Applied Thermodynamics for Engineers

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Lecture – 35
Theoretical and Actual Combustion Process

Hello friends, we are into the last leg of our course, that is we are into the module number 12. We have been discussing with each other about different topics of applied thermodynamics over in last 11 weeks and accordingly we you have gone through several kinds of topics like, we have discussed about different kinds of power producing cycles using non condensable gases as the working medium, using condensing vapor as a working medium and also we have discussed about the concept of combined cycles where generally combines two or three different kinds of powerful producing cycles in series, so that we can get higher efficiency from this combination of this powerful cycles.

We have also talked about the power absorbing cycles in the form of refrigeration cycles. Different kinds of refrigeration cycles were discussed, I also have discussed about one very important application of refrigeration cycle which is in the form of air conditioning. And there, air conditioning as it involves a mixture of the non condensable gas in the form of air and condensable vapour in the form of water vapour. So, we have talked in detail about the different properties of gas vapour mixtures, which of course we have primarily talked about from the point of view of moist air. However, that is equally applicable to any kind of mixture of gas and vapour.

In between you have also talked about the mixture of gases, mixture of real or ideal gases and we have seen how to assume in the properties of such gas mixtures. Now one important thing that we have always assumed throughout these 11 weeks of discussion was the presence of chemical equilibrium. We have always assumed that there is no unbalanced chemical potential present in the system and hence there is no form of chemical reaction that can be present inside the system. Accordingly, like you probably know from your basic thermodynamics that internal energy can have different kind of sources or different kinds of manifestations.

Internal energy can manifest in the form of sensible energy which macroscopic point of view leads to the change in temperature of the substance or internally as you can have latent form or latent energy which leads to the change in phase from macroscopic point of view. We have seen the application of both of these kinds of internal energy manifestations in power producing cycles. Like in case of gas power cycles or air standard cycles you have seen that the working medium was non condensable gases, so that it is temperature changes during the heat addition of heat reaction processes but there is no change of phase. And hence whatever internal energy change that was happening that was only in the sensible mode. Whereas when we talked about the vapour power cycles or the reverse of that one that is the refrigeration cycles, the vapour compression refrigeration cycles there we had change of phase.

So, there are sensible heating in certain parts like if you can think about the process that goes on expansion process, that goes on in a turbine. As long as it is limited to the superheated zone of the corresponding substance, superheated state that we are talking about, in that is also there is an energy change. But during the evaporation or condensation process that is definitely phase change process and so manifestations of the latent part of the internal energy.

Internal energy can also have its manifestation in the form of nuclear energy in certain nuclear fission reactions. However, there is another important manifestation of internal energy that is in the form of chemical energy. And that is present only when there is a chemical reaction goes on, there is change in the chemical combination or the chemical formula of the involved spaces. And that is something that we have neglected throughout this course.

But in this particular week, we are going to give you a little bit of touch on the thermodynamics of chemical reactions or chemical thermodynamics. Now before I go into the details of this, I must mention that what is the importance of studying that. Like say, we have always talked about heat engines as some kind of devices which receives energy from high temperature source and rejects heat to some low temperature sink. Now it is receiving energy from some high temperature source that means the source itself must have some kind of source of energy which it can supply to the heat engine.

Now from where that energy can come in? There are very few natural sources of heat in the environment or in the universe like sun can be one source of heat addition. But again, corresponding temperature corresponding solar temperature like when it reaches the surface of the earth can be quite low. Then what can be the most practicable source? Of course you know that the most common way of producing energy we have also discussed earlier that is to burn some kind of fuel via the process of combustion.

So that the fuel and oxidizer can combine together participate in some kind of chemical reaction and during this exothermic chemical reaction huge amount of energy can get released, which will be supplied to the heat engine for production of subsequent mechanical work. And therefore, chemical reaction is the essence of thermal energy production which can subsequently be utilized in any kind of heat engine. And therefore, wherever you are talking about any kind of heat engine application, we are talking about some kind of chemical reaction.

Like think about the air standard cycles, we have talked about the air standard cycles which are the common cycles you can find in different kind of automobile vehicles. But how we run automobiles from outside? Just do not bother about the engine, from outside from user point of view, we pour some kind of fuel in the fuel tank and we know that that fuel definitely is burning inside the cylinder and accordingly it is giving us energy.

Like in internal combustion engine we have seen that the combustion process goes inside the cylinder only. And therefore a chemical reaction is present to supply the energy. While performing a thermodynamic analysis of course we have neglected the chemical reaction we have assumed the heat addition in the thermodynamic cycle to be either in constant volume or constant pressure mode or maybe any combination of them in the dual pressure cycle or dual combustion cycle.

However, in practical engines it is a combustion reaction that goes inside the cylinder so chemical reaction is definitely present. If we talk about the external combustion engines like the gas turbine or steam turbine there again we are burning some kind of fuel like in gas turbine, we generally burn some kind of hydrocarbon fuels quite similar to the internal combustion engines and that produces energy and that energy is supplied to the gas when it passes through the combustor.

Similarly, in case of steam turbines we burn some common fossil fuels like coal or in lower scale, wood pieces etc, in certain limited cases maybe oil so that we can produce heat and that heat is added to the water when it passes to the water walls to raise the steam. Therefore, chemical reaction is very much the essence of thermal energy production for any kind of heat engine applications. And hence it is important to have some kind of idea about the thermodynamics of chemical reaction.

Of course, we do not have the scope of going to the details of this chemical reaction because that is another topic of advanced thermodynamics which is commonly taught at the master degree level. But still I would like to discuss about the most important concept and the several terminologies or definitions which are associated with the chemical thermodynamics. So, from now onwards we are going to talk about thermodynamic systems where we have multiple spaces present and the spaces can participate in some kind of chemical reaction.

Therefore, there is no kind no chemical equilibrium present in there inside the system rather the chemical part of the internal energy is getting manifested in the form of probably some change in temperature or something else.

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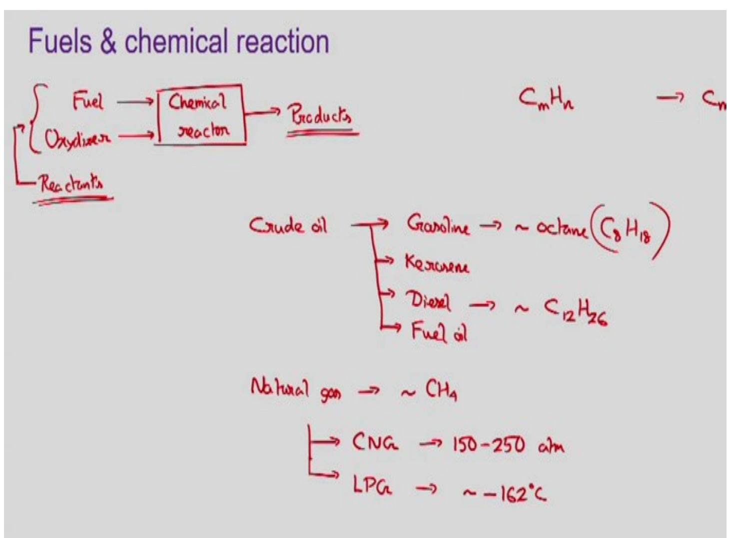

Now the first term that comes in combination with the chemical reactions that is fuel. Fuel is the substance which participates in the chemical reaction with some kind of oxidizer and accordingly it produces thermal energy. So, if we are talking about any kind of chemical reactor then we generally supply some fuel and we supply some oxidizer. I am not calling it oxygen rather I am writing oxidizer I shall be coming back to that very soon. And because of the combustion reaction some product comes out of this.

