Program : **B.Tech**

Subject Name: **Thermodynamics**

Subject Code: **ME-302**

Semester: **3rd**

UNIT-IV
FUEL AND COMBUSTION

1. INTRODUCTION

Combustion is the process of chemical reaction between fuel and oxygen (reactants). The process releases heat and produces products of combustion. The main elements which burn are:

CARBON HYDROGEN

SULPHUR

The heat released by 1 kg or m^3 of fuel is called the calorific value.

The oxygen used in combustion processes normally comes from the atmosphere and this brings nitrogen in with it which normally does nothing in the process but makes up the bulk of the gases remaining after combustion.

The main elements in combustion are then:

	Symbol	Atomic Mass	Molecular Mass	Product
Carbon	C	12		CO_2
Hydrogen	H_2	1	2	H_2O
Sulphur	S	32		SO_2
Oxygen	O_2	16	32	
Nitrogen	N_2	14	28	

If the water formed during combustion leaves as vapor, it takes with it the latent heat of evaporation and thus reduces the energy available from the process. In this case the calorific value is called the lower Calorific value (LCV). If the products cool down after combustion so that the vapor condenses, the latent heat is given up and the calorific value is then the higher calorific value (HCV).

Solid and liquid fuels are normally analyzed by mass to give the content of carbon, hydrogen, sulphur and any other elements present. Often there is silica, moisture and oxygen present in small quantities which have some effect on process. The silica leaves saggy deposits on the heat transfer surfaces in boilers.

Gaseous fuels are normally analyzed by volumetric content and are in the main hydrocarbon fuels.

For purposes of calculation, the content of air is considered to be:

	VOLUMETRIC	GRAVIMETRIC
Oxygen	21%	23%
Nitrogen	79%	77%

The sulphur content of the fuel is considered to be a pollutant and so undesirable. The theoretically correct quantity of air or oxygen required to just exactly burn the fuel expressed as a ratio to the fuel burned, is called the STOICHIOMETRIC RATIO. In practice it is found that not all the oxygen in the reactant reaches the fuel elements and that excess air is required in order to ensure complete combustion. This results in oxygen appearing in the products. If too little air or oxygen is supplied, the result is incomplete combustion resulting in the formation of carbon monoxide CO instead of carbon dioxide CO_2. The resulting products contain water H_2O. Industrial equipment for measuring the contents of the products usually remove the water from the sample and the products are then called the dry products.

2. COMBUSTION CHEMISTRY

2.1 SOLID AND LIQUID FUELS

In the case of solid and liquid fuels, we do the combustion of each element separately. The important rule is that you must have the same number of atoms of each substance before and after the process. This may be obtained by juggling with the number of molecules.

CARBON $C + O_2 = CO_2$
Mass ratio 12 + 32 = 44

Hence 1kg of C needs 32/12kg of O_2 and makes 44/12kg of CO_2

HYDROGEN $2H_2+O_2=2H_2O$
Mass ratio 4 + 32 = 36

Hence 1kg of H_2 needs 8kg of O_2 and makes 9 kg of H_22O

SULPHUR

$S + O_2= SO_2$
32+32 = 64

Hence 1 kg of S needs 1kg of O_2 and makes 2kg of SO_2.

2.2. GASEOUS FUELS

Typical hydrocarbons are:

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Ethene	C_2H_4(Ethylene)
Propene	C_3H_6 (Propylene)

Ethyne	C_2H_2 (Acetylene)
Benzenol	C_6H_6 (Benzene)
Cyclohexane	C_6H_{12}

The combustion equation follows the following rule :

$$C_aH_b + (a+b/4)O_2 = (a)CO_2 + (b/2)H_2O$$

If this results in fractional numbers of molecules, then the whole equation may be multiplied up.

EXAMPLE No.1

Write out the combustion equation for C_8H_{18}

SOLUTION

$C_8H_{18} + (8+18/4)O_2 = 8CO_2 + (18/2)H_2O$ C_8H_{18} +
$12½O_2 = 8CO_2 + 9H_2O$
$2C_8H_{18} + 25O_2 = 16CO_2 + 18H_2O$

There are other gases which burn and the main one to know about is Carbon Monoxide (CO) which is partially burned carbon. The equation for the combustion of CO is :

$$2CO + O_2 = 2CO_2.$$

3. COMBUSTION BY MASS

The only rule to be observed in deducing the quantities of each substance is the law of conservation of mass. The proportions of the mass are that of the molecular masses. This is shown in the following example.

