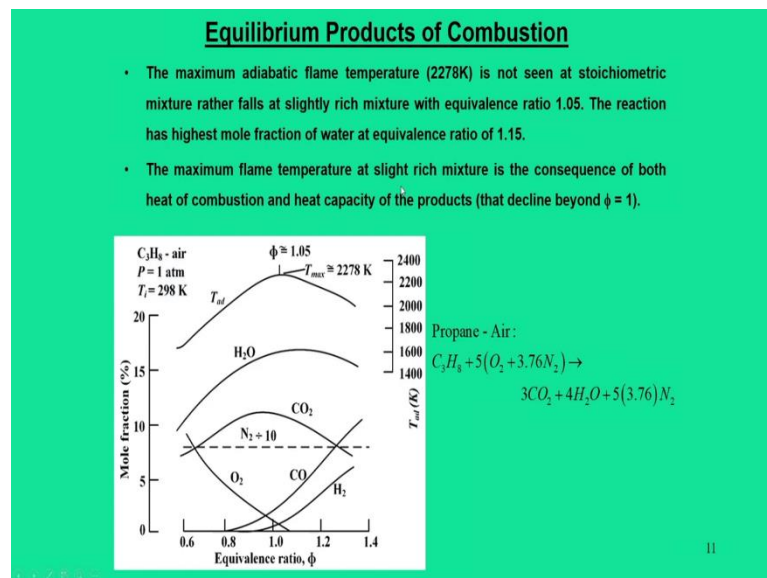
So, one interesting phenomenon is that that is quite obvious, this flame temperature increases, as and when the fuel quantity is increased or the fuel becomes richer and richer, but as and when the fuel becomes rich and rich, but subsequently at one point of time fuel does not find enough oxygen. So, after this the maximum flame temperature drops and the

maximum temperature is observed not exactly at $\phi = 1$, rather it is at $\phi = 1.05$ and this typical number is 2278 kelvin.

So, this is the benchmark or the maximum temperature that we can achieve through propane air combustion process and if you drop a vertical from this, then we can see what happens to other components, what happens to mole fraction of the other components. We see that the first thing the water formation and it is again is not seen at this maximum temperature rather it is seen when equivalence ratio is more than 1 and whereas, maximum for CO₂ is observed when the mixture is lean.

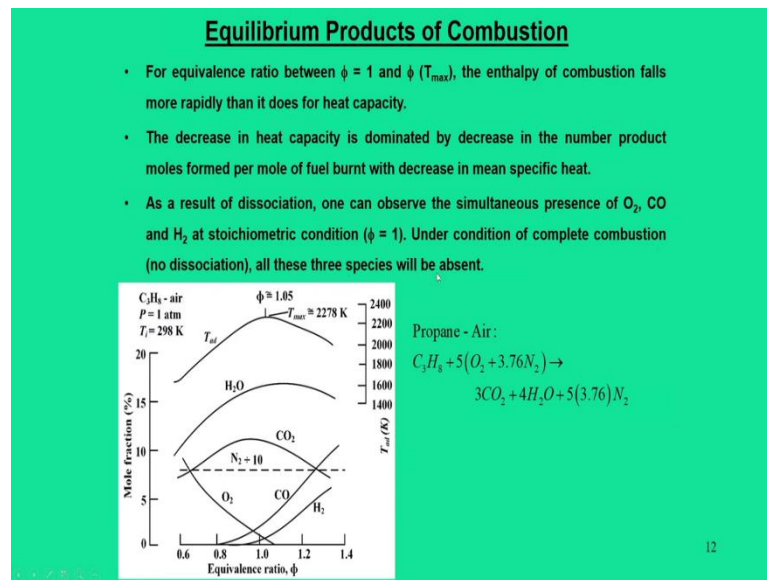
Of course, CO and H₂O concentration increases as and when we increase this equivalence ratio, our fuel becomes rich and rich, oxygen concentration drops and one point of time it becomes substantially 0 because we are moving towards rich mixtures. So, all these consequences happen.