So, these two together are generally called reactants because they participate in the chemical reaction. So, this side you have the reactants in the form of fuel and oxidizer and maybe something else as we shall be seeing shortly and this side, we have the combustion products. Now what can be the common fuel? Of course, common fuel can be the fossil fuels like coal or maybe the crude oil or petroleum. Crude oil can have different kind of variations for the process of distillation like when you take the crude oil and supply it to some kind of refineries then during the distillation process in different stages different elements comes up.

Like the one which is the most volatile one that comes out first which we commonly called the gasoline. As we have discussed in conjunction with our standard cycles the gasoline examples can be petrol or natural gases. Then as we the keep on going through this refining or distillation process then we keep on getting several other substances, like you may get something like kerosene afterwards it is slightly heavier, then we get diesel then finally we get the fuel oil etc.

This keeps on coming up at different temperature levels and accordingly we can have different forms of crude oil. Each of them has their own applications, like gasoline you can you know that patrols or necessarily gases they are used in lighter vehicles like in two wheelers or certain four wheelers. The gases like LPG or CNG they are used for cooking purposes particularly LPG and CNG again has application in automobiles.

Diesel is applied for running heavier automobiles or aircrafts or ships. Kerosene has generally application in the form of, in certain rural areas they keep on using the kerosene lamp still and fuel oil is used as the fuel in certain machineries, in certain heavy machinery. Now each of them particularly gasoline and diesel they are again not single substance they are rather a mixture of different gaseous, or no I should not say gaseous mixture of different kind of species. But still instead of considering them as a mixture different kind of liquids and gases we generally come assume them as a single substance like it is quite common to assume gasoline to be represented by octane.

Octane means C_8H_{18}, see whatever we are talking about as fuels under crude oil or maybe coals etc we are actually always talking about hydrocarbons. Hydrocarbon means which has carbon and hydrogen in the molecular structure. So something like say C_mH_n kind of combination. Now the most common kind of hydrocarbon that we can find in gasoline etc in they are alkenes where well their formula is something like C_mH_{2m+2}. Like in this case m is equal to 8, so for hydrogen the suffix is going to be $2 \times 8 + 2$, that is $16 + 2$, is equal to 18 which refers to octane.

So, while doing the analysis for gasoline we commonly assume it to be a single substance in the form of octane because the property of gasoline is quite similar to the property of octane. Whereas in case of diesel we generally assume this to be something like $C_{12}H_?$ what will be a subscript here? $12 \times 2 + 2$, that is 26. We commonly assume this one to be dodecane. Gasoline is commonly represented by the properties of octane whereas diesel is commonly represented by the properties of dodecane. And accordingly, we go for analysis by assuming they were single substance but truly speaking they are actually mixture of different kind of substances.

Similarly, the natural gas again can be a mixture of different kind of gaseous substances but the most common of that is CH_4, which is methane. And commonly we assume natural gas to be methane because other kind of gases are present in very small quantities is primarily methane only. Natural gas can be present in two forms one is CNG the compressed natural gas where you compress this natural gas to very high pressure levels. High pressure means we are talking about something in the level of say 150 to 250 atmospheric pressure level and it has application in automobile industries.

You know in several states of India it is already mandatory to run smaller vehicles, three wheelers or smaller four wheelers are using CNG's only and it is expected to gain more importance in near future. Whereas the other form of natural gas application is in the form of LPG, liquefied petroleum gas and CNG is compressed natural gas. Here you are talking about liquefied petroleum gas where the gas is liquefied by maintaining a very low temperature something in the range of $-162\ ^0C$, so that the gas remains in liquid form and we are able to store that in cylinders.

But why we are going either for liquification or to high pressure? Simply to reduce the volume. You know that the gas has lower volume only at higher pressure or at low temperature and accordingly we have these two routes of reducing the volume of a certain mass of gas. So, this way we can have this natural gas application in the form of CNG or LPG. There are several other fuels also, some newer renewable fuels that are coming up like ethanol can be on an example which is present in abundance in the nature and presently the blending of ethanol with diesel or its certain other fuels has been found to be quite popular, and probably you will find some kind certain kind of blended or mixed full applications very soon in automobile industries. But our point of discussion here is not on fuel and therefore I am not going any further into this fuel part.

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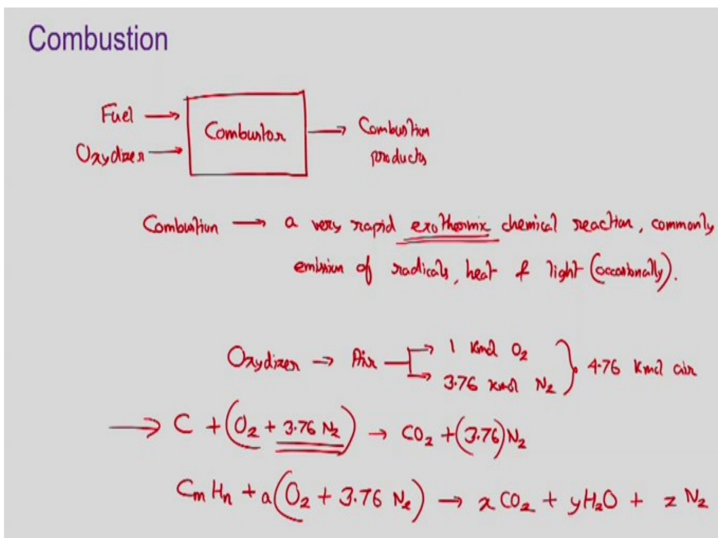

Rather let me proceed to combustion, what is combustion.? What do you mean by combustion? Just what I have shown in the previous slide I am drawing it again. So, here we have instead of calling this a reaction chamber, let us call this a combustion chamber or a combustor where we are supplying a fuel and some kind of oxidizer and we are getting the combustion products. Combustion can be defined as an exothermic chemical reaction between fuel and oxidizer which is generally very rapid in nature and is generally characterized by the emission of radicals and thermal energy and sometimes even light.

So, you can define combustion as a very rapid exothermic chemical reaction, commonly characterized by the emission of radicals, heat and light. Now light emission is not compulsory but it can be present, like if we take a piece of coal air or a piece of wood which is a common hydrocarbon and if you burn it in air then the air is acting as the oxidizer and you will find that the fire has come up which is nothing but this manifestation of this light and heat. So, combustion is generally associated with high temperature zone in a generally very thin or shallow high temperature zone we have this chemical reaction going on, which can be self-propagating in nature and often is extremely fast or rapid chemical reaction. But this exothermic part is important it has to be exothermic in nature otherwise we do not bother about this. Because in the reaction is endothermic then it is going to absorb energy and we are not gaining anything. Rather it has to be exothermic then only we can get useful thermal energy from this which can be supplied to the heat engine.

Now the oxidizer part, the most common oxidizer that you can think of, is air. Now we know that here is a combination primarily of oxygen or nitrogen it is a mixture of gaseous out of which oxygen and nitrogen are the most common one. And therefore, for combustion analysis generally we assume here to be comprising of, if there is 1 kmol of oxygen, then for every kmol of oxygen we are going to have 3.67 kmol of nitrogen, thereby giving you 4.676 kmol of air.