EXAMPLE No.2

A fuel contains by mass 88% C, 8%H_2, 1%S and 3% ash (silica). Calculate the stoichiometric air.

SOLUTION

Carbon mass ratio- $C + O_2 = CO_2$

$12 + 32 = 44$

Hence 0.88kg of C need (32/12)x0.88=2.347kg of oxygen.

It makes (44/12) x 0.88 = 3.227 kg of carbon dioxide.

Hydrogen mass ratio- $2H_2 + O_2 = 2H_2O$

$4 + 32 = 36$

Hence 0.08kg of hydrogen needs (32/4) x 0.08 = 0.64kg of oxygen.

Sulphur Mass ratio- $S + O_2 = SO_2$

$32 + 32 = 64$

Hence 0.01kg of sulphur needs 0.01kh of oxygen and makes 0.02kg of sulphur dioxide.

TOTAL OXYGEN needed is 2.347 + 0.64 + 0.01 = 2.997kg

TOTAL AIR needed is 2.997/23% = 13.03kg The

STOICHIOMETRIC air/fuel ratio is 13.03/1

EXAMPLE No.3

If the air supplied is 20% more than the stoichiometric value, find the analysis of the dry products by mass.

SOLUTION

If 20% excess air is supplied then the air supplied is:

120% x 13.03 = 15.637 kg

Oxygen is also 20% excess so 0.2 x 2.997 = 0.599kg is left over. Nitrogen in the air is 77% x 15.637 = 12.04kg

List of products :

Nitrogen	12.04kg	=75.8%
Carbon dioxide	3.227kg	=20.3%
Sulphur dioxide	0.02kg	=0.1%
Oxygen	0.599kg	=3.8%
Total dry product	15.886kg	=100%

It is of interest to note that for a given fuel, the % of any product is a direct indication of the excess air and in practice the carbon dioxide and/or oxygen is used to indicate this. This is important in obtaining optimal efficiency in a combustion process.

EXERCISE No. 1

1. A boiler burns fuel oil with the following analysis by mass :

80% C, 18% H_2, 2%S

30% excess air is supplied to the process. Calculate the stoichiometric ratio by mass and the % Carbon Dioxide present in the dry products.
(15.62/1 14.9% CO_2)

2. A boiler burns coal with the following analysis by mass :

75% C, 15%H_2, 7%S remainder ash

Calculate the % Carbon Dioxide present in the dry products if 20% excess air is supplied.
(16.5% CO_2)

3. Calculate the % of each dry product when coal is burned stoichiometrically in air. The analysis of the coal is:

80% C, 10% H_2, 5% S and 5% ash.

(76.7%N, 22.5% CO_2 0.8% SO)

COMBUSTION BY VOLUME

First we need to revise gas mixtures and understand the meaning of VOLUMETRIC CONTENT. To do this we must understand Dalton's law of partial pressures and Avagadro's Law.

First let us define the kmol. A kmol of substance is the number of kg numerically equal to the apparent molecular mass. For example 12 kg of Carbon is a kmol, so is 32 kg of O_2 and 2 kg of H_2 and 28 kg of N_2.

The molecular mass of a substance is expressed as kg/kmol so the molecular mass of O_2, for example, is 32 kg/kmol.

Avagadro's Law states :

1m^3 of any gas at the same pressure and temperature contains the same number of molecules. It follows that the volume of a gas at the same p and T is directly proportional to the number of molecules. From this we find that the volume of a kmol of any gas is the same if p and T are the same.

Dalton's law states:

The total pressure of a mixture is the sum of the partial pressures. The partial pressure is the pressure each gas would exert if it alone occupied the same volume at the same temperature.

Consider two gases A and B occupying a volume V at temperature T. Using the Universal gas law for each :

$$p_A V_A = m_A R_o T/\tilde{N}_A \qquad p_B V_B = m_B R_o T/\tilde{N}_B$$

where Ñ is the relative molecular mass.