(Refer Slide Time: 20:12)



So, this is what I have observed that what equivalence ratio of 1.05, we see the maximum flame temperature that is adiabatic flame temperatures, but the highest mole fraction is obtained at some higher equivalence ratio of 1.15. The maximum flame temperature is observed when the mixture is slightly rich.

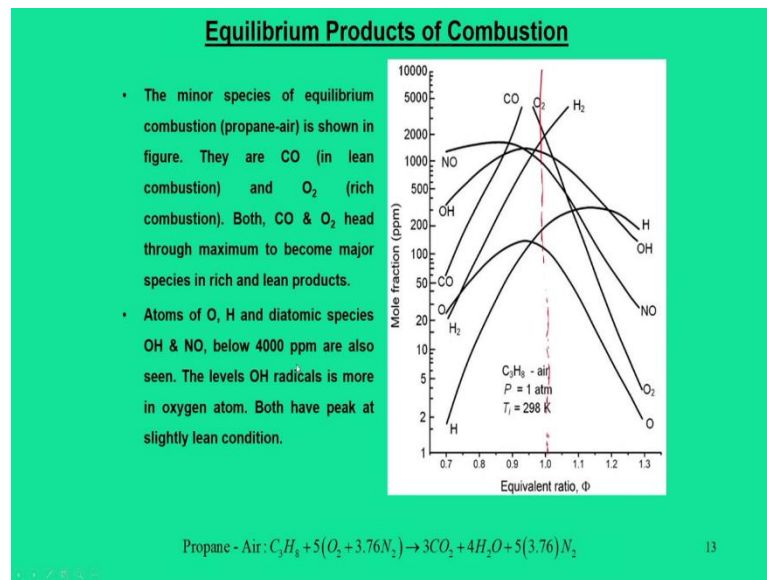
(Refer Slide Time: 20:36)



Other consequence we can draw that for equivalence ratio between $\phi = 1$ and $\phi(T_{max})$, the enthalpy of combustion falls more rapidly and this is one of the consequences why this maximum mole fraction of this is for H_2 is formed at higher equivalence ratio that is because the decrease in the heat capacity is dominated, by the decrease in the number of moles formed per mole fuel burnt with the decrease in the mean specific heat.

And, of course, when there is a dissociation, as a result of dissociation we can see simultaneous presence of oxygen, CO, H_2 at stoichiometric conditions. So, under condition of complete combustion or no dissociation all these three species will be absent. So, this is what we see the equilibrium products of combustion for major species.

(Refer Slide Time: 21:32)

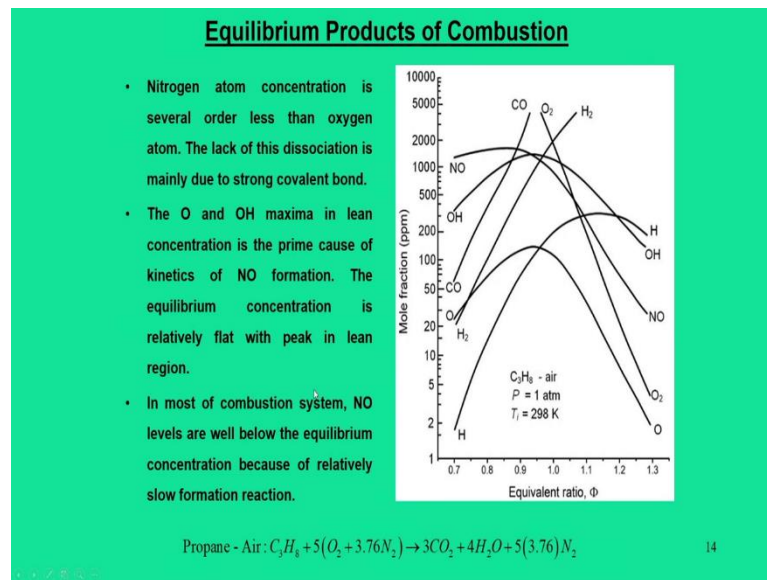


Now, let us understand what are the minor species that pops in. So, minor species as we say that in general minor species can be in the form of oxygen atom, hydrogen atom, OH NO all this formation can happen and all of them are plotted with respect to mole fractions. As we see that if you drop a vertical with equivalence ratio 1, we can get many information.

