Course Name: PETROLEUM TECHNOLOGY

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Lecture 36: Fundamentals of thermochemistry: Combustion

Hello and welcome to the 36th lecture of Petroleum Technology. In this lecture, we will learn about Fundamentals of Thermochemistry- Combustion. Let us talk about combustion. The combustible elements in solid and liquid fuels are carbon, hydrogen and sulfur. We know the liquid fuels, also you know the solid fuels, which may be coal. The major components that give us combustion are carbon, hydrogen, and sulfur.

The combustible components of gaseous fuel are hydrogen, carbon monoxide, methane, and unsaturated hydrocarbons. These are the components of gaseous fuels. The combustion process is always exothermic, and it liberates heat. You know that the burning process is an exothermic process; it is an exothermic reaction and liberates heat.

The combustion reaction may be written as fuel plus oxygen gives us combustible products, combustion products, and heat. Combustibles in solid and liquid fuels are expressed as the elements in weight percent, whereas, for gaseous fuel, it is given in volume percent or mole percent. The constituents of solid and liquid fuels, which are combustible in nature, are expressed in terms of weight percent of elements. For solid and liquid fuels, it may be a percentage of carbon, percentage of hydrogen, percentage of sulfur, percentage of oxygen, or whatever; this way, we can express. Whereas, for gaseous fuel, it is given in volume percent or mole percent, percentage of carbon monoxide, percentage of hydrogen, etcetera. The composition of the products of combustion, which is the flue gas after combustion, the gas generated is called flue gas, is first calculated as they are produced and expressed on a dry basis.

Dry basis is that when we burn a fuel, along with the carbon dioxide, carbon monoxide, or other gases produce sulfur oxide, etcetera, moisture is also produced; water is also produced. And the flue gas obtained, that is the gas after combustion generated due to the combustion process, can be expressed in terms of dry basis. That means, by subtracting the moisture content from the constituent of the flue gas. The term flue is there because of the reason that the duct through which the bond gases are flown before it goes to the stack for the removal is called the flue duct. So, the gas is called the flue gas. Further, sulfur dioxide and carbon dioxide are reported together as carbon dioxide because sulfur dioxide and carbon dioxide are absorbed in the same solvent or extractant.

Theoretical air is the amount of air stoichiometrically required for the complete combustion of the combustibles. Complete combustion of the combustibles is that where all the components of the combustible or all the components of the fuels are combusted completely without leaving any unburned constituents. So, theoretical air is the amount of air stoichiometrically required for this complete combustion. If we write an equation of combustion and calculate what is the air or oxygen required to burn that fuel, the stoichiometric coefficient gives us the idea of the moles of air or moles of oxygen required to combust that particular mole of fuel. So, that is the theoretical air we can say.

Excess air is the amount of air used in excess of the theoretical and expressed as the percentage of the fraction of the theoretical air. In most industries, the air supplied for combustion is not exactly stoichiometric air, not exactly theoretical air. Some excess air is also flown through the burner or through the furnace to ensure the complete combustion, and that is called excess air and expressed as the percentage of the fraction of the theoretical air. A useful basis of calculation is 100 kg of solid or liquid fuels and 100-kilo mole of gaseous fuels or flue gas, as the case may be. So, before we calculate any combustion problem, we have to fix a basis of solid or liquid fuel.

For solid or liquid fuel, we can go for the weight; that is, we can take 100 kg as the basis, and for gaseous fuel, we can go for the moles, 100 moles. Even sometimes for gaseous fuel, we can take the basis as in the volume in the form of volume either meter cube or feet cube as the case may be. The usual air is assumed dry and carbon dioxide-free in combustion calculations. So, the air that is supplied is assumed to be dry and does not contain any moisture or carbon dioxide; otherwise, that moisture and carbon dioxide will adapt to the flue gas composition. In dry air, the volume or mole ratio of the components of oxygen by nitrogen is 0.27. It is considered that in the air we consider oxygen is 21 percent and nitrogen is 79 percent. So, 21 by 79 is 0.27; oxygen by air is 21 by air is 100.