So, in every kmol of air or rather if for every kmol of oxygen, we have 3.76 kmol of nitrogen present in the chemical reaction. This nitrogen is almost inert, it hardly participates in any kind of chemical reaction and therefore it just comes out as it is during the reaction process and hence it is present on both the reactant and product side. Like if you think about a common chemical reaction which we are talking about is:

$$C + O_2 \rightarrow CO_2$$

Now truly speaking if we want to write this reaction properly then we should write this as:

$$C + (O_2 + 3.76\ N_2) \rightarrow CO_2 + (3.76)\ N_2$$

into this bracketed part is the air and the product of that is going to with carbon dioxide one mole of CO_2 and again 3.76 moles of nitrogen which has come out unaffected. The chemical reaction part that we are talking about, of course you can think that we can only use oxygen as the oxidizer but for that you need to go through details where simplification process or rather detailed kind of distillation process to separate the gases which is extremely difficult and expensive.

And hence we keep on using air which is almost a free source of oxidizer and during the combustion process, nitrogen comes out as it is. It just increases the total volume of the gases that we are dealing with and accordingly the size of the combustor may need to be much larger. But we cannot help, because we have hardly any option, realistic option of separating nitrogen from this air. And therefore, whenever you are talking about any kind of combustion reaction, we have to consider this nitrogen part as a part of the oxidizer.

Most of the hydrocarbon that we are talking about say if we write a hydrocarbon as C_mH_n then once it participated in combustion reaction with air which has oxygen and nitrogen, say some quantity of *a* mole of oxygen has been supplied then accordingly, we are going to get different kinds of products.

$$C_mH_n + a\,(O_2 + 3.76\,N_2) \rightarrow x\,CO_2 + y\,H_2O + z\,N_2 + b\,CO + (c)\,C + (d)\,O_2$$

So, you are getting x CO_2, y H_2O, z amount of nitrogen has come up, and depending upon the quantity of oxygen that you are supplying if your supplied oxygen is not sufficient then you may have certain other things also. You may have certain quantity of carbon monoxide present there, you may have certain quantity of just carbon that is we call soot, unburned carbon that is present there. If oxygen is more you may have certain quantity of unburned oxygen or unused oxygen that is coming out of this. So, it is not that your reaction is always going to be of this form same, your reaction can have several kinds of constituents on the product side.

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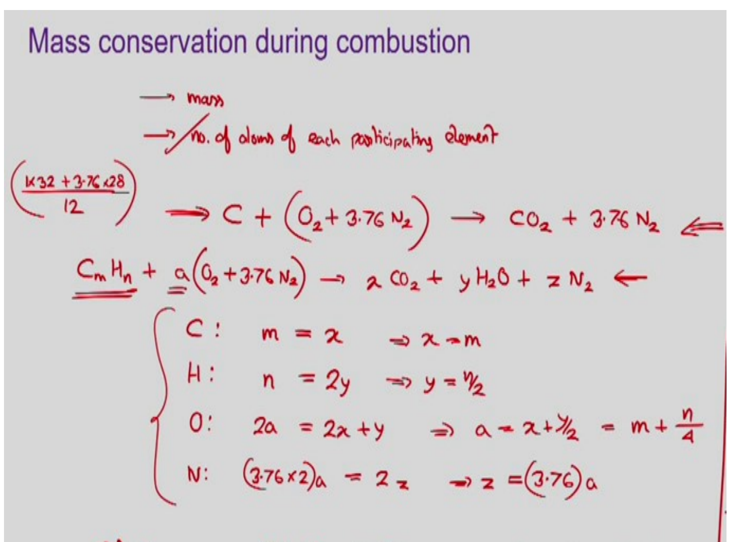

Now one important thing is that during the combustion process the mass has to be conserved. Of course, here we are neglecting the theory of relativity that is a conversion of mass to energy because that is applicable only during or that is significant only during the nuclear reactions. Here one thing you have to keep in mind that whenever we are having some kind of chemical reaction the exact mass on the product side and exact mass on the reactant side they are not going to match, truly speaking.

There will be very minute amount of difference because that small amount of difference of mass generally an exothermic reaction we are talking about there on the reactant side whatever mass you are getting on the product side the mass will be slightly lesser. And whatever difference of mass that you are getting which we commonly call the mass defect that actually gets converted to energy following the theory of relativity. However, that mass defect generally is so small that we do not need to bother about that during most of the common chemical reaction.

However, when you talk about a nuclear reaction the mass defect is quite significant compared to the mass of the original reactants which is not the case during chemical reactions. And therefore, in during chemical reaction you are going to neglect this mass defect we are going to assume that the mass of the reactant side and product side has to be equal to each other. So, there are two things that has to be conserved one is the mass, as we are talking about and second is the number of atoms of each participating element.

Whatever elements you are supplying their number of atoms they must be preserved which is also not true in case of nuclear reaction because there are atoms change during the reaction. There the subatomic particles like protons and neutrons and electrons they are conserved but not the number of atoms. However, during chemical reaction, a number of atoms are conserved but not the number of molecules. Number of molecules may change but number of atoms and accordingly the total mass has to be conserved.

Let us take the example that we are talking about in the previous slide. So, we have:

$$C + (O_2 + 3.76\ N_2) \rightarrow CO_2 + 3.76\ N_2$$

So, you can see that there are three participating elements: carbon, oxygen and nitrogen and the number of atoms has been conserved. And applying this principle we can easily balance any kind of chemical reaction. Like the one that I wrote in the previous slide, we have a hydrocarbon of the form C_mH_n and that is participating in a chemical reaction with *a* moles of oxygen.

$$C_mH_n + a\ (O_2 + 3.76\ N_2) \rightarrow x\ CO_2 + y\ H_2O + z\ N_2 + b\ CO + (c)\ C + (d)\ O_2$$

So, with every a mole of oxygen, 3.76 times of a moles of nitrogen will come as it is and on the product side we are then having x CO_2, y H_2O plus z N_2. And let us neglect any other products CO etc are not present. Then how can we get the values of this a, x, y and z. There are how many constituents there are there is carbon, hydrogen, oxygen and nitrogen, so there are four elements present there.

So, we have to write the balance equation for the number of atoms for each of the constituents. So, if we write for carbon then on the reactant side how many carbons you have? m number of carbons you have and that has to be equal to the number of carbons present on the product side which is x. And therefore, we know that

$$C: m = x \Rightarrow x = m$$

For hydrogen, on the reactant side we had n number of hydrogen and on the product side we have how many? we have 2H number of hydrogen atoms. So, from there we are getting that

$$H: n = 2y \Rightarrow y = n/2$$

whereas here we have got that $x = m$. Remember m and n are known quantities here. But this a is unknown similarly the x, y and z on the product side they are also unknown. We are trying to identify how many moles of air will be required for this. But C_mH_n , the hydrocarbon material is known. If we consider now oxygen, for oxygen on the reactant side we have twice of a and on the product side what do we have? We have twice of x on the product side from carbon dioxide plus y on the product side.

$$O: \ 2a = 2x + 2y \Rightarrow a = x + y/2 = m + n/4$$

and as we have already got the expression for x and y, so x can be replaced by m, y can be replaced by n to have n by 4. Once you know m and n, we also know the value of a. And finally, nitrogen, on the reactant side and product side we have:

$$N: (3.76 \times 2)\ a = 2\ z \Rightarrow z = (3.76)\ a$$

In fact in case of nitrogen and the number of moles are also getting or number of molecules or number of moles are also getting conserved but that is not the case for others.