With respect to this reference, first let us start one by one. The NO concentration drops when we are moving towards high equivalence ratio. OH concentration initially increases till this equivalence ratio and reaches maxima when it is mixture is slightly lean then it drops. The hydrogen concentration keeps on increasing; CO concentration is mostly found when the mixture is in the lean.

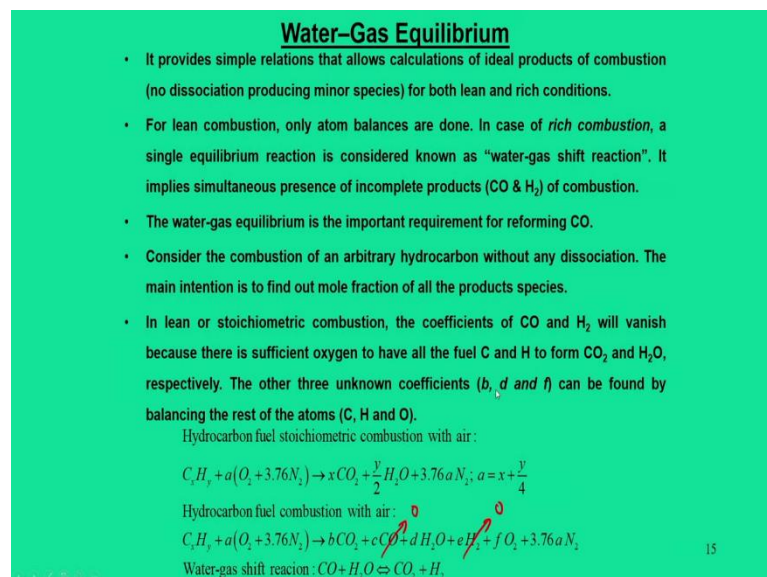
And, of course, for oxygen atom it increases and then towards the higher equivalence ratio this number drops out and the numbers are regarded as the minor species. And, minor species means that we are looking at, their numbers are not critical since they are below 4000 ppm.

(Refer Slide Time: 23:05)



Of course, for nitrogen atom, the concentration is several orders less than the oxygen atom and we do not find significant nitrogen, I mean reaction is not sufficient to give species of nitrogen, but it is giving in the form of NO. So, NO formation becomes vital when the mixture is in the lean side. So, this is all about the major and minor products during a combustion process of propane air mixture.

(Refer Slide Time: 23:37)



Now, we are going to discuss a very important topic that is called as water-gas equilibriums. So, water-gas equilibrium is simple chemical reactions that allows to control the composition in the products of combustion. So, how do you do that?

So, normally what happens first of all let us see what is this water shift reactions. So, water shift reaction is like we write this equation that $CO + H_2O \rightleftharpoons CO_2 + H_2$. So, this reaction is known as water shift reactions. So, it says that reaction can proceed in either directions; that means, CO when it mixes with water, it can produce CO_2 and H_2 and simultaneously, they can also decompose to form CO plus H_2O . So, this is called as water shift reactions.

Now, why it is required in the combustion process and now, if you look at any general hydrocarbon fuel stoichiometric combustion with air, we write $C_xH_y + a(O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{y}{2}H_2O + 3.76aN_2$; $a = x + \frac{y}{4}$. So, this is a balanced reaction general reaction for hydrocarbon fuel.