So, 0.21, 0.21; nitrogen is 21, air is 100, sorry, nitrogen is 79, air is 100. So, 0.79; air by oxygen is 4.76, that is 100 by 21.

So, 4.76; this way we can make the calculations. What is stoichiometric ratio? The ratio of actual air to stoichiometric air is called stoichiometric ratio. In fact, we supply excess air to the combustion process. So, actual air is the total air which is supplied for the combustion process, and stoichiometric air is according to the stoichiometric equation. What is the exact or theoretical air? For example, stoichiometric air for burning of a fuel gas is stoichiometric ratio is equal to actual air by stoichiometric air.

And what is excess air? That is the actual air minus stoichiometric air by stoichiometric air; this is another ratio. So, excess air is actual air by stoichiometric air, that is, stoichiometric ratio minus stoichiometric air by stoichiometric air, 1. So, stoichiometric ratio minus 1 whole into 100 percent is giving the excess air calculation. Say let us consider actual air is 120 and stoichiometric air is 100. So, stoichiometric ratio is 120 by 100.

And here again actual air if it is 120, stoichiometric air is 100, then it will be 120 by 100 minus 1 into 100 percent. So, 20 percent more air. Now coming to a numerical problem, if we do some exercise, some numerical problem, it will be easier to understand the combustion process. I am reading the numerical problem. Determine the flue gas analysis and air-fuel ratio by weight when a medium viscosity fuel oil with 84.9 percent carbon, 11.4 percent hydrogen, 3.2 percent sulfur, 0.4 percent oxygen and 0.1 percent ash is burnt with 20 percent excess air. Assume complete combustion that means, there is no carbon monoxide formation or any unburnt carbon remaining.

Let us come to the solution. The basis of the calculation is taken 100 kg of fuel oil; 100 kg of fuel oil is the basis. No change in the basis of expression is necessary. The data of the ultimate analysis is converted into the kilo mole. Ultimate analysis is the elemental analysis as there are carbon, hydrogen, sulfur, oxygen, etc., are elements, and its composition is given.

So, this is elemental analysis or ultimate analysis. In this table, if you see, all the elements are arranged in this leftmost column: carbon, hydrogen, oxygen, sulfur, and ash. Carbon kg of carbon per 100 kg of fuel oil because it is in percentage, and we have taken the basis as 100 kg of fuel oil, 84.9, which is given in the question.

Hydrogen is 11.4 here, oxygen is 0.4 oxygen, sulfur is 3.2, and ash is 0.1. Ash does not contribute to combustion, and ash is an inert substance.

Now, come to the next column, where kilo mole per 100 kg of fuel oil is calculated. Here 84.9 is the carbon. So, dividing the carbon by 12 we got 7.08, 84.9 divided by 12, where 12 is the molecular weight of carbon. So, it gives the 7.08. Similarly, for hydrogen 11.4, 11.4 divided by 2 giving us 5.7. Hydrogen is 4.

So, 0.4 by 4 giving us 0.01, sulfur is 32, 3.2 divided by 32 giving us 0.1. So, all these are divided by the molecular weight of respective elements, giving us the kilo mole per 100 kg of fuel oil, which is the basis.

Now, we have to see what amount of oxygen is required after the combustion. For carbon, as it is a complete combustion, the equation will be C plus O2, giving us CO2. So, 1 mole of carbon is producing 1 mole of carbon dioxide. So, 0.78 is 7.08 moles of carbon will require 7.08 moles of oxygen; this is kilo mole of oxygen. Hydrogen H2 plus half O2 gives us H2O. Hence, 5.7 moles of hydrogen will require half of the 5.7 moles of oxygen to produce 1 mole of water.

Hence, 5.7 divided by 2, 2.85 is the kilo mole of oxygen required to produce 1 mole of H_2O. Similarly, oxygen is not reacting with oxygen. So, it is extra, which is contributed from the weight of fuel. So, it is written as minus 0.01 as it is contributing; it is not getting consumed. Sulfur, the reaction is $S + O_2$ to give SO_2. 1 mole of sulfur reacts with 1 mole of oxygen to produce 1 mole of SO_2. Hence, 0.1 mole of sulfur will require 0.1 mole of oxygen to produce sulfur oxide gas.