And this way we can balance any chemical reaction, we can identify the number of moles of oxidizer required and similarly the constituents of the products. But of course, you need to know the information about this C_mH_n, the values of m and n needs to be known. And once we know that we can calculate this. As long as we are talking about an equation or a reaction like this. But of course, the number of moles is not getting conserved the number of moles may vary.

Like if we go back to this particular reaction, on the reactant side how many numbers of moles you have or how many molecules you have? 1 for carbon + 1 for oxygen + 3.76 from nitrogen. So, on the reactant side we have 5.76 number of molecules or 5.76 moles are participating in reaction. Whereas on the product side what we have? 1 mole of CO_2 + 3.76 moles of nitrogen that is 4.76. So that is not getting balanced and we do not need to bother about also we just bother about these particular things, as the total number of atoms of each participating element has to be balanced but not the number of molecules.

Let us use that to solve one exercise for this. But before that I would also like to mention that the chemical reaction that we have meant written here it is not guaranteed that you are only going to have only carbon dioxide, hydrogen and nitrogen under product side. Like one I wrote in a previous slide we may have several other participants also. Like if the combustion is not complete, like the amount of oxygen that you are supplying that is not complete you may have carbon monoxide or unburned carbon present there.

Also, you may have if the amount of oxygen is surplus you may have some oxygen present there also and secondly there is another possibility which we call dissociation. Dissociation, you have heard this term earlier in this course also refers to the reverse chemical reaction which generally happens at very high temperatures. Like this reaction C + O_2 go to CO_2, well the forward reaction is most common at low temperatures. Once you go to very high temperature the reverse reactions because applicable. And accordingly, we can have CO_2 breaking back to C + O_2 or rather more common form of the reaction is CO + O_2 producing CO_2.

Now when you go to high temperature than carbon dioxide breaks back to form carbon monoxide and when the forward reaction is exothermic, the reverse reaction is endothermic so that will lead to some loss of total thermal energy production. Similarly, hydrogen plus oxygen produces H_2O, I am not writing a balanced equation here. So, these are exothermic chemical reactions, but at higher temperatures once we cross 1000 K or 1200 K then the reverse reactions also starts to happen which we call the dissociation leading to the formation of hydrogen and oxygen.

And therefore, if we are talking about very high temperature which is very commonly the case in case of internal combustion engines or in case of any combustor, the dissociation reaction is may also be there and accordingly we may have several kind of substance present on the product side as well.

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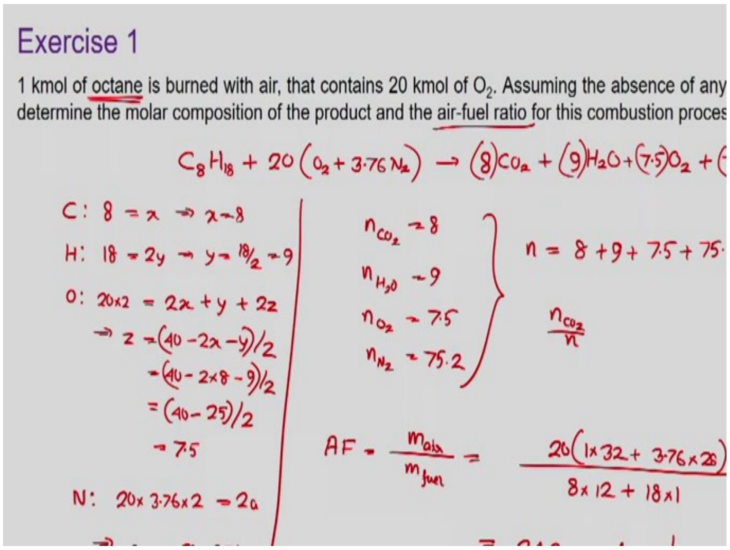

Now here we have one numerical exercise to deal with. The problem involves 1 kmol of octane, it is burned in air that contains 20 kmol of oxygen. Assuming the absence of any reverse reaction, so we are assuming there is no reverse reaction, there is no dissociation. So, the carbon dioxide and water vapour produced during the combustion reactions they are not breaking back to their constituents.

We have to determine the molar composition of the product and the air-fuel ratio for this combustion process. So, before solving this I have to mention what do you mean by air-fuel ratio. Air-fuel ratio is just from the point of view of this reaction, air-fuel ratio we generally write is as AF or sometimes also this A/F to indicate that you are talking about a ratio. It is nothing but the mass of air by mass of fuel or in case of open systems we talk about the mass flow rate of air with mass flow rate of fuel.

Now how to estimate this? Like the example that we had here how we can estimate the air-fuel ratio in this example? In this example we have to first estimate the mass of air, *a* mole of air has been supplied. For every mole of oxygen there is 3.76 moles of nitrogen. Now how much is the mass for that? 1 mole of oxygen has a mass of approximately 32 kg because you know that the molecular weight of oxygen is 32 kg/mol.

Truly speaking it is not perfectly 32 but here you are writing the whole number; we need more precise data if we want higher accuracy of calculation. For most of the combustion analysis actually the whole number is sufficient. So, 1 multiplied by 32 gives you the mass of 1 kmol of oxygen 32 kgs we are getting. And associated with that we have 3.76 moles of nitrogen and how much is the mass of 1 kmol of nitrogen? 28 kgs. So, once we multiply this bracketed quantity by *a* we are getting the total mass of air in kgs, that is participating in reaction for I kmol of C_mH_n. So, for 1 kmol of C_mH_n how much will be the mass? There is *m* amount of carbon and carbon has a mass of 12 plus *n* amount of hydrogen which is the mass of 1 and accordingly we can simplify this. So,

$$= \frac{a[1 \times 32 + 3.76 \times 28]}{(m)(12) + (n)(1)}$$

$$= \frac{(32 + 3.76 \times 28)a}{12\,m + n}$$

this is the air-fuel ratio for this particular chemical reaction. Similarly, if we want to calculate the air-fuel ratio for this particular one then:

$$= \left(\frac{1 \times 32 + 3.76 \times 28}{12}\right)$$

So, this is the air-fuel ratio for the first chemical reaction between carbon and oxygen. So, we have to calculate the air-fuel ratio in this example for that first we need to know the reaction. So, we have 1 kmol of octane, octane is C_8H_{18}. Octane gives you the idea that there will be subscript 8 with carbon and hydrogen substituent is indicated in following the formula C_mH_{2n+2} plus 20 kmol of oxygen is participating in reaction. So, 20 kmol of oxygen and with each kmol of oxygen 3.76 kmols of nitrogen also will be coming. So, we have complete description on the reactant side. So on the product side what we are having? We can see from here that:

$$C_8H_{18} + 2O\ (O_2 + 3.76\ N_2) \rightarrow x\ CO_2 + y\ H_2O$$

So, on the product side carbon is reacting with oxygen to form carbon dioxide, hydrogen reacting with oxygen to form H_2O, there is no reverse reaction. So, there is no carbon monoxide or etc present. Rather we may have some additional amount of oxygen present in the chemical reaction. So, let us write say *z* amount of oxygen present and let us say *a* amount of nitrogen is also present on the reactant side.