Now, we mentioned that not necessarily always CO_2 and H_2O will be present. So, we can have CO_2 , but any general reaction can have CO_2 , we can have CO, we can have H_2O , we can have H_2 , O_2 or N_2 . So, these are the major products that can form at any instant of time.

Now, the compositions like stoichiometric coefficient b, c, d, e, f all these things are regulated by the fact that whether the mixture is rich or lean. So, basically rich mixtures will say something and lean mixture will say something. So, what does it mean? Suppose first case we say that if the mixture is lean, in lean mixture what is going to happen? The coefficient of CO and H_2 will vanish. So, basically the reaction for a lean combustion would be that the hydrocarbon fuel when it reacts with oxidizer it will produce CO_2 , water, O_2 .

So, now, we can have a balanced equation. So, we have components like carbon atom, hydrogen atom and oxygen atom. So, by using these equations we can find out the unknowns like b, d, f. So, these three are unknown and a is already known because $a = x + \frac{y}{4}$. So, a is known already. So, b, d and f are unknown and this mass balance or atom balance can be done for carbon, hydrogen and oxygen to have a balanced equations.

So, basically what it means that during a lean or stoichiometric combustions, we do not require this water shift reaction because there is no CO, first thing. Second thing more or less we have sufficient equations to find the stoichiometric coefficients.

(Refer Slide Time: 27:26)

Water-Gas Equilibrium

- The total number of moles of products can be found by summing of the coefficients together with 3.76 moles of nitrogen.
- In rich combustion, no oxygen will appear and its coefficient will vanish. But, it leaves with four unknowns (b, c, d and e).
- So, three element (C, H and O) balance equation is employed along with water-shift equilibrium involving equilibrium constant (K_p) to find the unknown quantities.
- The equilibrium constant is a function of temperature and its value (0.16-0.22) is selected with respect to suitable combustion temperature (2000K - 2400K).

Hydrocarbon fuel stoichiometric combustion with air:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{y}{2}H_2O + 3.76aN_2; a = x + \frac{y}{4}$$

Hydrocarbon fuel combustion with air:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2$$

Water-gas shift reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$

Equilibrium constant: $K_p = \frac{(p_{CO_2}/p_{ref})(p_{H_2}/p_{ref})}{(p_{CO}/p_{ref})(p_{H_2O}/p_{ref})} = \frac{b \cdot e}{c \cdot d}$

16

Now, let us understand see if the mixture is rich, when the mixture is rich only thing that we can predict that no oxygen will appear; that means, f will be 0, because the mixture is rich there is no oxygen because it does not find sufficient quantity of air. Then what we see we have basically four unknowns; that means, the reaction will have the presence of CO₂, CO, H₂O, H₂ as well as N₂ and we have all four unknowns that is b, c, d, e, but the atomic balance will tell about three elements the carbon, hydrogen and oxygen.

So, we require another equation to find the all the stoichiometric coefficients this is where we realize the importance of this water shift reactions. So, if you look at this particular equation you can see this simultaneous presence of CO and H₂O in the products and they continuously react with each other and reaction can proceed in either side direction and the CO can form CO at the same time CO₂ can decompose to form CO. So, there is a simultaneous process of formation of CO₂, CO, H₂O and H₂.

To have this understanding we have to recall this water shift reactions, by doing so, what we are going to find out we are introducing a parameter what is called as equilibrium constant and that is defined with respect to partial pressures of each component that is a partial pressure of CO₂, CO, H₂O and H₂ and all these partial pressures are again controlled

with respect to their mole fractions and from this equation we can find $K_p =$

$$\frac{\left(\frac{p_{CO_2}}{p_{ref}}\right)\left(\frac{p_{H_2}}{p_{ref}}\right)}{\left(\frac{p_{CO}}{p_{ref}}\right)\left(\frac{p_{H_2O}}{p_{ref}}\right)} = \frac{b.e}{c.d}$$

So, basically now we have three equations with respect to carbon, hydrogen and oxygen atom; another equation will get through this equilibrium constants. Now, if you do this what is going to happen that we are going to see.