Ash is not taken into consideration. The total kilo mole of oxygen required is 10.02, 7.08 plus 2.85 minus 0.01 plus 0.1 gives 10.02. Now, in the problem, it is said that it is burnt with 20 percent excess oxygen; sorry, excess oxygen at 20 percent of the theoretical is 10.02 is the theoretical or stoichiometric oxygen into 0.2 is 2 moles of extra oxygen supplied by the air.

So, nitrogen also is supplied along with the air nitrogen from total air supplied 10.02 into 1.2, which means 120 percent into 3.76. 3.76 is nitrogen by oxygen ratio 79 by 21 is equal to 3.76. What does it mean that 10.02 into 1.2 is the oxygen total oxygen which has been supplied by the air into 79 by 21 gives us the nitrogen supplied in 120 percent excess air which is 45.25. Now, coming to the flue gas analysis carbon dioxide, what are the components of flue gas? Carbon dioxide, water, sulfur dioxide, nitrogen, and oxygen which which has come from the air excess oxygen and this nitrogen is also has come with the air this nitrogen did not take part in the combustion process, but it is a component of flue gas. So, what is the kilo mole of carbon dioxide 7.08 as per the previous equation which we have learnt water SO_2 nitrogen is 45.25 nitrogen is 2 mole extra. So, total kilo mole in flue gas is 60.13 this is the total kilo mole. How we can calculate the volume percent that is 7.08 divided by 60.13 into 100 gives us 11.78. 5.7 divided by 60.13 into 100 gives us the volume percent of water. This way, we have calculated all the volume percent of the respective components, which comes to a total of 100. Now, we have to express the flue gas composition on a dry basis, which means, excluding the moisture here, it is 60.13 minus 5.7, the quantity is the flue gas with flue gas kilo mole without water. So, 7.08 divided by 60.13 minus 5.7 gives us 13, 13 volume percent of carbon dioxide as we have excluded moisture. So, water we are not considering over here; similarly, we have calculated SO 2 that is 0.1 divided by 60.13 minus 5.7, giving us 3.7. Similarly nitrogen oxygen is 2 we are here it is not coming. So, total volume percent is 100. Now, air fuel ratio by weight how we can write it that 10.02 is the theoretical oxygen into 1.2 is the actual supplied air or actual supplied oxygen into 4.76, 4.76 is air by oxygen which is 100 by 21 4.76 we have to convert the oxygen into air from from the oxygen data we have to get the air data into 29, 29 is the molecular weight of air which is assumed calculated by 100, 16.6 is the air fuel ratio by weight. This gives us the answer of the numerical problem. Now, coming to the second one I am giving two different kind of problems. So, that it will give you a clear picture of how to calculate the combustion method of combustion gas or combustion percentage of excess air what is the is the answer how we can go through.

The reaction here is to calculate the percentage of excess air for methane burning. So, the methane burning reaction is CH_4 + $2O_2$ is equal to CO_2 + 2 H_2O. The flow rate of methane and air is given as 25 and 290 cubic meters per hour, respectively. In the reaction, you can see that one volume of methane reacts with two volumes of oxygen to produce one volume of carbon dioxide and two volumes of water. The basis is taken as one cubic meter of methane burning. So, stoichiometric air for methane burning is 9.524, which is 2 by 21 into 100, which is cubic meters per cubic meter of air. According to the given flow rate of methane (2, as assumed), the flow rate of methane is 25 cubic meters per hour, as already given in the question. The flow rate of air is 290 cubic meters per hour, and the stoichiometric air required is 25 times 9.524, which is 238.1 cubic meters per hour. The stoichiometric ratio will be 290 by 238.1. The excess air is 1.22 (stoichiometric ratio) minus 1, multiplied by 100, giving 22 percent excess air to be supplied.