$$C_8H_{18} + 20\,(O_2 + 3.76\,N_2) \rightarrow x\,CO_2 + y\,H_2O + z\,O_2 + a\,N_2$$

So, first you have to find the values of this product constituents. So, for carbon if we balance on the reactant side, we have 8, on the product side we have x. So accordingly, we are having

$$C: 8 = x \rightarrow x = 8.$$

For hydrogen side, we have 18 on the reactant side and twice y on the product side giving us,

$$H: 18 = 2y \rightarrow y = 18/2 = 9$$

So, for oxygen we have 20 multiplied by 2 that is 40 number of atoms of oxygen on the reactant side on the product side we have $2x$ coming from CO_2 plus y coming from H_2O plus some z.

$$O: 20 \times 2 = 2x + y + 2z \rightarrow z = (40 - 2x - y)/2 = (40 - 2 \times 8 - 9)/2 = (40 - 25)/2 = 7.5$$

So, 7.5 kmols of oxygen will be present on the product side. And finally, for nitrogen, nitrogen is not participating any chemical reactions so you have:

$$N: 20 \times 3.76 \times 2 = 2\,a \rightarrow a = 20 \times 3.76 = 75.2$$

So, we have the complete chemical reaction now. Accordingly, we can write the chemical reaction to be equal to:

$$C_8H_{18} + 20\,(O_2 + 3.76\,N_2) \rightarrow (8)\,CO_2 + (9)\,H_2O + (7.5)\,O_2 + (75.2)\,N_2$$

So, we have the complete chemical reaction present there. So, we can easily calculate the molar composition of the product. We know the molar composition; we know that on the product side for every kmol of octane we have 8 kmols of CO_2. So, here if our interest is to calculate the mole fraction that also you can do like here you know that,

$$n_{CO_2} = 8$$

$$n_{H_2O} = 9$$

$$n_{O_2} = 7.5$$

$$n_{N_2} = 75.2$$

So, total number of moles present on the products side is equal to:

$$n = 8 + 9 + 7.5 + 75.2$$

and then you can easily calculate the mole fraction for each of the components. Like if our interest is to calculate the mole fraction of carbon dioxide then you can easily calculate that as:

$$\frac{n_{CO_2}}{n}$$

to get the mole fraction for this. And if you want to calculate the mass fraction then also you know that we have to calculate the total mass of each of the constituents on the product side.

And summing that we are going to get the total mass then you can get the mass fraction. We have done this in earlier module number 10 when we talked about the mixture of gases. But now we have to calculate the air-fuel ratio for this combustion process. So, air-fuel ratio in this particular case is going to be:

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{20\ (1 \times 32 + 3.76 \times 28)}{8 \times 12 + 18 \times 1} = 24.2$$

The numerator in the above equation is the amount of air that you are putting in and denominator is that we are supplying. I have got the final numbers for you just 24.2 kg of air/kg of fuel. This is the air-fuel ratio that we are talking about it is a unit of kg of air per kg of fuel. So, in a way you can say that it is dimensionless. But actually, we are not talking about the same mass on numerator and denominator that is why it is better to you mention the unit as well, kg of air/kg of fuel.

Now in this particular chemical reaction we are seeing that there is additional oxygen present on the product side. That means that the amount of oxygen that we are supplying that is surplus. We could have supplied less amount of oxygen also. Like in this case issue of 20, had we supplied say $20 - 7.5$ that is 12.5 kmol of oxygen then you know there would have been no oxygen present on the product side and it would have got only carbon dioxide, H_2O and nitrogen on the product side.

So, the amount of oxygen that we are supplying, it is not that always we have to supply exactly this like the 12.5 number in this case you can supply higher amount of oxygen also.

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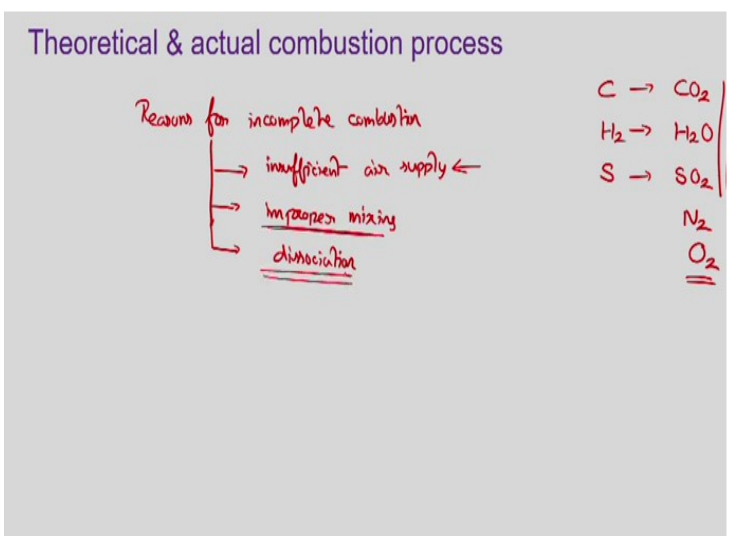

And that takes us to something called the actual combustion process. The theoretical combustion process refers to no presence of unburned fuel and again surplus oxygen on the product side. But practically during the actual combustion process it is always possible that some fuel may remain unburned. Now there are primarily three reasons for having unburned fuel or incomplete combustion. First reason can be insufficient air supply. Like in the previous case you have seen that if you have supplied 12.5 kmol of oxygen it should have given you a complete combustion.

Complete conversion of carbon to carbon dioxide and hydrogen to H_2O and that is what we refer by complete combustion. That is all the carbon atoms will get converted to carbon dioxide molecules, all the hydrogen will get converted to H_2O molecules and on the product side there will be no carbon monoxide present, that is what we call it complete combustion. Like in coal, quite often we a coal we quite have enough sulphur present then all the sulphur has to be converted to sulphur dioxide as well.

Then on the product side we are only going to get this reaction products plus nitrogen and maybe oxygen. That is what we call a complete combustion this oxygen is the surplus oxygen. But if the amount of oxygen is supplying that is not sufficient then you may have the carbon, a part of that gets converted to carbon dioxide and the remaining part because it is not getting sufficient air may just get converted to carbon monoxide.

And in certain rare cases you may have some unburned carbon as well which is called soot. Like when you burn a candle then the black smoke that comes out of this if you put your hand into this you will find fine carbon particles get deposited onto your hand, or if you put any piece of paper or something. That is what we call as soot, that is unburned carbon. So, if insufficient ai,r we are supplying then that will lead to incomplete combustion.

Second is, if you may have supplied exactly the amount of oxygen that is required. Like in the previous example if we have supplied 12.5 kmol of air or rather 12.5 kmol of oxygen for every kmol of octane, then you should have got theoretically a perfect combustion. But practically that may not be the case because of incomplete or insufficient mixing or you can say improper mixing, improper mixing of fuel and oxidiser. It is possible that in certain part of your combustion chamber you have too many in too much quantity of air present or in certain other part you have only fuel or a very rich quantity of fuel so that the fuel in that part is not getting sufficient oxygen to participate in combustion. This local imbalance may also lead to incomplete combustion. So, in such cases you are going to get both carbon monoxide and oxygen present in a combustion product. Like the part where you are having too much oxygen present there surplus oxygen will remain, whereas the part where you have too much fuel present there you are going to get unburned carbon or carbon monoxide.