(Refer Slide Time: 29:53)

Water-Gas Equilibrium

Lean and Stoichiometric combustion

Hydrocarbon fuel combustion with air:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2$$

At lean or stoichiometric condition ($\phi \leq 1$):

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + dH_2O + fO_2 + 3.76aN_2; a = \frac{x + \frac{y}{4}}{\phi}$$

C, H and O atom balance $\Rightarrow b = x; c = 0; d = y/2; e = 0; f = \left(\frac{1-\phi}{\phi}\right)(x + y/4)$

Total number of moles of product per mole of fuel burnt: $n_i = \left(x + \frac{y}{2}\right) + \left(\frac{x + \frac{y}{4}}{\phi}\right)(1 - \phi + 3.76)$

Mole fractions for combustion products:

$$\chi_{CO_2} = \frac{x}{n_i}; \chi_{CO} = 0; \chi_{H_2O} = \frac{y/2}{n_i}; \chi_{H_2} = 0; \chi_{O_2} = \frac{\left(\frac{1-\phi}{\phi}\right)(x + y/4)}{n_i}; \chi_{N_2} = \frac{3.76(x + y/4)}{\phi n_i}$$

So, this particular thing tells about when the mixture is lean or stoichiometric, we can say that we do not require water shift reactions, the entire equations can be solved with respect to carbon, hydrogen and oxygen atom balance. So, we can find out these stoichiometric coefficients, we can also find out the mole fraction of each combustion products.

(Refer Slide Time: 30:21)

Water-Gas Equilibrium

Rich combustion
 Hydrocarbon fuel combustion with air:
 $C_xH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2$
 Atrich condition ($\phi > 1$):

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + 3.76aN_2; a = \frac{x + \frac{y}{4}}{\phi}$$

C, H and O atom balance $\Rightarrow c = x - b; d = 2a - b - x; e = -2a + b + x + \frac{y}{2}; K_p = \frac{b \cdot e}{c \cdot d}$

$$b = \left[\frac{2a(K_p - 1) + x + (y/2)}{2(K_p - 1)} \right] - \frac{1}{2(K_p - 1)} \left[\left\{ 2a(K_p - 1) + x + (y/2) \right\}^2 - 4K_p(K_p - 1)(2ax - x^2) \right]^{1/2}$$

Total number of moles of product per mole of fuel burnt: $n_t = \left(x + \frac{y}{2} \right) + 3.76a$

Mole fractions for combustion products: $\chi_{CO_2} = \frac{b}{n_t}; \chi_{CO} = \frac{c}{n_t} = \frac{x - b}{n_t}; \chi_{H_2O} = \frac{d}{n_t} = \frac{2a - b - x}{n_t};$

$$\chi_{H_2} = \frac{e}{n_t} = \frac{\left(-2a + b + x + \frac{y}{2} \right)}{n_t}; \chi_{O_2} = 0; \chi_{N_2} = \frac{3.76a}{n_t}$$

18

But, here the challenge comes when we have rich combustions. So, in the rich combustions we have basically four unknowns like b, c, d, e, because f is 0. So, we have four unknown b, c, d, e at the same time we have to recall the equilibrium constant $K_p = \frac{b \cdot e}{c \cdot d}$. So, it will be a complicated equations which can be formed because this Kp is the equilibrium constant that has to be derived.

So, it is a very complicated equations and all these components we can find out, but what advantage we can get is that the simultaneous control of CO₂, CO, H₂O and H₂ can be regulated with a value Kp and this Kp can be controlled through the partial pressures of this each of these components.

So, basically it is a user defined parameters which you know it earlier by doing this all those things can be solved simultaneously to find out the products of combustion when the mixture is rich. Now, once you know all these numbers then it is easy to find out the composition or mole fraction of all the combustion products. So, this is all about when the mixture is lean or rich.