Now, coming to the mechanism and kinetics of combustion. The most essential thermodynamic parameter is the equilibrium constant as a function of temperature, required for the study of kinetics of combustion reaction. The equilibrium constant, denoted as K, is the ratio of the forward rate constant (k1) to the reverse rate constant (k2). Both rate constants are temperature-dependent, with each 10-degree rise in temperature doubling the rate of the reaction. Therefore, the equilibrium constant is also temperature-dependent, and thermodynamics handles temperature-related quantities. To calculate the equilibrium constant, we need to determine the rate constants k1 and k2, which are related to the kinetics of the reaction. Many steps in the combustion reaction are reversible in nature. In fact, almost all reactions are reversible, but for simplicity's sake, we sometimes consider the reactions to be irreversible.

The same is the case for combustion reactions; almost all combustion reactions are reversible in nature. Examples of some equilibrium reactions of combustion include:

1. $12H_2+12O_2 \rightarrow OH_{21}H_2+21O_2 \rightarrow OH$
   - This reaction involves the generation of free radicals. The equilibrium constant for this reaction, denoted as *Kp*, is given by $=[OH][H_2]1/2[O_2]1/2Kp=[H_2]1/2[O_2]1/2[OH]$.
2. $12H_2+12O_2 \rightarrow H_2O_{21}H_2+21O_2 \rightarrow H_2O$
   - This is a termination reaction. The equilibrium constant *Kp* for this reaction is $[H_2O][H_2]1/2[H_2]1/2[H_2O]$.

These equilibrium constants are denoted with *Kp*, with *p* indicating the partial pressures as all these reactions occur in the gaseous state. The expressions for these equilibrium constants are derived based on the stoichiometric coefficients.

Thermodynamics can describe the composition of the species at equilibrium steps in the overall mechanism, but it cannot predict the speed of the reaction. Thermodynamics helps us understand the composition of the species at equilibrium, revealing which different species are reacting at that moment. However, the speed of the reaction can only be predicted through the study of kinetics.

So, the knowledge of chemical kinetics is essential. A combustion reaction has a particular speed at a specified temperature, as I mentioned earlier that the rise in temperature causes the increase in the speed of reactions. Thus, at a specified temperature, we need to determine the speed of the reaction. In many cases, the mechanism of combustion follows complex kinetic phenomena with several elemental steps. A combustion reaction is not a single-step process; it involves a combination of complex kinetics in several elemental steps. Elemental steps, which determine the rate of the reaction, constitute the basis of the combustion reaction's complex kinetics.

The combustion process can be explained by a radical mechanism, specifically a free radical mechanism. This mechanism typically consists of initiation, propagation, branching, and termination steps, all associated with the free radical mechanism. It can be elucidated through the combustion of methane.

Let us examine the steps involved in the combustion of methane. These are the assumed steps given in the reactions, constituting a free radical mechanism.

1. **Initiation:** CH_4 may undergo initiation to form $CH_3\bullet + H\bullet$. O_2 is fragmented to $O\bullet$, and $O\bullet + H\bullet$ gives $HO\bullet$. This initiation results in the formation of free radicals.

2. **Propagation Reactions:** Propagation reactions may occur one after another through several steps:

   - $CH_4 + H\bullet \rightarrow CH_3\bullet + H_2$
   - $CH_4 + HO\bullet \rightarrow CH_3\bullet + H_2O$
   - $CH_3\bullet + O\bullet \rightarrow CH_2O + H\bullet$
   - $CH_2O + OH\bullet \rightarrow H_2O + CHO\bullet$
   - $CH_2O + H\bullet \rightarrow H_2 + CHO\bullet$

These are a series of chain propagation reactions associated with the combustion process.

3. **Branching:** Another assumed step in the process is branching, such as $CO + H\bullet + O_2 \rightarrow HO\bullet + CO_2$.

4. **Termination:** Once the reactions have propagated, the process may terminate. A termination reaction can be expressed as $H\bullet + R\bullet + M \rightarrow RH + M\bullet$, where M is a third body, possibly a wall or some other element that terminates the process.

This sequence illustrates an example of the combustion process. Methane, being a combustible gas, may undergo these steps during combustion.

These are the references through which you can go. Thank you for your attention.