$p_A/p_B = m_A \tilde{N}_B / m_B \tilde{N}_A$ = ratio of the kmol fractions.
p_A and p_B are the partial pressures.
V_A and V_B are the partial volumes.

These are the volumes each gas would occupy if they were separated and kept at the original p and T. This concept is very useful in problems involving the combustion of gases. It also follows that the partial volumes are directly related to the partial pressures so that $V_A/V_B = p_A/p_B$

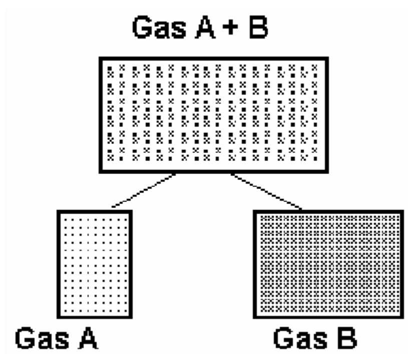

Figure 1

When not mixed the pressure is p and the volumes are V_A and V_B. Hence :

$pV_A/T = mR_o/\tilde{N}_A$ ` $\qquad p = m_A R_o T/\tilde{N}_A V_A$ ....(1)

$pV_B/T = mR_o/\tilde{N}_B$ $\qquad p = m_B R_o T/\tilde{N}_B V_B$ ....(2)

Since (1) = (2) then :

$m_A/\tilde{N}_A V_A = m_B/\tilde{N}_B V_B$ and so $V_A/V_B = (m_A/\tilde{N}_A)(m_B/\tilde{N}_B)$ which shows that in a mixture, the partial volumes are in the same ratio as the kmol fractions which in turn are in proportion to the number of molecules of each gas.

When mixed they both have volume V, hence:

$$p_A = m_A R_o T/\tilde{N}_A V \text{.........(3)}$$

$$p_B = m_B R_o T/Ñ_B V..........(4)$$

(3)/(1) gives $p_A/p = V_A/V$ and (4)/(2) gives $p_B/p = V_B/V$
hence $V_A/V_B = p_A/p_B$

Consider the combustion of Methane.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Since the volumetric content of each gas is in the same ratio as the kmol fractions then volumetric content is in the same proportion as the molecules. Hence it needs 2 volumes of oxygen to burn 1 volume of methane.

The volume of air needed is 2/21% = 9.52 volumes. Hence it burn 1 m^3 of methane we need 9.52 m^3 of air for stoichiometric combustion. If the products are at the same p and T as the original reactants, we would obtain 1 m^3 of carbon dioxide and 2 m^3 of water vapour which would probably condense and cause a reduction in volume and/or pressure.

EXAMPLE No.4

Calculate the % CO_2 in the dry products when methane is burned with 15% excess air by volume.

SOLUTION

	CH_4 +	$2O_2$ =	CO_2 +	$2H_2O$
Volume ratio	1	2	1	2

The stoichiometric air is 2/21% = 9.524 m^3 The actual air is 9.524 x 115% = 10.95 m^3

Analysis of dry products:

Nitrogen	79% x 10.95	8.65 m^3
Carbon Dioxide		1.00 m^3
Oxygen	15% x 2	0.30 m^3
Total		9.95 m^3

The % Carbon Dioxide = (1/9.95) x 100 = 10%

When the fuel is a mixture of gases, the procedure outlined must be repeated for each combustible gas and the oxygen deduced for the volume of each in 1 m^3 of total fuel.

EXAMPLE No. 5

A fuel is a mixture of 60% Methane and 30% carbon monoxide and 10% oxygen by volume. Calculate the stoichiometric oxygen needed.

SOLUTION

As before, the volume of oxygen required to burn 1 m^3 of methane is $2m^3$.To burn $0.6m^3$ needs $1.2m^3$ of oxygen. For carbon monoxide we use the combustion equation :

$$2CO + O_2 = 2CO_2$$

Hence to burn 1 m^3 of CO need 0.5 m^3 of oxygen, so to burn 0.3 m^3 needs 0.15 m^3 of oxygen.