(Refer Slide Time: 31:55)

Recuperation and Regeneration

- The effective energy utilization from the fuels can be achieved by approaching complete combustion.
- There are two practical applications to improve energy utilization through mechanical devices: (a) recuperation or regeneration; (b) exhaust gas recirculation.
- A recuperator is a heat exchanger in which energy from a steady flow of hot combustion products (i.e. flue gases), is transferred to the air supplied to the combustion process. They employ radiations from the flue gases as well as convection for effective utilization and increase adiabatic flame temperatures.

19

So, the next topic that we are going to discuss is a kind of some practical utility for example, we have a rich combustion and we are unable to burn the fuel sufficiently. So, what is the next approach? So, basically the fuel has to be circulated again as a reactant; that means, the products have to be recirculated again, that is one way. Second way, we can get that whatever energy that is carried by the exhaust product that can be tapped.

So, there are two approaches for effective utilization, one is by using certain mechanical devices we call it as recuperation or regeneration and second concept is the exhaust gas recirculation. So, basically this is a schematic diagram of a furnace maybe it can be a boiler or it can be any gas turbine engines where fuel and air get added, and we get required amount of heat and the combustion product goes out.

And, this combustion goes out; so, instead of releasing to the atmosphere. So, these products are nothing but your flue gases when they go out, we need to tap their heat. So, to tap that we can use a heat exchanger and with this prospective or application we call this as a recuperator and what it essentially does is tap the heat from the combustion product and it is to preheat the oxidizer or preheat the air.

So, this preheated air enters into the furnace. So, by this process what it does? It improves or it enhances the adiabatic flame temperatures. So, this is one way for effective utilization of energy.

(Refer Slide Time: 33:45)

Recuperation and Regeneration

- The effective energy utilization from the fuels can be achieved by approaching complete combustion.
- There are two practical applications to improve energy utilization through mechanical devices: (a) recuperation or regeneration; (b) exhaust gas recirculation.
- A regenerator transfers energy from flue gases to the incoming combustion air. In this case, an energy storage medium, such as corrugated steel or ceramic matrix, is alternatively heated by the hot gases and cooled by air. The stored energy may be utilized to preheat the incoming air, thereby increasing the adiabatic flame temperature.

20

Another way of looking at this instead of recuperator, people use regenerator. What it does is regenerator transfers the energy of the flue gases of incoming combustion of air. In this case this regenerator is considered as an energy storage medium and this storage can be in the form of a ceramic matrix or it can be a concrete, or it can be a steel or it can be a phase change material, it can be anything and this store energy is utilized whenever it is required either it can be used to preheat the air or it can be used for some other purposes.

And, if you preheat the air, I mean essentially what it does is improves or increases the adiabatic flame temperature. When such a regenerator or recuperator used, we can use this lean mixture because using during lean combustions, we have burnt the fuel sufficiently, but the exhaust product has sufficient heat.

So, in that such situations, the regeneration, recuperation concept can be used to tap the heat, but in other scenario when you have a rich mixtures; that means, we have not extracted the fuel energy completely. So, that means, the mixture is again still have some capability to initiate the reactions. So, during that conditions we use the concept called recirculation and we call this as a flue gas recirculation.

(Refer Slide Time: 35:29)

Flue Gas Recirculation

- The effective energy utilization from the fuels can be achieved by approaching complete combustion.
- There are two practical applications to improve energy utilization through mechanical devices: (a) recuperation or regeneration; (b) exhaust gas recirculation.
- In one strategy to decrease the amount of oxides of nitrogen (NO_x) formed and emitted from certain combustion devices, a portion of burned product gases is recirculated and introduced in air and fuel.
- The effect of the recirculated gases is to decrease the maximum temperature in the flame zone that leads to lowering NO_x. The flue gas recirculation (FGR) is very common in boilers/furnace while exhaust gas recirculation (EGR) system is mostly used in automotive engines.