And the third reason they have talked about that is a reverse reaction or dissociation. So, all of this will lead to the incomplete combustion procedure. And incomplete combustion is the reason for the presence of carbon monoxide in the reaction products. So, the quantity of air that we are going to supply that not only has to be sufficient rather often we have to supply surplus quantity of air or we need to ensure a better amount of mixing so that we can avoid this.

Similarly, for dissociation you have to control the temperature of the product, otherwise the reverse reaction will start that again will lead to an incomplete combustion because the reverse reactions are endothermic in nature.

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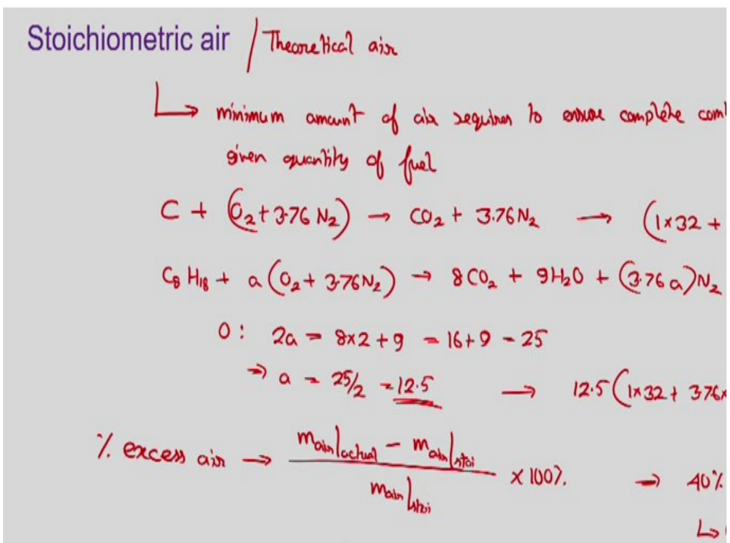

And in that context, I have this term to introduce to you which is called the stoichiometric air. Stoichiometric air requires the exact quantity of air requires to have complete combustion. Stoichiometric air quite often we also call it to be theoretical air. Stoichiometric air refers to the exact or quite often we call it a minimum amount of air required to ensure complete combustion of a given quantity of fuel. Like the reactions that we mentioned earlier,

$$C + (O_2 + 3.76\ N_2) \rightarrow CO_2 + (3.76)\ N_2$$

So, to have complete combustion of 1 kmol of carbon, just 1 kmol of oxygen is sufficient. And hence the stoichiometric air in this particular case is going to be this, the mass of air that we have written here that is:

$$1 \times 32 + 3.76 \times 28$$

this much kg of air is sufficient per kg of carbon. This is stoichiometric air for this. Or like the reaction that we wrote earlier with octane. Let me write it again just to ensure this and to calculate stoichiometric air for octane.

$$C_8H_{18} + a\ (O_2 + 3.76\ N_2) \rightarrow CO_2 + H_2O + N_2$$

where

a is the unknown quantity of air

Now if it is a perfect combustion process, complete combustion and we are talking about a minimum quantity of air, so no extra air present there and also no product like carbon monoxide because it is complete combustion. So, there are 8 carbon atoms on the reactant side, so there has to be 8 on the product side. There are 18 hydrogen atoms on the reactant side, so there has to be 18 by 2 that is 9 H_2O molecules. So, nitrogen we can always write it to be 3.76 multiplied by a, this is the quantity of nitrogen that you require.

$$C_8H_{18} + a\ (O_2 + 3.76\ N_2) \rightarrow 8\ CO_2 + 9\ H_2O + (3.76\ a)\ N_2$$

Then what is a in this case? Just balance the oxygen atoms. So, you have:

$$O:\ 2a = 8 \times 2 + 9 = 16 + 9 = 25$$

that gives your a as equal to:

$$a = 25/2 = 12.5$$

So, this 12.5 kmol of oxygen is required for you to ensure a perfect combustion and that is a minimum amount. Because if your supplied quantity of oxygen is less than 12.5, say 12.4 then all the carbon or hydrogen will not get combusted. Something will remain unburned in though either in the form of carbon or H_2 or maybe carbon monoxide.

And a 12.5 kmol of oxygen is a minimum that you need. So, in this case how much is your stoichiometric air? The stoichiometric air will be:

$$12.5\ (1 \times 32 + 3.76 \times 28)$$

whatever number you are getting this much kg of air will be required for it is a minimum quantity of air that is required for complete combustion of 1 kmol of C_8H_{18}. So, this stoichiometric or theoretical quantity of air is a very important quantity that we always need to be bothered about, we always have to ensure at least this quantity of air is supplied. But quite often we may supply higher amount of air or in certain cases less amount of air. So, if you are supplying higher quantity of air, they we call that excess air. Excess air refers to the amount of air that you are supplying generally it is excess in a percentage. We call it a percentage of excess air it is:

$$\%\ excess\ air = \frac{m_{air\,|actual} - m_{air\,|stoi}}{m_{air\,|stoi}} \times 100\ \%$$

that means in a certain case, suppose you have been given the information that the combustor has been supplied with 40% excess air. 40% excess air means the mass of actual air is the amount of air that you have been supplied, that is 140% of the stoichiometric air. 140% or 1.4 times of the stoichiometric that has been supplied. This is the percentage of excess air.

Similarly, the percent deficiency of here is the case when we talk when the amount of air supplied is insufficient. Here again we represent as a percentage that is we write here the other way around that is:

$$\%\ deficiency\ air = \frac{m_{air\,|stoi} - m_{air\,|actual}}{m_{air\,|stoi}} \times 100\ \%$$

So, in a certain case, if it is said that there is 20% deficiency of air that means the combustion has been actually supplied with 0.8 times or 80% of the stoichiometric air.

So, just from the chemical composition you can easily calculate the corresponding magnitude of stoichiometric air.

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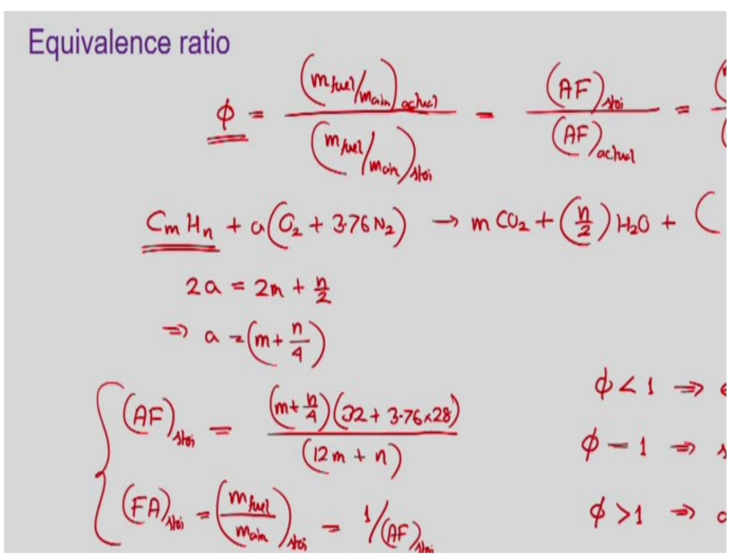