The total oxygen needed is 1.2 + 0.15 = 1.35 m^3 . However there is already 0.1 m^3 in the fuel so the **stoichiometric oxygen needed 1.25m^3**

EXERCISE No.2

1. Find the air fuel ratio for stoichiometric combustion of Ethane (26.19/1) by volume.

2. Find the air fuel ratio for stoichiometric combustion of Butane by volume.(30.95/1). Calculate the % carbon dioxide present in the dry flue gas if 30% excess air is used. (10.6%)

3. Find the air fuel ratio for stoichiometric combustion of Propane by volume.(23.81/1). Calculate the % oxygen present in the dry flue gas if 20% excess air is used. (3.8%)

4. A gaseous fuel contains by volume :

   5% CO_2, 40% H_2 , 40% CH_4, 15% N_2

   Determine the stoichiometric air and the % content of each dry product. (4.76 m^3, 89.7%,N_2 10.3% CO_2).

4. RELATIONSHIP BETWEEN PRODUCT AND EXCESS AIR.

It follows that if we can deduce the % product then given the figure, we can work backwards to determine the air or oxygen that was used.

EXAMPLE No.6

An analysis of the dry exhaust gas from an engine burning Benzole shows 15% Carbon Dioxide present by volume. The Benzole contains 90% C and 10% H_2 by mass. Assuming complete combustion, determine the air/fuel ratio used.

SOLUTION

1 kg of fuel contains 0.9kg of C and 0.1kg of H_2. Converting these into kmol we have 0.9/12 kmol of C and 0.1/2 kmol of H_2. For 1 kmol of dry exhaust gas we have :

0.15 kmol of CO_2
Y kmol of excess O_2

1 - 0.15 - Y = 0.85 - Y kmol of N_2

1 kmol of CO_2 is 44 kg
1 kmol of N_2 is 28 kg
1 kmol of O is 32 kg
0.15 kmol of CO_2 is 0.15 x 44kg
This contains (12/44) carbon so the carbon present is 0.15 x 12 kg
The carbon in the fuel is 0.9 kmol per kmol of fuel. Hence the number of kmols of DEG must be 0.9/(.15 x 12) = 0.5

There are 0.5 kmol of DEG for each kmol of fuel burned.

The Nitrogen present in the DEG is 0.85 - Y kmol per kmol of DEG. This has a mass of
28(0.85 - Y) per kmol of DEG
The oxygen supplied to the process must be :
(23.3/76.7) x 28 x (0.85 - Y) = 7.24 - 8.5Y kg per kmol of DEG.

(using precise proportions of air for accuracy).

The oxygen contained within the carbon dioxide is:

(32/44) x 0.15 x 44 = 4.8 kg per kmol DEG

1 kmol of CO_2 contains 44 kg and 32/44 of this is oxygen. The oxygen in the CO_2 is hence 32 x 0.15 kg per kmol DEG.

The excess oxygen is

32Y kg per kmol DEG

Total oxygen in the products excluding that used to make H_2O is :

32 x 0.15 + 32Y

The oxygen used to burn hydrogen is hence :

7.24 - 8.5Y - 32 x 0.15 + 32Y

O_2 used to burn H_2 is

2.44 - 40.5Y kg per kmol DEG

For 0.5 kmol this is

1.22 - 20.25Y kg

To burn hydrogen requires oxygen in a ratio of 8/1. There is 0.1 kg of H_2 in each kmol of fuel so 0.8 kg of O_2 is needed. Hence :

0.8 =1.22 - 20.25Y
Y = 0.208kmol per kmol DEG

The nitrogen in the DEG is 0.85 - Y = 0.642 kmol per kmol DEG The actual Nitrogen = 0.642 x 0.5 x 28 = 11.61 kg
The air supplied must be 11.61/.767 = 15.14kg per kg of fuel. A simple calculation shows

the stoichiometric mass of air is 13.73 so there is 10.3% excess air.

5. DISSOCIATION

At the high temperatures and pressures experienced in combustion, dissociation occurs. This results in some of the fuel not burning. CO is produced and in the case of hydrogen, some of it remains as hydrogen after the process even though oxygen is present. The reasons for this will not be covered here other than to say it is predicted by the 2nd law of thermodynamics and involves equilibrium in the chemical process.

When dissociation occurs, the energy released is reduced accordingly and if the amount of unburned fuel is known the previous examples may easily be modified to take account of it.