21

So, recirculation means like whatever exhaust product that comes, before it is being fed out, some part of these things is again fed into this system or the reactor. So, through this process what we are going to get is that we can tap this heat at the same time whatever unburnt fuel is there, they can be recirculated with the phase charge and as a result we can get an effective combustion.

One advantage of this is that we can lower the NO_x formations that is the essential advantage of this recirculation. So, there are two concepts associated with it, one is flue gas recirculation which are very common techniques when people used for boilers or furnace. Now, when you are doing research in IC engine, people used to take some part of exhaust gas and recirculate it and that they mix with the fresh air and such a concept we call is as a exhaust gas recirculation. And, that is very common in the automotive engines.

(Refer Slide Time: 36:39)

Numerical Problems

Q1. A stationary gas turbine engine operates at an equivalence ratio of 0.3 with an air flow rate of 950 kg/min. The equivalent composition of fuel is $C_{1.16}H_{4.32}$. Determine the mass flow rate of fuel and operating air-fuel ratio.

Soln

$\phi = 0.3, \dot{m}_a = 950 \text{ kg/min} = 15.8 \text{ kg/s}$

$C_x H_y + a(O_2 + 3.76 N_2) \rightarrow x CO_2 + \frac{y}{2} H_2O + 3.76 a (N_2)$ Recall,

$a = x + \frac{y}{4}, \quad x = 1.16, \quad y = 4.32$

$\Rightarrow a = 2.24$

$M_f = 12(1.16) + 1(4.32) = 18.24$

$M_a = 28.97$

$(A/F)_{stoic} = \left(\frac{\dot{m}_a}{\dot{m}_f}\right) = \left(\frac{4.76 a}{x}\right) \left(\frac{M_a}{M_f}\right) = 16.92$

$\phi = \frac{(A/F)_{actual}}{(A/F)} = 0.3 \Rightarrow A/F = \frac{16.92}{0.3} = 56.4$

$\frac{\dot{m}_a}{\dot{m}_f} = 56.4 \Rightarrow \dot{m}_f = \frac{15.8}{56.4}$

$\Rightarrow \dot{m}_f = 0.28 \text{ kg/s}$

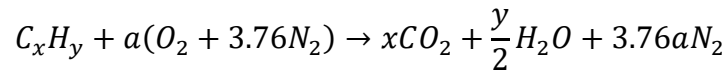
Now, with this I close this module, but before you complete this lecture let us understand some of the basic problems which you have covered in this class. So, again this we can say one particular problem which we typically use mainly while calculating the mass flow rate and air fuel mixture apart from the conventional fuel. Conventional fuel are normally petrol or diesels.

But, many a times we use some composition of fuel which is closely resembles to a into natural gas that is $C_{1.16}H_{4.32}$. So, this is another hydrocarbon fuel one can think of while using in any kind of gas turbine engines. So, what is given and basically what we are trying to say is that again we are revisiting to calculate the air fuel ratio, fuel-air ratio, mass flow rate all these fundamental concepts.

So, the problem that is given to us that we are known with the equivalence ratio which is 0.3, we are known with the air flow rate that is 950 kg/min, we have given with the composition of the fuel and we need to calculate the mass flow rate of the fuel and equivalence ratio.

$$\phi = 0.3; \dot{m}_a = 950 \frac{\text{kg}}{\text{min}} = 15.3 \frac{\text{kg}}{\text{s}}$$

Recall, $M_f = 12(1.16) + 1(4.32) = 18.24; M_a = 28.97$



$$a = x + \frac{y}{4} = 1.16 + \frac{4.32}{4} = 2.24$$

Now, we are in a position to calculate what is air-fuel ratio for the stoichiometries.

$$\left(\frac{A}{F}\right)_{sto} = \frac{\dot{m}_a}{\dot{m}_f} = \left(\frac{4.76a}{1}\right) \left(\frac{M_a}{M_F}\right) = 16.92$$

$$\phi = \frac{\left(\frac{A}{F}\right)_{sto}}{\left(\frac{A}{F}\right)} = 0.3; \frac{A}{F} = \frac{16.92}{0.3} = 56.4$$

$$\dot{m}_f = \frac{\dot{m}_a}{56.4} = 0.28 \text{ kg/s}$$

So, this system requires 0.28 kg per second of fuel while air quantity is 15.8 kg per second.