And in practical combustion cases generally we supply, we generally do not supply exactly the stoichiometric quantity of air, we always supply either more or less. And accordingly, we can have either a rich mixture or a lean mixture. And to take care of that we define this quantity which is known as the equivalence ratio which is nothing but another way of representing that excess air or deficiency of air. So, the equivalence ratio is defined as generally we use a symbol ϕ. ϕ is defined as the actual fuel-air ratio,

$$\phi = \frac{\left(m_{fuel}/m_{air}\right)_{actual}}{\left(m_{fuel}/m_{air}\right)_{stoi}}$$

Like the example that we have seen there, so 12.5 kmol of oxygen is required for every kmol of C_8H_{18}. So, this way we can write or we can write in the form of air-fuel ratio as well. So, if we want to write in terms of air-fuel ratio it will become:

$$\phi = \frac{(AF)_{stoi}}{(AF)_{actual}}$$

So, like in the previous question we have seen that 12.5 kmol of oxygen is required to form the stoichiometric one, then we can from there easily calculate the stoichiometric air-fuel ratio. Let us do a very quick exercise. If the composition of your hydrocarbon is given as:

$$C_mH_n + a\,(O_2 + 3.76\,N_2) \rightarrow m\,CO_2 + (n/2)\,H_2O + (\text{-})\,N_2$$

Then you know that C_m is always going to give you m CO_2 and this H_n is always going to give you (n/2) H_2O plus you have whatever may be the quantity of nitrogen left. Therefore the amount of oxygen requirement that is going to be:

$$2\,a = 2m + n/2$$

$$a = (m + n/4)$$

So, for a given hydrocarbon of the formulation C_mH_n you are always going to require (m + n/4) kmols of oxygen for complete combustion. That is the minimum quantity of oxygen required. Then your stoichiometric air-fuel ratio is always going to be:

$$(AF)_{stoi} = \frac{\left(m + \frac{n}{4}\right)(32 + 3.76 \times 28)}{12\,m + n}$$

So, once you know the value of m and n, you know the stoichiometric air-fuel ratio or fuel-air ratio whatever way you would like to represent. Like the fuel air ratio will be the opposite of this. Fuel-air stoichiometric or the way we write say we wrote earlier is:

$$(FA)_{stoi} = \left(\frac{m_{fuel}}{m_{air}}\right)_{stoi} = 1/(AF)_{stoi}$$

So, the stoichiometric value of air-fuel or fuel-air ratio is always known to you. Again. just the value of m and n are required.

So, you can easily calculate the theoretical quantity of air and from there you can easily calculate the stoichiometric air-fuel ratio. And then the equivalence ratio is going to give you the idea that whether you have been supplied with excess quantity of air or a deficient amount of air. If suppose,

$$\phi = 1$$

What does that mean ϕ equal to 1? It means your actual air-fuel ratio is equal to stoichiometric air-fuel ratio. So, you have been supplied with stoichiometric air only. Now when the ϕ is less than 1, ϕ less than 1 means your stoichiometric air-fuel ratio is less than the actual air-fuel ratio. So, just think about the definition let me write it in explicit form. So, you have:

$$\phi = \frac{\left({m_{air}}/{m_{fuel}}\right)_{stoi}}{\left({m_{air}}/{m_{fuel}}\right)_{actual}}$$

Now assume that the amount of fuel or mass of fuel remains constant in that case m_{fuel} you can cancel out and for the same quantity of air your equivalence ratio then becomes mass of actual air in stoichiometric case by mass of air in actual case.

So, then ϕ is less than 1, then the actual quantity of air that has been supplied that is actually more than stoichiometric here. Therefore, you have been supplied with excess air. So, when equivalence ratio is less than 1 you have been supplied with excess air, whereas the other case when ϕ is greater than 1 that means your stoichiometric air is more than the actual air and therefore you have deficiency.

Conventionally from combustion sense when you have been supplied with excess air then we call it a lean mixture. Whereas when it is deficient of here that is amount of fuel is more, then we call it a rich mixture. Whereas this is theoretical mixture. So, this equivalence ratio gives us an idea about the amount of air that has been supplied to you. That means once you know the chemical composition of the fuel that is the C_mH_n and you know the value of the equivalence ratio then more or less you have entire information about the amount of fuel and air that you are dealing with, you can easily form the corresponding chemical reaction as well.

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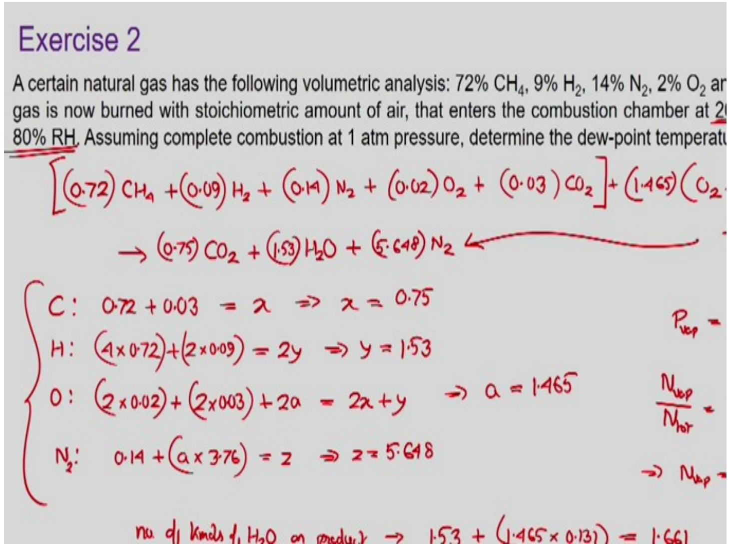

I will demonstrate that with this particular numerical example very quickly. So, a certain quantity of natural gas has been given which has a volumetric analysis given by this. Orsat apparatus is one of the apparatus using which you can get this volumetric analysis. So, it has CH_4, hydrogen, nitrogen, oxygen and some carbon dioxide as well. This gas is now bound with a stoichiometric amount of air that enters the combustion chamber at a given condition. We have to assume complete combustion at 1 atmospheric pressure and determine the corresponding dew point temperature of the product.

So, first we need to get the chemical reaction. Here the volumetric compositions are given. So, we can easily form the molar combination from there, how we can get this? The volumetric compositions are given means, the molar composition itself is given. So, for the fuel we have say for every kmol of fuel actually will comprise of:

$$(0.72)\ CH_4 + (0.09)\ H_2 + (0.14)\ N_2 + (0.02)\ O_2 + (-)\ CO_2$$

now how much is left you can easily add all of them that total has to be 100%. So, 72 + 9 is 81 + 14 is a 95 + 2 is 97, so we have 3% left 0.03 for carbon dioxide. Hence,

$$(0.72)\ CH_4 + (0.09)\ H_2 + (0.14)\ N_2 + (0.02)\ O_2 + (0.03)\ CO_2$$

So, this is for 1 kmol of fuel. For every kmol of fuel, let us assume a kmol of oxygen has been supplied so we have, a (O_2 + 3.76 N_2), this is your reactant side. Then on the product side you are going to have say x CO_2 it is a we are assuming complete combustion. So, and also stoichiometric amount of air has been supplied no excess air.