(Refer Slide Time: 42:23)

Numerical Problems

Q2. A natural gas fired industrial boiler operates with oxygen concentration of 4 mole percent of flue gases. Determine the operating air-fuel ratio and equivalence ratio.

Handwritten solution:

Natural gas: CH_4 - air combustion
 $CH_4 + a(O_2 + 3.76N_2) \rightarrow bCO_2 + 2H_2O + (b)O_2 + (3.76a)N_2$

O atom balance, $2a = 2 + 2 + 2b \Rightarrow b = a - 2$ (unknown a & b)

$x_{O_2} = 0.04$
 $\frac{N_{O_2}}{N_{mix}} = \frac{b}{1 + 2 + b + 3.76a} = 0.04$
 $\Rightarrow b = 0.12 + 0.04b + 0.1504a$

$\frac{A}{F} = \left(\frac{N_a}{N_f}\right) \left(\frac{M_a}{M_f}\right) = \frac{(2.52)(4.76)(28.97)}{(1) \times 16} = 21.72$

$(A/F)_{sto} = \frac{(2)(4.76)(28.97)}{(1)(16)} = 17.23$

$\phi = \frac{(A/F)_{sto}}{(A/F)} = \frac{17.23}{21.72} = 0.79$

Additional handwritten notes:
 After solving:
 $a = 2.52$
 $b = 0.52$
 $a = x + \frac{y}{4}$
 $(1.16) = 1 + \frac{y}{4}$
 $= 2$

23

Then moving further there is another problem which says that natural gas fired industrial boiler, it operates with oxygen concentration 4 mole percentage of flue gases. Now, let us see what is this mean by flue gases. Normally for hydrocarbon fuels when they burn, they produce CO_2 , H_2O , O_2 , N_2 . So, these are called as flue gases.

So, you should understand the term like flue gases. So, you can assume that normally when you say natural gas. Its main compositions one can blindly assume it is CH₄. So, we can say it is a methane air combustion. So, we can write this equation as $C H_4 + a(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + bO_2 + a(3.76)N_2$ and these are nothing but your flue gases and in this flue gases it contains 4 moles percent of oxygen.

So, if you make this oxygen atom balance one can write $2a = 2 + 2 + 2b; b = a - 2$.

$$X_{O_2} = 0.04; \frac{N_{O_2}}{N_{mix}} = \frac{b}{1 + 2 + b + 3.76a} = 0.04; b = 0.12 + 0.04b + 0.1504a$$

$$\text{Solving, } a = 2.52, b = 0.52$$

Now, with this number, we are now able to find out what should be the air fuel ratio. So, air fuel ratio would be number of moles of air by number of moles of fuel into molecular weight of air by molecular weight of fuel.

$$\frac{A}{F} = \left(\frac{N_a}{N_f}\right) \left(\frac{M_a}{M_f}\right) = \frac{(2.52 \times 4.76 \times 28.97)}{1 \times 16} = 21.72$$

Now, when I say A by F stoichiometric at the stoichiometric you have a is equal to x plus y by 4. So, x plus y by 4 means that is 1 plus 4 by 4, for methane, a is equal to 2.

$$\left(\frac{A}{F}\right)_{stoich} = \frac{(2 \times 4.76 \times 28.97)}{1 \times 16} = 17.23$$

$$\phi = \left(\frac{A}{F}\right)_{stoich} / \frac{A}{F} = \frac{17.23}{21.72} = 0.79$$

So, this is all about the type of fuel that we are using and how their compositions are going to affect the equilibrium products of combustions. So, with this I conclude.

Thank you for your attention.