So, on the product there will be no carbon monoxide present if as it is complete combustion also no oxygen present because it is stoichiometric quantity of air. So, we are having CO_2 and H_2O present there and of course some amount of nitrogen. That is the only thing that you can have on the product side.

$$[(0.72)\ CH_4 + (0.09)\ H_2 + (0.14)\ N_2 + (0.02)\ O_2 + (0.03)\ CO_2] \rightarrow x\ CO_2 + y\ H_2O + z\ N_2$$

So, you can easily balance them now. Let us balance the carbon first balancing carbon on the reactant side you have 0.72 coming from CH_4 and you have CO_2. So 0.03 coming from there is equal to x which gives:

$$C: 0.72 + 0.03 = x \rightarrow x = 0.75$$

Balancing hydrogen,

$$H: (4 \times 0.72) + (2 \times 0.09) = 2\,y \rightarrow y = 1.53$$

So, you have 4 multiplied by 0.72 coming from CH_4 plus 2 multiplied by 0.09 coming from H_2 and that is equal to on the product side we have twice y, giving you the value of y to be equal to 1.53.

Then let me write the balance of oxygen.

$$O: (2 \times 0.02) + (2 \times 0.03) + 2\,a = 2\,x + \mathrm{y} \rightarrow \mathrm{a} = 1.465$$

So, we have 2 multiplied by 0.02 on the reactant side also CO2 is there. So, 0.03 coming from CO_2 plus twice a coming from the air that is equal to twice x coming from CO_2 on the product side plus y on the product side. So, if you balance them then you are going to get this a to be equal to 1.465 as detailed in the above expression.

Finally, nitrogen, actually instead of writing N we can write this balance of N_2, as it is not participating in the reaction. It is 0.14 coming from the fuel side plus a multiplied by 3.76 coming from here that is equal to z giving the value of z is to be equal to 5.648 and is expressed as follows:

$$N_2: 0.14 + (a \times 3.76) = z \rightarrow z = 5.648$$

Similarly, we could have gone for O_2 also instead of writing oxygen. So, we have got the complete chemical reaction. That means here this a can be replaced by 1.465. Let me write in a clearer way. And here the carbon is 0.75, y becomes 1.53 and this z is 5.4648. I request you to recalculate these numbers just to avoid any possible kind of error. So, you have got the chemical composition of the product.

Now, in the chemical composition of the product we have carbon dioxide H_2O and nitrogen. Now here this entire reaction or rather this entire chemical reaction that we have done there we have assumed the air to be dry. But actually, the air that has been supplied that air is having in 80% relative humidity, that is here some amount of H_2O is also added. Now how much is the amount of H_2O? That is 80% relative humidity's we are talking about. So, how can you make use of that information?

Partial pressure of the air, the partial pressure of the water vapour present will be equal to the P of the total air that is 0.8, relative humidity is given to 0.8 and we need to know the saturation pressure of this air, saturation pressure corresponding is 20 ^{0}C. Now I have noted the value corresponding to 20 ^{0}C the saturation pressure for this water vapour is 2.3392 kPa. So, the partial pressure of the moisture present in the supplied air is equal to 1.871 kPa.

$$P_{vap} = \phi P_{sat} = (0.8)\ (2.3392) = 1.87 \text{ kPa}$$

And then, assuming this water vapour to be an ideal gas then we can easily calculate its mole fraction on the air also. How can you get this? It will be:

$$\frac{N_{vap}}{N_{tot}} = \frac{P_{vap}}{P_{tot}}$$

that this P total is this 1 atmospheric pressure from there we get the number of vapour molecules present if this to be equal to:

$$N_{vap} = 0.131$$

That is in this chemical reaction we also need to add 1.465 into 0.131 amount of H_2O and this one will directly come to the product side also. Because that never participate in chemical reaction that just comes out as it is. So, on the product side then number of kmols of H_2O on product side then, we already had 1.53 coming from the chemical reaction plus this new contribution of 1.465 times 0.131 that is giving you the additional contribution and it is now 1.661. This is the total number of moles of H_2O present in the product. That is the role of this 80% relative humidity.

So, now it is very easily you can calculate the dew point temperature, how can you do it? Now you can easily calculate the mole fraction, partial pressure, the vapour present on the product side that you can easily calculate as the ratio of the number of moles of H_2O present by the total number of moles. The term in the square bracket is the mole fraction and the entire thing is to be multiplied with the total pressure which is one atmosphere. So, 1 atmosphere can be written as 101.325 kPa giving me the partial pressure of this moisture present in the product to be equal to 20.88 kPa.

$$P_{v,product} = \left[\frac{1.661}{(0.75 + 1.661 + 5.648)}\right](101.325) = 20.88\ kPa$$

And finally, your dew point temperature is going to be the saturation temperature corresponding to this partial pressure on the product side, which you can check the chart it is going to be something in the range of 60.9 ^{0}C. So, this gives you a final result.

See while forming the chemical reaction you have neglected the moisture or present in the air because it never part is the same chemical reaction. Quite similar to nitrogen it is present in both reactant and product side. Therefore, we have added it later on just using the concept of this thing which you have discussed in the previous week. Like from the concept of RH how you can calculate the number of moles of water have present in the mixture by assuming to be an ideal gas.

We have calculated that we have added that to the H_2O that has been produced from chemical reactions so on the product the H_2O that we have here one part of this 1.53 kmol is coming from the chemical reaction where H_2 gets converted to H_2O plus this additional part is coming from the moisture which has already present on the supplied air giving you this total contribution 1.661.

And then it is very easy to calculate the mole fraction of this water vapour in the product and to get the corresponding dew point temperature.

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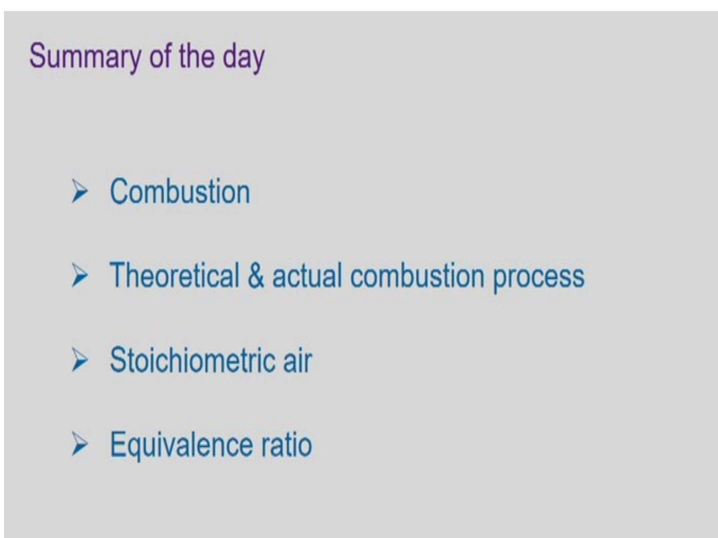

So, this takes us to the end of the day. Here we have discussed about the combustion process which is a chemical reaction between fuel and oxidizer you know one of the most important kind of chemical reaction that we can get in conjunction with thermodynamics. We have talked about the theoretical and actual combustion process, the theoretical quantity of air, the excess and deficiency of air that can be present which gives us the concept of stoichiometric air, stoichiometric air-fuel mixture and also the concept of equivalence ratio, we have discussed. So that is the end of today's discussion in the next lecture I shall be talking about the enthalpy of formation and enthalpy of reaction and also the maximum temperature that theoretically we can achieve during a chemical reaction process. Till then you please rehearse this lecture also try to go through your textbooks and if you have any query please write back to me, thank you very much.